

TURBIDIMETRIC DETERMINATION OF
ZIRCONIUM WITH MANDELIC ACID

by

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INTRODUCTION

Kumins' (5) discovery that mandelic acid is a highly selective precipitant for zirconium was published in 1947. He reported that it would separate zirconium quantitatively in the presence of a number of metallic ions by the formation of the relatively insoluble zirconium-tetramandelate. This precipitate was then ignited to zirconium oxide and weighed.

Oesper and Klingenberg (7) subsequently reported that other glycolic acid derivatives such as the para-halomandelic acids could also be used to precipitate zirconium. They reported some success with the direct weighing of the zirconium-halomandelic salts when precipitated from pure zirconyl chloride solution, but not with alloys and ores. Astanina and Ostroumov (1) obtained good results with the direct weighing of zirconium-tetramandelate. Belcher, et al., (2) investigated the direct weighing of zirconium-tetramandelate and zirconium-parabromomandelate. The former was found to be almost constant and stoichiometric in composition, though varying slightly with the amount of zirconium in the solution being tested. With the latter, ignition to the oxide was found necessary.

The use of mandelic acid for the quantitative determination of small amounts of zirconium has been investigated by Hahn (3). He used the gravimetric method with ignition to the oxide for 0.00015 g. to 0.015 g. of zirconium oxide. Astanina and Ostroumov (1) found that zirconium in quantities below 1 mg. did not precipitate at once, particularly in the presence of other elements.

They recommended that the precipitation time be extended to one or more days. Mills and Hermon (6) separated small amounts of zirconium with mandelic acid. They reported good results down to 3 mg., but poor results when only 1 mg. of zirconium oxide was found. An overnight digestion period was advocated by them for less than 15 mg. of zirconium.

Kumins (5), in his report on mandelic acid, mentioned that zirconium-tetramandelate dissolved in aqueous ammonia to form a clear colorless solution. This property was used by Hahn and Weber (4) who reported an ultraviolet spectrophotometric determination of zirconium in the range of 0.5 mg. to 50 mg. In this method the precipitate of zirconium-tetramandelate was collected, washed, and then dissolved with 6M ammonia, the resulting solution being diluted to a specified volume with water. The absorbance of this solution at 258 millimicrons was then determined and compared with a previously prepared standard curve. The mandelate ion absorbs at this wavelength, and the amount present is dependent upon the amount of zirconium with which the mandelic acid has chelated. A digestion period of 24 hours was required. Relative errors of 50 to 100 per cent were reported for 2 mg. or less of zirconium.

There are, of course, many other reported methods of determining zirconium quantitatively. Cupferron and phosphate are well known as precipitants, but are not as selective as mandelic acid.

The present work is a continuation of the investigations into the quantitative determination of zirconium by the use of mandelic

acid as the precipitating agent. The proposed method is a turbidimetric procedure, using mandelic acid, to determine zirconium in the range of 6 to 200 p.p.m. No accurate method, with mandelic acid as the precipitant, has been reported for this range.

REAGENTS AND EQUIPMENT

A stock solution of $ZrOCl_2 \cdot 8H_2O$ was prepared in 2 per cent HCl. This solution was standardized by the method of Kumins (5), and found to contain 0.435 mg. of zirconium per ml. The various zirconium samples used in the investigations were all prepared by taking an aliquot of this stock solution and diluting to volume with 2 per cent HCl.

The mandelic acid solution was prepared by adding 140 g. of mandelic acid to a one-liter flask and diluting to the mark with 2 per cent HCl.

A "magne-stir" from the Laboratory Appliance Corporation, Chicago, Illinois, with a plastic-covered magnetic stirring bar $1 \frac{3}{8}$ by $\frac{3}{8}$ inches, was used to stir the solution during the formation of the turbidity. It appeared to have a higher stirring speed than some of the other magnetic stirrers. A Raytheon voltage stabilizer was used in conjunction with the stirrer to minimize voltage fluctuations.

To insure a constant temperature while stirring, a 5 by $2 \frac{1}{4}$ inches copper water bath was placed on the magnetic stirrer, and water from a constant temperature bath pumped into it. The water in the copper water bath was returned to the constant temperature

water bath by gravity flow through a hose connected to the steam outlet pipe on the side of the copper water bath.

