Spectrophotometric Determination of Beryllium, Copper and Iron with Sodium-2'', 6''-dichloro-4'-hydroxy-3, 3'-dimethylfuchsone-5, 5'-dicarboxylate

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Several organic compounds which have the hydroxydimethylfuchsone dicarboxylic acid structure have been used as the reagents for the determination of certain trace metals. Typical of these are eriochrome cyanine R for the colorimetric determination of aluminum[1] and beryllium[2], and chrome azurol S as an indicator for the complexometoric titration of aluminum, copper, iron and zirconium[3-5]. Sodium - 2'', 6'' - dichloro - 4' - hydroxy - 3, 3' - dimethylfuchsone - 5, 5' - dicarboxylate (pontachrome azure blue B) has been examined spectrophotometrically for the determination of beryllium in an alkaline solution[2], but was not satisfactory because of the overlap of the absorption peak of the reagent with that of its beryllium complex. This paper reports an extensive study of the color reaction between the compound and metallic ions and procedures for its use as a reagent for the spectrophotometric determination of beryllium, copper and iron.

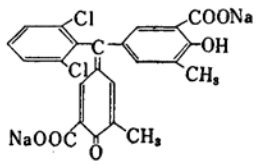

Fig. 1. Sodium-2'', 6''-dichloro-4'-hydroxy-3, 3'-dimethylfuchsone-5, 5'-dicarboxylate.

Experimental

Apparatus and Reagent.—A Shimadzu spectrophotometer model QB-50, with 1.00 cm. glass cells and a Hitachi photoelectric photometer Type-FPW 4 with 1.00 cm. glass cells were used.

Amberlite IRA 410 (50 to 100 mesh) was used in a goose-neck type column (30 cm. in height and 10 mm. in inside diameter).

The reagent solution was prepared by dissolving 0.2 g. of sodium-2'', 6''-dichloro-4'-hydroxy-3, 3'-dimethylfuchsone-5, 5'-dicarboxylate in 100 ml. of 99% ethanol and filtering off the residue.

The standard solution containing 0.1 mg. of beryllium per milliliter was prepared by dissolving beryllium chloride (analytical grade) in distilled water. The standard copper solution containing 0.1 mg. of copper per milliliter was prepared by dissolving pure crystals of $CuSO_4 \cdot 5H_2O$ in distilled water. The standard iron(III) solution was prepared by dissolving crystals of pure $Fe_2(SO_4)_3(NH_4)_2SO_2 \cdot 24H_2O$ in dilute sulfuric acid to give a solution containing 0.1 mg. of iron per milliliter. Five grams of 8-hydroxyquinoline was dissolved in 12 ml. of 17 N acetic acid and diluted to 100 ml. with distilled water.

Concentrated ammonium hydroxide (130 ml.) was neutralized with 120 ml. of glacial acetic acid and diluted to 100 ml. with distilled water to give ammonium acetate solution.

Determination of Beryllium.—*Separation of Beryllium.*—Acidify slightly a solution, containing interfering ions such as Al^{3+}, Co^{2+}, Cu^{2+}, $Fe^{2+,3+}$ and Ni^{2+}, with dilute acetic acid, and warm it on a steam bath to 60~70°C. Add the oxine-acetic acid solution in 50% excess, and then add the ammonium acetate solution slowly, until precipitation is complete. Let stand for one hour with frequent stirring, filter off the precipitate and wash with dilute acetic acid. Determine the beryllium in the filtrate.

Procedure of Determination.—Transfer the solution (not more than 1.5 ml.) containing 2 to 20 p.p.m. of beryllium to a 25 ml. volumetric flask, add about 10 ml. of the acetate-acetic acid buffer solution (pH 5.8) and mix well. Then add 1 ml. of the 0.2% reagent solution, shake well, and make up to the

1) F. J. Welcher, "Organic Analytical Reagents", Vol. IV, D. Van Nostrand Co., Inc., New York (1949), p. 355.
2) S. Umemoto, This Bulletin, **29**, 845 (1956).
3) M. R. Lewis and P. P. Goland, *Cancer Research*, **13**, 130 (1953).
4) J. S. Fritz and C. L. Ford, *Anal. Chem.*, **25**, 1640 (1953).
5) M. Theis, *Z. anal. Chem.*, **144**, 275 (1955).
6) K. A. Kraus and G. E. Moore, *J. Am. Chem. Soc.*, **75**, 1460 (1953).

mark with the buffer solution. After 20 min., measure the absorbance at 570 mμ, using a reagent blank solution (or distilled water) as a reference.

