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SPECTROPHOTOMETRIC DETERMINATION OF CERIUM WITH TIRON

ABSTRACT

A spectrophotometric method for the determination of cerium with Tiron (disodium-1,2-dihydroxybenzene-3,5-disulfonate) was applied to the determination of cerium in samples which contain uranium and zirconium. The cerium-Tiron complex in solutions of pH 8 or greater exhibits an absorption maximum at 500 mμ. This reagent does not react with any other lanthanide element. The interference of iron, uranium, and zirconium was eliminated by extracting these interfering elements with a solution of trioctylphosphine oxide in cyclohexane.

SPECTROPHOTOMETRIC DETERMINATION OF CERIUM WITH TIRON

B. L. McDowell, A. S. Meyer, Jr., and J. C. White

Oak Ridge National Laboratory
Oak Ridge, Tennessee

A rather limited number of methods has been proposed for the spectrophotometric determination of cerium. These have included several methods which are based on the measurement of the yellow color of the cerium(IV) ion in either the visible or ultraviolet region of the spectrum.[1,2,3,5,7] Freedman and Hume[2] and Medalia and Byrne[5] measured the color intensity in the ultraviolet region in order to increase the sensitivity. The measurement of the absorbance of various complexes of cerium has also been investigated. Telep and Boltz[9] proposed a procedure for the measurement of the absorbance of the cerium-hydrogen peroxide complex in a concentrated solution of potassium carbonate in the ultraviolet region of the spectrum. In order to avoid the difficulties due to flocculated colloids when the determination is made in the potassium carbonate-hydrogen peroxide solution, Conca and Merritt[1] carried out the measurement in a solution of potassium carbonate.

Gordon and Feibush[3] reported an indirect spectrophotometric method for the determination of cerium. The cerium(III) is oxidized to cerium(IV), after which the unstable cerium(IV) is immediately reacted with a measured excess of ferrous ammonium sulfate. The excess iron(II), which is determined spectrophotometrically with o-phenanthroline, is a measure of the cerium content of the solution.

Sarma[8] reported that cerium(IV) forms a soluble violet colored complex in a nearly neutral or alkaline medium with the disodium salt of 4,5-dihydroxy-m-benzenedisulfonic acid (Tiron), which was first introduced by Yoe and Jones[12] as a very sensitive reagent for the determination of iron. Yoe and Armstrong[11] later described Tiron as a reagent for the determination of titanium. They list VO^{+2}, MoO_4^{-2}, OsO_4^{-2}, and UO_2^{+2} as interfering ions which form colored complexes, and Al^{+3}, Ca^{+2}, Ce^{+3}, Hg^{+2}, Pb^{+2}, Sn^{+4}, Th^{+4}, ZrO^{+2}, and WO_4^{-2} as ions which consume reagent but do not form colored complexes.

The purpose of this investigation was to make a detailed photometric study of the cerium-Tiron system; to establish optimum conditions for color formation in sulfate solutions of samples which also contain uranium and zirconium; to determine the nature and extent of interferences, and methods for their elimination; and to attempt to establish the complex form(s).

EXPERIMENTAL

Apparatus

Absorbance measurements were made with a Beckman Model DU spectrophotometer, using 1.000-cm matched Corex cells.

Measurements of the pH value of solutions were made with a Beckman Model H2 pH meter with a glass-calomel electrode system.

Reagents

A standard solution of cerium(III) was prepared by dissolving especially prepared cerium(III) fluoride in sulfuric acid.

Eastman's white label 4,5-dihydroxy-m-benzenedisulfonic acid disodium salt (Tiron) was used as the chromogenic reagent. The Tiron was added either as a weighed quantity of the solid reagent or as a measured volume of an aqueous solution which contained 5 mg per ml of Tiron.

Sodium acetate solution, 25 w/v per cent, was prepared from reagent grade sodium acetate.

An 0.1 M solution of trioctylphosphine oxide (TOPO) in cyclohexane, which was used for the extraction of some interfering ions, was prepared by dissolving 38.6 g of trioctylphosphine oxide in cyclohexane and then diluting the solution to a volume of one liter with cyclohexane.

Sodium sulfate solution, 25 w/v per cent, was prepared from reagent grade sodium sulfate.

Test paper, pHydroin, which is manufactured by the Micro Essential Laboratory of Brooklyn, New York, was used as an indicator for the estimation of the pH of the solutions.

