Spectrophotometric Determination of Beryllium with Eriochrome Cyanine R

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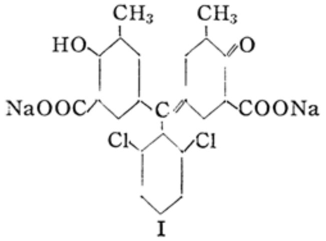
For the colorimetric determination of beryllium with organic reagents, various reagents have been used. The following reagents are known; *p*-nitrobenzeneazoorcinol[1,2,3,4,5], quinalizarin[6,7,8,9] curcumin[2,10], alkanin[11,12], naphthazarin[11,12], naphthacrome green G[13] aluminon[14,15,16], quinizarine-2-sulfonic acid[17,18,19], acetylacetone[20], sulfo-salicylic acid[21], sodium salt of chlorophenol-azo-dioxy-naphthalene disulfonic acid[22], 8-hydroxy-quinaldine[23] solochrome cyanine[24], benzene-2-arsonic acid-(1-azo-2)-1, 8-dioxynaphthalene-3, 6-disulfonic acid[25], solochrome brilliant blue B (sodium salt of sulfo-dichloro-hydroxy-dimethyl fuchson dicarboxylic acid[26] etc.. Beryllium fails to give a specific color change on a reaction with these reagents; but in general some other ions including iron, aluminum, alkali earth metals and rare earth metals give color change. Therefore, on their application, any of the above mentioned reagents is to be chosen according to the purpose. The method here proposed also seems possible of utilization for some purpose.

Introduction

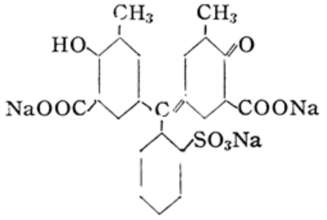
The color reaction of the following three organic reagents of a similar structure with beryllium was examined at pH 1.42–11.0.

To 2 ml. of the buffer solution, 2 drops of metal solutions containing 50 p. p. m. metals



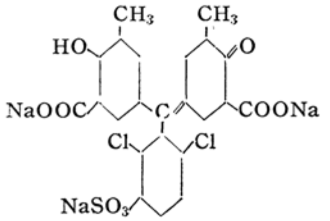
I

Sodium salt of dichloro-hydroxy-dimethyl fuchson dicarboxylic acid



II

Sodium salt of sulfo-hydroxy-dimethyl fuchson dicarboxylic acid (Eriochrome cyanine R)



III

Sodium salt of sulfo-dichloro-hydroxy-dimethyl fuchson dicarboxylic acid (Solochrome brilliant blue B)

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and 2 drops of 0.1% reagent solution were added. After three hours the color change was observed. For the pH ranges of 1.42–5.2, 7.0–9.2 and 9.2–11.0, the following buffer solutions were used respectively; hydrochloric acid–sodium acetate, hydrochloric acid-barbital and borax–sodium carbonate. In a buffered solution, pH 9.2, the color is yellow for all three blanks (water), and in the presence of beryllium, the color changes to brownish red (I), pinkish red (II) and dark reddish brown (III) respectively. Titanium changes the color of I to brownish yellow. But the same amounts of alminum, iron (ferric and ferrous), titanium (with II and III), copper, thorium and zirconium do not give any color change. The same amounts of calcium, magnesium, manganese and uranium ($(UO_2)^{2+}$) also fail to give any color change to II. In the other buffered solution, beryllium gives a color change, but fails to give a specific color change on reaction with these reagents as in pH 9.2.

Concerning eriochrome cyanine R[27] and solochrome brilliant blue B[26], their application to spectrophotometric determination has been already suggested.

Apparatus

Light absorption was measured against water by means of Shimadzu photoelectric spectrophotometer with 10 mm. absorption cells.

Reagents

Distilled Water.—Redistilled water is obtained by using a water distilling apparatus made of quartz.

Standard Beryllium Solution.—In 5 ml. of concentrated sulfuric acid, 0.1417 g. of beryllium oxide is dissolved. The resulting solution is transferred to a 500 ml. measuring flask containing about 100 ml. of water and is diluted to volume. This solution contains 0.1022 mg. of beryllium per ml.

*0.05*M *Borax Buffer Solution.*—In 1000 ml. of distilled water, 19.10 g. of borax are dissolved.

