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DIFFERENTIAL SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM

D. L. Manning
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ABSTRACT

Differential spectrophotometry has been applied to the determination of zirconium as the alizarin sulfonate complex in perchloric acid solution. Under ideal conditions the coefficient of variation is less than one per cent and compares favorably with the best precision obtainable by gravimetric procedures. The method is rapid and particularly suited for samples when the zirconium concentration is generally known. There are few interferences; fluoride, sulfate, and phosphate are the primary interferences.

DIFFERENTIAL SPECTROPHOTOMETRIC DETERMINATION OF ZIRCONIUM

INTRODUCTION

The ever-increasing importance of zirconium and its compounds has led to the development of a number of methods for its determination. Most of the investigations have been concerned with the development of organic precipitants such as mandelic acid and its halo-derivatives(5,10). These reagents are decidedly superior to phosphate(6) and cupferron(7) as quantitative reagents. In order to eliminate the ignition step, and save time, volumetric modifications have been devised. White(12) developed a titrimetric method based on the separation of zirconium as the halo-mandelate. Kolthoff and Johnson(9) reported on an amperometric method based on the use of m-nitrophenylarsonic acid. Recently Fritz and Fulda(3) demonstrated that zirconium can be titrated with ethylenediaminetetraacetic acid (EDTA).

This investigation was undertaken to apply the advantages of differential spectrophotometry to the determination of trace amounts of zirconium. Hiskey(8) and Bastian(1) have emphasized that the accuracy and precision which can be attained by differential spectrophotometry are equivalent to volumetric and gravimetric techniques. In the differential method the optical density 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 the given component are then measured against this zero point in the usual way. In order to obtain the increased light needed to adjust the zero scale by this procedure, the spectrophotometer slit is set at wider apertures than normal. For systems obeying Beer's

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law at wider slit openings, the resultant optical density readings are directly proportional to the difference in concentration between the zero point standard and the solution in question.

The reaction between zirconium and sodium alizarin sulfonate is an excellent color reaction for the determination of zirconium and was used in this study.

EXPERIMENTAL

Application of Differential Spectrophotometry to the Zirconium-Alizarin-Red-S Reaction

Green(4) applied the reaction between zirconium and alizarin-red-S to the determination of low concentrations of zirconium. The "lake" is formed in either hydrochloric or perchloric acid media and its absorbancy is measured at 530 mμ. Since zirconium forms a very weak complex with perchloric acid, this medium was used in this study. The concentration of acid present is not critical over the range of acidity from pH 0 to 2. The acidity generally used is in the pH range of 1 to 2. Higher acid concentrations tend to cause a decrease in intensity of the color formed; while hydrolysis readily occurs in less acidic solutions. In this particular application, sensitivity is of minor importance so some sensitivity is sacrificed to permit the use of 1 M $HClO_4$ and thereby prevent hydrolysis. The color formed in this medium reaches its maximum intensity within one-half hour as shown in Figure 1 and is stable for at least three hours. Reproducible measurements can be made after 30 minutes, however.

For systems which obey Beer's law, the accuracy possible by differential colorimetry increases as the absorbancy of the zero point standard (reference standard) increases. Eventually, however, because of the combined effects of broadening band widths of light emitted by the widening slit apertures,