A Klett and Summerson industrial model photoelectric colorimeter was used for the turbidimetric readings. The 40 mm. light path of a 40 mm. by 20 mm. glass cell was used. A 420 millimicron filter was used at all times except during the interference study of ferric ion, when a 560 millimicron filter was used.

RECOMMENDED PROCEDURE

Twenty ml. of the stock mandelic acid solution was pipetted into a 50 ml. erlenmeyer flask to which was added 5 ml. of a zirconium-containing solution. The magnetic stirring bar was placed in the flask, which was then lightly stoppered to allow for air expansion. The flask was mounted in the copper water bath on the magnetic stirrer and held firmly in position with a burette clamp so that the flask rested on the bottom of the copper water bath. The flask was placed in the same position each time. The stirrer was then turned on at maximum speed, and the pump started, to supply water from the constant temperature bath to the copper water bath. After about a minute the stopper was pressed firmly into the flask.

At the end of 25 or 40 minutes, depending upon the concentration, the stirrer was shut off and the contents of the flask poured into the glass cell, and the turbidity measured by the Klett. Two minutes from the time of pouring the solution into the cell, the turbidity was read. A time interval of one to four

minutes was not critical, though upon prolonged standing some of the material would settle.

A blank was prepared by combining 20 ml. of the mandelic acid stock solution with 5 ml. of 2 per cent HCl in a 50 ml. erlenmeyer flask, and then following the above procedure of stirring, five or ten minutes being sufficient. The blank was then poured into the cell, and after two minutes the Klett was balanced at zero by adjusting the shutter. Throughout a day of determinations it was found inconvenient to use the working cell for a blank. An alternative was provided by using the 40 by 10 mm. glass cell which also accompanies the instrument. This cell was filled to a suitable height with distilled water. After the instrument was set at zero with the aforementioned blank, the cell containing the distilled water was placed in the Klett, with the 10 mm. width in the light path. The scale reading was recorded and the instrument was then set at this value with the distilled water blank before each determination.

INVESTIGATION OF VARIABLES

Stirring Equipment

Initial investigations into the development of a turbidimetric method of determining zirconium with mandelic acid, were concerned with finding a satisfactory stirring method. High speed air-driven and motor-driven stirrers were tried, but discarded when it was found that a magnetic stirrer gave higher and more precise turbidities.

Selection of a suitable stirring flask was somewhat difficult. A 50 ml. erlenmeyer flask was an ideal size, considering the volume of 25 ml. that was to be stirred. A number of these flasks were tried, and found to produce varying turbidities. The bottoms of all the flasks were convex, but to an individual degree. If the stirring appeared to be quite smooth, low turbidities were obtained. Very irregular stirring caused the stirring bar to lose contact with the magnetic field, and stop. The flask used, was selected because it produced reasonably high and precise turbidities. It was found necessary to place the flask in the same position on the magnetic stirrer each time.

A 1 3/8 by 3/8 inches plastic-covered magnetic stirring bar was used during the investigations.

Varying the stirrer speed did affect the turbidity somewhat, but by interposing a voltage stabilizer between the stirrer and the power source, and setting the stirrer at full speed, a constant speed was assured.

Stirring Time and Temperature Study

A study was made to determine the optimum stirring time. For this purpose a concentration of 65.2 p.p.m. of zirconium was used, the stirring temperature being maintained at 27-28 degrees C. Plate I, Fig. 1 shows that there is no difference in turbidity between a 35 and a 45 minute stirring period, so a 40 minute period was selected.

The next investigation was concerned with the determination

of a satisfactory temperature. Here a concentration of 10.9 p.p.m. of zirconium was used. The temperatures at which the samples were stirred were 28, 38, 48, and 53 degrees C. The results are shown in Plate I, Fig. 2. The turbidities obtained at 38 and 48 degrees were not significantly different. On the basis of these results, 45 degrees was selected as the stirring temperature, since it was apparent that a variation of several degrees either side of 45 degrees would not affect the results.