Determination of Copper and Iron(III).—*Separation of Copper and Iron.*—Separate copper and iron(III) by the method of Kraus[6], using an anion exchange resin. (Copper and iron do not interfere with each other's determination if the solution is adjusted to pH 7.2 for copper and 3.5 for iron.)

Procedure of Determination.—Transfer 1.00 ml. of the neutralized sample solution containing 10 to 100 p.p.m. of copper (or iron) to a 25 ml. volumetric flask containing about 10 ml. of borax-succinic acid buffer solution (pH 7.2 for copper or 3.5 for iron). Then add 2 ml. of the reagent solution, mix thoroughly, and fill up to the mark with the buffer solution. After 20 min., measure the absorbance at 610 mμ, using a reagent blank solution (or distilled water) as a reference.

For all these measurements, a photoelectric photometer equipped with 570 and 610 mμ filters was used.

Results and Discussion

Color Reactions.—Sodium-2'', 6''-dichloro-4'-hydroxy-3, 3'-dimethylfuchsone-5, 5'-dicarboxylate is a red-brown solid, soluble in water and ethanol. It was stable indefinitely in the solid state and for at least one month when dissolved in ethanol. The effect of pH on the reagent solution is shown in Fig. 2. Its color reaction was tested on a spot plate with 52 ions. Some metallic ions in an acid or a neutral medium reacted with it to give the colors shown in Table I. In an ammoniacal solution, only large amounts of calcium, magnesium and nickel ions gave blue solutions.

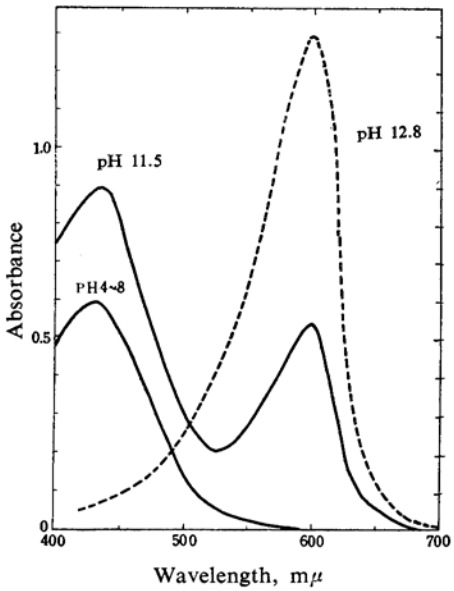

Fig. 2. Effect of pH on the reagent. Reagent: 40 ppm. pH was adjusted by HCl and NaOH solutions.

Seven of the colored complexes were examined spectrophotometrically. The results are summarized in Table II.

Absorption Spectra. — *Beryllium Complex.* — Absorption spectra of the reagent solution and

Table I. Color produced with ions in an acid or a neutral solution

Li^+	*Be^{2+}*													
	Mg^{2+}										*Al^{3+}*			
K^+	Ca^{2+}	*Sc^{3+}*	Ti^{4+}	Cr^{3+}	Mn^{2+}	**Fe^{3+}**	Co^{2+}	**Ni^{2+}**	**Cu^{2+}**	Zn^{2+}	**Ga^{3+}**		As^{3+}	SeO_3^{2-}	Br^-
						Fe^{2+}									
Rb^+	Sr^{2+}	Y^{3+}	Zr^{4+}			Ru^{3+}	Rh^{3+}	Pd^{3+}	Ag^+		In^{3+}	$Sn^{2+,4+}$	Sb^{3+}		
Cs^+	Ba^{2+}		Hf^{4+}				Ir^{4+}			Hg^+	Tl^{3+}	Pb^{2+}	Bi^{3+}		
				UO_2^{2+}											
*La^{3+}	Ce^{3+}	**Pr^{3+}**	**Nd^{3+}**		Eu^{3+}	**Gd^{3+}**		Dy^{3+}		Er^{3+}	Tm^{3+}	Yb^{3+}			
	Ce^{4+}														

Three ions shown in italic types give green solution.
Ten ions shown in gothic types give blue solution.