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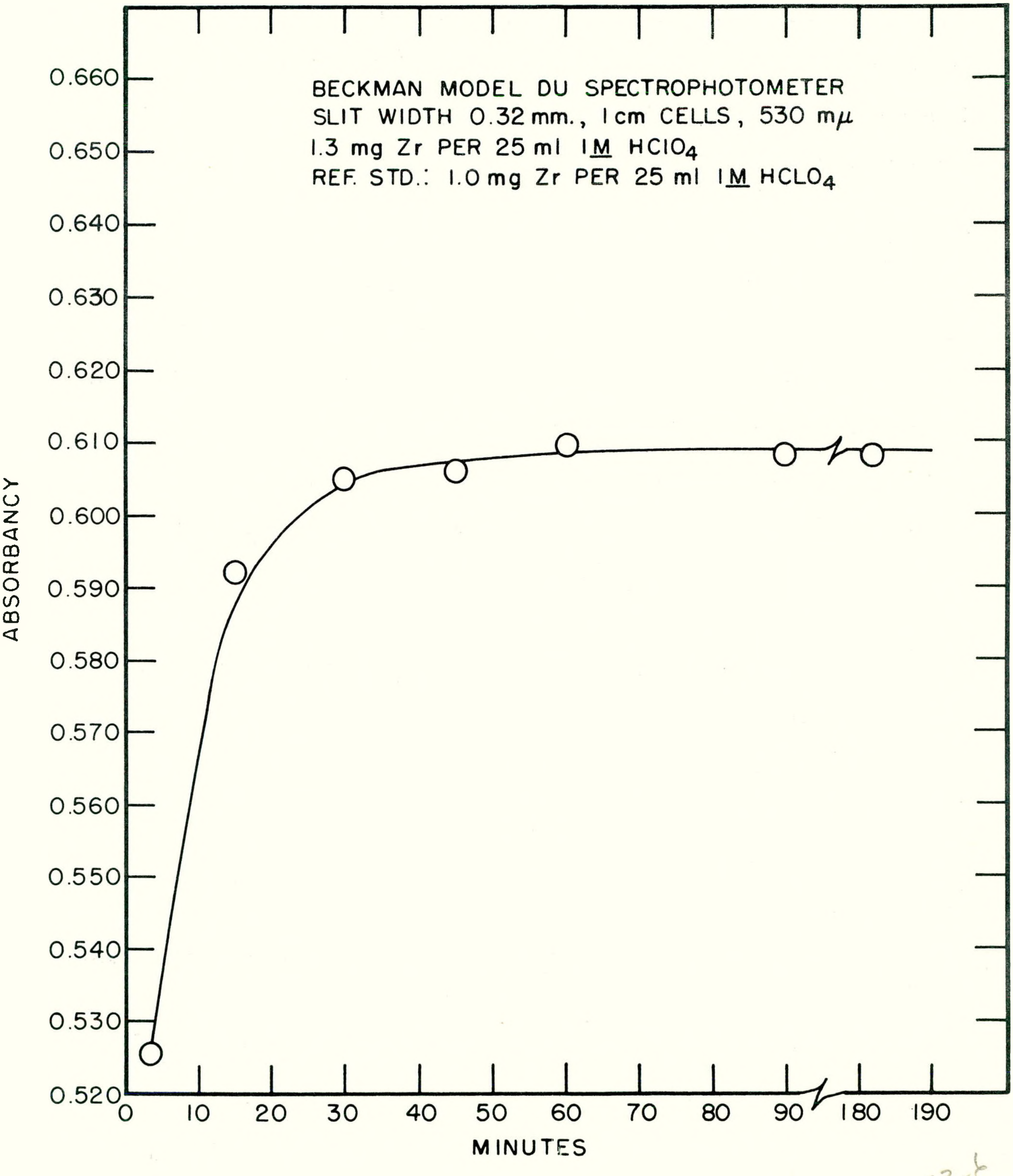
FIGURE 1. EFFECT OF TIME ON THE COLOR DEVELOPMENT OF THE ZIRCONIUM-ALIZARIN RED-S COMPLEX.



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and excessive concentrations, an optimum concentration is reached beyond which decreased accuracy results. A thorough discussion of these effects and a detailed procedure for the determination of the optimum reference standard is presented by Bastian(2). The optimum concentration of zirconium in the reference standard as determined by Bastian's procedure was 1.0 mg in a final volume of 25 ml of 1 M $HClO_4$. With this solution as a reference, a standard zirconium curve was prepared.

Reagents

Standard Zirconium Stock Solution, 2.5 mg per ml. Dissolve 9.3 g of zirconium nitrate in 10 ml of concentrated nitric acid and 200 ml of concentrated perchloric acid by heating to fumes for one hour. Cool and dilute with approximately 200 ml of water. Cool and filter through Whatman No. 2 paper, or equivalent, and dilute to exactly 500 ml. Standardize by determining the zirconium gravimetrically in a 25-ml aliquot of the solution.

