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DIFFERENTIAL SPECTROPHOTOMETRIC DETERMINATION OF BERYLLIUM

J. C. White
A. S. Meyer, Jr.
D. L. Manning

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June 6 , 1955

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ABSTRACT

Differential spectrophotometry was applied to the determination of beryllium as the p-nitrobenzeneazoorcinol complex in basic solution. The absorbance of the complex is measured against a reference standard which contains 1.0 mg of beryllium per 100 ml of solution. The coefficient of variation of the method is less than one per cent on duplicate determinations. The method is essentially free from interferences and is applicable to the determination of beryllium in the presence of moderate amounts of uranium and aluminum. Relatively large amounts of fluoride can be tolerated without interference.

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INTRODUCTION

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Beryllium and beryllium compounds have many unique chemical and physical properties[5] which have won for this element increasing applications and widespread interest. As the use and availability of beryllium increase many new problems have arisen in the analysis of this element which have resulted in the development of new and modified methods of determination.

The gravimetric methods[13] most widely used for the determination of beryllium include: the precipitation of beryllium as the hydroxide and ignition to beryllium oxide for weighing, and the precipitation of beryllium as the ammonium phosphate salt with subsequent ignition to $Be_2P_2O_7$ for weighing. The determination of beryllium as the oxide is subject to many interferences. The solution from which beryllium hydroxide is to be precipitated must be free from all other cations that form insoluble hydroxides with ammonium hydroxide. The precipitation of beryllium ammonium phosphate with subsequent ignition to beryllium pyrophosphate has the advantage of almost four times as much mass per equivalent beryllium content as in the beryllium oxide method. If the conditions of precipitation are not meticulously controlled, however, slight departures from the theoretical composition of beryllium pyrophosphate may occur, thus resulting in a loss of accuracy.

A volumetric method[8, 13] for beryllium has been reported in which beryllium is first precipitated as the hydroxide at a pH of 8.5. If an excess of sodium fluoride is then added, beryllium is converted to the very stable fluoride complex, K_2BeF_4, and an amount of hydroxyl ions equivalent to beryllium is found as sodium hydroxide. This alkalinity is determined by titration with standard acid and calculated as a measure of the concentration of beryllium present. The method, although empirical, is rapid and precise under ideal conditions. Aluminum reacts in a similar manner to beryllium and will be included with the beryllium. Although it is possible to correct for the aluminum present, the precision of the method is seriously affected. Zirconium, hafnium, rare earths, uranium and thorium interfere and must be separated.

Colorimetric reagents that have been used for the determination of microgram quantities of beryllium include quinalizarin[10], curcumin[6], alkanin[12], p-nitrobenzeneazoorcinol[13], and many others[7,3,11,14].

This investigation was undertaken to apply the advantages of differential spectrophotometry to the determination of relatively large amounts of beryllium. Hiskey[4] and Bastian[1] have emphasized that the accuracy and precision which can be obtained by differential spectrophotometry are equivalent to that obtainable by volumetric and gravimetric techniques. In the differential method the absorbance scale is set at zero with a solution of a highly colored or light-absorbing substance in the place of a reagent blank. Higher concentrations of a given component are then measured against this reference solution in the usual manner. In order to obtain the increased light intensity required to adjust the zero scale by this method, the spectrophotometer slit is set at wider apertures than normally used. For systems which obey Beer's law at wider slit openings, the resultant absorbance measurements are directly proportional to the difference in concentration between the zero point standard and the solution in question.

The reaction between beryllium and p-nitrobenzeneazoorcinol to produce a highly colored complex was used for the differential spectrophotometric determination of beryllium in this study because of its simplicity and stability.

Application of Differential Spectrophotometry to the Beryllium-p-nitrobenzeneazoorcinol Reaction

When a solution of p-nitrobenzeneazoorcinol[13] in 0.1 N sodium hydroxide (amber-colored) is added to a moderately alkaline solution which contains beryllium, a red color is formed. By carefully controlling such conditions as alkalinity and the concentration of chromogenic reagent, the relationship of the absorbance of the complex to beryllium concentration can be fixed. Optimum alkalinity is maintained by means of a sodium borate-sodium citrate buffer. The chromogenic reagent is almost specific for beryllium; it reacts in an interfering manner only with magnesium and to a much smaller extent with zinc[13] by forming colored complexes with these elements. Many metals, if present in limited amounts, that would ordinarily precipitate in alkaline solutions are rendered soluble through the formation of soluble citrate complexes.