Table II. Optimum conditions for analytical use

Ion	Optimum pH	Wavelength at max. absorbance	Buffer soln.	Ion p.p.m. per 0.1 abs. unit
Fe^{3+}	2.8~4.2	610 mμ	B. S.*	0.22
Be^{2+}	5.6~6.2	570	A. A.**	0.02
Al^{3+}	5.6~6.2	600	B. S.	0.06
UO_2^{2+}	5.2	610	—	1.04
Cu^{2+}	6.8~7.8	610	B. S.	0.42
Ca^{2+}	9.0	580	NH_4OH-NH_4Cl	20.0
Mg^{2+}	11.0	570	NH_4OH-NH_4Cl	0.71

* Borax-succinic acid ** Acetate-acetic acid

of its beryllium complex solution are shown in Fig. 3. All solutions were adjusted to pH 5.8, using the acetate-acetic acid buffer solution. The beryllium complex had a maximum absorption at 570 mμ. However, the reagent appreciably absorbed light at 570 mμ when its concentration was more than 50 p.p.m.

Copper and Iron(III) Complex. — The copper complex in a solution of pH 7.2 had a maximum absorption at 610 mμ; the reagent did not appreciably absorb light at this wavelength when its concentration was less than 100 p.p.m. The iron(III) complex in a solution of pH 3.5 had also a maximum absorption at 610 mμ.

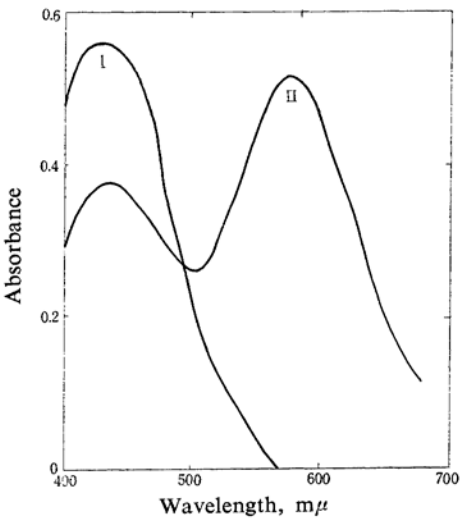

Fig. 3. Absorption spectra.
I: Reagent, 30 p.p.m.
II: Reagent (30 p.p.m.) + Be(0.1 p.p.m.)
pH: 5.8

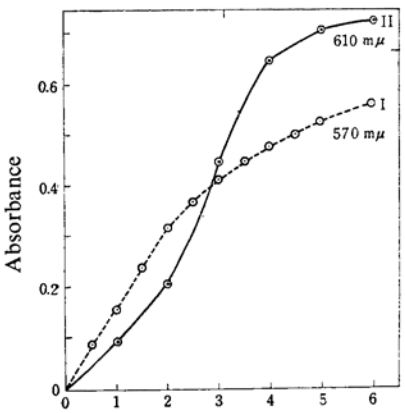

Fig. 4. Application of the mole ratio method.
I: Beryllium complex (pH 5.8)
II: Copper complex (pH 7.2)

7) J. H. Yoe and A. I. Jones, *Ind. Eng. Chem., Anal. Ed.*, **16**, 111 (1944).

Mole Ratio Studies.—*Beryllium Complex.* — Application of the mole ratio method[7] showed no sharp break or leveling-off to a constant absorbance for ratios up to as high as one mole of beryllium to six moles of reagent. The results are shown in Fig. 4.

Obviously the colored complex is appreciably dissociated and hence a large excess of the reagent is required to cause the reaction to proceed completion. By the application of the continuous variation method[8], the ratio of beryllium to the reagent was shown to be 1 to 2 (see Fig. 5).

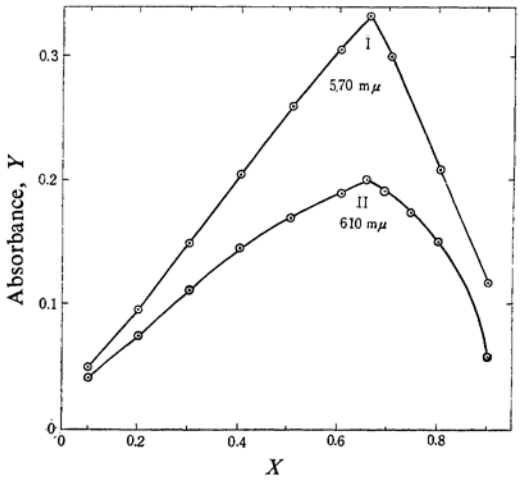

Fig. 5. Application of the method of continuous variation.
I: Be-complex (pH 5.8), II: Cu-complex (pH 7.2).