Zirconium Standard Solutions

A. Zirconium, 1 mg per ml. Dilute an appropriate aliquot of the stock solution with water.

B. Zirconium, 0.10 mg per ml. Dilute 10 ml of solution A to 100 ml with 1 M $HClO_4$.

C. Zirconium, 0.05 mg per ml. Dilute 5 ml of solution A to 100 ml with 1 M $HClO_4$.

Sodium Hydroxide, 0.25 M Solution. Dissolve 10 g of sodium hydroxide in 1 liter of water.

Perchloric Acid, 1 M. Dilute 86 ml of perchloric acid, 70-72 per cent, to one liter with water.

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Sodium Alizarin Sulfonate. Prepare by dissolving 0.5 g in approximately 80 ml of water. Filter and adjust the acidity of the solution to pH 1 with perchloric acid and dilute to 100 ml with 0.1 *M* perchloric acid.

Procedure

Transfer the appropriate volumes of standard solutions of zirconium into 25-ml volumetric flasks so that they contain 1.00, 1.05, 1.10, 1.20, 1.30, 1.40, and 1.50 mg of zirconium respectively. Dilute to about 15 ml with 1 *M* $HClO_4$ and add 3 ml of alizarin-red-S reagent. Swirl, add 5 ml of acetone. Dilute to volume with 1 *M* $HClO_4$ and shake. Allow the color to develop for one-half hour and read the optical density of each of the solutions on the Beckman Model DU spectrophotometer at 530 $m\mu$ in 1-cm cells against the reference standard, which is the solution containing 1 mg zirconium. In order to obtain the proper slit width, zero the galvanometer by setting the slit width constant and make the necessary adjustments with the sensitivity control. Plot the optical density as the abcissa versus the concentration of zirconium on the ordinate. Since the reference standard must remain in the cell for some time it may be necessary to place a cap on this cell. Acetone was added to the solution following formation of the complex to prevent its precipitation in the aqueous medium. The solubility product in aqueous solution is exceeded above 1.2 mg of zirconium in the 25-ml final volume.

RESULTS

With the establishment of a standard curve, shown in Figure 2, the method was tested by determining zirconium in a solution containing 0.38 mg per ml in 1 M $HClO_4$. Aliquots of 3 ml were taken and the procedure, as previously described, was followed. The difference in optical density was used in calculating the concentration of zirconium present. The results of these tests are shown in Table 1. Additional tests were made on solutions with known concentrations of zirconium in the presence of such cations as sodium, potassium, iron, nickel, chromium, and uranium. These data are shown in Table 1 also.

Table 1

Determination of Zirconium in Standard Solutions by the Differential Spectrophotometric Method

Reference Solution - 1 mg Zr per 25 ml
Slit Width - 1.7 mm, Beckman Model DU Spectrophotometer

	Standard Solution	
Zirconium, mg per ml	Pure	Mixed
Taken	1.27	3.80
Found	1.27	3.79
Difference	0.00	0.01
Number of Determinations	6	4
Standard Deviation, mg per ml	0.02	0.03

The method was also applied to a number of solutions of mixtures of sodium and zirconium fluorides. These samples had been previously analyzed by the mandelic acid method(10). The procedure consisted of the following steps.

Dissolve 0.1 g samples in 10 ml of concentrated HNO_3 and 15 ml of 72 per cent $HClO_4$. Avoid evaporation of the solution to near dryness