For systems which obey Beer's law, the accuracy which is theoretically obtainable by application of differential spectrophotometry increases with increasing absorbancy of the reference standard. Eventually, however, because of the combined effects of broadened band widths of light which are transmitted as a consequence of the widened slit apertures and high concentrations of the complex, an optimum concentration is reached beyond which a decrease in accuracy results. These effects are discussed in detail by Bastian[2]. The concentration of the reference standard used in this study was 1 mg of beryllium in a final volume of 100 ml. The absorbance of this solution versus a reagent blank was approximately unity. The concentration of the reference standard could have been increased somewhat; however, 1 mg per 100 ml was chosen in order that absorbance measurements could be made with a Beckman Model B spectrophotometer or similar type instrument. With this solution as a reference standard, a standard beryllium curve was prepared.

REAGENTS

p-Nitrobenzeneazoorcinol, 0.025 per cent W/V. Weigh out 0.125 g of p-nitrobenzeneazoorcinol reagent, then add to a solution of 300 ml of water and 25 ml of 2 N NaOH. Stir the mixture until the reagent is dissolved (4 to 6 hours). Transfer the solution to a 500-ml volumetric flask, then dilute to volume with water, finally transfer the reagent into an amber storage bottle.

Buffer solution, pH 12.7 ± 0.1. Dissolve 178 g of sodium citrate$\cdot 2H_2O$, 92 g of sodium borate$\cdot 10\,H_2O$ and 143 g of sodium hydroxide in about 600 ml of water by stirring with a magnetic stirrer until all the salts are dissolved. Transfer the solution to a 1-liter volumetric flask then dilute to volume with water. Mix thoroughly.

Sodium hydroxide, 2 N. Dissolve 40 g of sodium hydroxide in 500 ml of water.

Beryllium standard solution, 0.100 mg per ml. Add 0.278 g of National Bureau of Standards beryllium oxide to a solution containing 150 ml of water and 56 ml of concentrated H_2SO_4. Heat until the appearance of fumes of SO_3, then continue heating until the oxide is in solution. If,after one hour of heating, all of the beryllium oxide is not in solution, add about 100 ml of water, then heat to fumes of SO_3 again. If undissolved beryllium oxide is still present, cool the mixture then add about 400 ml of water and filter off the undissolved beryllium oxide. Fuse the beryllium oxide with about 0.5 gram of potassium pyrosulfate, then dissolve the fusion mixture in water. Combine the solution with the filtrate. Transfer the solution to a one-liter volumetric flask and dilute to volume with water. The final concentration is then 0.100 mg of beryllium per ml in a 2 N solution of H_2SO_4.

PROCEDURE

Transfer appropriate aliquots of the standard beryllium solution into separate 50-ml beakers so that they contain 1.0, 1.1, 1.2, 1.4, and 1.6 mg of beryllium, respectively. Adjust the pH of the solutions to 5 to 6 by adding 2 N NaOH. Transfer the solutions to 100-ml volumetric flasks, add 10 ml of buffer solution then 20 ml of color reagent and dilute to volume with water. Allow the color to develop for at least 10 minutes, then measure the absorbance of each of the solutions with a Beckman Model DU spectrophotometer at 510 mμ in 1-cm cells against the reference standard, which is the solution containing 1 mg of beryllium. In order to obtain the proper slit width, adjust the galvanometer to zero by setting the slit width at a constant value. Make the necessary adjustments with the sensitivity control. Plot the absorbance as the ordinate versus the concentration of beryllium in mg per 100 ml as the abcissa. Since the reference standard must remain in the cell for some time, it is desirable to place a cap on this cell to avoid changes in concentration as a consequence of evaporation.