With the selection of a stirring temperature, the question arose as to whether or not a shorter stirring period might be found, since the original experiments had been conducted at a lower temperature. Subsequent investigations indicated that for the lower concentrations of zirconium, a 40 minute stirring period was satisfactory, whereas for the higher concentrations, a 25 minute stirring period was adequate, when a temperature of 45 degrees was used. Plate II, Fig. 1 shows the results when a stirring time study at 45 degrees C. was made on 5.4 p.p.m. of zirconium, the lowest concentration used in these investigations. The turbidity increases rapidly up to 35 minutes. Since there is little increase in turbidity beyond 35 minutes stirring time, 40 minutes was chosen as an ample stirring time for low concentrations of zirconium. A concentration of 21.9 p.p.m. zirconium was chosen as the division point between high and low concentrations of zirconium, because there was no change in the turbidity between 25 and 45 minutes stirring time at this concentration as is indicated in Plate II, Fig. 2. Lower concentrations were to be stirred for

EXPLANATION OF PLATE I

- Fig. 1. Development of turbidity with stirring time, of a 65.2 p.p.m. zirconium solution at 27-28 degrees C.
- Fig. 2. Development of turbidity with increasing temperature, of a 10.9 p.p.m. zirconium solution at 40 minutes stirring.

Fig. 1

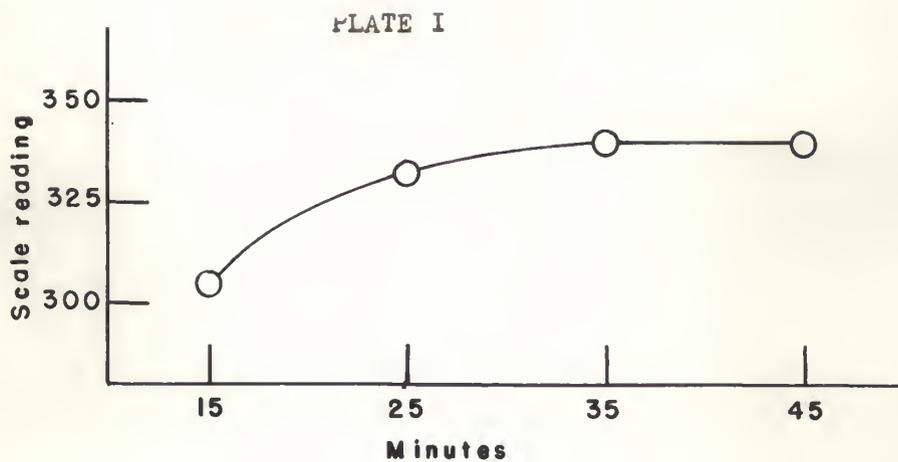
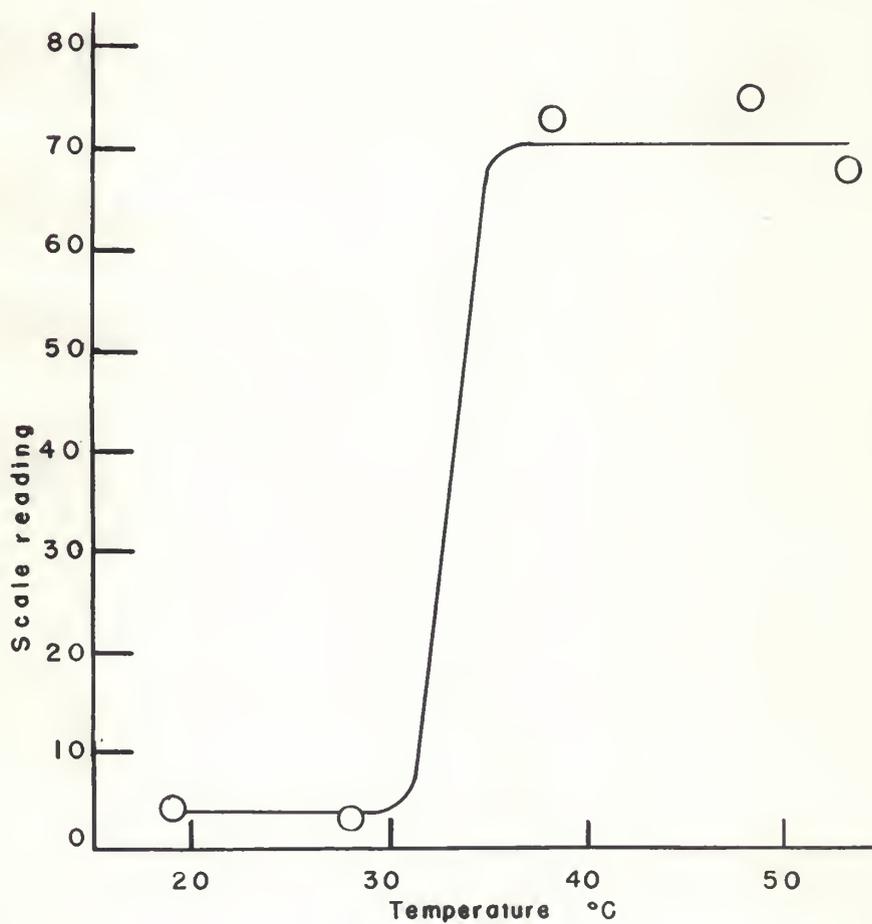


