BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 42 2998—3000 (1969)

The Spectrophotometric Determination of Beryllium with Chromal Blue G

Katsuya UESUGI

Laboratory of Chemistry, Himeji Institute of Technology, Himeji

(Received January 16, 1969)

The present author and his co-workers[1-5] have studied the methods of the spectrophotometric determination of several metals using dyes of the triphenylmethane series, and have previously reported[5] a spectrophotometric determination of scandium with chromal blue G (sodium-2''-chloro-4''-nitro-4'-hydroxy-3,3'-dimethylfuchsone-5,5'-dicarboxylate, color index 43835), and found that a very small amount of beryllium also reacts with this reagent in a weakly acidic medium to form a complex. This paper will describe a spectrophotometric determination of beryllium using this reagent. The proposed method is not selective, like other reagents for beryllium, but it is more sensitive than the methods using chromazurol S,[6] eriochrome cyanine R,[7] or xylenol orange,[8] which have structures similar to that of this reagent.

Experimental

Reagents and Apparatus. *Standard Beryllium Solution.* A standard beryllium solution was prepared by dissolving 1.964 g of beryllium sulfate tetrahydrate (Mitsuwa Chemicals) in distilled water, then adding 10 m*l* of hydrochloric acid and diluting the solution to 1 *l*. The solution contained 100 μg of beryllium per milliliter. This standard stock solution was then further diluted to 10 ppm with distilled water.

Chromal Blue G Solution. The chromal blue G (Geigy Chemicals, New York, U. S. A.) was purified by recrystallization from ethanol before use, and then 0.1 g of it was dissolved in 100 m*l* of 95% ethanol. This solution was stable for at least a month.

All the other reagents and the apparatus used were the same as those reported previously.[5]

The Standard Procedure for Beryllium Determination. To a sample solution containing from 1 to 8 μg of beryllium, add 2 m*l* of the chromal blue G solution, then add 10 m*l* of an acetate buffer solution (pH 6.0), mix well, and make up to 25 m*l* with distilled water. Determine the absorbance at 610 mμ against a reagent blank solution treated in a similar manner. From the measured absorbance, determine the beryllium concentration of the sample solution by the use of a calibration curve.

Results and Discussion

Absorption Curves. The absorption curves of chromal blue G have been presented in a previous paper;[5] the maximum absorption is at 480 mμ below pH 4.0, at 430 mμ over the pH range from 5.5 to 10.0, and at 590 mμ above pH 10.5. The absorption curves of the beryllium-chromal blue G complex at various pH values are shown in Fig. 1. These curves were obtained by measuring the absorbance of the solution containing 0.12 ppm of beryllium and 80 ppm of chromal blue G at various pH values against a reagent blank solution. Above pH 5.0, the solutions give essentially identical absorption curves, with an absorption maximum

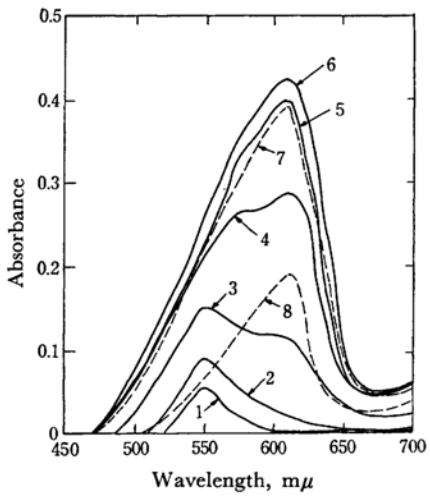

Fig. 1. Absorption spectra of beryllium complex at various pH.
Be 0.12 ppm, Reagent 80 ppm, Reference: Reagent blank
pH 1 : 3.5, 2 : 4.0, 3 : 4.5, 4 : 5.0, 5 : 5.5, 6 : 6.0—6.3, 7 : 7.0, 8 : 8.0

1) Y. Katsube, K. Uesugi and J. H. Yoe, This Bulletin, **34**, 72 (1961).
2) Y. Katsube, K. Uesugi and J. H. Yoe, *ibid.*, **34**, 829 (1961).
3) K. Uesugi, Y. Katsube and J. H. Yoe, *ibid.*, **35**, 516 (1962).
4) T. Shigematsu, K. Uesugi and M. Tabushi, *Bunseki Kagaku (Japan Analyst)*, **12**, 267 (1963).
5) K. Uesugi, This Bulletin, **42**, 2051 (1969).
6) L. Silverman and M. E. Shideler, *Anal. Chem.*, **31**, 152 (1959).
7) U. T. Hill, *ibid.*, **30**, 521 (1958).
8) M. Otomo, This Bulletin, **38**, 730 (1965).

at 610 mμ. However, the reagent solution has a slight absorption at this wavelength in the pH range from 5.5 to 7.5. Below pH 4.5, the position of the maximum absorption shifts to 570 mμ. The curve obtained at pH 5.0 has a shoulder at about 580 mμ.