RESULTS

The differential spectrophotometric method was tested by applying the method to sulfuric acid solutions of beryllium and lithium that had been analyzed previously for beryllium by the indirect fluoride titration method[8,13]. The solutions were approximately 1 N with respect to H_2SO_4. Aliquots of the standard beryllium solution which contained 1.0, 1.1, 1.4, 1.5, and 1.6 mg of beryllium were treated along with the samples as described previously. Absorbance measurements of the standards and samples were made after allowing the color to develop for a period of at least 10 minutes. The beryllium content of the samples was calculated by comparison with the absorbance of the standard solutions. The following formula, which is based on linear relationship of absorbance to concentration over the range 1.1 to 1.6 mg of beryllium per 100 ml of solution, was used for purposes of calculation.

$$C_s = C_r \quad 1.1 + 0.5\left(\frac{(A_s - A_{1.1}}{(A_{1.6} - A_{1.1})}\right)$$

Where C_s = concentration of beryllium in sample aliquot

C_r = concentration of beryllium in reference solution (1.0 mg in this case)

A_s = absorbance of sample aliquot versus reference solution

$A_{1.1}$ = absorbance of standard containing 1.1 mg of beryllium versus reference solution

$A_{1.6}$ = absorbance of standard containing 1.6 mg of beryllium versus reference solution

0.5 = difference between concentration of standard containing 1.6 mg and that containing 1.1 mg of beryllium

Table I

Comparison of the Differential Spectrophotometric Method for the Determination of Beryllium with the Indirect Fluoride Titration Method

			Beryllium, mg		
Sample	Absorbance versus Reference Standard	Dilution Factor	Differential Spectrophotometry A	Volumetry B	Difference A-B
1	0.288	13.3	17.7	17.7	0.0
2	0.264	13.3	17.2	17.5	-0.3
3	0.446	13.3	20.3	19.7	+0.6
4	0.525	12.5	20.4	20.5	-0.1
5	0.500	25.0	40.0	39.7	+0.3
				Average Difference	0.3

Beryllium Standards

Reference Standard - 1.0 mg Be per 100 ml

Be, mg per 100 ml	Absorbance
1.0	0.000
1.1	0.105
1.2	0.195
1.4	0.354
1.6	0.500

Since the volumetric, fluoride-complex method[8] had been standardized against a standard solution of beryllium, the results by this method can be considered as reliable values. Hence, the excellent order of agreement between the two methods is indicative of the reliability of the differential spectrophotometric method.

The particular method of calculation used was chosen because of the failure of the plot of the absorbance versus concentration to go through the origin. Further tests were then made on the conformity of the complex to Beer's law. The absorbance of the complex for beryllium concentrations of 1.1 to 1.9 mg per 100 ml was measured daily over a period of 10 days. The plot of the average absorbance versus concentration is shown in Figure 1. Excellent conformity to Beer's law is demonstrated for the range of concentration of 1.1 to 1.6 mg per 100 ml. Higher concentrations deviate sharply. It is of interest to note that the concentration of Sample No. 4 of Table 1 exceeded the range of conformity, yet the agreement is still very good.

Optimum Wavelength for Absorbance Measurements

The partial absorption spectrum of the beryllium-p-nitrobenzeneazoorcinol complex, shown in Figure 2, exhibits a broad maximum from 505 to 515 millimicrons with the center point at about 510 millimicrons, the point which was chosen as the optimum wavelength for the absorbance measurements. The existence of the broad maximum makes it possible to apply a Beckman Model B spectrophotometer, or its equivalent, in these measurements of absorbance.

The Effect of Time on the Absorbance of the Beryllium-p-Nitrobenzeneazoorcinol Complex

The color of the complex is at its maximum intensity, as seen in Figure 3, within ten minutes after the addition of the color reagent and is stable over a period of at least three hours. Subsequent tests showed that the absorbance of the complex diminished about five per cent after 15 hours.

