

DIFFERENTIAL SPECTROPHOTOMETRIC
DETERMINATION OF HAFNIUM IN
THE PRESENCE OF ZIRCONIUM

by

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Typed by Sharon Johnson

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DIFFERENTIAL SPECTROPHOTOMETRIC
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INTRODUCTION

In 1922 it was discovered that all naturally occurring zirconium contains a small amount of hafnium. These two elements are so similar in their chemical behavior that virtually no qualitative and only minor quantitative differences have been observed up to the present time. This similarity is associated with the identical arrangements of the electrons in the outermost quantum levels and to the nearly identical atomic radii. However, a complete explanation of the exceptional similarity of hafnium and zirconium is not known at the present time. Contributing also to this similarity is the fact that their compounds almost always occur with oxidation number four and covalently bonded to the maximum extent that is sterically possible. These conditions limit the possibilities for valence hybridizations which might tend to increase the differences between the compounds of hafnium and zirconium. They are both in Group IV of the Periodic Table and should therefore have a normal valence of four and a maximum coordination number of eight (9, p. 3-5, 25-26, 35-38).

As a result of similarities noted above, practically all experimental data on zirconium have been determined

on materials containing 0.5 to 2.0 % hafnium. For most practical purposes this can be ignored; however in the atomic energy field this is not true. As a result of this interest much research has been carried out using X-ray fluorescence and optical spectroscopic methods. An excellent survey of these methods is given by Goward and Jacobs (29). Since the differences in the physical properties of hafnium and zirconium are more readily measured than the chemical properties, these physical methods are used almost exclusively for the determination of hafnium in the presence of zirconium, especially at low concentration levels of hafnium.

Solvent extraction, ion exchange, fractional crystallization etc., have been applied to the separation of hafnium and zirconium from each other. Because many of these processes involve multiple batch or continuous operation, their use for quantitative analytical chemistry application has been rather limited with the exception of certain of the ion exchange techniques (29).

Since ion exchange techniques lend themselves most readily to laboratory scale type separations, their application is the most promising approach to separations from a quantitative analytical viewpoint. A number of separations based on election from cationic or anionic exchange resins by the use of various complexing agents have been

described. Although separation by means of liquid-liquid extraction has taken precedence over ion exchange insofar as the large scale separation of hafnium from zirconium is concerned, the complexity of the equipment needed for continuous extraction makes this method less attractive for analytical scale separations (29). Unfortunately, none of these separation methods has successfully been applied to the quantitative determination of small amounts of hafnium in zirconium. In addition to the relative difficulty of these separation methods, the great increase in the availability of precise and rapid spectrochemical methods for the determination of hafnium in the presence of zirconium has tended to discourage the development of analytical chemical methods of separation. Since no adequate chemical methods have been developed, a definite need exists for a chemical method capable of determining 0 to 5% HfO_2 in ZrO_2 . This would then make it possible for laboratories lacking the more elaborate equipment needed for the X-ray and spectroscopic methods to determine hafnium in the presence of zirconium. It would also make available an independent procedure for checking the instrumental methods.

A brief review of the gravimetric and colorimetric methods for zirconium and hafnium will be found in the following sections. These will be followed by the methods available at the present for the indirect chemical

determination of hafnium - zirconium ratios and then by a discussion of differential spectrophotometry and its application to the determination of HfO_2 in ZrO_2 .

Gravimetric Methods

All classical methods of analysis determine the total hafnium and zirconium present. Zirconium and hafnium are both precipitated as the hydrous oxides from a basic solution. Unfortunately, most of the other metals occurring with zirconium and hafnium are also precipitated thus making this procedure applicable only to pure samples of hafnium and zirconium. The resulting precipitate must then be ignited to the oxides. In practically all gravimetric methods for these two metals, the final weighing form is the ignited oxide. Some of the more important methods for the separation and determination of both metals will be outlined in the following paragraphs.

For the purposes of this research, a good method for the separation of zirconium and hafnium from all other metals was desired as well as one which would give the oxides upon ignition.

Mandelic Acid Method - Mandelic acid (phenylglycolic acid) is probably the most useful and convenient reagent for the separation and determination of zirconium and hafnium. Mandelic acid and the p-bromo- and p-chloro-derivatives

are the most selective reagents known for these two metals. The use of mandelic acid as a specific reagent for zirconium and hafnium was first described by Kumins (48) in 1947. He found that zirconium was quantitatively separated from Ti, Fe, V, Al, Cr, Th, Ce, Sn, Ba, Ca, Cu, Bi, Sb and Cd in hydrochloric acid solution. It was also shown that the complex formed was $\text{Zr} \left[\text{O}-\overset{\text{O}}{\underset{\text{H}}{\text{C}}}-\overset{\text{OH}}{\text{C}}-\text{C}_6\text{H}_5 \right]_4$. In 1949 Hahn (32) found that Co^{++} , Mg^{++} , Hg^{++} , Ni^{++} , UO_2^{++} , and Zn^{++} do not interfere with the mandelic acid precipitation. It was also found that hafnium precipitates quantitatively with this reagent. Oesper and Klingenberg (58) suggested that the glycolic acid group ($-\text{CHOH}-\text{COOH}$) might be specific for zirconium. Several glycolic acid derivatives were therefore studied by these authors. They found that mandelic, p-bromomandelic acid, p-chloromandelic acid, the sodium salt of p-iodomandelic acid, sodium salt of benzilic acid, and the sodium salt of 2-naphthylglycolic acid were all suitable for the quantitative precipitation of zirconium. However, of these, only the p-chloromandelic acid and p-bromomandelic acid were considered to have advantages worth further consideration. These two derivatives were claimed to be very water insoluble, thus making it possible to wash them with water. Hahn and Joseph (33) found that 1-naphthylglycolic acid compares favorably with mandelic acid but it offers no advantage over it.

Klingenberg and Papucci (45) have indicated that in the determination of zirconium in steels using p-bromo or p-chloromandelic acid, the precipitates can be weighed directly without conversion to the oxide. However, Belcher, Sykes and Tatlow (8) found that it was necessary to ignite mandelic acid and p-bromomandelic acid to the oxides for the best accuracy. With the aid of the Chevenard thermobalance, Stachtchenko and Duval (73) carried out thermogravimetric analysis of zirconium mandelate and zirconium p-bromomandelate and as a result, observed that the formula of the first compound closely approximates $\text{Zr}(\text{C}_6\text{H}_5\text{CHOHCOO})_4$ while the second one had no definite formula. Hahn and Baginski (36) postulated that compounds of varying amounts of basic salts such as $\text{ZrO}(\text{C}_8\text{H}_7\text{O}_3)_2$ and $\text{Zr}(\text{OH})(\text{C}_8\text{H}_7\text{O}_3)_3$ along with the pure zirconium tetramandelate were formed. This suggested that best results should be expected in strongly acid solutions. They found that the concentration of hydrochloric acid present at the time of precipitation greatly influenced the composition of the precipitate. The normal zirconium tetramandelate was obtained only in strong acid solution (5 M or greater). However, it was found that quantitative precipitation of zirconium occurred at all acidities. The proper conditions for precipitation to be followed by direct weighing were also outlined. Mandelic acid, p-chloro and p-bromomandelic acid have been

utilized for the gravimetric determination of zirconium in titanium, magnesium and aluminum alloys quite successfully (39, 61, 62, 63).

Hahn (34) has determined zirconium - hafnium ratios using p-bromomandelic acid. The mixed zirconium and hafnium tetramandelates were weighed directly and then ignited to the oxides and weighed. From these data, simultaneous equations were set up and the hafnium content calculated. An accuracy of about 0.5% (absolute) was claimed for samples containing more than 10% hafnium oxide.

Cupferron Method - Cupferron is the ammonium salt of phenyl-nitrosohydroxylamine ($\text{C}_6\text{H}_5\text{N}(\text{O}=\text{N})\text{O}-\text{NH}_4$) and has been known since 1909 when it was introduced as an analytical reagent (78). This reagent forms insoluble compounds with a number of metals but is more specific in strong acid solution (72). In addition to zirconium and hafnium, it will precipitate ferric iron, titanium, vanadium and tin in 5 to 10% sulfuric or hydrochloric acid solution. In weakly acid solutions copper, mercury, bismuth, molybdenum, tungsten, niobium, tantalum, and others are precipitated. It has therefore been widely used for separation of the above metals when they are present as interferences. However, it is an excellent reagent for standardization or determination of solutions known to contain only zirconium and hafnium and those metals which will not interfere. The precipitate

cannot be weighed as mixed cupferrates, but must be ignited to the oxides. Hillebrand, Lundell, Bright and Hoffman (40, p. 572-5) and Scott (70, p. 1099-1100) give detailed directions for the use of Cupferron in the analysis of zirconium and hafnium (See Appendix also). Olson and Elving (60) have described a gravimetric cupferron precipitation procedure for the determination of zirconium in a thousandfold excess of fluoride. This would be valuable in those cases where hydrofluoric acid is used to put samples into solution.

Phosphate Method - Lundell and Knowles (56) have described the use of alkali phosphates as precipitants in the determination of zirconium and hafnium. They found that in 20% sulfuric acid by weight, zirconium can be quantitatively separated as the phosphate from iron, aluminum, chromium, cerium, thorium and in the presence of hydrogen peroxide from titanium. The phosphate was then ignited to the pyrophosphate for weighing. This method was found to be accurate only for small amounts of zirconium (up to 20 mg. of the oxide). Willard and Hahn (79) found that 2 to 60 mg. of zirconium oxide could be determined by homogeneous precipitation from 3.6 N hydrochloric or sulfuric acid solution with trimethyl phosphate after 12 to 15 hours of heating. The resulting phosphates were then ignited to the pyrophosphate. Antimony, bismuth, cerous and stannic

ions interfered and large amounts of ferric, titanium, thorium and uranyl ions gave high results. These authors also found that metaphosphoric acid can be used for samples containing from 0.2 to 200 mg. of the oxide. Successful separations were made from aluminum, arsenate, borate, cadmium, chromic, cerous, cobalt, cupric, magnesium, manganous, mercuric, nickel, potassium, sodium, tartrate, vanadyl, yttrium and zinc ions. Bismuth, stannic and perchlorate ions interfered as well as ferric ions, thorium and titanium oxide in large amounts.

Goward and Jacobs (29, p. 289) claim that only tantalum, niobium, thorium and protoactinium cause high results and that the thorium interference can be eliminated by solution of the phosphate and reprecipitation. Hillebrand et al. (40, p. 569-571) and Scott (70, p. 1102) give detailed directions for the phosphate method.

A great disadvantage of this method for the purpose of this research arises from the fact that the oxides are not obtained directly upon ignition. In order to obtain the oxides with this method, the pyrophosphate must be fused with sodium carbonate and then with pyrosulfate and finally precipitated with one of the reagents that will give the oxide upon ignition (40, p. 571).

Other Reagents - Zirconium and hafnium may be precipitated as the basic selenites by using selenious acid as the

precipitant. The selenites can then be ignited to the oxides. Zirconium and hafnium can be separated from aluminum, certain rare elements, moderate amounts of iron and titanium if hydrogen peroxide is present. Thorium, phosphate, sulfate, niobium and tantalum interfere (40, p. 573-4; 70, p. 1101).

Phenylarsonic acid separates zirconium and hafnium from most other elements. Hydrogen peroxide must be added if titanium or niobium is present. Tantalum interferes (40, p. 567; 70, p. 1102-3).

Normal propylarsonic acid can be used to separate zirconium and hafnium from titanium, aluminum, chromium, cobalt, nickel, copper, uranium, vanadium, thorium, molybdenum and traces of silicon and tungsten. The precipitate can be ignited to the oxide (40, p. 567-8).

Tannin can be used for the quantitative separation of titanium, niobium, tantalum, aluminum, iron, chromium, neodymium, yttrium, uranium, beryllium, manganese and nickel from zirconium and hafnium (40, p. 568).

The phenylhydrazine, sulfurous acid and iodate are useful only with pure zirconium and hafnium solutions (40, p. 575). A method which should be useful for the separation of zirconium and hafnium from niobium, titanium, tantalum, molybdenum, tungsten, lead, iron, copper and tin is that in which the zirconium and hafnium are

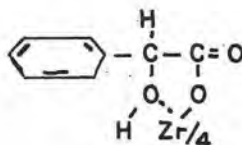
precipitated from hydrofluoric acid solution as the barium fluorzirconate and fluohafnate (29, p. 290-1). Bainlescu and Trucu (1) have recently introduced the use of tartrazine and 2-hydroxy-5-methylazobenzene-4'-sulfonic acid for the selective determination of zirconium. The precipitate formed with the tartrazine was filtered through a filtering crucible and dried at 100°C for an hour and then weighed directly. Aluminum, titanium, uranyl, lanthanum, cerium, potassium, cadmium, zinc, cobalt, nickel, copper, magnesium, sodium, lithium, iron and calcium did not interfere. Sulfate, tartaric and citric acids interfered.

Colorimetric Methods

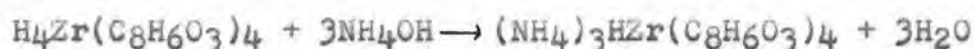
Quite a number of colorimetric reagents have been reported for the determination of hafnium and zirconium. Some of the more important ones which have been considered are briefly described in the following paragraphs.