5% Potassium Sodium Tartrate Solution.—In 1000 ml. of distilled water, 50 g. of potassium sodium tartrate are dissolved.

Dye Solutions.—In 1000 ml of distilled water, 1, 3 or 5 g. of dyes are dissolved. The solutions thus obtained contain 0.1, 0.3 or 0.5% of dyes. Dye solutions should not be stored for more than one week.

Absorption Spectra

Absorption spectra of the reagents I, II and III, and of the complexes formed with beryllium are respectively presented in Figs. 1, 2 and 3. These curves were measured in buffered solutions of pH 9.2. The blank solution was prepared by mixing 20 ml. of 0.05 M borax solution with 1 ml. of water and 1 (I) or 2 ml. (II, III) of 0.1% reagent solution, whilst for the preparation of the complex solution 1 ml. of beryllium solution (50 micrograms of beryllium) was used in place of water. The solutions were made to stand for three hours at room temperature before the light absorption was measured.

Inspection of the curves shows that the reagent II is the most desirable for the spectrophotometric determination and that a wave length of 527 mμ gives the greatest difference in light absorption between the blank and the complex of reagent II, eriochrome cyanine R.

Therefore, the following experiments were carried out only with eriochrome cyanine R.

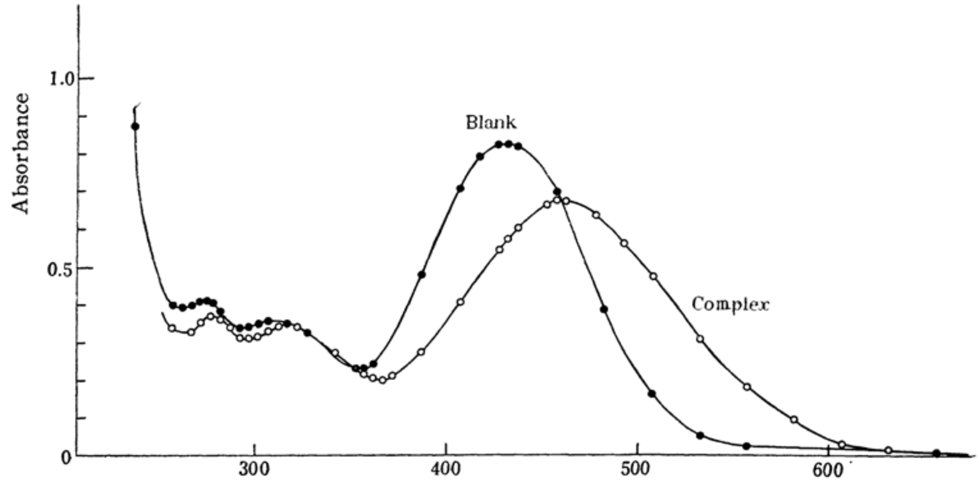

Fig. 1. Absorption spectra of reagent I and its complex.

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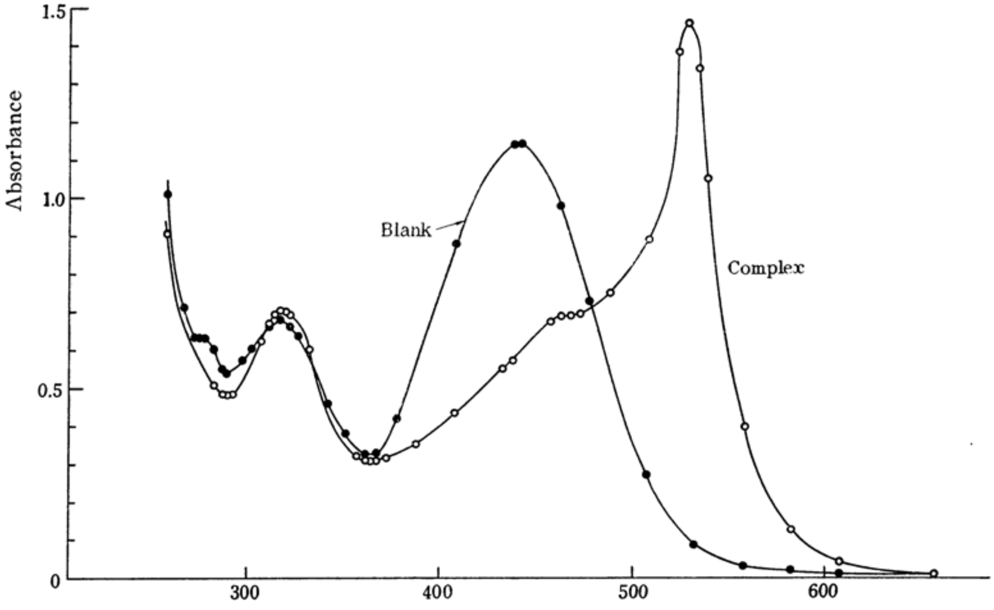