The best analytical results were obtained when the concentration of unreacted reagent was between 50 and 80 p.p.m.

Copper and Iron(III) Complexes.—Mole ratio studies for copper complex solution (pH 7.2) gave results similar to those for beryllium; the copper complex was appreciably dissociated and the ratio of copper to the reagent was 1 to 2 (see Figs. 4 and 5). The iron complex was also studied in a solution of pH 3.5. The ratio of iron to the reagent was 1 to 3.

Effect of pH. — Borax-succinic acid buffer and acetate-acetic acid buffer were satisfactory for the determination of beryllium, copper and iron. For an accurate measurement it was necessary to hold the pH fairly constant. The effect of pH on the color intensities of the metal complexes is shown in Fig. 6. The optimum pH range for the determination is listed in Table II.

Effect of Temperature.—There was no variation in the absorbance of the color systems

8) W. C. Vosburgh and G. R. Cooper, *J. Am. Chem. Soc.*, **63**, 437 (1941).

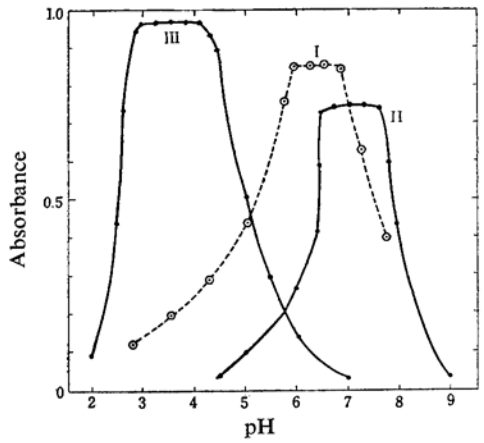

Fig. 6. Effect of pH.
I: Be^{+2}, 0.17 p.p.m., II: Cu^{+2}, 3.0 p.p.m., III: Fe^{+3}, 2.0 p.p.m.

over a temperature range of 15 to 30°C Hence, normal temperature changes in the laboratory introduce no error.

Rate of Color Development. — At room temperature the color intensities increased during the first 20 min. then remained constant for 40 to 50 min.

Interfering Ions.—Color reactions of 52 ions are listed in Table I. The limiting concentrations of seven ions in the determination of beryllium are given in Table III. The concentration of an ion that causes a diviation of 0.01 unit in the absorbance of a solution containing 0.1 p.p.m. of beryllium was taken to be the limiting concentration.

TABLE III. LIMITING CONCENTRATIONS OF INTERFERING IONS FOR DETERMINATION OF BERYLLIUM

Ion	Added as	Limiting concentration p.p.m.
Al^{+3}	$K_2SO_4Al_2(SO_4)_3$	0.09
Co^{+2}	$Co(NO_3)_2$	20.0
Cr^{+3}	$Cr_2(SO_4)_3$	3.0
Cu^{+2}	$CuSO_4$	0.22
Fe^{+3}	$K_2SO_4Fe_2(SO_4)_3$	0.27
Ni^{+2}	$Ni(NO_3)_2$	16.4
UO_2^{+2}	$UO_2(NO_3)_2$	1.9

Several methods were tried to eliminate the interfering ions for the determination of beryllium. The 8-hydroxyquinoline method[9] effected a good separation of beryllium. Interfering ions for the determination of copper and iron, such as Al^{+3}, Be^{+2}, Co^{+2} and Cr^{+3}, were eliminated by the method of Kraus[6].

9) E. B. Sandell, "Colorimetric Determination of Traces of Metals", 3rd Ed., Interscience Publishers, Inc., New York (1959), p. 306.