Mandelic Acid - Kumins (48) observed that zirconium tetramandellate dissolves in dilute sodium hydroxide followed by immediate precipitation of the hydrous oxide. He found, however, that with ammonium hydroxide no precipitate was formed, thus indicating the probable formation of a soluble complex. Hahn and Weber (37) further studied this reaction and subsequently (38) developed an ultraviolet spectrophotometric method for zirconium. They found that the amount of

ammonia used to dissolve the zirconium tetramandellate was not critical. An alcohol and ether wash served to remove the excess mandelic acid from the zirconium tetramandellate. After two days, the solutions started to hydrolyze with precipitation of the hydrous oxide. Absorbance measurements were made at a wavelength of 258 mμ. It was postulated that the absorbance was caused by the phenyl groups of the zirconium tetramandellate, as ammonium mandelate solutions give an identical absorbance spectrum. These authors (37) also concluded from their studies on zirconium tetramandellate that it must be a chelate type compound as postulated by Feigl (21).



The reaction of ammonia with excess zirconium tetramandellate was thought to be

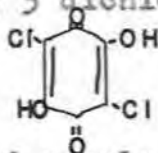


and with excess ammonia some $(\text{NH}_4)_4\text{Zr}(\text{C}_8\text{H}_6\text{O}_3)_4$ was believed to have formed.

Bricker and Waterbury (10) attempted to use p-bromomandelic acid instead of mandelic acid but found that each bottle of reagent was sufficiently different so that consistent and reproducible results could not always be obtained.

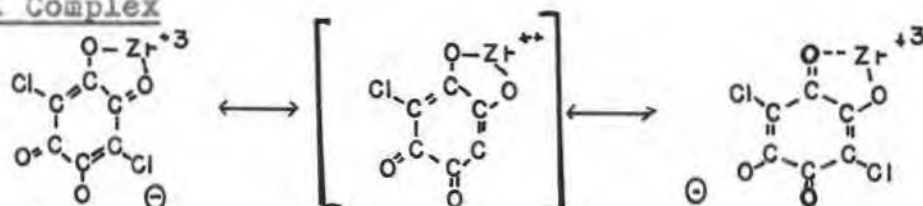
Chloranilic Acid - Thamer and Voigt (74; 75) found that

chloranilic acid (2, 5 dichloro-3, 6 dihydroxy-p-quinone)

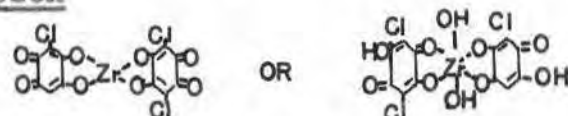


forms soluble colored complexes with zirconium in perchloric acid solution. The color reaction was rapid and a true solution that was stable indefinitely was claimed. A spectrophotometric method for zirconium at formalities of 2×10^{-6} to 5×10^{-5} was developed with the absorption being measured at 340 mμ. Although both a 1:1 and 1:2 complex was formed, the color was found to be due principally to the 1:1 complex. The structure postulated for these complexes is shown below.

1:1 Complex



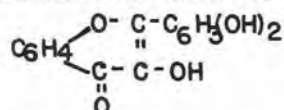
1:2 Complex



Frost-Jones and Yardley (28) determined zirconium with chloranilic acid in the visible range at 525 mμ. At this wavelength, the sensitivity is much less than at 340 mμ thus making it possible to determine considerably larger amounts of zirconium. Concentration of zirconium should not be greater than 1.5 mg. per 50 ml. as solutions may become cloudy. The color intensity was found to decrease sharply over the range of 0 to 3.5 molar perchloric acid.

Bricker and Waterbury (10) used chloranilic acid to determine zirconium in microgram amounts in plutonium alloys. For best results, the zirconium was separated from other metals by a double precipitation with p-bromomandelic acid. Absorbance measurements were made at 350 mμ. Hahn and Johnson (35) analyzed for zirconium in steel using the chloranilate complex. Interfering ions were first removed by electrolysis with a mercury cathode. Methods were described for samples containing 0.1 % zirconium or more and for those containing less than 0.1%. Measurements on the 0.1% zirconium or more samples were made at 525 mμ and for the less than 0.1% samples at 330 mμ. Interferences were found to be the same at both wavelengths. Quantitative results were obtained in solutions 1.5 to 2.5 M in perchloric acid. Acid concentrations lower than 1.5 M gave high results and concentrations greater than 2.5 M gave low results.

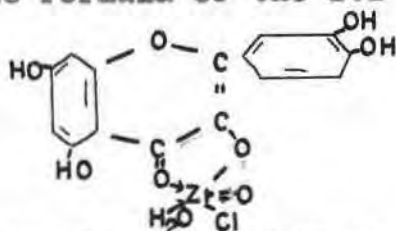
Quercetin - Grimaldi and White (31) have used quercetin



for the determination of trace quantities of zirconium. The reaction for this determination was carried out in 0.5 N hydrochloric acid. Under the conditions used, quercetin forms a 1:2 complex although a 1:1 complex may exist under certain conditions. Absorption measurements were made at 440 mμ. It was necessary to use alcohol to

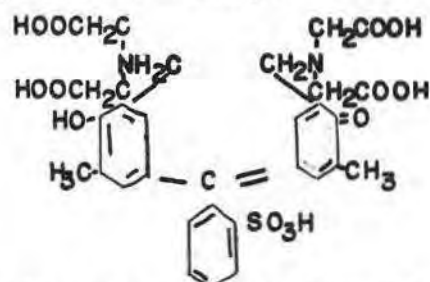
prevent precipitation of the quercetin. The absorbancy was found to be almost independent of acid concentration in the range 0.1 to 1 N. The color reaction could also be carried out in nitric or perchloric acid but not in sulfuric.

The formula of the 1:1 complex was postulated to be:



From the data given in this paper, the molar absorbance was found to be about 26,000 which makes this a very sensitive reagent for zirconium. The authors recommend this reagent for macro determinations as well as micro.

Xylenol Orange - The use of Xylenol Orange (3:3'-bis-N:N-di(carboxymethyl)-aminomethyl -o-cresolsulphonphthalein)



as a colorimetric reagent for the determination of zirconium and hafnium has been investigated extensively by Cheng (12; 13; 14; 15; 16). These papers have shown Xylenol Orange to be one of the most sensitive and selective colorimetric reagents for zirconium and hafnium. The molar absorbance of the zirconium complex in 0.2 N sulfuric acid

was reported to be 33,840 at 535 μ . Since Xylenol Orange is an acid-base indicator, it was found to change color from yellow to purple at about pH 6. The yellow solution of the dye was found to show maximum absorption at 437 μ . Optimum acid concentration for the complex was 0.15 to 0.25 N with sulfuric acid, and both perchloric and hydrochloric acids gave their maximum absorbance at 0.8 N concentration. With perchloric acid, the complex should stand two hours or more for maximum color development. Effect of interferences was also studied extensively by the author.

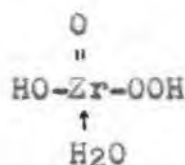
It was found that the maximum absorption of the hafnium - Xylenol Orange complex was at 530 μ in 0.3 N perchloric acid. According to Cheng (14) the molar absorption of the hafnium - Xylenol Orange complex was found to be 25,100 at 535 μ as compared with 38,800 for the zirconium - Xylenol Orange complex at 540 μ in 0.8 N perchloric medium. However, in 0.3 N perchloric acid the molar absorption of the hafnium complex was found to be 48,700 which was much greater than that of the zirconium complex.

In reference (14) this same author reports the molar absorptivity of the zirconium complex in 0.8 N perchloric acid to be 24,200 at a wavelength of 535 μ and 15,700 for the hafnium complex in 0.2 N perchloric acid at

530 mμ. No explanation was offered for the large differences reported in these papers.

One of the most valuable findings to come out of this work was in observing the masking effect of hydrogen peroxide on the zirconium complex. The masking effect on the hafnium complex was only slight. This, therefore, made possible the development of an analytical method for the determination of trace amounts of zirconium and hafnium when present together.

The masking effect of the hydrogen peroxide on the zirconium - Xylenol Orange complex was postulated to be due to the formation of a relatively stable zirconyl peroxide complex:



It is also interesting to note that hydrogen peroxide will mask niobium which is often one of the chief interferences with zirconium and hafnium.

Alizarin Red S, Alizarin, Quinalizarin and Purpurin -

Liebhafsky and Winslow (54) first described the use of alizarin, quinalizarin and purpurin for the determination of zirconium and hafnium. They found that quinalizarin was the most sensitive reagent followed by purpurin, and alizarin was the least sensitive but it adhered to Beer's law over a wider range of concentrations. The alizarin

and purpurin formed red complexes and the quinalizarin purple. They found that no matter which of these dyes were used, a precipitate eventually settled out. The purpurin and quinalizarin settled out most rapidly. It was claimed that zirconium and hafnium formed lakes with these dyes and evidence was presented to show that the hafnium - alizarin lake was a 1:1 compound. Flagg, Liebhafsky and Winslow (22) found that zirconium also formed a 1:1 compound with alizarin, quinalizarin and purpurin.

Green (30) developed a colorimetric method for the determination of zirconium in clays using the red complex formed by sodium alizarin sulfonate and zirconium. Color development was found to be complete in one hour and stable at least four hours. This method was capable of detecting from 0.003 mg. to 0.275 mg. of ZrO_2 in clays. Absorbance readings were made at 520 m μ . Wengert (77) used this reagent for the analysis of zirconium in magnesium - base alloys. He found it to be equal to or better than gravimetric methods and applied it to samples containing 0.10 to 1.00% zirconium. This author found that optimum color development required about 15 minutes and was stable for two or three days. Silverman and Hawley (71) used alizarin Red S to determine 0.005 to 0.350% of zirconium in thorium. They found that many interferences were reduced by adjusting the pH to 0.70. They also found that acetone

and heat will accelerate the rate of color development and increase the stability of the color. Manning and White (57) and Freund and Holbrook (27) have successfully applied differential spectrophotometric methods for the determination of zirconium and hafnium in zirconium, respectively, using alizarin Red S. These will be discussed in a following section.

It can be seen from above that alizarin is one of the most widely used of the colorimetric reagents for the determination of zirconium and hafnium.

Other Colorimetric Reagents - Horton (44) has described a method for the determination of zirconium using "Thoron". Measurements were made at 555 m μ and covered a range of 10 to 100 ppm. of zirconium. Fletcher and Milkey (24), in a study of the Thorium - Morin color system included data which suggested the application of Morin to the determination of zirconium and hafnium.

The blue color of the zirconium - pyrocatechol violet complex was utilized by Young, French and White (82) for the microdetermination of zirconium in sulfuric acid solutions with Pyrocatechol Violet. Measurements were made at 650 m μ and its molar absorbance at this wavelength was claimed to be 32,600 which would make this a very sensitive colorimetric reagent. As would be expected, hafnium was found to form a complex of equivalent molar absorbancy.

Fletcher (23; 25) has recently introduced the use of 2, 2', 4'-Trihydroxyazobenzene-5-Sulfonic acid as a colorimetric reagent for zirconium. These papers were principally theoretical studies. It was found that both a 1:1 and a 2:1 complex of dye to zirconium were formed. Both complexes were found to be true chelates. Still more recently Rolf (68) extracted zirconium with di-n-butyl phosphate and determined it directly in the organic phase with 1-(2-Pyridylazo)-2-naphthol. This method was claimed to be very sensitive and selective for the separation and determination of microgram quantities of zirconium in Al-Mg alloys. The system obeyed Beer's law from 10 to 65 ug. of zirconium per 25 mls. The molar absorptivity was claimed to be about 32,000.

There are a few additional colorimetric reagents for zirconium which have not been described. However, these are of limited value.

Indirect Chemical Determination of Hafnium - Zirconium Ratios

A number of indirect chemical methods have been described for the determination of hafnium in the presence of zirconium. However, most of these have serious limitations and none are completely adequate in the 0 to 10% HfO_2 range.

These indirect chemical methods are adequately reviewed by Goward and Jacobs (29, p. 300-2). All of these methods involve the determination of the total hafnium and zirconium by two independent chemical methods, one of which is usually the weighing of a mixture of the pure ignited oxides and the other a gravimetric, volumetric or spectrophotometric procedure. The composition of the mixture is then found by solving two simultaneous equations or determined on the basis of a calibration curve in which a fixed weight of known oxide mixtures are used. Some of these indirect chemical methods will be briefly mentioned in the following paragraphs.

A phosphate precipitation method has been described for the determination of hafnium in zirconium. These metals were isolated as the pure oxides, weighed, dissolved and reprecipitated with ammonium phosphate and ignited to the pyrophosphates for the second weighing. The reverse procedure has also been used (29, p. 301).

Werniment and DeVries (76) based a method on the increased effect of hafnium over zirconium on the optical rotation of solutions of tartaric acid. Claassen (17) and Schumb and Pittman (69) utilized a mixed selenite procedure to determine the zirconium - hafnium ratios.

As previously mentioned, Hahn (34) determined the ratios using p-bromomandelic acid as a weighing form

in conjunction with a mixed oxide weight.