Fig. 2. Absorption spectra of reagent II and its complex.

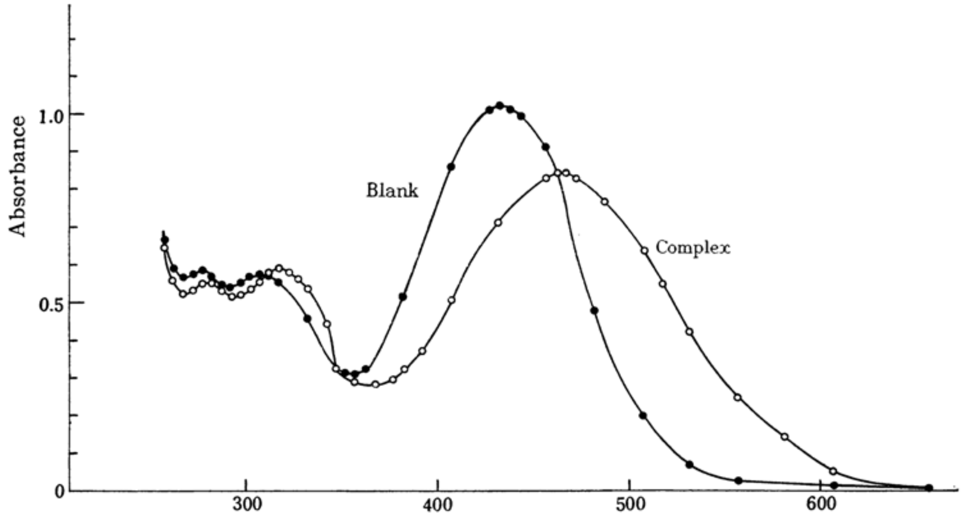

Fig. 3. Absorption spectra of reagent III and its complex.

Effect of Temperature and Time

In general, the organic reagents and beryllium may react slowly in an alkaline medium and at a low temperature. Consequently the effect of temperature and time of standing on the color change was studied.

Five ml. of beryllium solution and 100 ml. of 0.05 M borax solution were mixed, and made to stand for one hour in an ice box or in an air bath, its temperature being controlled. Five ml. of 0.1% eriochrome cyanine R solution were added. Light absorption at 527 mμ was measured ten, twenty and thirty minutes, one, two, three, five, eight, twenty-four and forty-eight hours after the development of the color for aliquots of the beryllium solutions of various concentrations. The results are presented in Table I and II and also in Fig. 4.

From these results, the color intensity was found to be dependent on the temperature and on the time after color development. At a lower temperature, color intensity is high but develops slow, but at a higher temperature, color intensity is low but develops fast. Therefore, the temperature has to be strictly controlled and the mesure-