Specially prepared, spectrochemically pure, cerium(III) fluoride was used to prepare a standard cerium(III) solution. A 712-mg portion of cerium(III) fluoride was dissolved by repeated heating to fumes of sulfur trioxide with a 3:1 mixture of hydrochloric and sulfuric acids. A concentration of 4.99 mg of cerium per ml was determined titrimetrically by the sodium bismuthate method of Metzger.[6]

Formation of the Cerium-Tiron Complex

Sarma[8] recommended that the complex be formed in a neutral or slightly alkaline solution which contained one w/v per cent Tiron and 10 w/v per cent sodium acetate. He found the absorption maximum at 500 mμ. He also noted that while several hours were required for complete color development of the solution which contained cerium(III), the color development of the solution of cerium(IV) was instantaneous.

The absorption spectra of these solutions was determined using the procedure suggested by Sarma. The partial spectra are shown in Figure 1. The data essentially confirm Sarma's findings. Apparently the same complex is formed regardless of oxidation state of the cerium. Since color development is slow for cerium(III) but rapid for cerium(IV), several methods were tested as a means of accelerating the oxidation process. Standard cerium(III) solutions were heated to 100° C for 30 minutes but still did not attain full color intensity until they had aged for nearly six hours. Chemical oxidants such as hydrogen peroxide and potassium iodate were investigated but proved ineffective. As a result of this experience, a standard color development period of some six hours was adopted.

The method of Job[4] was used to characterize the complexes which are formed between Tiron and cerium(III) and cerium(IV). The data for both of these characterization studies are presented in Figure 2. The spectral measurements at 500 mμ indicate that the stoichiometry of the complexes is three to one.

Effect of pH and Ionic Strength

Sarma stated that the color was developed in nearly neutral or slightly alkaline media. Preliminary tests were carried out in which the color was developed in solutions at pH seven and 10. At pH seven, immediate color development was not observed even in solutions that contained cerium(IV). However, at pH 10, the maximum absorbance was reached within 30 minutes for either cerium(III) or (IV).

A series of solutions was then prepared each of which contained 500 µg of cerium(III) and 250 mg of Tiron. The solutions were adjusted to various pH values from three to 10 with either dilute (1:1) H_2SO_4 or NaOH (50 w/v per cent). The solutions which had been adjusted to pH values of 8.5, 9.0, 9.5, and 10.0 showed a constant absorbance value at 500 mµ which indicated maximum color development at this range of pH. The absorbance values for solutions below pH 8.5 decreased rapidly to pH five, below which a relatively constant absorbance value of approximately 10 per cent of the maximum value was measured.

Sodium acetate is an inefficient buffer in the solution since the pH of the solutions was observed to vary by as much as two pH units within the period of color development. No satisfactory buffer is available for this system. Ammonium and phosphate salts, the most likely buffers, are not tolerable since the ammonium ion interferes by reacting with Tiron and phosphate by reacting with cerium.

In order to determine whether ionic strength as well as pH is a critical factor in color development, several solutions were prepared which contained a constant amount of $NaClO_4$ (3 g). The solutions were adjusted to pH values of 6.0, 7.0, 8.0, 9.0, and 10.0. For these samples which contained added salt, the region of constant absorbance for varying pH values was found to extend from 8.0 to 10.0. More precise results were obtained with the added salt for constant ionic strength.

Since the samples for which this method was developed would be contained in a sulfuric acid solution, sodium sulfate rather than sodium perchlorate was investigated as a means of maintaining a constant ionic strength in the solution. As much as 2.5 g of sodium sulfate was found to have no effect on the absorbance of solutions of pH 10 or greater which contained either cerium(III) or cerium(IV).

Effect of Tiron Concentration

The effect of concentration of Tiron on the color development was determined in solutions which contained a constant amount of cerium(III), 10 ppm in the final solution, and amounts of Tiron from one to 250 mg. On the basis of the data shown in Table I, it is indicated that 5 mg of Tiron is sufficient to develop full color intensity with 250 μg of cerium(III). This quantity is considerably less than that recommended by Sarma. A quantity of 25 mg of Tiron was selected as sufficient for complete development of the color of solutions of cerium whose absorbance could be conveniently measured photometrically in one-cm cuvettes.