A differential spectrophotometric method using alizarin Red S was developed by Freund and Holbrook (27). 10 to 50% ZrO_2 in HfO_2 was determined by measuring the absorbance against a permanent standard prepared from strips of colored cellophane. A calibration curve was prepared from known mixtures of HfO_2 and ZrO_2 all at the same total oxide level.

A number of other methods based on the determination of mixed halides, sulfates etc. have been proposed but have not received much attention because of the difficulty of obtaining these compounds in a reproducibly pure form. Density measurements have also been used but have not proved very satisfactory.

None of these methods above except that of Freund and Holbrook hold much promise of being applied to the determination of 0 to 5% HfO_2 in ZrO_2 . The method of Freund and Holbrook will be further discussed in a later section.

Differential Spectrophotometry

Differential spectrophotometry refers to that technique in which the concentration of an unknown sample is determined by measuring its transmittance or absorbance relative to a standard solution of known concentration.

This is usually done with the specific objective of reducing the relative concentration error.

A differential method can decrease the relative error in the determination of concentrations in two ways. The determination of the concentration of an unknown by measuring its transmittance or absorbance relative to a reference solution of known concentration can result in an increase in the relative precision of the concentration measurement. This is true since any error in the spectrophotometric measurement will result only in an error in the difference in concentration between the unknown and reference solutions. The second way in which a differential method may reduce the relative error is in the compensation of systematic errors. For example, a slight error in setting the wavelength for a given solution will affect both the reference and sample absorbances to approximately the same extent when the concentrations are the same or nearly so (59).

In 1955, Reilley and Crawford (65) described theoretically, four spectrophotometric methods and called these Method I, II, III and IV. Methods I and II had been described previously, but III and IV were newly proposed methods. These four methods of operation are described below:

Method I. "Ordinary" Method. The instrument is set

to read 0 with the photocell in darkness and to read 100 when exposed to light which has passed through pure solvent.

Method II. "Transmittance-Ratio" Method. The instrument is set to read 0 with the photocell in darkness and to read 100 when exposed to light which has passed through a reference solution more dilute than the sample.

Method III. "Trace Analysis" Method. The instrument is set to read 100 when exposed to light which has passed through the pure solvent and to read 0 when exposed to light which has passed through a reference solution somewhat more concentrated than the sample.

Method IV. "General" Method. Reference solutions are used to set both the 0 and 100 end of the scale.

Method II was known, used and discussed by many investigators previous to this paper of Reilley's. Interest in the "transmittance-ratio" method was promoted by the papers of Kortüm (47), Kortüm and Seiler (46), Ringbom (67), Bastian (5; 7), Bastian, Weberling and Palilla (6), Hiskey (42), Hiskey and Firestone (41), Hiskey, Rabinowitz and Young (43), Young and Hiskey (81) and Ringbom and Osterholm (66). These papers were concerned primarily with the theory and principles of this method

which will be further discussed later. Papers subsequent to these have been concerned with application, evaluation and extension of Methods II, III and IV. Among these are articles by Lothe (55), Freeland and Fritz (26), Banks, et al (4), Banks, Spooner and O'Laughlin (2; 3), Manning and White (57), Carvallo (11), Reilley and Hildebrand (64), Freund and Holbrook (27), and Crawford (18).

The principles of differential spectrophotometry are also briefly discussed in many of the more recent instrumental analysis books such as Willard, Merritt and Dean (79, p. 50-5) and Ewing (20, p. 57-60).

Since this thesis work has been principally concerned with Method II described above, in general the remaining discussion will be confined to this method.

As previously mentioned, the principle objective in using a differential method is to reduce the relative error. This is designated as dC/C or $\Delta C/C$. Bastian, Weberling and Palilla (6) developed an equation relating this relative uncertainty in concentration, $\Delta C/C$ to the uncertainty in absorbance, ΔA . This is given by

$$\Delta C/C = \Delta A/SxC$$

where S is the slope of the absorption - concentration curve at any concentration C . This equation is independent of Beer's law which is a special case when S is

constant. From this relationship it can be seen that in order to make $\Delta C/C$ as small as possible, A should be as small as possible and SxC as large as possible. Since ΔA is usually relatively constant for a given instrument S or C or S and C must be increased in order to decrease $\Delta C/C$.

Using Method II, the SxC product is maximized by increasing C where C is the concentration of the reference solution. As C is increased, then wider slit widths than normal must be used to balance the instrument. This results in less monochromatic light and eventually in an apparent deviation from Beer's law. When this happens the slope, S , begins to decrease. Therefore, it is apparent that the optimum conditions for a minimum $\Delta C/C$ will occur when SxC is a maximum. From this it is seen that if SxC vs. C is plotted, the curve will rise to a maximum and then decline. The optimum concentration is then taken at the point where SxC is a maximum.

In order to determine the best transmittance and absorbance range for finding C relative to a reference standard, we will consider the following. The relationship for finding the concentration C for a sample using the "transmittance-ratio" method is given by

$$(1) C = \frac{1}{ab} \log \frac{1}{T_1} + \frac{1}{ab} \log \frac{1}{T_R}$$

and the relative uncertainty in this concentration is

given by

$$(2) \Delta C/C = \frac{\Delta T}{T_1(\ln T_1 + \ln T_R)}$$

where T_1 is the transmittance relative to the reference solution and T_R is the transmittance of the reference solution. The $T_1(\ln T_1 + \ln T_R)$ term increases with T_1 if the transmittance of the reference solution relative to solvent is 0.368 or smaller and $\Delta C/C$ will be at a minimum when $T_1 = 1$, and also if the absorbance of the reference solution relative to solvent is 0.4343 or larger, the absorbance of the unknown sample relative to the reference should be as small as possible (59; 6; 42). The useful transmittance range for this method is from 20 to 100.

O'Laughlin and Banks (59) expressed the opinion that the compensation of systematic errors which is inherent in this method may be equally as important as the theoretical increase in precision.

Lothe (55) and Reilley and Hildebrand (64) have described indirect "transmittance-ratio" methods which potentially are very useful. In the indirect methods, the substance to be determined is added to a colored solution which is bleached as a result of the addition. The extent of the bleaching can then be related to the amount of the substance added. Lothe (55) shows that for the ideal case, the optimum absorbance of the sample solution in indirect spectrophotometry is zero. He also developed

an equation for the relative error when the instrument is balanced at the 100 end of the scale with a reference solution slightly more bleached than the same solution,

$$\frac{\Delta C_1}{C_1} = \frac{T_1}{T_1'(\ln T_1' - \ln T_u)}$$

and where $\Delta C_1/C_1$ is the relative concentration error of the bleached solution T_1 and T_u is the transmittance of the original unbleached solution.

Using the indirect approach there is no instrumental limit on how high the absorbance of the unbleached solution is made since it is not necessary to make any spectrophotometric measurements on it. It would therefore appear that there would be no instrumental limit to the possible gain in relative precision by this procedure. O'Laughlin and Banks (59) have labeled this the "ultimate method" but have qualified this by admitting that this approach is greatly limited by the lack of suitable color systems. It should also be recognized that none of these methods are any better than the chemical manipulations which accompany them. In many cases these will be the limiting factors rather than the instrumental measurements.

Now that the differential method has been described, as well as the various color systems available for hafnium and zirconium, it is possible to outline the experimental approach to the thesis problem of determining 0 to 5%

HfO₂ in the presence of ZrO₂. This will be taken up in the next section on "Approach to the Problem"

APPROACH TO THE PROBLEM

With the background which has been included in the preceeding sections it is now possible to state the problem and to outline theoretically the experimental approach to it.

The problem was to find a method for determining accurately 0 to 5% HfO_2 in the presence of ZrO_2 by utilizing the differential spectrophotometric Method II.

As previously stated, the molar absorptivities of given zirconium and hafnium complexes are essentially identical. Therefore, for the same weight of ZrO_2 and HfO_2 , the difference in absorbance (ΔA) will be due to the difference in their atomic weights. This can be seen from the following relationships:

$$(1) \quad A_{\text{ZrO}_2} = \epsilon \times b \times C \times 1/\text{ZrO}_2$$

$$(2) \quad A_{\text{HfO}_2} = \epsilon \times b \times C \times 1/\text{HfO}_2$$

where ϵ is the molar absorbtivity of the complex, b is the cell path length and C is the weight concentration in grams per liter. The A 's shown would actually be for the complexes but they are written in terms of the oxides for convenience.

If the total weight of the oxides are held constant, $W_{\text{ZrO}_2} + W_{\text{HfO}_2} = W_t = \text{constant}$, it can then be seen that the absorbance of any mixture of HfO_2 and ZrO_2 must lie

between limiting values set by the pure components. The relationship of A_{HfO_2} to A_{ZrO_2} can be found by dividing equation (2) by (1), then:

$$(3) \frac{A_{HfO_2}}{A_{ZrO_2}} = \frac{\epsilon \times b \times C \times 1/HfO_2}{\epsilon \times b \times C \times 1/ZrO_2}$$

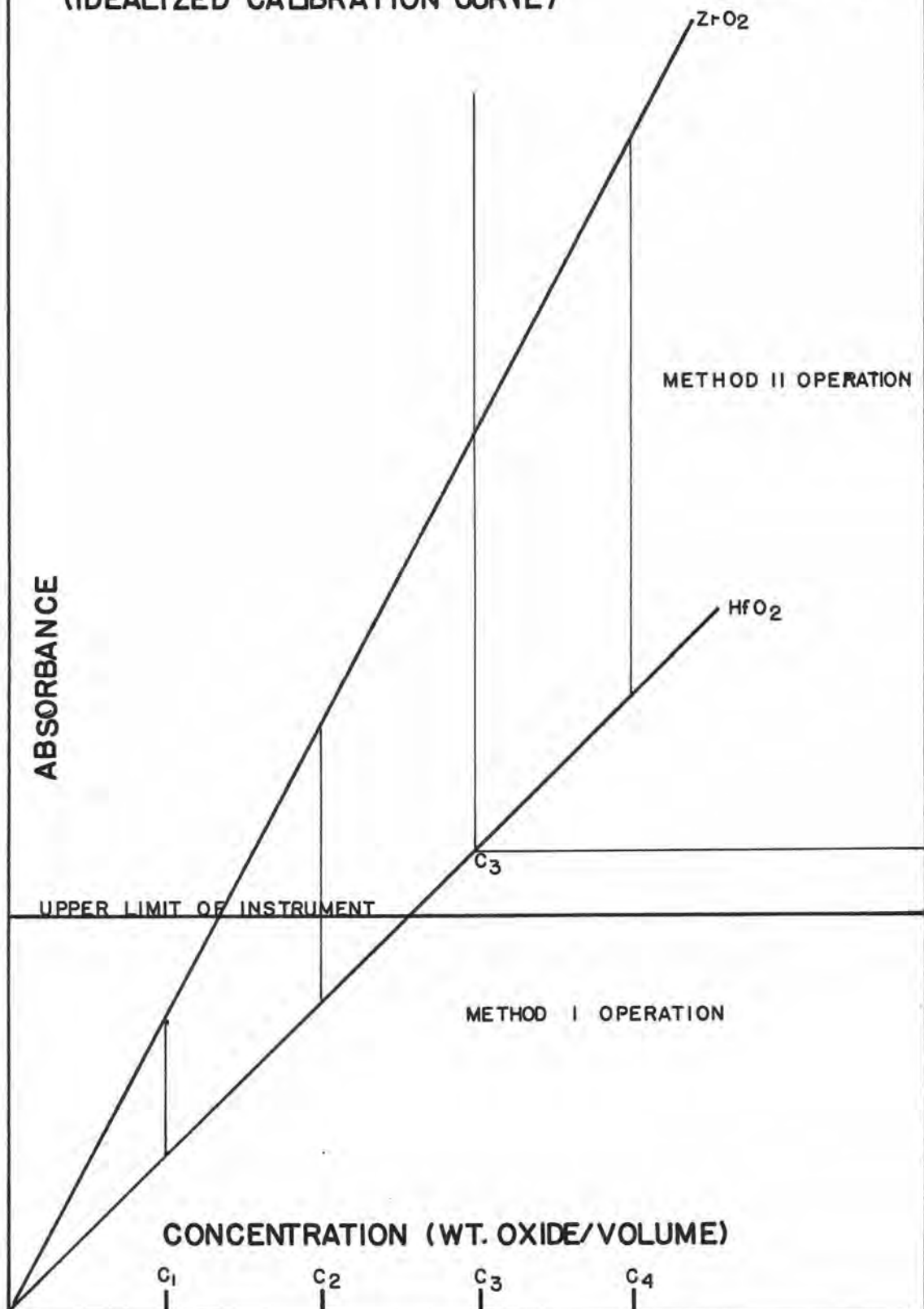
$$(4) \frac{A_{HfO_2}}{A_{ZrO_2}} = \frac{ZrO_2}{HfO_2} = \frac{123.2}{210.5} = 0.585$$

Then for a given concentration (Wt./vol.) of HfO_2 and ZrO_2 , the absorbance of the HfO_2 solution would be $0.585 \times A_{ZrO_2}$. It can therefore be seen that ordinary spectrophotometry would be completely inadequate for small amounts of HfO_2 in ZrO_2 . However, Method II (transmittance-ratio) operation, in effect, permits a scale expansion since an absorbing solution is used as the reference solution. These relationships can more clearly seen from Figure 1.