Table I
Effect of temperature and standing time

Temperature °C	Concentration of Beryllium Solution Mixed with Borax Solution p. p. m.	Standing Time									
		10min.	20min.	30min.	1 hr.	2 hr.	3 hr.	5 hr.	8 hr.	24 hr.	48 hr.
0	25	34.2	39.9	43.4	51.0	65.1	75.1	88.3	97.9	100	98.6
	20	37.8	41.3	44.6	52.9	66.2	74.5	89.1	100	100	100
	15	47.0	50.1	53.1	60.5	69.6	78.7	90.6	99.7	99.5	100
	10	58.9	63.1	63.7	70.3	76.7	83.3	92.5	99.6	98.9	100
	5	79.9	80.8	83.0	87.9	89.7	92.4	96.0	98.2	97.3	100
	0	90.9	96.1	92.2	94.8	98.7	100	96.1	97.4	97.4	97.4
15	25	39.7	66.8	73.4	89.0	94.3	100	100	100	87.7	82.7
	20	61.8	71.2	76.9	87.1	93.3	99.9	100	99.9	88.5	84.1
	15	72.7	80.2	83.5	92.7	97.3	100	100	100	94.0	89.3
	10	86.6	88.3	90.4	96.8	99.1	100	99.4	100	97.1	94.8
	5	90.9	93.9	94.4	97.0	98.5	100	98.0	99.0	94.4	92.9
	0	97.1	92.9	94.3	100	100	100	100	100	95.7	100
25	25	92.2	99.4	99.9	99.7	98.7	99.3	100	99.0	91.3	77.3
	20	89.6	100	98.0	98.7	98.2	97.7	97.3	97.5	91.0	89.6
	15	93.5	99.3	100	98.6	98.6	98.8	99.3	98.8	93.3	92.3
	10	97.7	100	100	100	98.0	99.3	99.7	99.7	96.7	93.0
	5	91.9	99.5	100	98.4	98.9	100	99.5	99.5	94.1	91.4
	0	87.2	87.2	93.6	97.4	94.9	93.6	94.9	92.3	100	97.4
50	25	99.3	98.5	97.6	98.2	97.5	98.4	100	98.5	71.8	65.4
	20	98.9	98.7	99.3	99.6	99.8	100	100	99.1	77.3	72.6
	15	99.2	100	97.2	98.1	97.8	96.7	95.0	96.7	87.3	82.3
	10	96.3	98.1	98.9	100	98.1	98.9	100	100	93.7	92.6
	5	94.1	97.1	96.5	95.9	100	97.1	98.8	100	94.1	89.4
	0	89.5	89.5	96.1	100	97.4	96.1	97.4	94.7	98.7	98.7

Figures shown are the percentages of light absorptions for the maximum light absorption of the solutions which contained same amount of beryllium and were kept at the same temperatures.

Table II
Analysis of variance

Source of Variation		Degrees of Freedom	Sum of Squares	Mean Square
Main Effects	Temperature (T)	3	9,681.15	3,227.05**
	Time (H)	9	7,217.42	801.94**
	Concentration (C)	5	3,930.46	786.09**
2-Factor Interactions	T×H	27	16,846.31	623.94**
	C×H	45	2,052.73	45.62**
	T×C	15	4,018.36	267.89**
3-Factor Interaction	T×H×C	135	3,097.32	22.94
Total		239	46,843.45	

** Highly significant * Significant

Table III
Effect of dye concentration and tartrate

Figures are the readings of the photometer

	20 ml. 0.05M Borax				10 ml. 0.05M Borax +10 ml. 5% Tartrate			
	Concentration of Beryllium Solutions Added p. p. m.*							
	0	3	7	10	0	3	7	10
0.1% Eriochrome Cyanine R	0.090	0.152	0.234	0.314	0.092	0.152	0.223	0.273
0.3% Eriochrome Cyanine R	0.267	0.393	0.593	0.769	0.273	0.423	0.609	0.755
0.5% Eriochrome Cyanine R	0.442	0.616	0.880	1.10_0	0.452	0.663	0.947	1.15_3

* Beryllium content of the solutions, the light absorptions of which were measured is 1/22 of these figures.