Table I

Effect of Concentration of Tiron on Determination of Cerium

Conditions: 250 μg of cerium(III)
25-ml volume
5 per cent Na_2SO_4

Weight of Tiron, mg	Absorbance
1	0.081
5	.321
10	.327
25	.328
50	.327
75	.327
250	.328

The use of 25 mg of Tiron rather than the 250 mg quantity suggested by Sarma resulted in a new, second absorption peak, as shown in Figure 3 at 440 mμ of much greater intensity than the 500 mμ maximum.

This maximum almost coincides with the wavelength of a less intense maximum which was observed for solutions of Tiron alone at high pH values. This phenomenon is much more pronounced in solutions of trivalent cerium, and under some conditions the absorbance at 440 mμ is five times as great as that at 500 mμ. The intensity of the absorbance at 440 mμ is an extremely sensitive function of the pH of the solution. Attempts to characterize the interaction between cerium and Tiron by measurement at 440 mμ were unsuccessful because of the poor reproducibility of absorbance measurements at this wavelength.

Calibration Curve

Since Tiron can react with strong oxidizing agents which are required for the oxidation of cerium(III) to cerium(IV) and since almost identical molar absorbance indices were obtained for solutions prepared from cerium(III) and cerium(IV), standard calibration curves were obtained from solutions which were prepared from trivalent cerium. In accordance with the observations which were noted during the exploratory experiments, the following procedure was followed. The desired volume of the standard cerium solution was transferred to a 50-ml beaker and if necessary acidified to a pH of less than three with a few drops of H_2SO_4. The Tiron reagent was added to the acid solution as 5 ml of an 0.5 w/v per cent solution. Tiron should be added before adjustment of pH since cerium will precipitate in neutral or alkaline solution. The pH of the solution was adjusted to pH of approximately 10 with a 10 w/v per cent solution of sodium hydroxide as indicated by pHydroin paper. The solution was transferred to a 25-ml volumetric flask and diluted to volume. Despite the fact that complete color development had been noted in less than one hour, the solutions were aged for a period of six hours before the absorbance was measured. All absorbance measurements were made with a Beckman Model DU spectrophotometer at 500 mμ against a reference solution of reagents which was prepared in the same manner. The data for these standards, which are presented in Figure 4, conform to Beer's law up to a concentration of 60 ppm of cerium(III). On the basis of standards, the precision of the method was found to be less than three per cent.

Interfering Substances

In order to determine the limiting concentration of interfering substances, a solution of the interfering ion in either water, dilute HCl, or dilute H_2SO_4 was added to the cerium standard, which contained 400 µg of cerium, before the color was developed. Since the precision of the method was found to be three per cent, concentrations of ions which produced this magnitude of deviation was considered as an interfering concentration. In Table II some of the cations are listed which, on the basis of the work of Yoe et al,[11,12] might be expected to interfere with the determination of cerium. Also, the concentration which was experimentally determined as causing interference is shown in this table.

Table II

Effect of Diverse Ions

Interfering Substance	Concentration for Relative Error of 3 Per Cent or Greater, ppm
Al	320
Ca	80
Cr(III)	320
Cr(VI)	15
Cu	40
Dy	> 15
Fe(III)	0.2
Gd	> 15
La	> 10
Mg	160
Mo	400
Nd	> 15
Nb	4
Ni	100
Pr	> 15
Sm	> 15
Ti	80
U	5
V	40
W	160
Y	> 15
Yb	> 15
Zr	45

Iron(III), uranium, and niobium interfere seriously with the determination of cerium by forming colored complexes with the Tiron and must be removed. Also, zirconium interferes with the determination of cerium by forming a colorless complex with Tiron; therefore, enough reagent must be added to complex all of the zirconium as well as the cerium, or the zirconium must be separated.

Of the common anions, chloride, carbonate, bicarbonate, perchlorate, and sulfate in concentrations up to several thousand parts per million produced negligible errors in the determination of cerium. Nitrate, however, oxidizes the reagent and must be absent from the final solution. If any fluoride is present in the solution, it complexes the cerium more strongly than the Tiron and bleaches the color of the complex. Phosphate in low concentration bleaches the color of the cerium-Tiron complex and must be absent from the solution. Citrate, tartrate, oxalate, and salicylate were found to have a slight bleaching effect on the complex when they were present in high concentrations; however, these anions were not investigated thoroughly and no definite conclusions can be drawn as to their interference.