It is clear from this diagram of idealized calibration curves that as the concentration increases, the curves become more widely separated. However, as we go to higher concentrations such as C_2 , C_3 , etc; where the absorbance curves are sufficiently separated, the limits of the instrument are exceeded for Method I. However, using these higher concentrations (C_1 , C_2 , C_3) as reference solutions to set the 100% T scale reading of the instrument, acceptable Method II calibration curves are obtained. It is also seen that the greater the

ABSORBANCE VS. CONCENTRATION
(IDEALIZED CALIBRATION CURVE)

FIGURE 1



concentration of reference solution, the greater the separation of calibration curves and the more sensitive the method becomes to the detection of hafnium. In an actual case, the optimum concentration will produce the largest separation of curves with minimum relative error.

The optimum concentration was discussed briefly in the preceeding section where the relation

$$\frac{\Delta C}{C} = \frac{\Delta A}{Sx C}$$

was given. Since this equation was not derived at that point, it is derived below starting with the fundamental equation suggested by Reilley (65).

(1) $R = kI + k'$ where R = instrument dial reading, k = sensitivity, I = amount of light issuing from the sample, k' = dark current setting. A linear relationship between I and R is assumed.

(2) Boundary conditions for R , 0 and 100

$$R = 100 \text{ when } I = I_1$$

$$R = 0 \text{ when } I = I_2$$

(3) When $R = 100$,

$$100 = kI_1 + k'$$

$$\text{and when } R = 0,$$

$$0 = kI_2 + k'$$

then

$$100 = kI_1 - kI_2$$

$$k = \frac{100}{I_1 - I_2}$$

$$k' = -kI_2 = \frac{-100 I_2}{I_1 - I_2}$$

- (4) Substituting these relations into (1),

$$R = \frac{100}{I_1 - I_2} \times I - \frac{100 I_2}{I_1 - I_2}$$

and therefore,

$$R = 100 \frac{I - I_2}{I_1 - I_2}$$

- (5) Assuming that Beer's law is valid

$$I = I_0 10^{-abC} = I_0 e^{-2.303abC} = I_0 e^{-uC}$$

where $u = 2.303ab$

- (6) Substituting into equation (4)

$$R = 100 \frac{(e^{-uC} - e^{-uC_2})}{(e^{-uC_1} - e^{-uC_2})}$$

and solving for C

$$e^{-uC} = R/100 \quad e^{-uC_1} - e^{-uC_2} + e^{-uC_2}$$

$$C = -1/u (\ln R/100) e^{-uC_1} - e^{-uC_2} + e^{-uC_2}$$

- (7) Applying boundary conditions of Method II.

$$R = 100, C_1$$

$$R = 0, C_2 =$$

$$C = -1/u (\ln R/100) e^{-uC_1} - 0 + 0$$

$$C = -1/u \ln R/100 + \ln e^{-uC_1}$$

- (8) $C = C_1 - 1/u (\ln R/100)$

$$C = C_1 - \frac{1}{2.303ab} (2.303 \log R/100)$$

$$C = C_1 - 1/ab (\log R/100)$$

Substituting $A = -\log R$ into this equation

we obtain

$$C = C_1 + \frac{A}{ab} - \frac{2}{ab}$$

(9) Differentiating gives

$$dC = \frac{dA}{ab}$$

and dividing both sides of the equation by C

$$\frac{dC}{C} = \frac{dA}{abC}$$

$$\text{or } \frac{\Delta C}{C} = \frac{\Delta A}{abC}$$

where $\Delta C/C$ is the relative uncertainty in concentration and ΔA is the minimum difference in absorbance that can be detected.

(10) Substituting, $a = \frac{\Delta A}{\Delta C} = S$ into equation (9),

$$\frac{\Delta C}{C} = \frac{\Delta A}{Sx C} \text{ when } b = 1 \text{ cm.}$$

Equation (10) is correct if Beer's law is followed and therefore the greater the concentration the smaller the relative error in the determination of concentration. However, a concentration level is reached ultimately where for both chemical and instrumental reasons deviations from Beer's law results in an increase in this relative error. This suggests that an optimum concentration should exist.

Negative deviations from Beer's law caused by chemical deviations may be due to the presence of more than one absorbing species, polymerization, or to excessive concentration. This latter case may also result in

instrumental deviations as well as chemical.

As solutions of increasing concentrations are employed less and less, radiant energy will strike the detector. Ultimately, a point must be reached even though the system obey's Beer's law perfectly, where the signal to noise ratio will limit the useful operation of the detector. Failure of the equation $R = kI + k'$, or its equivalent, $R = k k_c I + k'$ will also occur when such concentrated solutions are used that no radiant energy issues from the sample and I will then become zero. If k , the photocell sensitivity at a given wavelength is not great enough to sufficiently detect the extremely small signal received by it through the highly absorbing sample solution or k_c , the circuit sensitivity is not great enough to adequately amplify the signal from the photocell, then the equation $R = kI + k'$ will become non-linear. In order for this equation to be applicable, I must be large enough so that k does not have to be made so large that instrumental instability will result. The maximum usable amplification is fixed by the signal-to-noise ratio.

An excellent way in which to increase k , without increasing k_c , when I is relatively small is to replace the ordinary phototube with a photomultiplier tube. This can increase k as much as 100 to 200 times without

increasing k to a degree that will result in instability. Ordinary vacuum phototubes have a maximum photocurrent sensitivity of 10 to 40 microamperes per lumen while photomultiplier tubes have sensitivities of the order of 20 to 20000 amperes per lumen. In practice however, the actual photocurrent must be of the order of microamperes as excessive currents will damage the tube (50).

Photomultipliers are generally useful from about 10^{-14} to 10^{-4} lumens. The continuous current flowing from the anode should be kept below 1 milliampere to avoid fatigue effects. For maximum stability, the current should be in the range 0.1 to 0.001 milliamperes (51). These tubes have a linear response over a wide range of light intensities leading to anode currents of 10^{-12} to 10^{-5} amperes. Amplification can be pushed to the limits imposed by shot - effect noise, approximately 6×10^{-12} amperes, without seriously increasing the number of erratic excursions of the indicating meter. This limit may be diminished by reducing the temperature at which the tube is operated, the reason for which will be given in a later paragraph.(19).

The superiority of a photomultiplier tube over an ordinary photocell, with respect to random noise, increases as the illumination decreases. The photomultiplier can measure intensities about $1/200$ as strong as

those measurable with an ordinary photocell(19). In the case of the Beckman Model DU Spectrophotometer, the electrometer - amplifier circuit is sensitive to phototube currents as small as 10^{-13} amperes. This amounts to an IR drop in the phototube resistor (2000 megohms), produced by the light induced photocurrent, of 0.2 millivolts. If a photomultiplier tube is used in place of the ordinary phototube the sensitivity is increased 100 times (53).

The sensitivity of a spectrophotometer is ultimately limited by the signal - to - noise ratio. Electrical noise arises in electronic circuits from the random motion of electrons in conductors, resistors, and vacuum tubes, generating spontaneous voltage fluctuations that are superimposed on whatever directed voltages are present. The three types of noise commonly encountered in electronic circuits are thermal - resistor, or Johnson noise, noise from fluctuations in plate and grid currents, and shot effect noise. The magnitude of the noise voltage associated with a resistance, R is given by the equation:

$$e_n^2 = 4kTR(f_2 - f_1)$$

where e_n^2 is the root - mean - square value of the noise voltage, k is the Boltzman constant, T the absolute temperature, and $(f_2 - f_1)$ is the band width, or range of frequencies under consideration (52).

Whenever the voltage drop produced by a photocurrent

in an input resistor R is applied to the grid of the input tube of an amplifier, thermal resistance noise is added to the shot noise in the photocurrent. Whenever the voltage drop in the resistor produced by the total photocurrent i is less than 0.05 volt, the thermal resistance noise exceeds the shot noise. Since the input resistance cannot be increased without limit, this condition is commonly found. The total noise voltage at the input is given by the equation:

$$e_n^2 = (2eiR^2 + 4kTR)(f_2 - f_1)$$

From this it would then appear that it would be desirable to preamplify the photocurrent to a relatively high value by some method which does not introduce thermal noise. This can be accomplished by the use of a photomultiplier tube. Detailed analysis has shown that the mean square noise current in the output of a photomultiplier exceeds only slightly the mean square noise current in the emission of the photocathode multiplied by the square of the gain of the multiplier tube. This excess decreases as the gain per stage of the photomultiplier is increased. Secondary - emission amplification in the photomultiplier tube raises the level of the signal current to a point at which the amplified shot noise in the original photocurrent, overrides the thermal noise generated in the input resistance of a succeeding

conventional amplifier, as well as the tube noise of the amplifier. This is accomplished without appreciably reducing the signal - to - noise ratio to a value below that of the original photocurrent. The noise output of an n - stage photomultiplier with a gain G per stage is given by the following formula,

$$i_n^2 = 2e i_0 (f_2 - f_1) \frac{G^{2n} + 1 - G^n}{G - 1} = 2e i_0 (f_2 - f_1) (1 + \frac{1}{G} + \dots) G^{2n}$$

The i_0 term is the emission current from the photocathode, comprising both photoemission and thermionic emission (dark current). Since the output signal current is $i_s G^n$, i_s being the photocurrent generated by the light, the ratio of signal to noise current becomes,

$$\frac{i_s G^n}{(i_n^2)^{\frac{1}{2}}} = \frac{i_s}{[2e i_0 (f_2 - f_1) (1 + 1/G + \dots)]^{\frac{1}{2}}} \quad (83).$$

At this point a little more will be said about the dark current previously mentioned. Any phototube to which voltage is applied will pass a certain amount of current even if the photocathode is unilluminated. Such dark currents are most significant in devices employed for the measurement of very small amounts of light such as photomultiplier tubes where the relatively high potential differences present in these tubes may accentuate these currents (83). At the normal operating voltages of photomultiplier tubes (and at room temperature) thermionic emission is the principle source of dark

currents. Thermionic emission depends only upon the work function of the emitting surfaces and their temperature. The specific emission of a surface is given by the formula:

$$j = AT^2e^{-W/kT} = AT^2e^{-11.607W/T}$$

where T is the absolute temperature of the surface, W its work function in electron volts, and k the Boltzman constant. The constant A is, for pure metals, of the order of 1.2×10^6 amperes per square meter per degree squared. The exponential factor is therefore very small and varies very rapidly with temperature. This relation also holds for composite surfaces, although in this case A is much smaller than the value given. It is therefore possible to greatly reduce the dark current by cooling the photomultiplier tube, for example, in liquid air. It has been shown that the dark current can be reduced from about 10^{-13} amperes at 40°C to 10^{-17} amperes at -120°C (83).

Deviations from Beer's law may also result from the use of excessive slit widths (or spectral band widths). In a prism instrument such as the Beckman Model DU Spectrophotometer, the spectral band width will increase as the slit width is increased. This will result in a decrease in the absorption maxima and it is therefore desirable to use small slit widths. The minimum slit

width at which measurements can be made with a given solution is dependent upon the energy of the light source, the sensitivity of the detector, and the absorbance of the solution. In a prism instrument the light dispersion depends upon wavelength and therefore the minimum slit width will depend upon the wavelength at which the solution is measured. A photomultiplier will of course, make it possible to use much smaller slits than would otherwise be possible, thus minimizing deviations due to excessive spectral band widths and making it possible to measure much more highly absorbing solutions than would otherwise be possible.

In addition to the above considerations, the 2,000 megohm phototube load resistor as used in the Model DU may show nonlinearities of as much as 0.2%. These departures from Ohm's law are largest at low current and represent an important reason for operating at as high light levels as other conditions permit when measurements of the highest accuracy are required (53).

When measuring very low incident light intensities, the sensitivity of different regions of the photosensitive surface may vary significantly and may be a source of error (80).

Experimentally, the optimum concentration previously mentioned, can be determined as follows. A series of

standard solutions of the complex, differing by a fixed increment, is prepared and the absorbance of each solution is measured against the solution of the next lowest concentration as reference. In making these measurements, the spectrophotometer is balanced at 0 absorbance, ($R = 100$) with the reference solution in the light path, making a rough adjustment with the slit control and the fine adjustment with the sensitivity control. O'Laughlin and Banks (59) claim that the sensitivity should remain essentially constant as changing it will change ΔA which is assumed to be constant. It is not clear however, how significant this is.

If the relative absorbance (ΔA) values measured are divided by the concentration increment ΔC then the average value for the slope, S , of the absorbance vs. concentration curve is obtained for the concentration range of the two solutions. The optimum concentration will then be that concentration at which $S \times C$ is a maximum.

In order to assist in the selection of color systems which might be suitable for the differential Method II approach, the following derivation was made in which the relative absorbance or relative $\log R$ can be estimated between any two solutions.