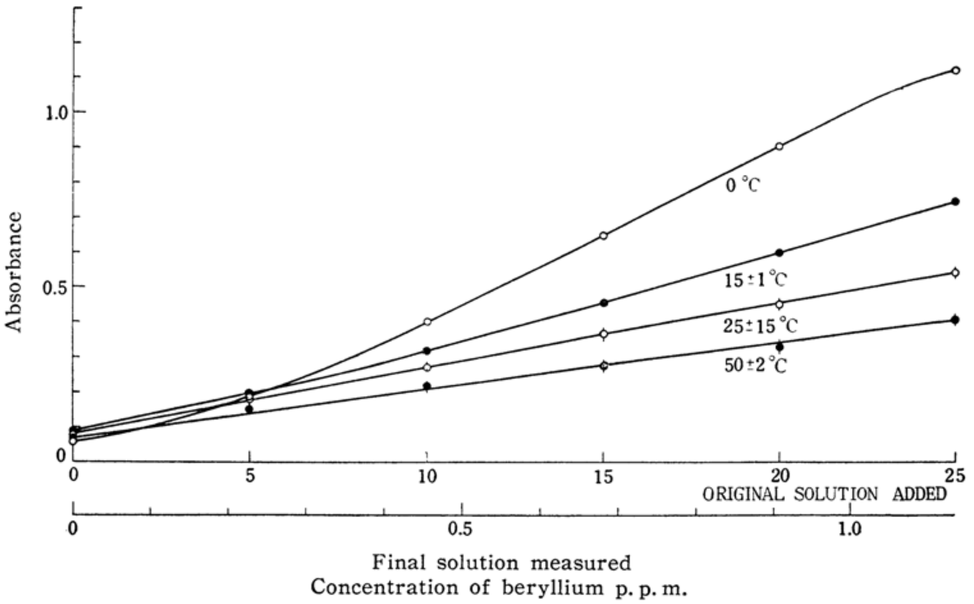

Fig. 4. Effect of temperature and relations between beryllium content and maximum light absorption.

ment of the maximum absorption has to be made at an adequate time after color development.

For an easier control, it seems convenient to select the temperature at 15–30°C and the measuring time in accordance with the temperature.

Effect of Dye Concentration and Tartrate

At pH 9.2, various metals are precipitated; when these elements are present in a large amount, beryllium is coprecipitated and the color change of eriochrome cyanine R by beryllium is inhibited. To avoid this, the presence of potassium sodium tartrate is desirable.

To determine the effect of potassium sodium tartrate and of the concentration of eriochrome cyanine R solution, 0.1, 0.3 and 0.5% eriochrome cyanine R solutions, 3 p.p.m., 7 p.p.m. and 10 p.p.m. of beryllium solutions and 5% potassium sodium tartrate in 0.05 M borax solution were used respectively. One ml. of beryllium solution and 10 ml. of tartrate solution were mixed and 10 ml. of 0.05 M borax solution were added. After standing for one hour in an air bath of 15°C (±1°C), 1 ml. of eriochrome cyanine R solution was added. After four hours, light absorptions were measured at 527 mμ. The results are shown in Table III and IV and in Fig. 5.

The larger the quantity of eriochrome cyanine R, the more intensive is the color (see the inclination of the curve in Fig. 5). Since, however, the light absorption of the blank should not be too high for an accurate determination, the concentration of eriochrome cyanine R cannot be higher than 0.5%.

As the results of presence of tartrate, the relations between the beryllium concentration and the light absorption of the complex holds linear. Moreover, the rate of increase in light absorption with increase in the concentration of eriochrome cyanine R is greater in the presence of tartrate than in its absence.

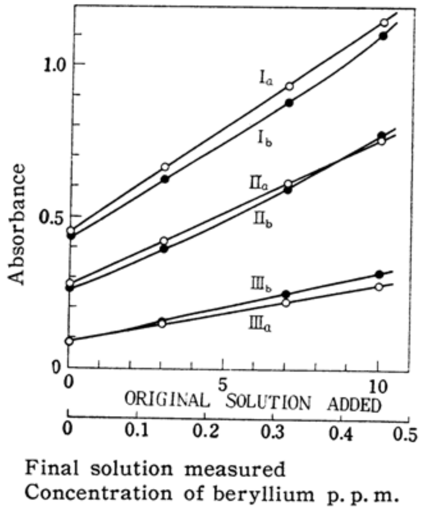

Fig. 5. Effect of dye concentration and tartrate.

Ia: 0.5% dye solution, presence of tartrate

Ib: 0.5% dye solution, absence of tartrate

IIa: 0.3% dye solution, presence of tartrate

IIb: 0.3% dye solution, absence of tartrate

IIIa: 0.1% dye solution, presence of tartrate

IIIb: 0.1% dye solution, absence of tartrate

TABLE IV

ANALYSIS OF VARIANCE

Source of Variation		Degrees of Freedom	Sum of Squares	Mean Square
Main Effects	Concentration of Dye (D)	2	1,397,195	698,597.5**
	Concentration of Beryllium (B)	3	728,133	242,711.0**
	Tartrate (T)	1	1,135	1,135.0**
2-Factor Interactions	D×B	6	135,318	22,553.0**
	T×D	2	3,274	1,637.0
	B×T	3	771	257.0
3-Factor Interaction	D×B×T	6	1,220	203.3
Total		23	2,267,046	

** Highly significant * Significant

Thus, the addition of tartrate gives many benefits for an accurate determination.