Effect of pH. The effect of pH on the color development of the complex was examined by measuring, at 610 mμ, the absorbance of a solution containing 0.12 ppm of beryllium and 80 ppm of the reagent at different pH values from 4.5 to 9.0. The results are shown in Fig. 2, from which it can be seen that the maximum absorbance of the beryllium complex occurs in the pH range from 5.8 to 6.4. The amount of the buffer solution (pH 6.0 and 0.2 M in acetate) was found to have no effect on the absorbance over the range from 5 to 10 ml per 25 ml of the solution.

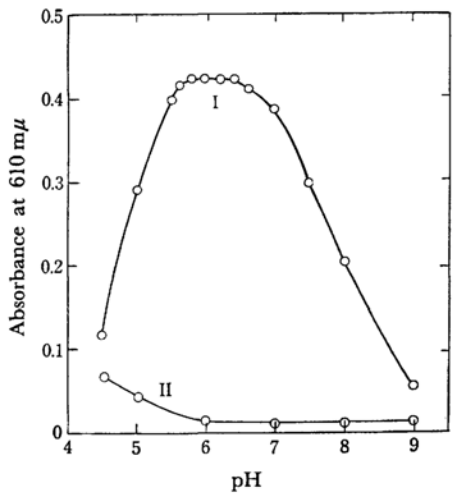

Fig. 2. Effect of pH on color development.
I: Be 0.12+Reagent 80 ppm (Reference: Reagent blank)
II: Reagent 80 ppm (Reference: Water)

Stability of Color. The color development between beryllium and the reagent occurs instantaneously at room temperature. The color intensity of the solution remains almost constant for at least 2 hr after preparation when measured against a reagent blank.

Effect of Reagent Concentration. The effect of the chromal blue G concentration on the color development was examined by varying the concentration of the reagent at a constant beryllium concentration. The absorbance of the beryllium complex at 610 mμ gradually increases at higher reagent concentrations. However, above 1.0 ml of a 0.1% reagent solution, the rate of the increase of the absorbance is relatively small. On the basis of these data, 2.0 ml of 0.1% reagent solution was chosen as the fixed quantity to be added. Two milliliters of a 0.1% chromal blue G solution for 25 ml of the solution was found to be a sufficient amount for less than 0.3 ppm of beryllium.

Effect of Temperature. The effect of the temperature on the color development was examined by measuring the absorbance of colored solutions kept at various temperatures for 20 min after preparation. There was no variation in the absorbance of the colored complex over the temperature range from 10 to 40°C. At temperatures over 40°C, however, the color intensity decreased.

Beer's Law and Sensitivity. The linearity between the absorbance of the beryllium-chromal blue G complex and the beryllium concentration was examined by varying the beryllium concentration and by measuring the absorbance at a wavelength of 610 mμ and at pH 6.0. The beryllium complex was found to follow Beer's law up to a beryllium concentration of at least 0.3 ppm. The molar absorptivity is 31000 at 610 mμ. The spectrophotometric sensitivity[9] is estimated to be 3×10^{-4} μg of beryllium per cm², corresponding to $\log I_0/I=0.001$.

Effect of Diverse Ions. A study was made of the effect of several cations and anions. The most commonly-encountered ions were added individually to a solution containing 10 μg of beryllium. From the results, it can be concluded that copper(II), aluminum, iron(III), nickel, scandium, yttrium, and rare earth elements interfere seriously with the determination of beryllium.

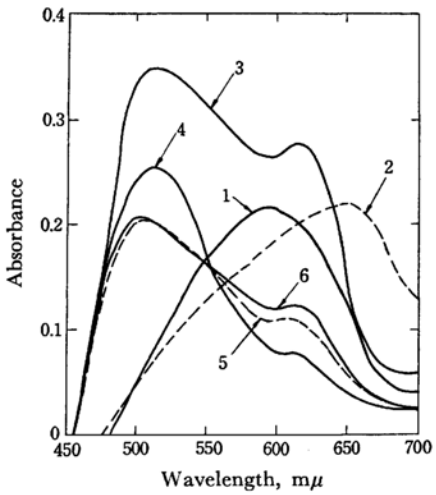

Fig. 3. Absorption spectra of aluminum, iron(III), yttrium, lanthanum, gadolinium, and erbium complexes at pH 6.0.
Reagent 80 ppm, Reference: Reagent blank
1 : Al 0.13 ppm, 2 : Fe(III) 0.26 ppm, 3 : Y 1.5 ppm, 4 : La 1.5 ppm, 5 : Gd 1.5 ppm, 6 : Er 1.5 ppm

9) E. B. Sandell, "Colorimetric Determination of Traces of Metals," 3rd Ed., Interscience Publishers, New York (1959), p. 83.