Starting with the relationship already derived,

$$(1) \quad C = C_1 - \frac{\log R/100}{\epsilon \times b}$$

and applying to the determination of HfO_2 in ZrO_2 .

$$(2) \quad C = \frac{fW_t}{\text{HfO}_2} + \frac{W_t(1-f)}{\text{ZrO}_2}$$

$$C_1 = \frac{f_0W_t}{\text{HfO}_2} + \frac{W_t(1-f_0)}{\text{ZrO}_2}$$

where $W_t = W_{\text{ZrO}_2} + W_{\text{HfO}_2} = \text{constant} = g/1$

f_0 = weight fraction of HfO_2 in solution 1, C_1 .

f = weight fraction of HfO_2 in any solution, C .

Substituting into equation (1) gives,

$$(3) \quad \frac{fW_t}{\text{HfO}_2} + \frac{W_t(1-f)}{\text{ZrO}_2} = \frac{f_0W_t}{\text{HfO}_2} + \frac{W_t(1-f_0)}{\text{ZrO}_2} - \frac{1}{b} \log R/100$$

When $f = 0$, and $b = 1 \text{ cm.}$, equation (3) becomes

$$\frac{W_t}{\text{ZrO}_2} = \frac{f_0W_t}{\text{HfO}_2} + \frac{W_t(1-f_0)}{\text{ZrO}_2} - \frac{1}{\epsilon} \log R/100$$

$$\frac{W_t}{\text{ZrO}_2} - \frac{f_0W_t}{\text{HfO}_2} - \frac{W_t(1-f_0)}{\text{ZrO}_2} = \frac{1}{\epsilon} \log R/100$$

$$\frac{W_t}{\text{ZrO}_2} - \frac{f_0W_t}{\text{HfO}_2} - \frac{W_t}{\text{ZrO}_2} + \frac{f_0W_t}{\text{ZrO}_2} = -\frac{1}{\epsilon} \log R/100$$

$$\epsilon \left[\frac{f_0W_t}{\text{HfO}_2} - \frac{f_0W_t}{\text{ZrO}_2} \right] = \log R/100$$

$$\epsilon f_0W_t \left(\frac{1}{\text{HfO}_2} - \frac{1}{\text{ZrO}_2} \right) = \log R - \log 100$$

$$\epsilon f_0W_t \left(\frac{1}{210.6} - \frac{1}{123.2} \right) = \log R - 2.000$$

$$(4) \quad \log R = 2.000 - \epsilon f_0W_t \times 3.365 \times 10^{-3}$$

This relationship will then give $\log R$ for a solution containing only ZrO_2 when measured against a reference solution containing some fraction of HfO_2 .

The derivation above was checked by another approach

which is found in appendix D.

It can be seen from these derived relations that it is desirable to have the molar absorbanoy (ϵ) and the total weight of oxides as large as possible in order to permit the fraction of HfO_2 to be small. The optimum total weight of oxide (W_t) to be used can be found by following the procedure previously described.

In selecting the color systems to be investigated, the literature was consulted (see preceeding section) and those systems which seemed to have desirable characteristics and would lend themselves to this type of treatment were investigated.

The mandelic acid system was first investigated since it could be used to separate as well as determine zirconium and hafnium. In this approach, the sample was precipitated with mandelic acid to give the zirconium and hafnium tetramandelates which were weighed directly. These were then dissolved in ammonia and the absorbance measured.

The second system to be tried was one utilizing chloranilic acid. This seemed to have possibilities due to its large molar absorptivity and stable color complexes formed with hafnium and zirconium.

Quercetin was the third system to be utilized. It has an even higher molar absorptivity than chloranilic

acid.

The final system to be investigated was Xylenol Orange. This system offered the possibility of an indirect "transmittance-ratio" approach and proved to be the most fruitful one.

Details of these investigations will be found in the experimental sections.

INVESTIGATION USING MANDELIC ACID

Objective

The objective of this research was to develop a differential spectrophotometric method for the determination of hafnium in zirconium. It was hoped that this could be accomplished by precipitating standard solutions prepared from known weights of ZrO_2 and HfO_2 with mandelic acid, filtering and drying the precipitates and finally weighing out exactly the same weight of each tetramandellate standard and dissolving it in 1 M ammonium hydroxide to a given volume. These solutions should then be able to be measured differentially by the "transmittance-ratio" method, the standard containing the largest amount of Hf being used as the reference solution. Each of the other standards should then be measured and a calibration curve of relative absorbance (ΔA) versus percent $Hf(M)_4$ constructed.

In order to accomplish this objective it was necessary to establish or confirm:

1. The conditions for quantitative precipitation of hafnium and zirconium with mandelic acid.
2. The absorption curves for mandelic acid, zirconium tetramandellate and hafnium tetramandellate in 1 M ammonium hydroxide.

3. The optimum concentration of zirconium and hafnium tetramandelate in 1 M ammonium hydroxide.

Apparatus

All absorbance measurements were made with the Beckman Model DU Spectrophotometer equipped with photomultiplier and ultraviolet light source. Matched silica cells were used for all absorbance measurements.

Reagents

1. Zirconium Oxide - High purity ZrO_2 obtained from the United States Bureau of Mines, Albany, Oregon was used as the source of zirconium for all zirconium solutions. Zirconium solutions were standardized by the cupferron method. (See Appendix).

2. Hafnium Oxide - High purity HfO_2 , $HfCl_4$ and $HfOCl_2 \cdot 8H_2O$ from the Bureau of Mines were used as the sources of all hafnium solutions. Hafnium solutions were standardized by the cupferron method. (See Appendix).

3. Mandelic Acid - Reagent grade mandelic acid (melting point, 118-119°C) available from Matheson, Coleman and Bell, Norwood, Ohio, was used for preparation of mandelic acid solutions.

4. Potassium Pyrosulfate - Reagent grade. Used for fusion of ZrO_2 and HfO_2 . May be obtained from J. T. Baker Chemical Co., Phillipsburg, New Jersey.

5. Wash Solutions -

A. Saturated zirconium tetramandelate solution. Added distilled water to a bottle containing excess solid zirconium tetramandelate and agitated.

B. Saturated hafnium tetramandelate solution. Same as (A) except solid hafnium tetramandelate was used.

Mandelic Acid Precipitation in Presence of Sulfate

Three 0.2 g. samples and three 0.05 g. samples of ZrO_2 and HfO_2 were weighed exactly into crucibles, 5 g. and 2 g. respectively of potassium pyrosulfate was added to each and the samples were fused until a clean melt was observed. The contents were then dissolved in 100 mls. of 2 M HCl solution, 50 mls. of 15% mandelic acid was added and the temperature was slowly raised to $85^{\circ}C$ and held there for about half an hour. The resulting precipitates were filtered through previously weighed medium porosity sintered glass crucibles and washed with a hot 2% HCl and 5% mandelic acid wash solution. Each sample was then washed three times with acetone and twice with ether. Air was then drawn through the precipitates for a few minutes and they were then placed in an oven at

110°C overnight. The results are summarized in Table I and II.

Although the zirconium gave essentially 100% yields with mandelic acid, the hafnium was low in each case. In order to determine whether this was due to the method of precipitation, a dropwise addition of mandelic acid solution was made. The ZrO_2 and HfO_2 samples were fused in pyrosulfate and dissolved as previously. The solutions were then heated to 85°C and 15% mandelic acid was added dropwise with constant stirring. They were digested for thirty minutes at this temperature and allowed to cool. They were filtered, washed and dried as previously described. The results are summarized in Table III and IV.

This procedure gave essentially the same results as the previous one. However, the precipitates obtained were grainier and more easily filtered but the procedure was much more time consuming.

Since actual standards and samples would be composed of the mixed oxides, a series of synthetic standards were prepared containing from 0% HfO_2 in ZrO_2 to 10% HfO_2 in ZrO_2 . These were fused with 2 g. of potassium pyrosulfate and the melts dissolved in 50 mls. of 2 M hydrochloric acid. 35 mls. of 15% mandelic acid was added to each solution and they were slowly heated to 85°C and

TABLE I

MANDELIC ACID PRECIPITATION
OF Zr IN PRESENCE OF SULFATE

Sample No.	ZrO ₂ Added (g)	Zr(M) ₄ Found (g)	ZrO ₂ Found (g)(calc)	Error (g)	%Recovery
1	0.2023	1.1583	0.2053	+0.0030	101.5
2	0.2082	1.1739	0.2081	-0.0001	100.0
3	0.1706	0.9752	0.1728	+0.0022	101.3
4	0.0520	0.2914	0.0517	-0.0003	99.4
5	0.0565	0.3163	0.0561	-0.0004	99.3
6	0.0630	0.3551	0.0629	-0.0001	99.8

TABLE II

MANDELIC ACID PRECIPITATION
OF Hf IN PRESENCE OF SULFATE

Sample No.	HfO ₂ Added (g)	Hf(M) ₄ Found (g)	HfO ₂ Found (g)(calc)	Error (g)	%Recovery
1	0.1847	0.6712	0.1804	-0.0043	97.7
2	0.1982	0.7235	0.1945	-0.0037	98.1
3	0.2034	0.7354	0.1977	-0.0057	97.2
4	0.0653	0.2350	0.0632	-0.0021	96.8
5	0.0580	0.2100	0.0565	-0.0015	97.4
6	0.0574	0.2091	0.0562	-0.0012	97.9

TABLE III

DROPSWISE MANDELIC ACID
PRECIPITATION OF Zr IN
PRESENCE OF SULFATE

Sample No.	ZrO ₂ Added (g)	Zr(M) ₄ Found (g)	ZrO ₂ Found (g)(calc)	Error (g)	%Recovery
1	0.0520	0.2914	0.0517	-0.0003	99.4
2	0.0565	0.3163	0.0561	-0.0004	99.3
3	0.0630	0.3551	0.0629	-0.0001	99.8

TABLE IV

DROPSWISE MANDELIC ACID
PRECIPITATION OF Hf IN
PRESENCE OF SULFATE

Sample No.	HfO ₂ Added (g)	Hf(M) ₄ Found (g)	HfO ₂ Found (g)(calc)	Error (g)	%Recovery
1	0.0653	0.2350	0.0632	-0.0021	96.8
2	0.0580	0.2100	0.0565	-0.0015	97.4
3	0.0574	0.2091	0.0562	-0.0012	97.9

were allowed to remain for thirty minutes. They were then allowed to stand overnight before filtering through sintered glass crucibles as previously described. These experimental results are summarized in Table V.

No explanation can be given for these generally high results especially since they ordinarily seem to be slightly low in presence of sulfate.

A series of experiments were carried out to determine whether precipitation in absence of sulfate would be advantageous. These results will be found in the following paragraph.

Mandelic Acid Precipitation in Absence of Sulfate

Standard sulfate free solutions of ZrO_2 and HfO_2 were prepared from $ZrOCl_2 \cdot 8H_2O$ and $HfOCl_2 \cdot 8H_2O$ respectively. Since $ZrOCl_2 \cdot 8H_2O$ was not available as such, it was prepared from ZrO_2 . (See Appendix). The standard ZrO_2 solution contained 3.248 mg./ml. of the oxide and the standard HfO_2 solution 4.692 mg./ml. of oxide in 2 M HCl solution.

25.00 ml. aliquots of both standards were precipitated and filtered in the same manner as previously except that they were filtered while still hot. These data will be found in Table VI and VII.

In general these data seem to show improvement over

TABLE V

MANDELIC ACID PRECIPITATION
OF SYNTHETIC SAMPLES IN
PRESENCE OF SULFATE

Sam- ple No.	ZrO ₂ Added (g)	HfO ₂ Added (g)	Total Oxide (g)	Mandelate (Theory) (g)	Mandelate (Found) (g)	Differ- ence (g)	%Er- ror
1	0.0982	-	0.0982	0.5540	0.5584	+0.0044	0.79
2	0.0992	0.0009	0.1001	0.5629	0.5612	-0.0017	0.24
3	0.0973	0.0029	0.1002	0.5597	0.5651	+0.0054	0.97
4	0.0958	0.0050	0.1008	0.5591	0.5649	+0.0058	1.0
5	0.0084	0.0084	0.1047	0.5745	0.5813	+0.0068	1.2
6	0.0096	0.0096	0.0994	0.5423	0.5466	+0.0043	0.78

TABLE VI

MANDELIC ACID PRECIPITATION OF
Zr IN ABSENCE OF SULFATE

Sample No.	ZrO ₂ Added (g)	Zr(M) ₄ Found (g)	ZrO ₂ Found (g)(calc)	Difference (g)	%Error
1	0.0812	0.4577	0.0811	-0.0001	0.12
2	0.0812	0.4565	0.0809	-0.0003	0.37
3	0.0812	0.4581	0.0812	-0.0000	0.00
4	0.0812	0.4542	0.0805	-0.0008	0.98
5	0.0812	0.4497	0.0797	-0.0015	1.8
6	0.0812	0.4540	0.0805	-0.0008	0.98

TABLE VII

MANDELIC ACID PRECIPITATION OF
Hf IN ABSENCE OF SULFATE

Sample No.	HfO ₂ Added (g)	Hf(M) ₄ Found (g)	HfO ₂ Found (g)(calc)	Difference (g)	%Error
1	0.1173	0.4384	0.1179	+0.0006	0.51
2	0.1173	0.4374	0.0076	+0.0003	0.26
3	0.1173	0.4397	0.1181	+0.0008	0.68
4	0.1173	0.4389	0.1180	+0.0007	0.60
5	0.1173	0.4382	0.1178	+0.0005	0.43
6	0.1173	0.4383	0.1178	+0.0005	0.43

those obtained in the presence of sulfate. This is especially true for the hafnium. Subsequent precipitations were therefore made in absence of sulfate.