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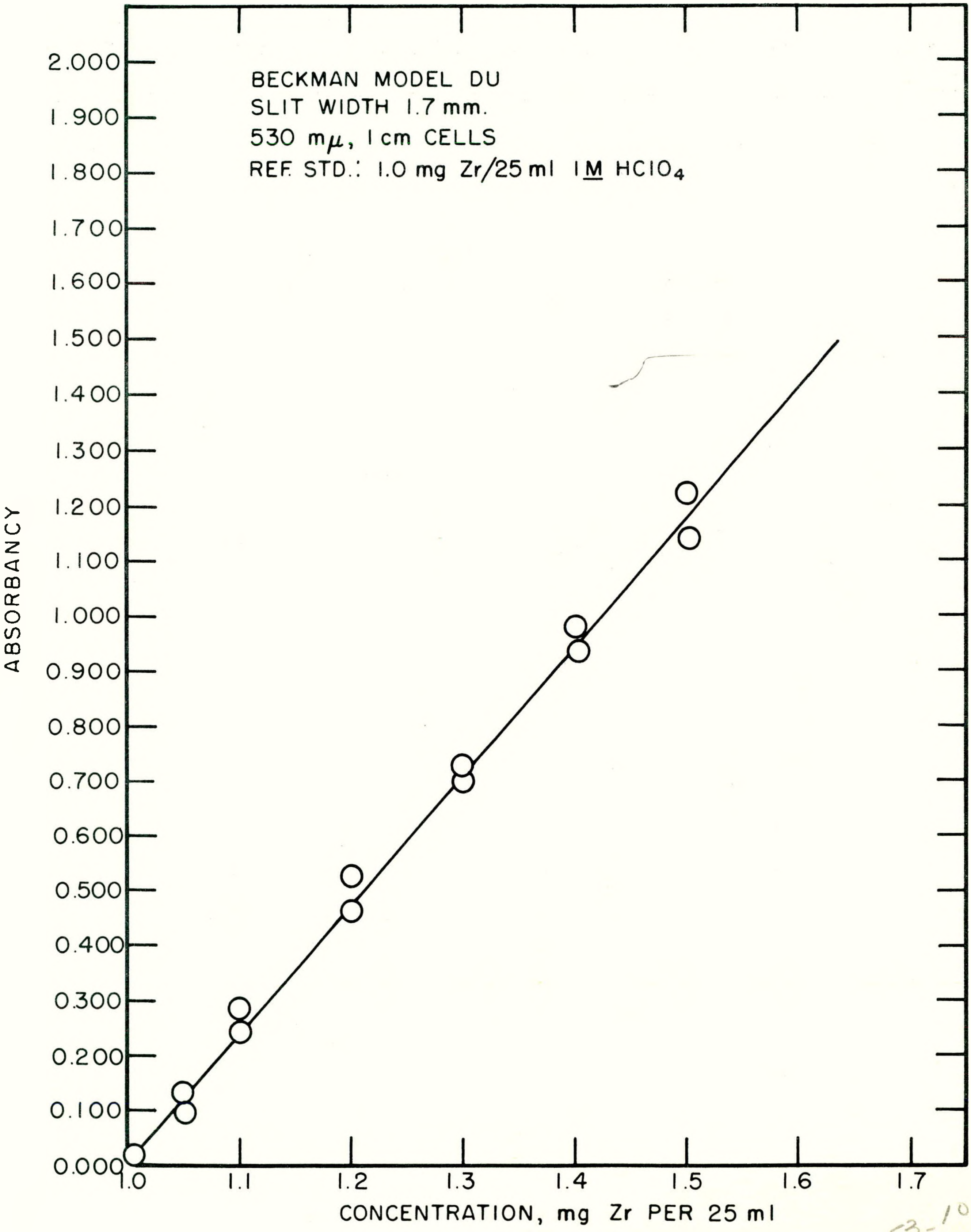
FIGURE 2. STANDARD CURVE FOR THE DETERMINATION OF ZIRCONIUM WITH ALIZARIN RED-S BY DIFFERENTIAL SPECTROPHOTOMETRY.



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because the dehydrated zirconium salts do not dissolve readily upon dilution. Add 10 ml of 1 M $HClO_4$, cool, transfer to a 150-ml beaker and dilute with 25 ml of water. Adjust the pH to 0 with sodium hydroxide. Transfer to a 100-ml volumetric flask and dilute to the mark with 1 M $HClO_4$. Transfer an aliquot containing between 1 and 1.5 mg of zirconium to a 25-ml volumetric flask and follow the procedure outlined on page 5. The results are shown in Table 2.