For the most sensitive condition at 15°C, i.e. for the application of 0.5% eriochrome cyanine R and the presence of tartrate, the calibration curve for beryllium is shown in Fig. 6.

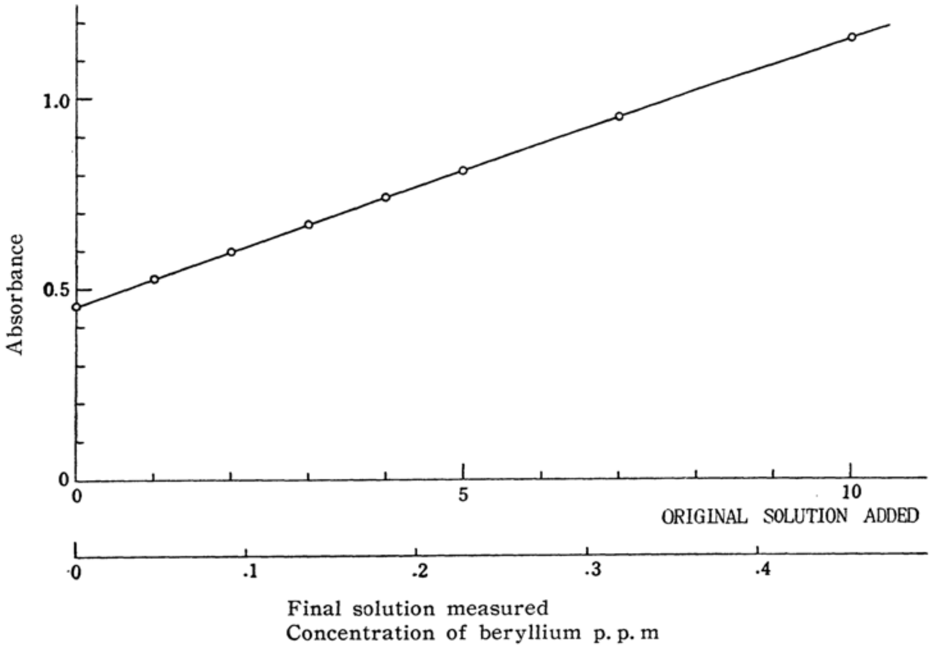

Fig. 6. Calibration curve of beryllium.
(15°C, presence of tartrate, 0.5% eriochrome cyanine *R* solution)

Effect of Metals and Anions

It has already been mentioned that small amounts of various metals fail to give any color change to eriochrome cynine R in a medium of 0.05 M borax solution, pH 9.2. In the presence of tartrate, however, many metal ions can be held in solution and are expected to give color change of the dye.

In order to disclose the limit of interference of various metals and anions with the color development of beryllium, one series of solutions containing 3 p.p.m. of beryllium and various amounts of a metal or of an anion were prepared. One ml. of a metal or anion solution and 10 ml. of 5% potassium sodium tartrate solution were mixed with 10 ml. of 0.05M borax solution, and set aside for one hour at 15°C. One ml. of 0.5% eriochrome cyanine R solution was added, and the light absorption at 527 mμ was measured after four hours. The limit and mode of interference of various metals and anions were shown in Table V.

When a dilute solution of eriochrome cynine R was used, the limit of interference of each metal or anion became greater and the color change caused by beryllium smaller. An example is shown in Table VI and VII (c.f. Table V). Experimental conditions were the same as in the case of the above experiment except for the use of 0.1% dye solution instead of 0.5%.

TABLE V

INTERFERENCE LIMIT OF METALS AND ANIONS

Metal or Anion	Compound	Interference Limit: For the Metal or Anion Solutions Mixed with Tartrate Solution	Interference Limit: For the Final Solutions, Light Absorption of which were measured p. p. m.†	Mode of Interference
Fe^{3+}	Ferric chloride	250	12	Color enhancement
Al^{3+}	Alum	250	12	ditto
Ti^{4+}	Titanium sulfate	>300	>14	—
Mg^{2+}	Magnesium sulfate	250	12	Color inhibition
Ca^{2+}	Calcium chloride	700	32	ditto
Th^{4+}	Thorium nitrate	2000	91	ditto
Fe^{2+}	Ferrous ammonium sulfate	—*	—*	—
$(ZrO)^{2+}$	Zirconium oxychloride	100	4.5	Color inhibition
$(UO_2)^{2+}$	Uranyl acetate	>1000	>45	—
SiO_3^{2-}	Sodium silicate	300	14	Color inhibition
F^-	Sodium fluoride	1000	45	ditto
PO_4^{3-}	Potassium phosphate, monobasic	3000	136	ditto

* For standing, Fe^{2+} is oxidized to Fe^{3+}, and same figure was obtained as Fe^{3+}.