Soon after this investigation, the paper of Hahn and Baginski (9) was consulted in which the optimum conditions for the direct weighing of zirconium tetramandelate was given. The next phase of this work was therefore concerned with testing these conditions for both zirconium and hafnium. The conditions outlined by these authors were:

1. The solution should be 5 M or greater hydrochloric acid.
2. The mandelic acid should be added dropwise with constant stirring to the hot (85°C-90°C) acid solution.
3. The solution should be cooled before filtration.
4. The precipitate should be washed with a saturated solution of zirconium tetramandelate followed by alcohol and ether.

Mandelic Acid Precipitation in Strong Hydrochloric Acid Solution

The standard sulfate free zirconium solution for this investigation contained 2.828 mg./ml. of ZrO_2 and the hafnium contained 3.740 mg./ml. of HfO_2 both in 6 M

hydrochloric acid.

Twenty-five mls. aliquots of these standards were used. 25 mls. of concentrated hydrochloric acid was added to each standard and was then heated to 85°C. 50 mls. of 15% mandelic acid was added dropwise with constant stirring. These solutions were digested for thirty minutes after the mandelic acid had been added. The precipitates were allowed to stand overnight before filtering through sintered glass crucibles. The zirconium and hafnium tetramandellate precipitates were washed with saturated solutions of the same, followed by acetone and ether. The results are summarized in Table VIII and IX.

The zirconium results look very good but the hafnium values are high. This is rather interesting since in all previous runs the hafnium had a tendency to be low. The only explanation that seems reasonable is that these hafnium precipitates were not washed enough to remove all the excess mandelic acid or that the ratio of mandelate to hafnium was slightly greater than 4:1. The latter explanation seems to be the more likely one. The hafnium standard was analyzed using exactly the same procedure as that for the direct weighing of the hafnium tetramandellate except that the precipitates were filtered through Whatman #42 filter paper and ignited to the oxide and weighed. These values checked with the original ones

TABLE VIII
MANDELIC ACID PRECIPITATION
OF Zr IN STRONG HCl

Sample No.	ZrO ₂ Added (g)	Zr(M) ₄ (Theory) (g)	Zr(M) ₄ Found (g)	Difference (g)	%Error
1	0.0707	0.3988	0.3980	-0.0008	0.20
2	0.0707	0.3988	0.3991	+0.0003	0.08
3	0.0707	0.3988	0.3973	-0.0015	0.38
4	0.0707	0.3988	0.3988	0.0000	0.00
5	0.0707	0.3988	0.3979	-0.0009	0.23
6	0.0707	0.3988	0.4003	+0.0015	0.38
7	0.0707	0.3988	0.3993	+0.0005	0.13
8	0.0707	0.3988	0.4000	+0.0012	0.30

TABLE IX
MANDELIC ACID PRECIPITATION
OF Hf IN STRONG HCl

Sample No.	HfO ₂ Added (g)	Hf(M) ₄ (Theory) (g)	Hf(M) ₄ Found (g)	Difference (g)	%Error
1	0.0935	0.3478	0.3543	+0.0065	1.9
2	0.0935	0.3478	0.3536	+0.0058	1.7
3	0.0935	0.3478	0.3500	+0.0022	0.63
4	0.0935	0.3478	0.3500	+0.0022	0.63
5	0.0935	0.3478	0.3543	+0.0065	1.9
6	0.0935	0.3478	0.3532	+0.0054	1.6
7	0.0935	0.3478	0.3514	+0.0036	1.0
8	0.0935	0.3478	0.3517	+0.0039	1.1

using cupferron.

At this time it seemed worthwhile to determine the effect of varying the ratio of zirconium to mandelic acid. For this work new standard solutions containing 4.196 mg./ml. of ZrO_2 and 4.012 mg./ml. of HfO_2 were prepared. The concentration of zirconium and hafnium were varied by using 5.00, 10.00, 25.00 and 50.00 mls. of each standard solution. 50 mls. of concentrated hydrochloric acid was added to each solution and then 50 mls. of 15% mandelic acid was added dropwise at $85^{\circ}C$ followed by a thirty minute digestion. They were finally cooled, filtered, washed and dried. These data are summarized in Tables X and XI.

These data seem to indicate that a large excess of mandelic acid gives the best results with zirconium and that no significant difference is observed for hafnium. This would imply that a large excess of mandelic acid should be used for precipitation of mixed oxides of zirconium and hafnium where the zirconium content is high. It should also be noted that the present figures for the hafnium agree very closely to theory, whereas the last series were consistantly high. No explanation for this can be made unless it had something to do with the use of different standard solutions for the two runs. This latter run certainly indicates that this method is

TABLE X

EFFECT OF VARIATION OF ZIRCONIUM
TO MANDELIC ACID RATIO

Sample No.	Volume ZrO ₂ (ml)	ZrO ₂ Added (g)	Zr(M) ₄ (Theory) (g)	Zr(M) ₄ Found (g)	Difference (g)	%Error
1	5.00	0.0210	0.1184	0.1184	0.0000	0.00
2	5.00	0.0210	0.1184	0.1189	+0.0005	0.42
3	25.00	0.1049	0.5918	0.5889	-0.0029	0.49
4	25.00	0.1049	0.5918	0.5892	-0.0026	0.44
5	10.00	0.04196	0.2367	0.2376	+0.0009	0.38
6	10.00	0.04196	0.2367	0.2365	-0.0002	0.085
7	50.00	0.2098	1.1836	1.1686	-0.0150	1.27
8	50.00	0.2098	1.1836	1.1694	-0.0142	1.20

TABLE XI

EFFECT OF VARIATION OF HAFNIUM
TO MANDELIC ACID RATIO

Sample No.	Volume HfO ₂ (ml)	HfO ₂ Added (g)	Hf(M) ₄ (Theory) (g)	Hf(M) ₄ Found (g)	Difference (g)	%Error
1	10.00	0.04012	0.1492	0.1513	+0.0021	1.40
2	10.00	0.04012	0.1492	0.1505	+0.0013	0.87
3	5.00	0.02006	0.0746	0.0755	+0.0009	1.20
4	5.00	0.02006	0.0746	0.0743	-0.0003	0.42
5	25.00	0.1003	0.3731	0.3737	+0.0006	0.16
6	25.00	0.1003	0.3731	0.3731	-0.0016	0.43
7	50.00	0.2006	0.7462	0.7476	+0.0014	0.19
8	50.00	0.2006	0.7462	0.7460	-0.0002	0.027

applicable to hafnium as well as zirconium.

A series of precipitations were also run in which time of digestion varied from no digestion (after initial precipitation) to eight hours digestion at 70°C. No significant differences were observed for either zirconium or hafnium. The thirty minute digestions which have been used for all runs therefore seems to be adequate.

The next step in this study was the precipitation of several solutions containing both zirconium and hafnium in varying amounts. These solutions were prepared by measuring different volumes of standard zirconium solutions containing 2.072 mg./ml. of ZrO_2 and standard hafnium containing 0.988 mg./ml. of HfO_2 into beakers and precipitating, filtering and weighing as done previously. The results are tabulated below in Table XII.

In general these values seem to fall in line with previous results for the individual metals.

Since it was shown that both hafnium and zirconium can be quantitatively precipitated with mandelic acid, the next phase of this study was concerned with the determination of absorbance curves for mandelic acid, zirconium tetramandelate and hafnium tetramandelate in 1 M ammonium hydroxide.

TABLE XII

MANDELIC ACID PRECIPITATION
OF MIXED OXIDES IN
STRONG HYDROCHLORIC ACID

Sam- ple No.	ZrO ₂ Added (g)	HfO ₂ Added (g)	Zr(M) ₄ +Hf(M) ₄ (Theory) (g)	Zr(M) ₄ +Hf(M) ₄ (Found) (g)	Dif- fer- ence (g)	%Er- ror
1	0.0497	0.000988	0.2841	0.2825	-0.0016	0.56
2	0.0497	0.000988	0.2841	0.2824	-0.0017	0.60
3	0.0477	0.00198	0.2765	0.2733	-0.0032	1.15
4	0.0477	0.00198	0.2765	0.2727	-0.0038	1.37
5	0.0456	0.00296	0.2683	0.2675	-0.0008	0.30
6	0.456	0.00196	0.2683	0.2667	-0.0016	0.60
7	0.0435	0.00395	0.2601	0.2576	-0.0025	0.96
8	0.0435	0.00395	0.2601	0.2586	-0.0015	0.58
9	0.0414	0.00494	0.2520	0.2505	-0.0015	0.59
10	0.0414	0.00494	0.2520	0.2506	-0.0014	0.56
11	0.0332	0.00889	0.2204	0.2183	-0.0021	0.95
12	0.0332	0.00889	0.2204	0.2192	-0.0012	0.54
13	0.0249	0.0128	0.1881	0.1876	-0.0005	0.27
14	0.0249	0.0128	0.1881	0.1862	+0.0001	0.053
15	0.0207	0.0148	0.1719	0.1721	+0.0002	0.17
16	0.0207	0.0148	0.1719	0.1701	-0.0018	1.05

Mandelic Acid Absorption Curves

The UV absorption of 5.04×10^{-3} M and 1.008×10^{-3} M mandelic acid in 1 M ammonium hydroxide solutions were determined by plotting absorbance vs. wave length (λ) from a wavelength of 242 μ to 270 μ . These curves are shown in Figure 2. It can be seen from these curves that the maximum absorption peak occurs at 258 μ . The 1 M ammonium hydroxide solution was used as a blank in these measurements.

Zirconium Tetramandellate Absorption Curves

Absorption curves for zirconium tetramandellate in 1 M ammonium hydroxide solution were determined for 9.95×10^{-4} M and 2.49×10^{-4} M solutions in the same manner as those for the mandelic acid. The curves obtained are shown in Figure 2.

Hafnium Tetramandellate Absorption Curves

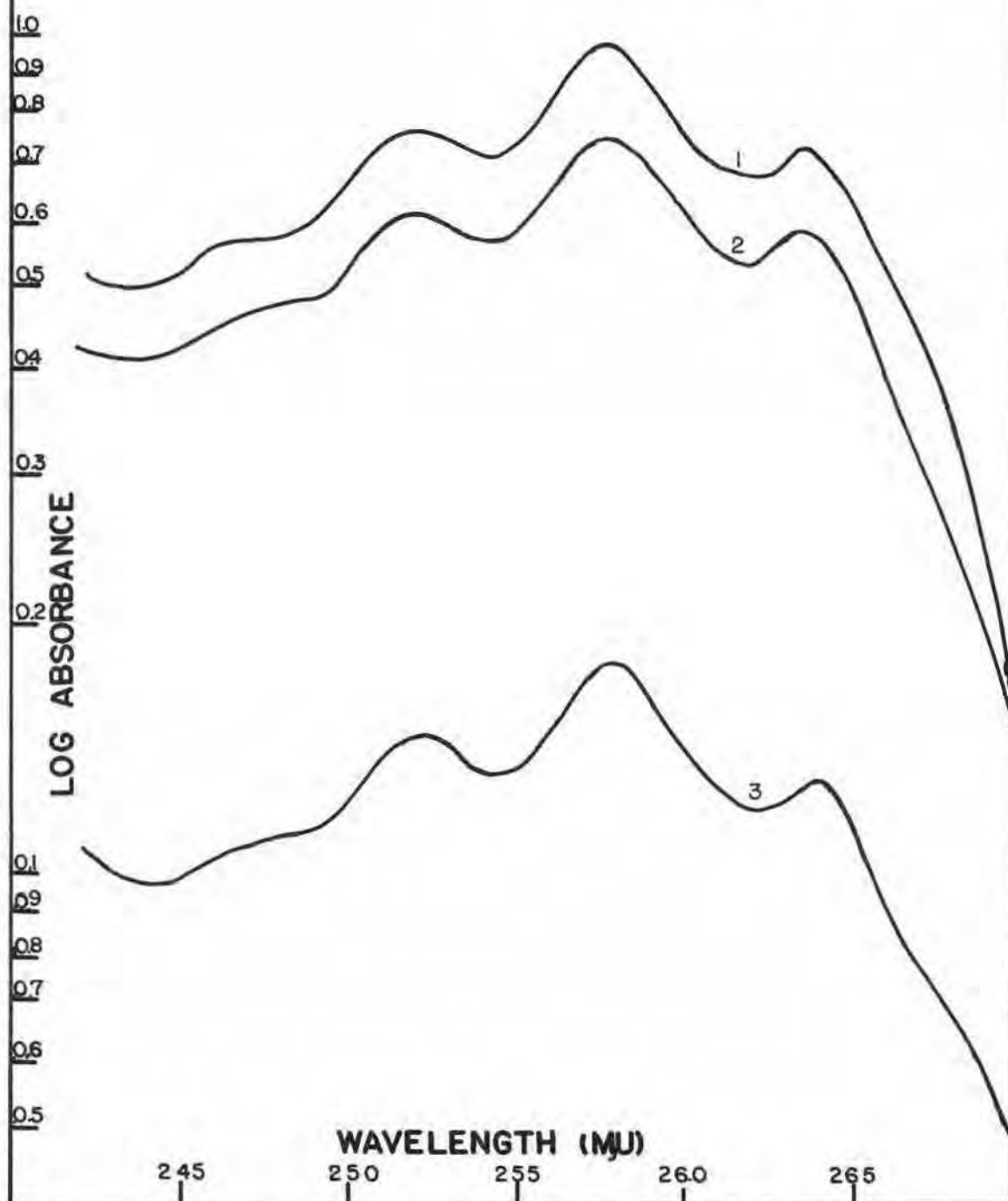
These curves were determined in the same manner as those above except that 9.86×10^{-4} M and 2.47×10^{-4} M solutions of hafnium tetramandellate in 1 M ammonium hydroxide were used. These curves are also indicated in Figure 2.