Fig. 2



EXPLANATION OF PLATE II

Fig. 1. Development of turbidity with stirring time, of a 5.4 p.p.m. zirconium solution at 45 degrees C.

Fig. 2. Development of turbidity with stirring time of a 21.9 p.p.m. zirconium solution at 45 degrees C.

PLATE II

Fig. 1

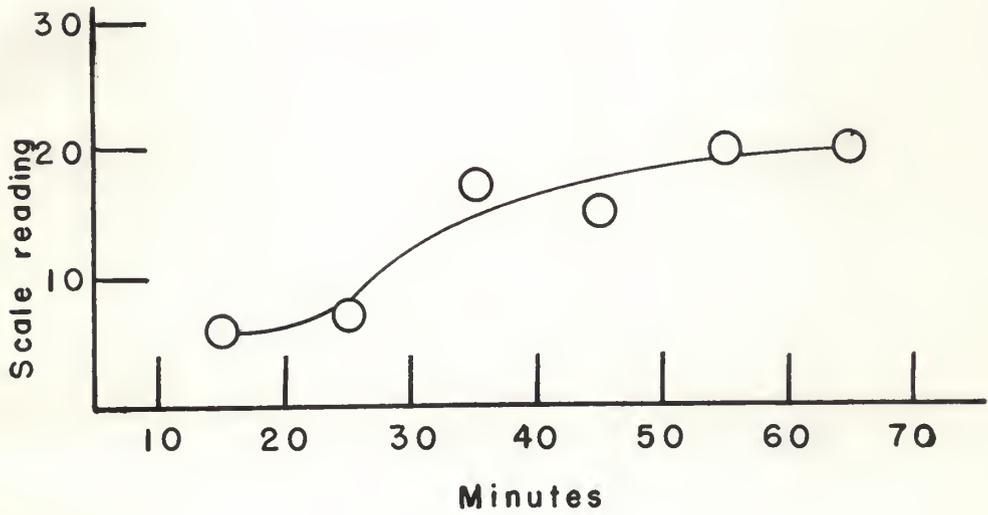
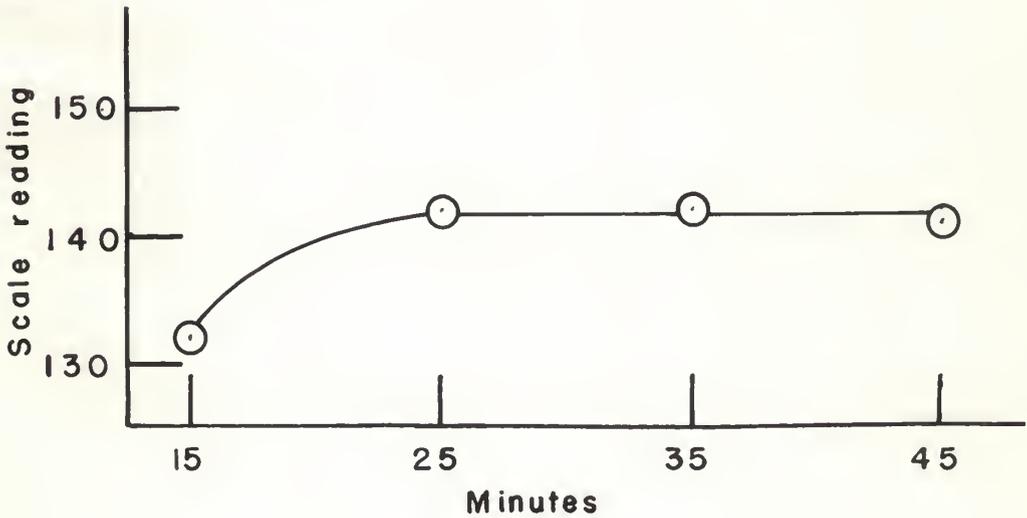


Fig. 2



40 minutes, and higher concentrations for 25 minutes.