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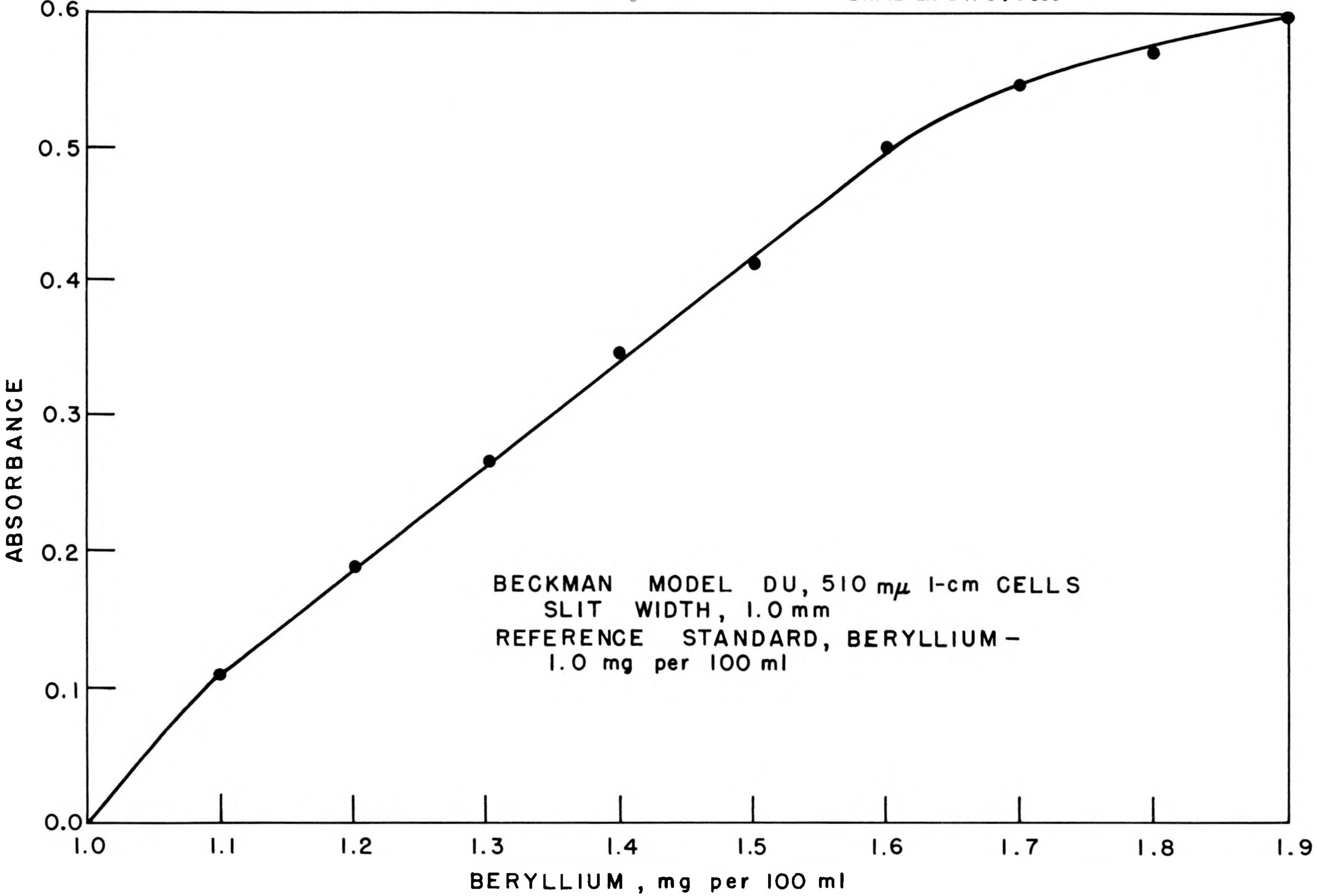

FIGURE 1. STANDARD CURVE FOR THE DETERMINATION OF BERYLLIUM WITH p-NITROBENZENEAZOORCINOL BY DIFFERENTIAL SPECTROPHOTOMETRY