Upon examination of these absorption curves it can

LOG ABSORBANCE
VS.
WAVELENGTH

FIGURE 2

- 1- 5.04×10^{-3} M MANDELIC ACID
2- 9.95×10^{-4} M $Zr(M)_4$
 9.86×10^{-4} M $Hf(M)_4$
3- 1.008×10^{-3} M MANDELIC ACID
 2.49×10^{-4} M $Zr(M)_4$
 2.47×10^{-4} M $Hf(M)_4$



be seen that they are all essentially identical thus showing that the absorption is due to the mandelate ion.

It is of interest to note that when the molar absorptivities are calculated for the above solutions, they are found to be greater for the more concentrated solutions than for the dilute. This is rather unusual as it would result in a positive deviation from Beer's law when absorbance vs. concentration is plotted, while the usual case is to find a negative deviation.

In order to find the optimum concentration for the zirconium and hafnium tetramandelates, the following investigation was carried out.

Optimum Concentration

The optimum concentrations were determined by preparing a series of solutions containing zirconium and hafnium tetramandelate in 1 M ammonium hydroxide at a constant weight increment of the tetramandelate. Starting with a 1 M ammonium hydroxide solution as reference, the absorbance of the most dilute solution was measured. Then using this solution as reference, the absorbance of the solution of higher concentration was determined and so on until all solutions were measured. Using these absorbance values and knowing the concentration increment (in g./l.) the slope was calculated, $S = \Delta A / C$. The

optimum concentration then is that concentration at which $S \times C$ is a maximum since $\Delta C/C = \Delta A/S \times C$. These data are found in Table XIII and XIV.

From these data it was concluded that the optimum concentration of zirconium tetramandelate was about 2.4 g./l. and of hafnium tetramandelate about 2.8 g./l. or $3.46 \times 10^{-3} \text{ M}$ and $3.58 \times 10^{-3} \text{ M}$ respectively. If no deviation from Beer's law occurred, then the product of $S \times C$ would continue to increase until the instrument could no longer be balanced. Perhaps this deviation from Beer's law can be more clearly seen if these same data are used to determine the absorbance of each solution relative to the initial zero reference and the resulting values then plotted against concentration. These are found in Figure 3. It can be seen from these figures that, as expected, rather severe deviation is starting to occur just beyond the optimum concentrations.

Using the optimum concentration of 2.400 g./l. of total mandelate, a standard curve was next determined.

Standard Curve for Determination of Hafnium Tetramandelate in Presence of Zirconium Tetramandelate

A series of standard solutions containing from 5.00 to 50.00% hafnium tetramandelate in zirconium tetramandelate were prepared by weighing out the proper amounts

TABLE XIII

OPTIMUM CONCENTRATION OF
ZIRCONIUM TETRAMANDELATE

Solution Zr(M) ₄ (g/l)					
To Set Zero	To Obtain Reading	Slit (mm)	ΔA	Slope (S)	S x C
0.0000	0.4175	0.0225	0.461	1.104	-
0.4175	0.8350	0.04	0.502	1.202	0.502
0.8350	1.2525	0.07	0.460	1.102	0.920
1.2525	1.6700	0.13	0.495	1.186	1.485
1.6700	2.0875	0.24	0.438	1.149	1.752
2.0875	2.5050	0.40	0.434	1.140	2.171
2.5050	2.9225	0.64	0.318	0.62	1.909
2.9225	3.3400	0.88	0.269	0.644	1.882
3.3400	3.7575	1.15	0.130	0.311	1.039
3.7575	4.1750	1.30	0.112	0.268	1.007

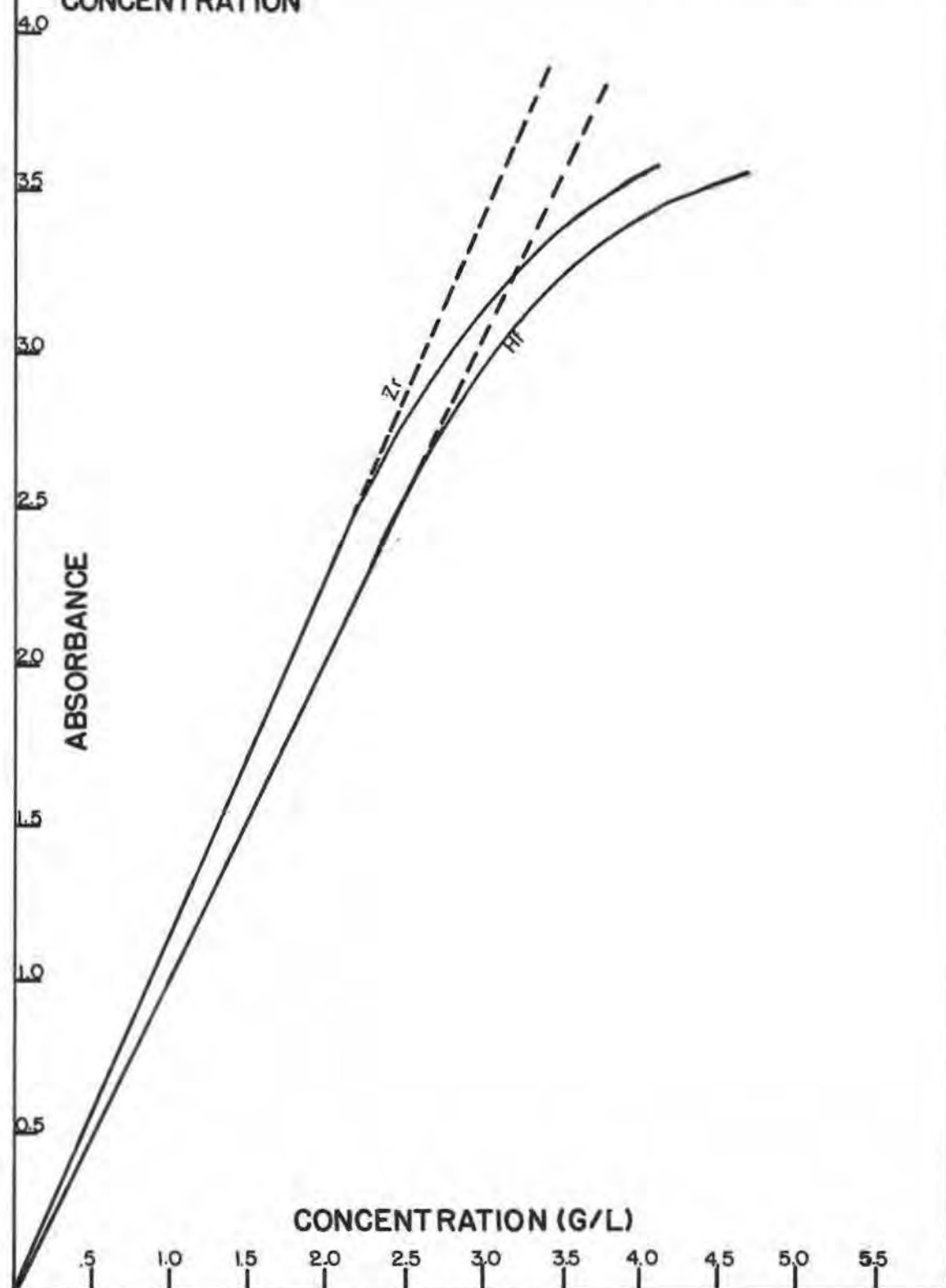
TABLE XIV
OPTIMUM CONCENTRATION OF
HAFNIUM TETRAMANDELATE

Solution
Hf(M)4 (g/l)

To Set Zero	To Obtain Reading	Slit (mm)	ΔA	Slope (S)	S x C
0.0000	0.4698	0.0225	0.469	0.998	-
0.4698	0.9396	0.04	0.500	1.064	0.500
0.9396	1.4094	0.07	0.456	0.971	0.912
1.4094	1.8792	0.13	0.498	1.060	1.494
1.8792	2.3490	0.24	0.432	0.920	1.728
2.3490	2.8188	0.40	0.443	0.943	2.215
2.8188	3.2886	0.64	0.434	0.924	2.604
3.2886	3.7584	0.88	0.146	0.311	1.022
3.7584	4.2282	1.15	0.135	0.287	1.080
4.2282	4.6980	1.30	0.109	0.232	0.098

ABSORBANCE
VS.
CONCENTRATION

FIGURE 3



of each compound and made up to volume with 1 M ammonium hydroxide so that each solution contained exactly 2.400 g./l. of mixed mandelates. The absorbance of each of these solutions was then measured relative to the 50% hafnium tetramandellate as reference since it was the least absorbing. A standard curve of ΔA vs. % $Hf(M)_4$ was then drawn. This is shown in Figure 4.

It is fairly obvious from this curve that the 0 to 3.5% $Hf(M)_4$ (0 to 5.2% HfO_2) range which is really the desired range, could not be used due to the small ΔA .

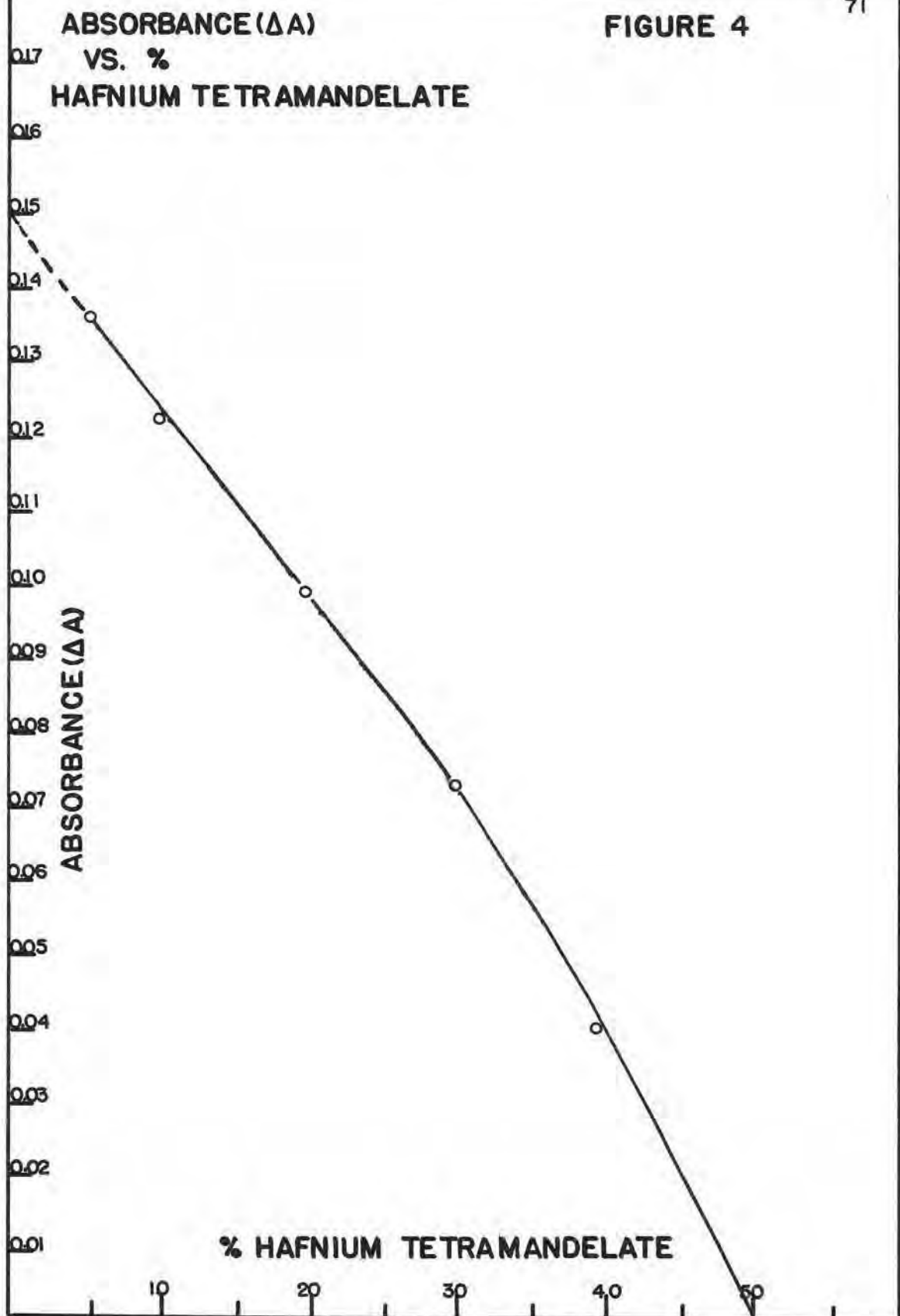
Discussion

Although this procedure using mandelic acid cannot be applied to the determination of 0 to 5% HfO_2 in ZrO_2 , it certainly could be applied to samples containing a large ratio of HfO_2 to ZrO_2 . However, this application was not pursued any further.