HCl Concentration

The mandelic acid solution and the zirconium solutions used in these investigations were both contained in 2 per cent HCl, as has been mentioned. In practical applications of this quantitative method a higher HCl concentration might be necessary. With this possibility in view, a study was made of the effect of increased HCl concentration in the zirconium solutions, upon the turbidity. Five solutions were prepared at concentrations of 2, 4, 6, 8, and 10 per cent HCl, each containing 21.9 p.p.m. zirconium. The turbidities were determined at 45 degrees and 25 minutes stirring; three samples of each HCl concentration being run. The results indicated that the turbidity was not affected by varying the HCl concentration of the zirconium solutions between 2 and 10 per cent.

Mandelic Acid Concentration

A study was made of the effect of varying the mandelic acid concentration. Normally 20 ml. of 14 per cent mandelic acid in 2 per cent HCl was used to precipitate the zirconium. Lower concentrations of mandelic acid were tried by placing an aliquot of the mandelic acid stock solution in the 50 ml. flask and adding 2 per cent HCl so that a final volume of 20 ml. was attained. Five ml. of solution containing 87 p.p.m. zirconium was then added, and the usual turbidimetric procedure followed. Although the precision was not affected, lower concentrations of mandelic acid did produce lower turbidities.

STANDARD CURVES

Two standard curves were prepared; one for 5.4 to 21.9 p.p.m. of zirconium, using a 40 minute stirring time, and the other for 21.9 to 219 p.p.m. with a stirring time of 25 minutes. Four samples of each concentration were determined. The first curve is shown in Plate III, and is seen to be nearly linear. The second curve is shown on Plate IV.

INTERFERENCES

A number of ions were investigated to determine the effect of their presence. Zirconium solutions at 10.9 and 87 p.p.m. were prepared, containing the individual ions to be studied. Ten samples each, of these two zirconium concentrations, but containing no added ions, were used to determine the standard deviations. These were calculated to be 1.6 p.p.m. for the lower concentration of zirconium, and 2.5 p.p.m. for the higher.

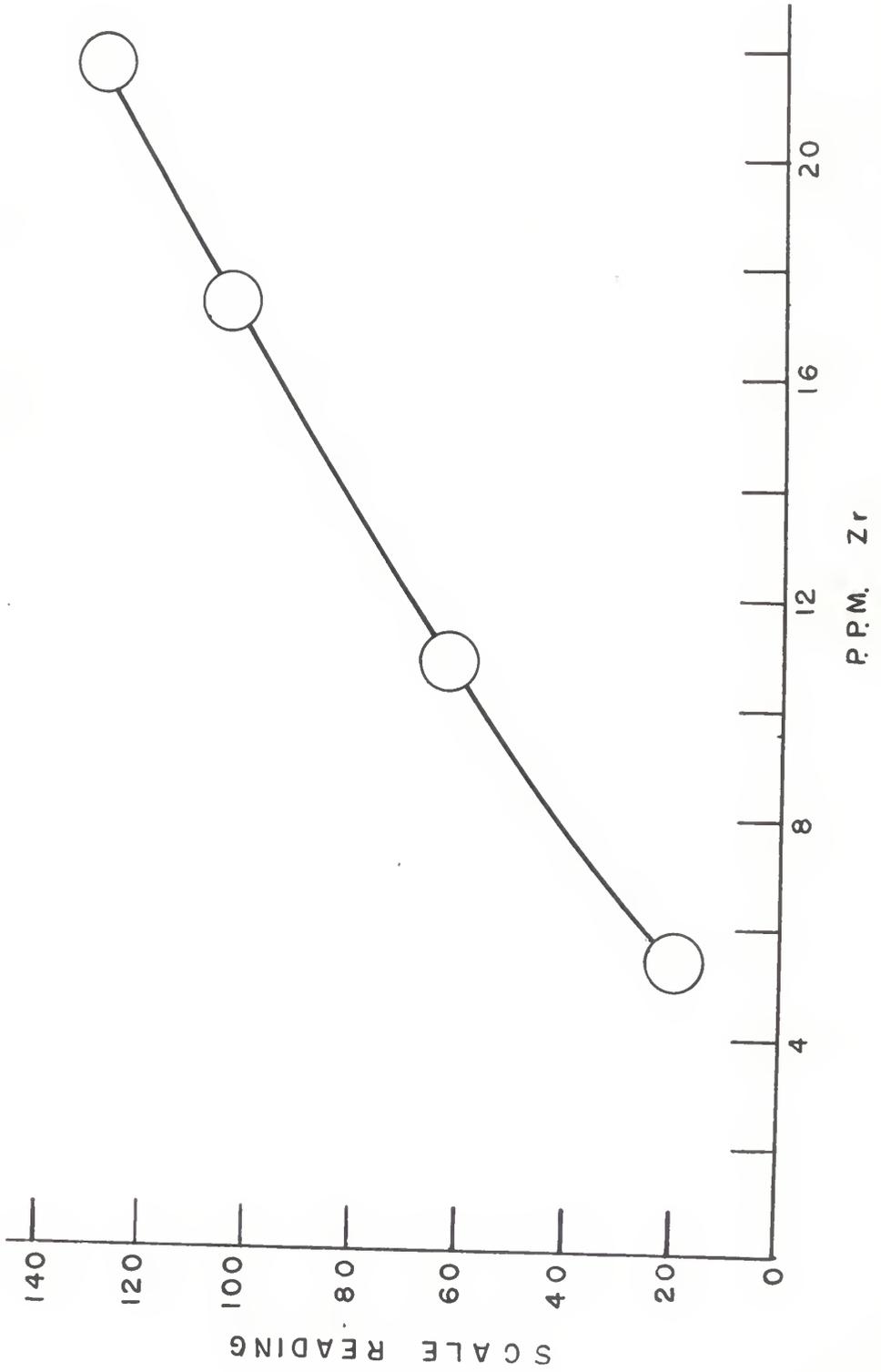
Two or more samples of each ion-containing zirconium solution were determined, along with a reference zirconium sample. Interference was considered to have occurred if the standard deviation was exceeded.