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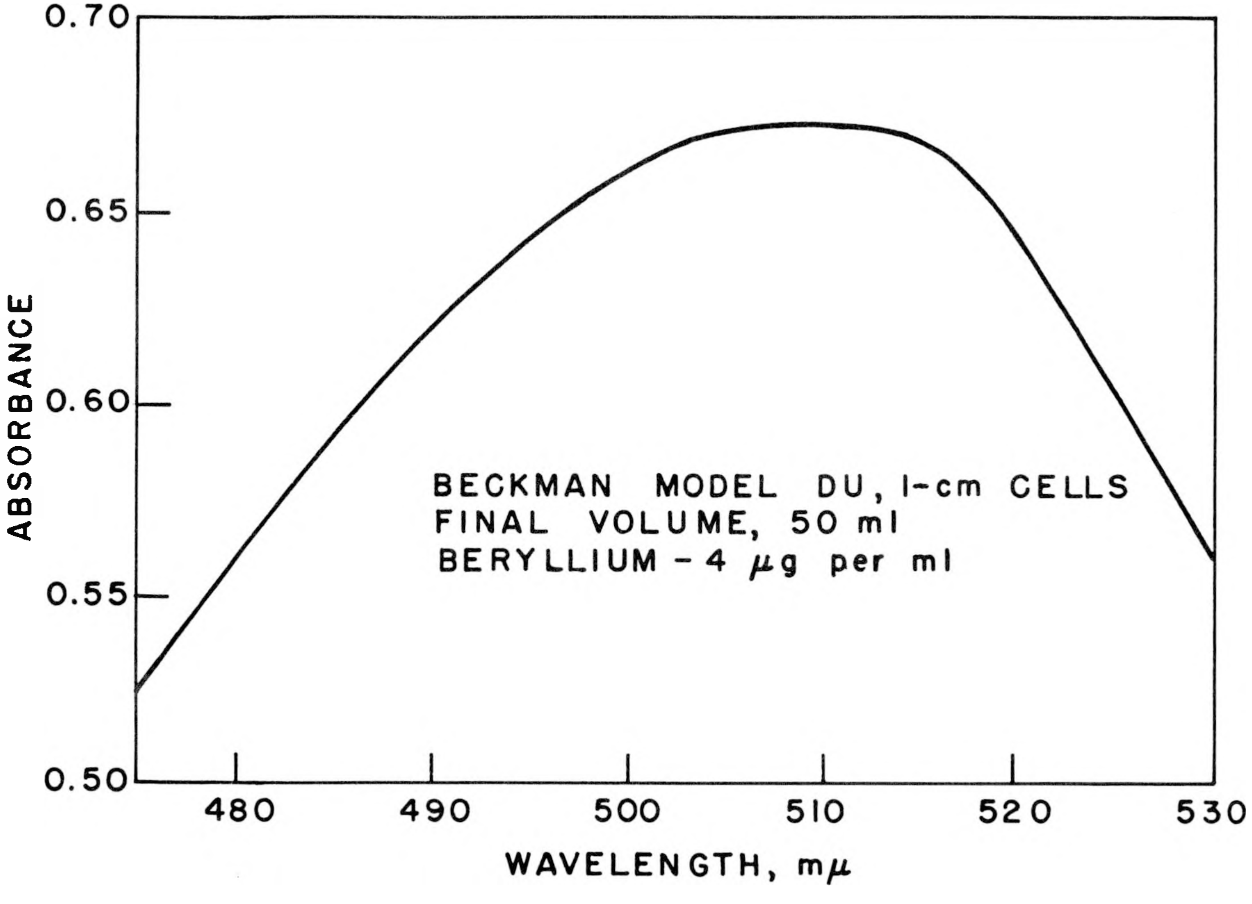