Sulfate, chloride, nitrate, and acetate ions, on the other hand, do not interfere. Oxalate, fluoride, citrate, phosphate, and EDTA bleach the complex.

The absorption curves of the complexes of aluminum, iron(III), yttrium, and some of the rare earth elements at pH 6.0 are shown in Fig. 3. The maximum absorption of the aluminum complex is at 590 mμ, much like that of the scandium complex,[5] while that of the iron(III) complex is shifted toward a longer wavelength. The complexes of yttrium, lanthanum, gadolinium, and erbium at pH 6.0 have two absorption maxima, as is shown in Fig. 3.

Complex Formation. The composition of the beryllium-chromal blue G complex was established by the continuous variation method.[10] The results are shown in Fig. 4, which indicates that a 1-to-2 complex is formed between beryllium and chromal blue G at pH 6.0. Similar relations were also observed for scandium and the chromal blue G complex.[5] In order to estimate the composition of the complex formed below pH 4.5, the method of continuous variation was employed. The results indicated that the combining ratio of beryllium and chromal blue G is 1 to 1. These results were confirmed by the mole ratio method.

The formation constant of the beryllium complex was determined spectrophotometrically by the method used in a previous paper.[5] The conditional formation constant for the complex at pH 6.0 and 20°C was calculated, from the curves of the continuous variation, to be 4.3×10^{10}.

The proposed method was compared with the methods using some other reagents with structures similar to that of this reagent. The results are listed in Table 1. The proposed method using chromal blue G has some advantages: the sensitivity is very high, the solution is stable and the calibration curve is very reproducible, and the procedure is simple.

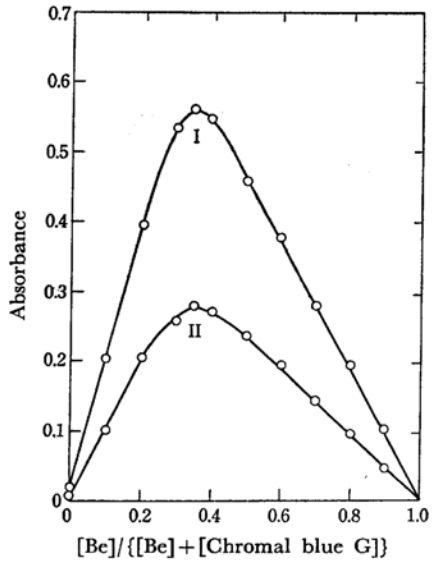

Fig. 4. Continuous variation method.
pH 6.0, Wavelength: 610 mμ
I: [Be]+[Chromal blue G]=8.52×10^{-5} M
II: [Be]+[Chromal blue G]=4.26×10^{-5} M

Table 1. Comparisone with other method

Method	Molar absorptivity [Sensitivity]	Precision
Aluminon[11]	*2.6×10^{3} (535 mμ)	$\sigma=12\%$
Eriochrome cyanine R[7]	*2×10^{4} (512 mμ)	
Chromazurol S[6]	*1.55×10^{4} (575 mμ)	*$\sigma=1.15\%$
Naphthochrome green G[12]	3.88×10^{4} (652 mμ)	Error$\leqq$3%
Xylenol orange[8]	*1.5×10^{4} (495 mμ) [6×10^{-4} μg/cm^2]	
Pontachrome azure blue B[1]	4.5×10^{4} (570 mμ)	$\sigma=1.8\%$
Chromal blue G	3.1×10^{4} (610 mμ) [4×10^{-4} μg/cm^2]	$\sigma=0.65\%$

* Calculated from the reference
σ : Relative standard deviation

The author wishes to express his hearty thanks to Professor Tsunenobu Shigematsu of the Institute for Chemical Research, Kyoto University, for his kind guidance.

10) P. Job, *Ann. Chim.*, **9**, 113 (1928).

11) G. E. Kosel and W. F. Neuman, *Anal. Chem.*, **22**, 936 (1950).

12) T. Fujinaga, T. Kuwamoto, K. Kuwabara and S. Ikezawa, *Bunseki Kagaku (Japan Analyst)*, **12**, 1213 (1964).