A precipitate of the metal hydroxide formed in some of the solutions which were prepared for the interference studies when the pH of the solution was adjusted to 10 or greater. These precipitates were removed by filtration before the absorbance of the solutions was measured.

Application to Sulfate Solutions of Zirconium and Uranium

The method was applied to sulfate solutions of zirconium and uranium which also contained some iron. Since iron interferes strongly as does uranium, a method of removal was required. White and co-workers[10] have demonstrated that trioctylphosphine oxide (TOPO) will extract iron, uranium, and zirconium under certain conditions but will not extract cerium. The following procedure was found to be satisfactory for the removal of the interfering elements, zirconium, uranium, and iron, prior to the development of the cerium-Tiron color. The volumes of the TOPO solution which are specified are sufficient to remove 20 mg of zirconium and 10 mg of uranium from a solution which contains sulfate if the solution is at least 6 M with respect to hydrochloric acid.

The aqueous phase was made at least 6 M with respect to hydrochloric acid by the addition of concentrated hydrochloric acid. After the addition of 10 ml of an 0.1 M solution of TOPO to the aqueous solution, the phases were equilibrated for three minutes. After the phases had been separated, the aqueous phase was extracted with another 10-ml portion of the solution of TOPO. A suitable volume of the aqueous phase was taken as a test portion for the development of the cerium-Tiron color according to the procedure which was given previously. The aqueous to organic volume ratio was maintained at approximately one. By using correspondingly larger portions of the solution of TOPO, larger amounts of uranium and zirconium can be removed.

Iron(III) is extracted from a chloride solution into a solution of TOPO with the uranium and, unless the amount of iron(III) in the sample is sufficiently large to complex an appreciable amount of the TOPO, no added volume of the solution of TOPO is necessary.

Results of determinations of cerium in samples of alkali metal fluoride which contain zirconium and uranium are included in Table III.

Table III

Determination of Cerium in Samples of Sulfuric Acid

	Cerium, Per Cent	
Sample Type	Volumetric[a]	Spectrophotometric
Alkali Metal Fluorides		
A	6.19	6.11
B	6.28	6.21
C	6.26	6.25
D	5.67	6.06
Alkali Metal Fluorides Which Contain Zirconium and Uranium[b]		
A	2.85	2.76
B	2.63	2.62
C	5.33	5.13
D	2.73	3.01

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[a] Cerium was determined by the method of Metzger.[6]

[b] These samples were extracted with TOPO to remove iron, zirconium, and uranium.

CONCLUSION

The data which has been obtained is not sufficient to characterize completely the interaction of Tiron and cerium. Nevertheless, the absorbance at 500 mμ is reproducible under a considerable variation of conditions and suitable for a spectrophotometric determination of cerium.

Since the variation of absorbance with solution conditions at 440 mμ does not parallel those at 500 mμ, it would appear that more than one chromogenic species is present in the solution. The maximum at 440 mμ almost coincides with the wavelength of the absorption maximum of the reference solutions and thus might represent a product of a reaction of Tiron which is merely catalyzed by cerium. Since the maximum disappears with increasing concentrations of Tiron, the previous postulation does not appear to be tenable. In the continuous variation plots (Figure 2) slight anomalies in the absorbances are observed for ratios of Tiron to cerium between three to one and 0.25 to one, where precipitation occurs. This anomalyous behavior could be explained on the basis of partial hydrolysis or a complex of lower order. Exact characterization of lower order complexes and possible application to a more sensitive determination of cerium would require a suitable buffer. Such a buffer must furnish a reasonable buffering capacity in the region of pH 10 and must be inert toward Tiron and cerium and not absorb excessively at 440 mμ. Of the commonly used buffers salts of the polybasic acids complex cerium and ammonium salts and borates react with Tiron.

The cerium-Tiron system shows conformity to Beer's law for the range of cerium concentrations from 0.8 to 60 ppm with an optimum concentration range of three to 30 ppm of cerium. The method is precise. A standard deviation of three per cent was noted for both standards and samples.

A number of ions interferes with this determination of cerium, but a method is proposed for the elimination of several of these ions.