Beer's Law.—As a large excess of the reagent required for the determination of beryllium, was copper and iron, the calibration curves of water blank did not pass through the origin because of the absorption of the reagent solution at 570 or 610 mμ. The use of these curves provided satisfactory results whenever the same concentration of the reagent was used for

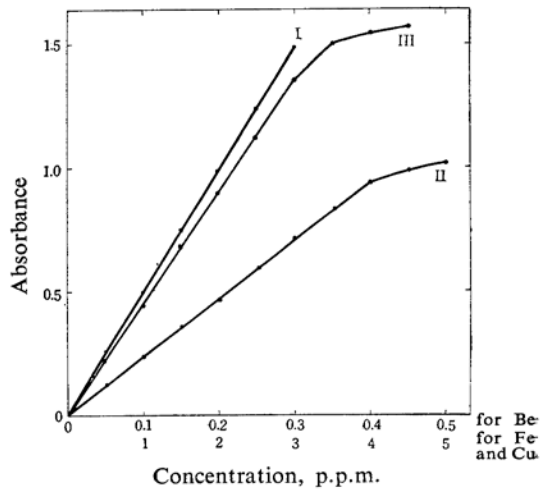

Fig. 7. Calibration curves for the determination.
I: Be^{+2}, pH 5.8, II: Cu^{+2}, pH 7.2, III: Fe^{+3}, pH 3.5, reference: reagent blank.

TABLE IV. DETERMINATION OF BERYLLIUM

	Solution analized		Found Be* p.p.m.	Error %
	Ion	Added p.p.m.		
1)	Al^{+3}	0.16		
	Fe^{+2}	0.16		
	Co^{+2}	0.16		
	Ni^{+2}	10.00		
	Cu^{+2}	20.00		
	Zn^{+2}	20.00		
	Be^{+2}	0.16	0.16	0.0
2)	Al^{+3}	8.00		
	Fe^{+3}	10.00		
	Co^{+2}	10.00		
	Ni^{+2}	20.00		
	Cu^{+2}	20.00		
	Ti^{+4}	20.00		
	Be^{+2}	0.16	0.15	−6.3
3)	Al^{+3}	10.00		
	Cr^{+3}	10.00		
	Cu^{+2}	10.00		
	Fe^{+3}	20.00		
	Ca^{+2}	20.00		
	Mg^{+2}	20.00		
	Ni^{+2}	10.00		
	Be^{+2}	0.08	0.08	0.0

* These values are the averages of six repeated determinations.

standards and unknowns. However, color intensities measured with the reagent solution as a blank obeyed Beer's law better than those with a water blank; Beer's law was obeyed up to about 0.3 p.p.m. of beryllium, about 4.0 p.p.m. of copper and about 3.0 p.p.m. of iron (see Fig. 7). In addition, the absorbances were sufficiently reproducible to permit beryllium to be determined up to 0.4 p.p.m., but for the best precision the concentration range should be 0.05 to 0.3 p.p.m.

TABLE V. DETERMINATION OF COPPER AND IRON

	Solution analyzed		Found*		Error
	Ion	Added p.p.m.	Cu p.p.m.	Fe	%
1)	Cu^{2+}	2.00	2.01		+0.5
	Fe^{3+}	2.00		1.96	−2.0
2)	Al^{3+}	20.00			
	Ca^{2+}	20.00			
	Be^{2+}	2.00			
	Cu^{2+}	1.00	1.01		+1.0
	Fe^{3+}	1.00		0.97	−3.0
3)	Al^{3+}	200.00			
	Ca^{2+}	200.00			
	Mg^{2+}	200.00			
	Cu^{2+}	2.00	1.88		−6.0
	Fe^{3+}	2.00		1.86	−7.0

* These values are the averages of three repeated determinations.

Determination of Beryllium in Solutions Containing Various Ions. — Beryllium has been determined in three solutions containing various amounts of certain foreign ions, after separation of the latter by oxine precipitation. The results are listed in Table IV.

Determination of Copper and Iron in Solutions Containing Various Ions.—Copper and iron(III) have been determined in three solutions, after separation of the foreign ions by the exchange resin. The results are given in Table V.

Summary

Procedures have been developed for the spectrophotometric determination of trace amounts of beryllium, copper and iron(III) with sodium-2″, 6″-dichloro-4′-hydroxy-3, 3′-dimethylfuchsone-5,5′-dicarboxylate. Certain ions that interfere with the beryllium determination are removed by an oxine precipitation. Ions that interfere with the analysis of copper and iron(III) are removed with an anion exchange resin column.

Accuracy and precision are good. Beer's law is obeyed up to about 0.3 p.p.m. of beryllium, about 4 p.p.m. of copper and about 3 p.p.m. of iron.

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