Chromic, cobaltous, and uranyl solutions required the subtraction of a blank because they absorbed at the wavelength used. This was accomplished by combining 5 ml. of the ion-containing zirconium solution with 20 ml. of 2 per cent HCl in the 40 by 20 mm. glass cell, stirring slightly, and determining the scale reading on the Klett. This reading was then subtracted from the turbidity

EXPLANATION OF PLATE III

Standard curve for 5.4 to 21.9 p.p.m. of zirconium with 40 minute stirring at 45 degrees C.

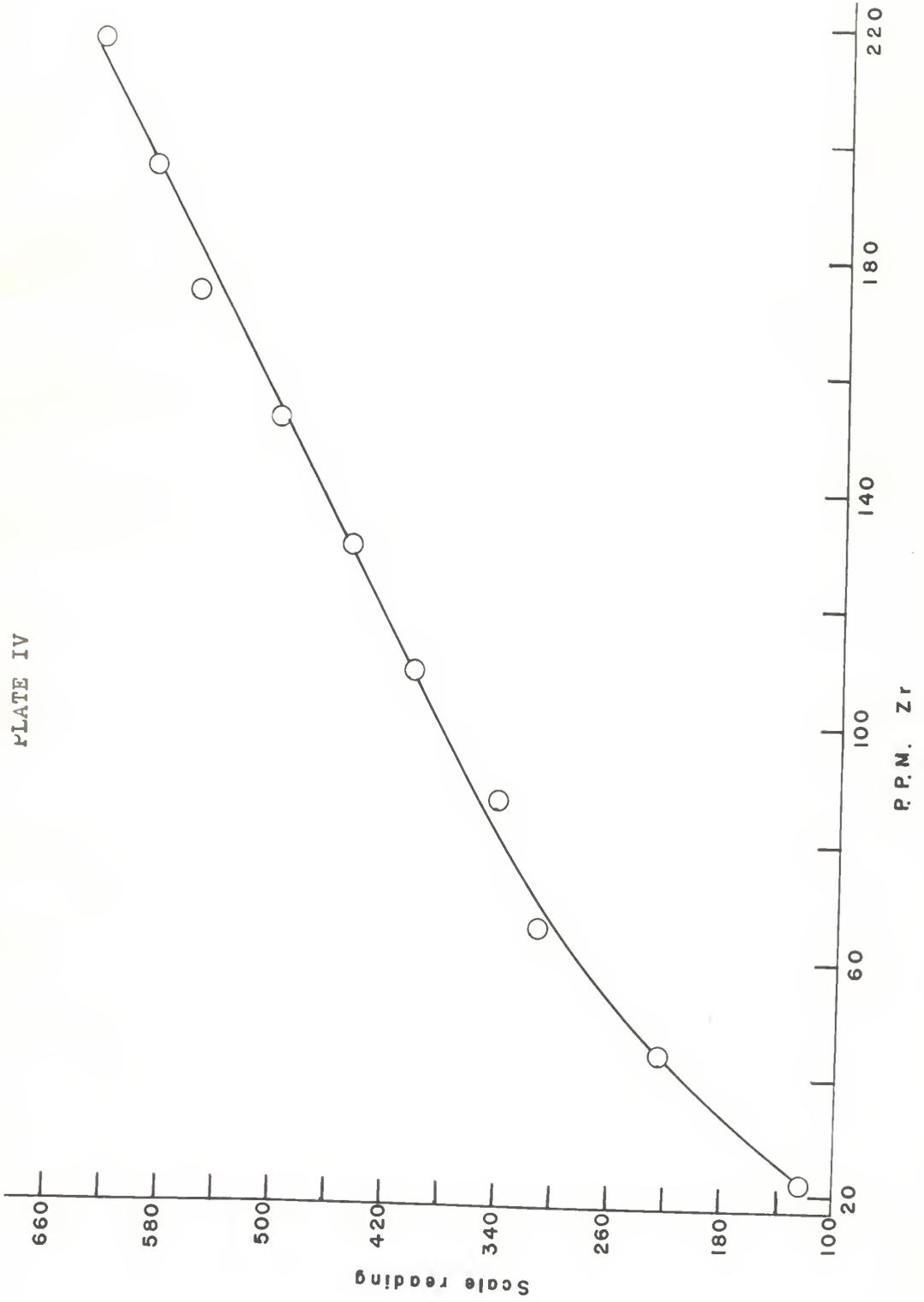
PLATE III



EXPLANATION OF PLATE IV

Standard curve for 21.9 to 219 p.p.m. of zirconium with 25 minutes stirring at 45 degrees C.

PLATE IV



reading.

Ferric ion, because it was temperature sensitive and absorbed highly in the region of 420 millimicrons, did not permit the subtraction of a blank. Investigation of its absorbance spectrum disclosed that ferric ion did not absorb highly in the region of 560 millimicrons. At this wavelength, subtraction of a blank gave good results for the determination of zirconium in the presence of iron.

A list of the ions studied, and their permissible concentration, is shown in Table 1. No studies were made at higher than 2000 p.p.m. concentrations of these ions.

Table 1. Effect of interfering ions on the turbidimetric determination of a 10.9 and 87 p.p.m. solution of zirconium.

Compound used	Calculations based on	Concentration below which no interference noted (p.p.m.)
KNO_3	NO_3^-	2000
Na_2SO_4	SO_4^{--}	2000
NaClO_4	ClO_4^-	2000
$\text{Al}_2(\text{SO}_4)_3$	Al^{+++}	2000
$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$	Cu^{++}	2000
$\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$	Cr^{+++}	2000 1
$\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$	Mn^{++}	2000
$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	Co^{++}	2000 1
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	Ni^{++}	2000
$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	Zn^{++}	2000
$\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	UO_2^{++}	2000 1
$\text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$	Fe^{+++}	2000 1,2
TiCl_4	Ti^{++++}	1500
NaF	F^-	10

1. Required subtraction of a blank.
2. Required a 560 millimicron filter.

DISCUSSION

The most difficult part of establishing this method was the selection of a suitable stirring flask which would produce high and reasonably precise turbidities. The turbidity was found to be a function of the individual stirring flask, the position in which it was placed on the magnetic stirrer, and the magnetic stirring bar.

The concentration of mandelic acid was found to be a factor in the turbidity produced, but this was easily controlled. Stirring speed, another variable, was kept constant by using a voltage stabilizer and setting the stirrer at maximum speed.