FIGURE 2. PARTIAL ABSORPTION SPECTRUM OF THE BERYLLIUM-p-NITROBENZENEAZOORCINOL COMPLEX

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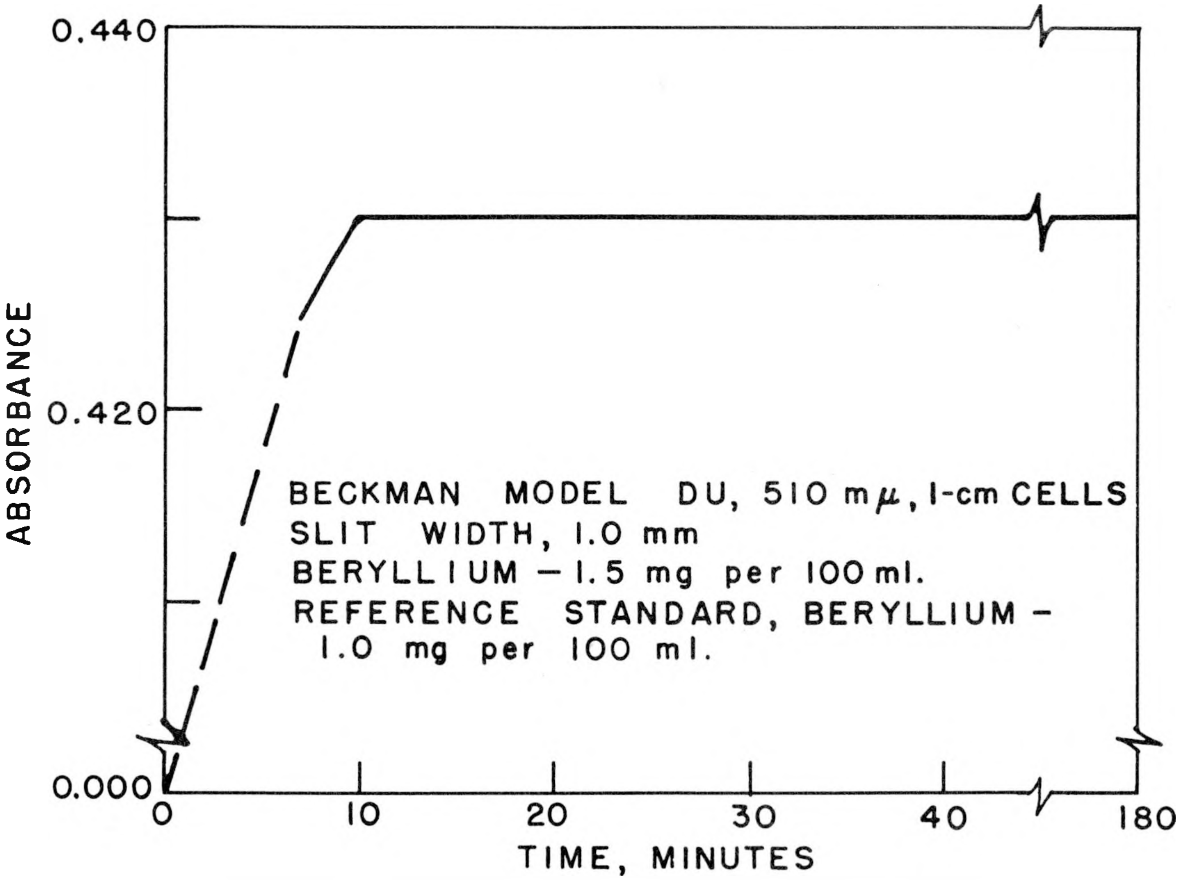

FIGURE 3. EFFECT OF TIME ON THE COLOR DEVELOPMENT AND STABILITY OF THE BERYLLIUM - p - NITROBENZENEAZOORCINOL COMPLEX

Effect of Alkalinity on the Beryllium p-Nitrobenzeneazoorcinol Complex

Vinci[13] reported that the absorbance of the complex is dependent upon the alkalinity and recommended the use of the sodium borate-sodium citrate buffer solution to maintain constant alkalinity. Since solutions of beryllium are of necessity maintained quite acidic to avoid hydrolysis, a step was added to the procedure whereby the original acidity was essentially neutralized with 2 N sodium hydroxide. The addition of the buffer solution thus provided the rather rigid control of the basicity that the method requires.

Interferences

Since zinc and magnesium also form colored complexes with p-nitrobenzeneazoorcinol, these elements also interfere. Those cations that would normally precipitate as hydrous oxides in alkaline solution were complexed with citrate ion and their interference is thereby prevented.

It was of interest to ascertain the extent of interference of uranium, aluminum, and fluoride ions which present certain difficulties in most methods of analysis.

The effect of uranium and aluminum was determined by adding varying amounts of the metals to two series of solutions containing a known amount of beryllium. The complex was formed and absorbance measurements were made versus the reference standard that did not contain any interfering metal. The data are shown in Table 2. The interference of fluoride was determined by adding known amounts of sodium fluoride to several solutions containing 1 mg of beryllium. The complex was formed and its absorbance was measured versus a reagent blank containing 10 ml of buffer and 20 ml of color reagent in a volume of 100 ml. The results are shown in Table 3.