† The concentration of beryllium was 0.17 p. p. m. in this experiment.

TABLE VI

EFFECT OF METAL IONS

One milliliter of 20 p. p. m. beryllium solution containing various amounts of metals and 10 ml. of tartrate solution were mixed and added 10 ml. of 0.05M borax solution. After standing for one hour at 15°C, 1 ml. of 0.1% eriochrome cyanine R solution is added and after four hours light absorption of the solution was measured. Figures of light absorptions are as follows.

Concentration of Iron p. p. m.*	Concentration of Titanium p. p. m.* 0			50		
	Concentration of Aluminum p. p. m. 0	200	1000	0	200	1000
0	0.441	0.453	0.446	0.452	0.452	0.451
200	0.446	0.447	0.448	0.449	0.453	0.445
1000	0.456	0.459	0.451	0.452	0.442	0.447

* These concentrations are the concentration of the metal solutions mixed with tartrate. For the final solutions, these concentrations must be devided by 22.

Discussion

In the case of the determination of beryllium using eriochrome cyanine R, temperature, standing time, concentration of the dye solution, the presence of tartrate, and the concentration of various other ions are the factors which regulate the accuracy, precision and reproducibility.

Above all, the concentration of dye solution should be as high as possible. When it is high, one of the beneficial effects of tartrate, increase in color intensity, is promoted.

Concerning further advantages brought about by tartrate, it makes the working curve linear and prevents the coprecipitation of beryllium with metal ions such as iron, aluminum, calcium and magnesium. Thus, the addition of tartrate is essential.

Temperature is also an important factor; at a lower temperature the color intensity is

TABLE VII

ANALYSIS OF VARIANCE

Source of Variation		Degrees of Freedom	Sum of Squares	Mean Square
Main Effects	(Ti)	1	1.39	1.39
	(Fe)	2	31.45	15.73
	(Al)	2	24.11	12.06
2-Factor Interactions	(Ti)×(Fe)	2	141.44	70.72
	(Fe)×(Al)	4	46.22	11.56
	(Al)×(Ti)	2	44.11	22.06
3-Factor Interaction	(Ti)×(Fe)×(Al)	4	75.56	18.89
Total		17	364.28	

** Highly significant   * Significant

higher, but to get maximum light absorption it requires a long time to obtain it and the temperature control is difficult; at a higher temperature standing time for obtaining the maximum light absorption is shorter but the resulting color intensity is lower, the temperature control being also difficult.

Consequently, temperature of 15–30°C will also be recommended from these respects. The interfering cations and anions should not be present with beryllium over the interference limit. The latter is a function of the concentration of the dye solution as mentioned above.

The following procedure is recommended.

One ml. of the sample solution containing from 1 to 10 micrograms of beryllium and 10 ml. of 5% potassium sodium tartrate solution are mixed with 10 ml. of 0.05M borax solution. After standing for one hour at 15°C, 1 ml. of 0.5% eriochrome cyanine R solution is added. After three hours the light absorption of the colored solution is measured at 527 mμ. With the aid of the calibration curve, the amounts of beryllium can be determined (see Table V and Fig. 6).

To a dilute solution of beryllium containing from 0.05 to 0.5 milligram Be per liter, the following procedure is applied. Into a 25 ml. measuring flask, 0.5 g. of potassium sodium tartrate is taken and 20 ml. of the sample solution are poured. After dissolution of tartrate, 0.191 g. of borax is added, dissolved and the whole diluted to 25 ml. After being kept for one hour at 15°C, 1 ml. of 0.5% eriochrome cyanine R solution is added and the light absorption is measured at 527 mμ after four hours. In this case, the calibration curve must be used, which is prepared by the same procedure for a standard beryllium solution.

In any case, when an interfering substance is present in greater quantity than the interfering limit, its amount has to be diminished below the interfering limit.

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