REFERENCES

1. Conca, N., Merritt, C., Anal. Chem., <u>28</u>, 1264 (1956).
2. Freedman, A. J., Hume, D. N., Ibid., <u>22</u>, 932 (1950).
3. Gordon, L., Feibush, A. M., Ibid., <u>27</u>, 1050 (1955).
4. Job, P., Ann. chim., [11] <u>6</u>, 97 (1936).
5. Medalia, A. J., Byrne, B. J., Anal. Chem., <u>23</u>, 453 (1951).
6. Metzger, F. J., J. Am. Chem. Soc., <u>31</u>, 523 (1909).
7. Plank, J., Z. Anal. Chem., <u>116</u>, 312 (1939).
8. Sarma, B., J. Sci. Industr. Res., <u>14B</u>, 538 (1955).
9. Telep, G., Boltz, D. F., Anal. Chem., <u>25</u>, 971 (1953).
10. White, J.C., "Extraction of the Elements with Trioctylphosphine Oxide from Acidic Solutions," Report No. ORNL-CF-56-9-18, Sept.6,1956.
11. Yoe, J. H., Armstrong, A. R., Anal. Chem., <u>19</u>, 100 (1947).
12. Yoe, J. H., Jones, A. L., Anal. Chem., <u>16</u>, 111 (1944).