Table 2

Comparison of Differential Spectrophotometric Method for Determination of Zirconium with Gravimetric Mandelic Acid Method

Sample	Zirconium, per cent Spectrophotometric A	 Gravimetric B	 Difference B-A
1	37.1	37.9	0.8
2	38.2	38.3	0.1
3	37.8	38.1	0.3
4	38.9	38.2	-0.7
5	37.9	38.3	0.4
6	37.4	38.3	0.9
7	39.0	38.3	-0.7
8	39.1	38.4	-0.7
9	38.7	39.6	-0.9
10	37.3	37.9	0.6
11	38.7	38.3	-0.4
12	39.2	38.9	-0.3
13	39.4	39.0	-0.4
14	38.1	38.3	0.2
15	43.0	43.2	0.2
16	35.3	34.9	-0.4
17	43.7	43.1	-0.6
18	31.7	31.5	-0.2
19	30.0	30.2	0.2
20	39.2	38.5	-0.7
		Average Difference	0.5

DISCUSSION

The data indicate that results by the spectrophotometric method are in essential agreement with those by the mandelic acid method. The statistical "F" test was applied to the results on samples 1 through 14. The experimental "F" was less than the theoretical "F" value at the 95 per cent confidence level. This test reveals that the precisions of the two methods are essentially the same and that no significant difference exists.

Since the method of differential colorimetry involves the measurement of optical density of an unknown solution versus a reference standard, it is apparent that it is essential that extreme care be exercised in the preparation of the zirconium standards for establishing the reference curve and for the reference standards.

Zirconium metal and zirconium hydride were used initially to prepare standard solutions because of the high purity of these materials (in excess of 99 per cent). These materials were dissolved in dilute hydrofluoric acid and taken to fumes of perchloric acid several times. The standard curves, which were prepared from solutions of these reagents, were not reproducible. This difficulty was considered to be due to the presence of traces of fluoride ion. Fluoride is the most serious interference in this method because of the strong complex it forms with zirconium which effectively bleaches the alizarin complex. Zirconium oxide is available in a pure state, but must be dissolved in either fluoride or sulfate media. Sulfate, like the fluoride, forms a strong complex with zirconium and also diminishes the intensity of the complex. Zirconium nitrate is readily soluble in perchloric acid. The nitrate is easily removed by increasing the temperature of the solution. Zirconium nitrate, however, is relatively impure and therefore requires standardization. The reproducibility of the standard curve, which was prepared from a solution of zirconium nitrate, was determined by repeating the procedure on five different occasions. The results are shown in Table 3.

Table 3

Reproducibility of Standard Zirconium Curve

Reference Standard - 1.0 mg Zr
Acidity - 1 M $HClO_4$
Final Volume - 25 ml
Slit Width - 1.7 mm, Beckman Model DU
Spectrophotometer, 1-cm cells

Zirconium, mg	Average Optical Density	Coefficient of Variation Per Cent
1.05	0.122	3.1
1.10	0.262	2.0
1.20	0.504	2.8
1.30	0.708	1.8
1.40	0.946	2.9
1.50	1.153	1.1
	Average	2.3

An evaluation of the data reveals that the curve can be reproduced to within 2.3 per cent. The importance of the standard reference curve is illustrated by this data. In order to obtain an order of precision comparable to that obtainable by gravimetric methods, the standard reference curve should be re-established with each set of determinations. The precision of the method can be considered to be less than one per cent under these conditions. If the curve is not established with the set of determinations, the maximum precision obtainable is represented by the reproducibility of the standard curve, approximately 2.5 per cent.

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CONCLUSION

Overall evaluation of the data obtained by this method leads to the conclusion that the differential spectrophotometric method, under ideal conditions, is satisfactory for the determination of zirconium with a coefficient of variation of less than one per cent. The method has the major advantage of being considerably less time-consuming than precipitation methods. It is particularly suited for samples in which the concentration of zirconium is generally known. The interferences are relatively few. Cationic interferences, with the exception of aluminum, are eliminated by the use of 1 M perchloric acid. Such anions as fluoride and sulfate, which form strong complexes with zirconium, interfere seriously. Phosphate forms an insoluble zirconium salt and must be absent also.

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