Ten samples each were run at 10.9 p.p.m. for the "40 minute" curve, and at 87 p.p.m. zirconium for the "25 minute" curve. For the former, the maximum deviation was 3.2 p.p.m., the average deviation 1.3 p.p.m., and the standard deviation 1.6 p.p.m. For the latter, the maximum deviation was 5 p.p.m., the average deviation 1.7 p.p.m., and the standard deviation 2.5 p.p.m.

Sometimes a series of readings would vary from those obtained on a previous day, though having a like precision. The reason for this was not established. However, this difficulty may be circumvented by running standard samples along with the unknowns and relating them to the standard curves. Occasionally rather high or low individual readings were obtained, particularly with low concentrations of zirconium.

Freedom from interfering ions was excellent and is one of the attributes of the use of mandelic acid as a precipitating agent

for zirconium.

This method can be used for concentrations of 200 p.p.m. or less of zirconium, a range for which no accurate method has been reported. The gravimetric procedure at this low concentration requires exacting technique. In addition, the gravimetric procedure and other published procedures, using mandelic acid, required at least an overnight digestion period when micro amounts of zirconium were determined. The turbidimetric method presented, involved only a 25 to 40 minute period for the formation of the turbidity.

SUMMARY

A simple and direct turbidimetric method has been presented for the determination of small amounts of zirconium in the range of 5 to 200 p.p.m. No other published procedure, using mandelic acid, is satisfactory in this range. Freedom from interferences was excellent.

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In 1947 mandelic acid was reported as a highly selective precipitant for zirconium, and one that would separate zirconium quantitatively in the presence of a number of metallic ions, by the formation of the relatively insoluble zirconium-tetramandelate. This precipitate was then ignited to zirconium oxide and weighed.

When small amounts of zirconium were determined, a digestion period of eighteen or more hours was necessary. An ultraviolet spectrophotometric procedure was reported for 0.5 to 50 mg. of zirconium. In this method, the zirconium-tetramandelate was dissolved in aqueous ammonia to form a clear colorless solution. The ultraviolet absorbance of the mandelate ion in this solution was then determined and compared with a standard curve. Relative errors for this method, of 50 to 100 per cent were reported for 2 mg. or less of zirconium.

No accurate method of determining 1 mg. or less of zirconium, using mandelic acid, has been reported.

The proposed method is a turbidimetric procedure, using mandelic acid, to determine zirconium in the range of 6 to 200 p.p.m. Aliquots of a mandelic acid stock solution and a zirconium solution were placed in a 50 ml. erlenmeyer flask, and stirred at constant temperature on a magnetic stirrer. After a timed interval of stirring, the resulting turbid solution was poured into a glass cell of a Klett and Summerson photoelectric colorimeter and the turbidity determined.

A study was made to determine the variables, and to develop methods of controlling them. The turbidity was found to be a

function of the stirring flask, stirring speed and temperature, magnetic stirring bar, and mandelic acid concentration.

A stirring time and stirring temperature investigation was made. This disclosed that a stirring temperature of 45 degrees C was satisfactory, though not critical. A stirring time of 40 minutes for 6 to 22 p.p.m. zirconium, and of 25 minutes for 22 to 220 p.p.m. was found adequate. A standard curve was made for each of these two concentration ranges.

The mandelic acid solution and the zirconium solutions used in these investigations were both contained in 2 per cent HCl. When the HCl concentration of a zirconium solution was varied from 2 to 10 per cent HCl, no effect on the turbidity was noted.

Fourteen ions were studied individually for possible interference. All, except two, did not interfere at a concentration of 2000 p.p.m. This was the highest ion concentration used. Titanium interfered when present in concentrations above 1500 p.p.m., and fluoride, when above 10 p.p.m. Several ions required the subtraction of a blank. Ferric ion required the use of a 560 millimicron filter in place of the 420 millimicron filter which was used on all other occasions. The ion study was made at two different concentrations of zirconium. Ten samples each, of these two zirconium concentrations, but containing no added ions, were used to determine the standard deviation. Interference was considered to have occurred when the standard deviation was exceeded.

The lower concentrations of zirconium, requiring a 40 minute stirring period, had a standard deviation of 1.6 p.p.m., an

average deviation of 1.7 p.p.m., and a maximum deviation of 3.2 p.p.m. The higher concentrations, requiring a 25 minute stirring period, had a standard deviation of 2.5 p.p.m., an average deviation of 1.7 p.p.m., and a maximum deviation of 5 p.p.m.