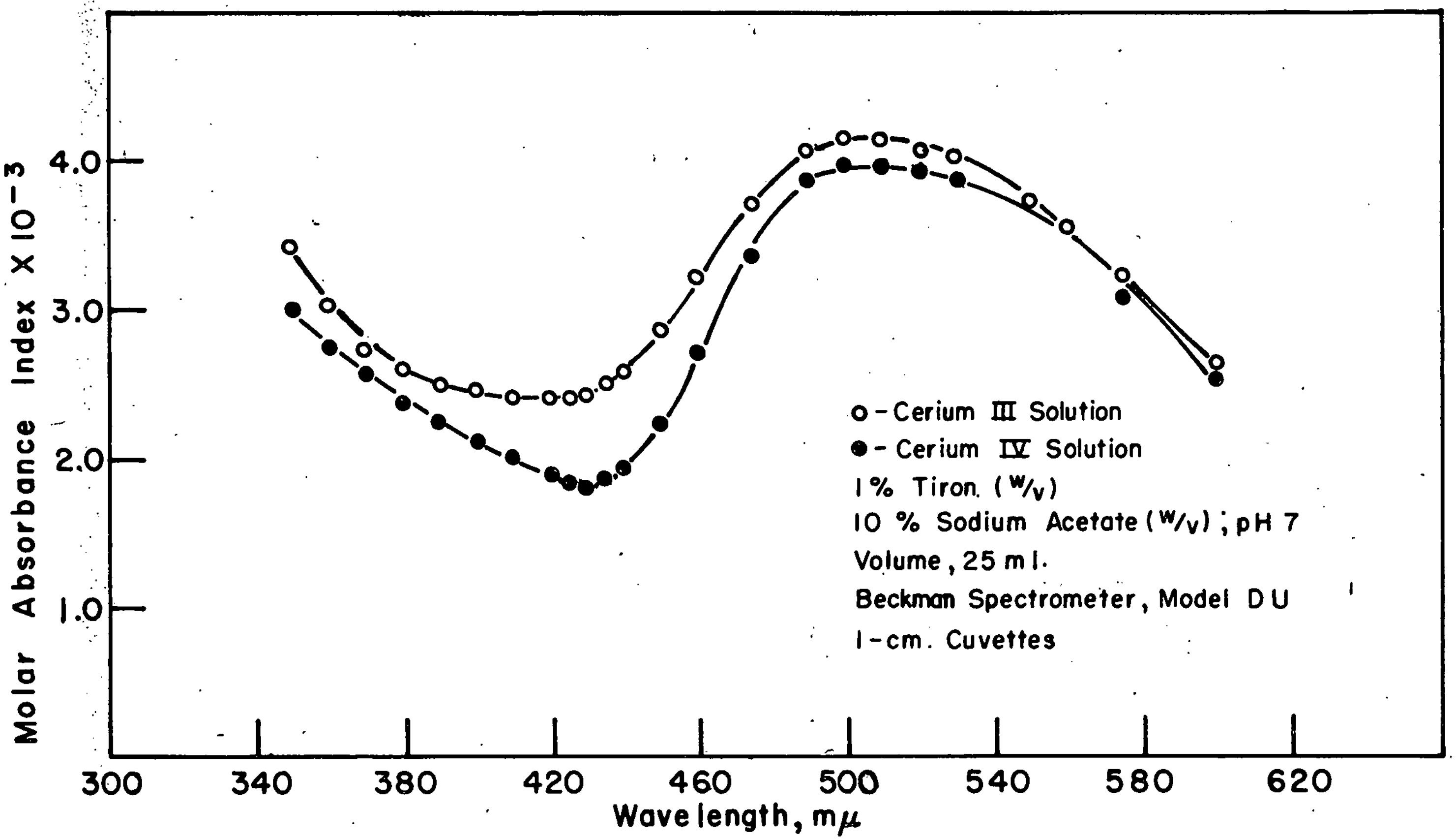

FIGURE 1, PARTIAL ABSORPTION SPECTRUM OF THE CERIUM TIRON COMPLEX

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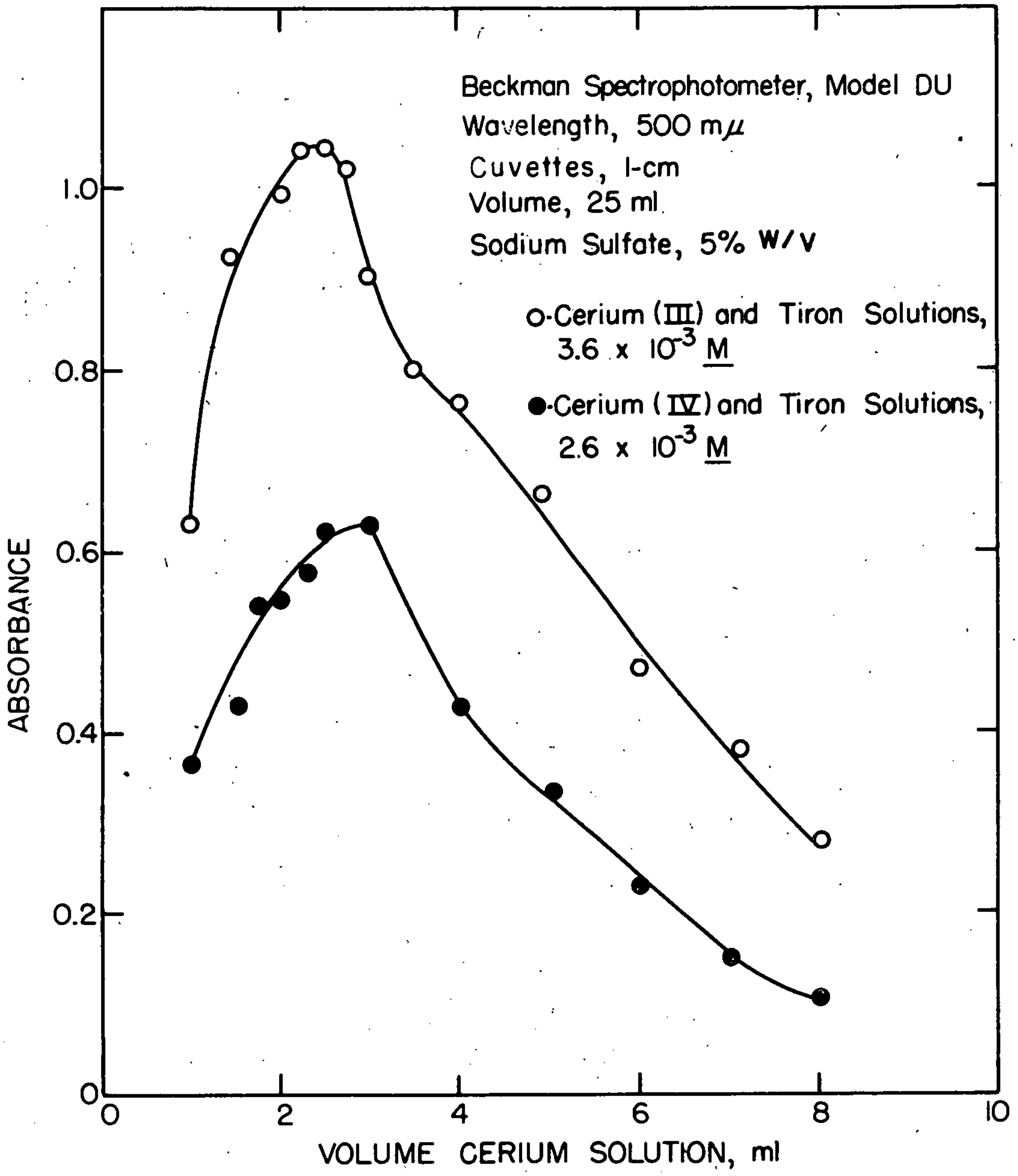