Table 2

The Effect of Uranium and Aluminum on the Color Intensity of the Beryllium-p-Nitrobenzeneazoorcinol Complex

Beckman Model DU, 510 mμ, 1-cm cells
Slit, 1.0 mm
Final volume, 100 ml
Reference Standard, 1.0 mg per 100 ml
Beryllium present, 1.2 mg per 100 ml

Weight Ratio Metal to Beryllium	Absorbance	Beryllium Found, mg	Correction Factor Ratio: Be present / Be found
Uranium			
0	0.187	1.20	1.000
2.5	0.193	1.21	0.995
5	0.205	1.22	0.984
10	0.220	1.24	0.972
Aluminum			
0	0.194	1.20	1.000
0.05	0.195	1.20	0.998
1	0.196	1.20	0.998
5	0.206	1.21	0.987
10	0.230	1.24	0.973

Table 3

The Effect of Fluoride on the Color Intensity of the Beryllium-p-Nitrobenzeneazoorcinol Complex

Beryllium, 1.0 mg per 100 ml
Buffer, 10 ml
Color reagent, 20 ml
Reference Solution - Reagent Blank

Weight Ratio F/Be	Absorbance
0.0	1.45
1.0	1.45
5.0	1.45
50	1.43
110	1.40

The data indicate that a five-fold excess of either uranium or aluminum can be tolerated without causing an error greater than 2 per cent. By means of the appropriate correction factor, however, the interference of larger amounts of uranium and aluminum can be corrected for by multiplying the apparent amount of beryllium found by the factor corresponding to the metal: beryllium weight ratio.

The tests indicate that rather large amounts of fluoride can be tolerated without affecting the color of the beryllium complex. The fact that moderate amounts of fluoride produced no fading leads to the conclusion that the colored complex is more associated than the beryllium fluoride complex.

Precision of the Method

The precision of the method was determined by analyzing a number of solutions containing about equal concentrations of beryllium and uranium. From the data obtained, the coefficient of variation was calculated for each sample type from the difference between duplicates[9]. The data are shown in Table 4.

Table 4

Determination of Beryllium by Differential Spectrophotometry. Calculation of the Coefficient of Variation for Each Sample from the Difference Between Duplicates

Sample	Beryllium Per Cent	Average $\overline{x}$	Difference Per Cent
1	8.18 8.29	8.24	1.34
2	6.80 6.91	6.86	1.60
3	8.02 7.97	8.00	0.62
4	5.69 5.64	5.66	0.88
5	6.71 6.68	6.69	0.45
6	8.53 8.79	8.66	3.00
7	8.47 8.43	8.45	0.47
8	8.00 8.00	8.00	0.00
9	8.09 8.23	8.16	1.72
10	9.00 8.93	8.96	0.78
11	3.66 3.65	3.65	0.27
12	7.26 7.24	7.25	0.27
13	7.15 7.13	7.14	0.28
14	8.31 8.29	8.30	0.24
15	8.24 8.27	8.25	0.36

Table 4 continued on Page 15

Table 4 (Continued)

P = number of pairs of duplicates

V = coefficient of variation, per cent

D = difference between duplicates, per cent

$$V^2 = \frac{\Sigma D^2}{2P} = \frac{18.87}{30} = 0.628$$

$$V = \sqrt{0.628} = 0.8 \text{ per cent}$$

The coefficient of variation of the differential spectrophotometric method is less than one per cent for duplicate determinations. This order of precision is equal to that which can be obtained by either gravimetric or volumetric methods, and, more important, this precision is achieved with far greater ease and rapidity than by other methods.

The results in Table 4 were calculated by the use of the equation shown previously. There are obviously alternate methods for calculating the beryllium content. An obvious one is to refer to the standard curve, as shown in Figure 1, which is a composite curve compiled over a period of several days. Since the method is dependent for its high degree of precision on the reliability of the reference solution and the differences in absorbance of standard solutions from this reference solution, in order to achieve the maximum precision of the method, the standard curve should be re-established each time the method is used. For routine usage, calculation from a standard curve, which is rechecked periodically, is quite satisfactory.

SUMMARY

Overall evaluation of the data obtained by the differential spectrophotometric method leads to the conclusion that this method is satisfactory for the determination of beryllium with a coefficient of variation of less than one per cent. The method is less time-consuming than precipitation methods and is particularly suited for samples in which the concentration of beryllium is generally known. The method is essentially free from interferences and is applicable to the determination of beryllium in the presence of moderate amounts of uranium and aluminum, whereas the indirect fluoride titration method and gravimetric techniques require a prior separation. Relatively large amounts of fluoride can be tolerated without interference. Other metals, present in small amounts, are rendered inactive through the formation of citrate complexes.

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