FIGURE 2, CURVES FOR THE CHARACTERIZATION OF THE CERIUM (III) AND CERIUM (IV) - TIRON COMPLEXES BY THE METHOD OF CONTINUOUS VARIATION

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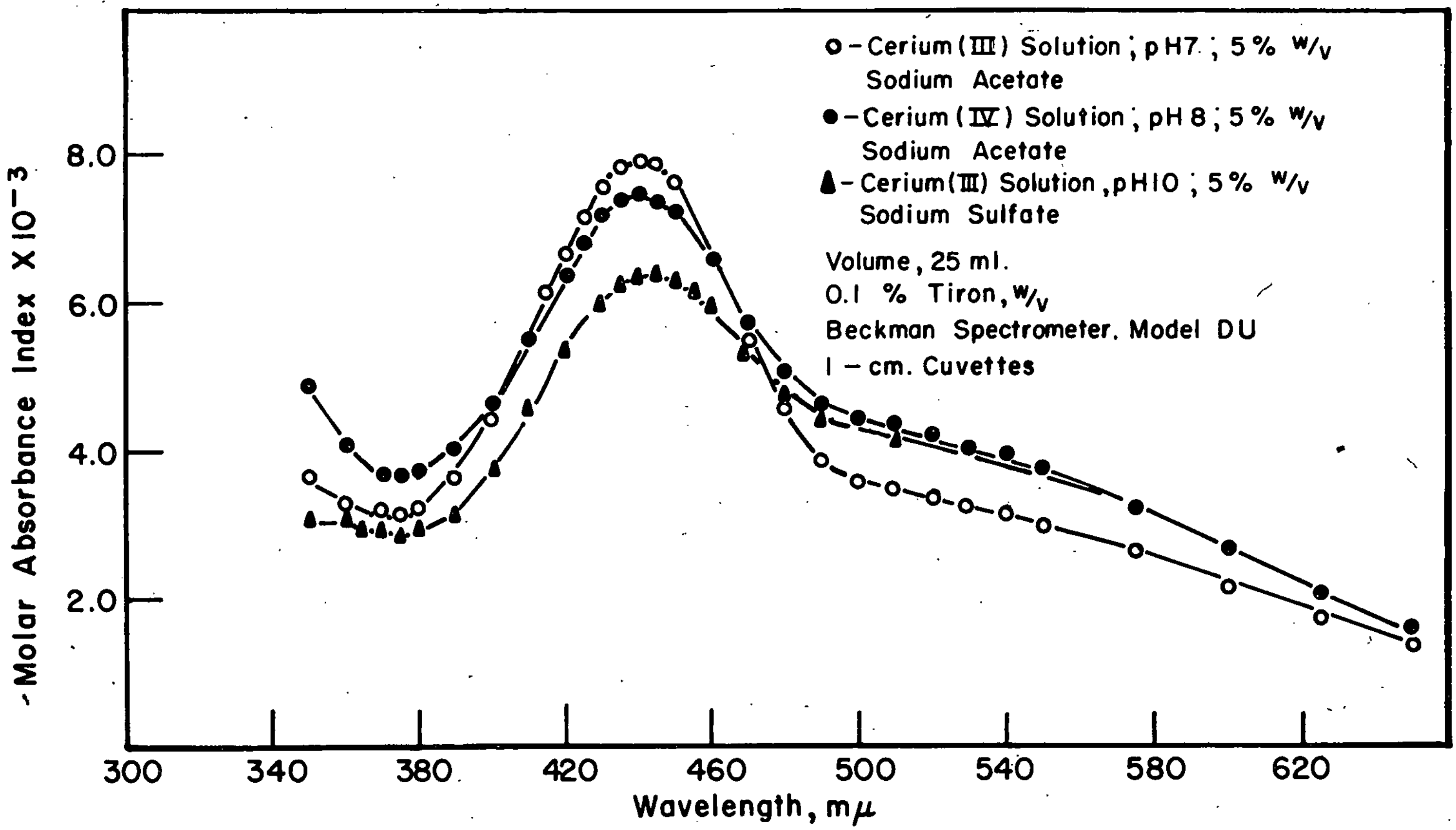

FIGURE 3, ABSORPTION SPECTRA OF THE CERIUM TIRON COMPLEX EFFECT OF LOW TIRON CONCENTRATION

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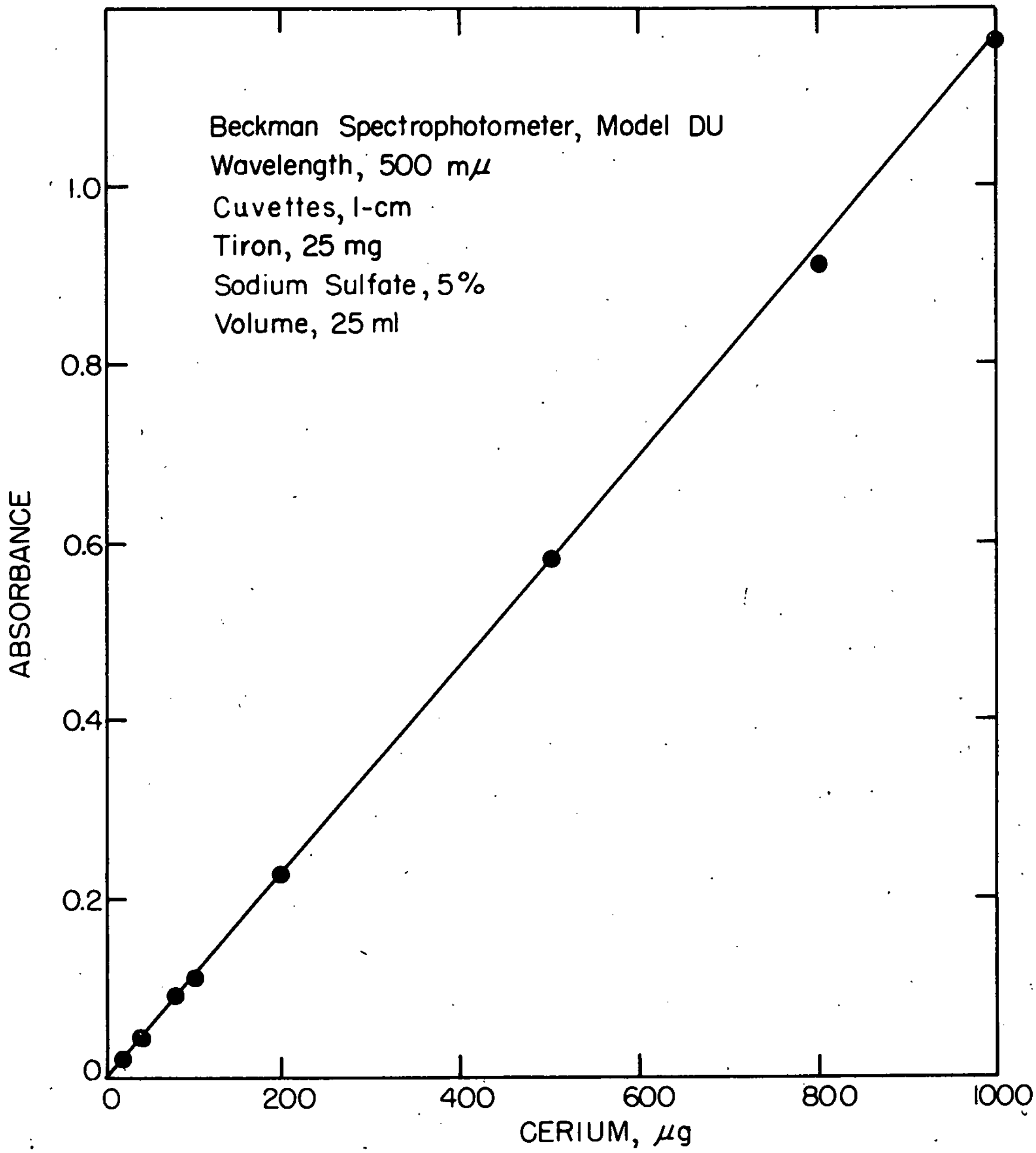

FIGURE 4, STANDARD CURVE FOR THE DETERMINATION OF CERIUM WITH TIRON