This method failed in the 0 to 5% HfO_2 range due to the low optimum concentration and low molar absorptivity of the system being used. This of course could have been predicted, using the formula developed for calculating ΔA , had the optimum concentration and molar absorbance of the zirconium and hafnium tetramandellate been known previous to this experimental work.

The chloranilic acid system with its high molar

FIGURE 4



absorbance, seemed to offer some possibilities for the solution of this problem and was investigated next.

INVESTIGATION WITH CHLORANILIC ACID

Chloranilic acid with its high molar absorptivity and other desirable characteristics seemed to offer hope for successful application to the determination of small quantities of HfO_2 in ZrO_2 . The investigation of the application of chloranilic acid to this determination will therefore be described. As was seen in the introduction, a considerable amount of work pertaining to this reagent had been carried out previously. In view of this, a minimum amount of preliminary work was necessary in running absorption curves, etc. This made possible the determination of the optimum concentration and its application to the determination of HfO_2 in a minimum of time.

Experimental Approach

The experimental approach used for the determination of hafnium in the presence of zirconium with chloranilic acid was based on the following considerations:

1. Hafnium and zirconium will react in an identical manner with chloranilic acid.
2. The intensity of the colored complex found with the chloranilic acid and mixtures of hafnium and zirconium will depend on their ratio when the total weight concentration is held constant.
3. Differential spectrophotometry will provide

sufficient gain in accuracy and sensitivity to permit accurate analysis by this method.

Apparatus

The apparatus was identical to that utilized for the mandelic acid work.

Reagents

1. Perchloric acid, 4 M. Diluted 684 mls. of 70% (11.7 N) perchloric acid, reagent grade, to two liters with distilled water.

2. Chloranilic acid, (2, 5-dihydroxy-p-quinone. Eastman no. P4539), 0.10% (4.78×10^{-3} M). Dissolved exactly 0.500 g. of purified chloranilic acid in distilled water and diluted to exactly 500 mls. See Appendix for method of purification.

3. ZrO_2 , standard solution. Dissolved about 3 g. of $ZrOCl_2 \cdot 8H_2O$ in distilled water and precipitated with ammonia. Washed precipitate with distilled water to remove the chloride ion. The precipitate was then dissolved and diluted to 500 mls. with 2 M perchloric acid. This solution was standardized by the cupferron method and was found to contain 2.624 mg./ml. of ZrO_2 .

4. HfO_2 , standard solution. This solution was prepared in the same manner as the ZrO_2 standard except

that 0.9 g. of $\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$ was used. This solution upon standardization with cupferron was found to contain 0.988 mg./ml. of HfO_2 . It was further diluted ten times with 2 M perchloric acid so that the final concentration was 0.0988 mg./ml. of HfO_2 .

Absorption Curves of Chloranilic Acid and Zirconium
Chloranilate In the UV

UV absorption curves from 240 to 380 $\text{m}\mu$ were determined on 1 M perchloric acid solutions of the following:

1. 8.12×10^{-6} M chloranilic acid.
2. 8.12×10^{-5} M chloranilic acid.
3. 8.12×10^{-5} M Zr and 8.12×10^{-6} M chloranilic acid.
4. 8.12×10^{-5} M Zr and 8.12×10^{-5} M chloranilic acid.
5. 8.12×10^{-6} M Zr and 8.12×10^{-5} M chloranilic acid.

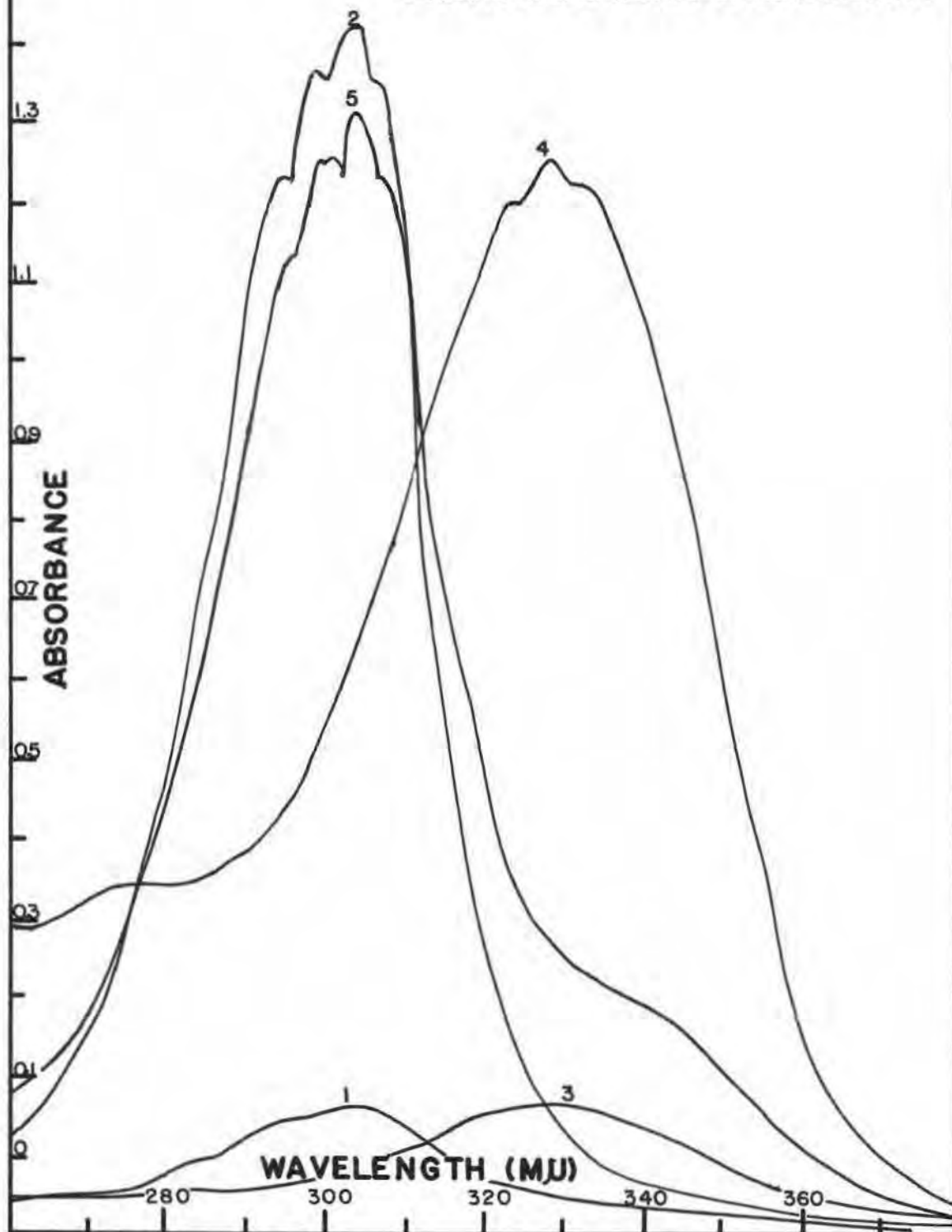
All measurements were made against water as the reference solution. The curves are shown in Figure 5. It can be seen from these figures that the absorption maximum occurred at about 328 to 330 $\text{m}\mu$ for solution 3 and 4 where the zirconium to chloranilic acid ratio was 10:1 and 1:1 respectively. However, the maximum seemed to be shifted to about 335 $\text{m}\mu$ when chloranilic acid was in ten fold

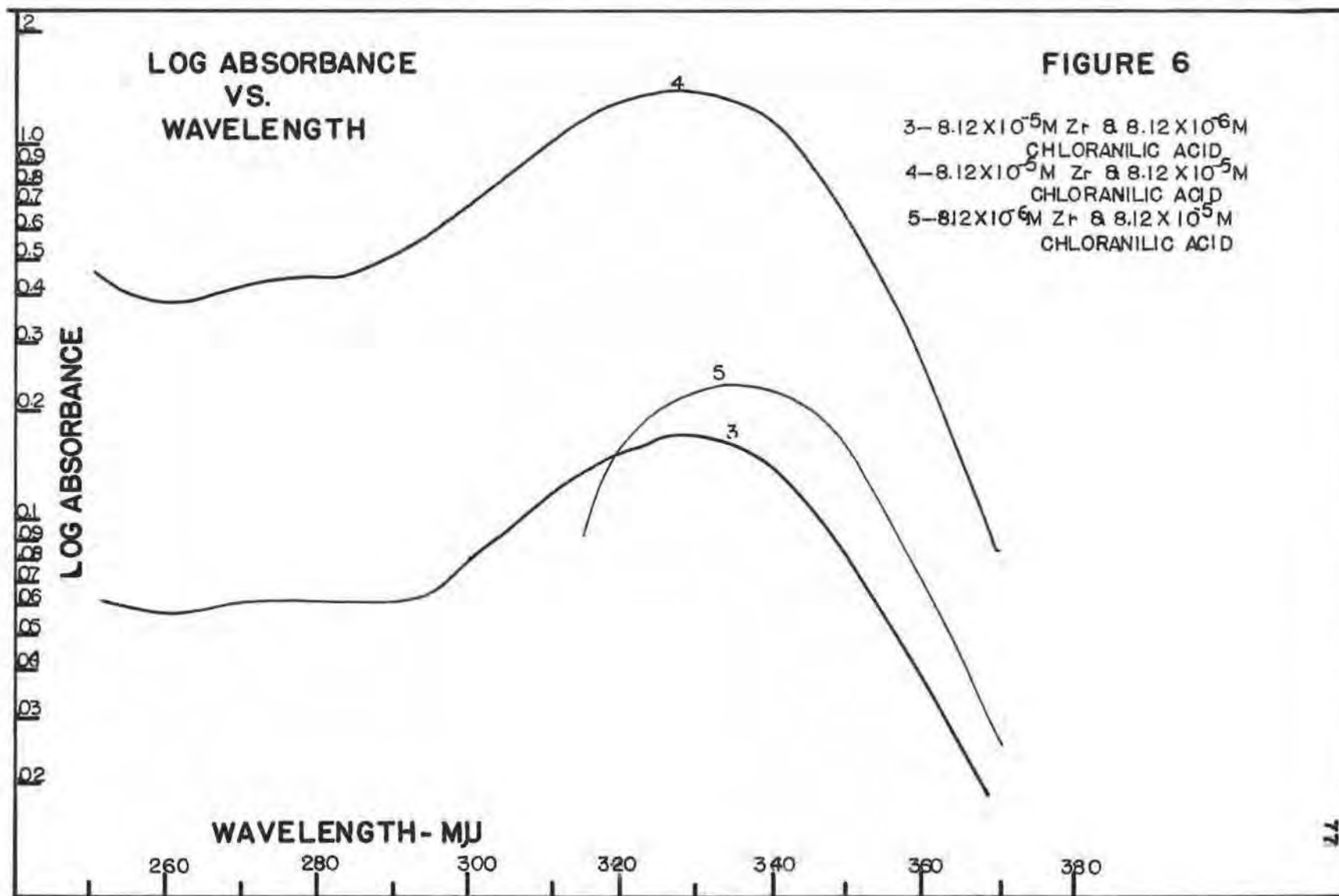
**ABSORBANCE
VS.
WAVELENGTH**

FIGURE 5

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- 1- 8.12×10^{-6} M CHLORANILIC ACID
- 2- 8.12×10^{-5} M CHLORANILIC ACID
- 3- 8.12×10^{-5} M Zr & 8.12×10^{-6} M CHLORANILIC ACID
- 4- 8.12×10^{-5} M Zr & 8.12×10^{-5} M CHLORANILIC ACID
- 5- 8.12×10^{-6} M Zr & 8.12×10^{-5} M CHLORANILIC ACID





excess (solution 5). This shift was probably due to the formation of a 1:2 zirconium to chloranilic acid complex whereas a 1:1 complex was present in solutions 3 and 4. The curves in Figure 6, where the log of absorbance vs. wavelength is plotted, seem to support this interpretation. Curves 3 and 4 were plotted directly but curve 5 was corrected for absorbance due to excess chloranilic acid. It can be seen that curves 3 and 4 are essentially identical but curve 5 is shifted to the right. An increase in molar absorptivity accompanies this shift to higher wavelengths. However, for all practical purposes it should be possible to make absorbance measurements at any given wavelength from about 328 μ to about 345 μ . Absorbance measurements for this work on chloranilic acid were made at 330 μ .

It was next necessary to determine the optimum concentration for this system. This investigation is described in the following section.

Optimum Concentration

A series of solutions containing from 0.05 mg./25 ml. of ZrO_2 were prepared. A five fold excess of chloranilic acid was added to each solution and diluted to volume with sufficient perchloric acid to make the final solution 2 M in this acid.

The optimum concentration was then determined in the same manner as previously described. These data are summarized in Table XV.

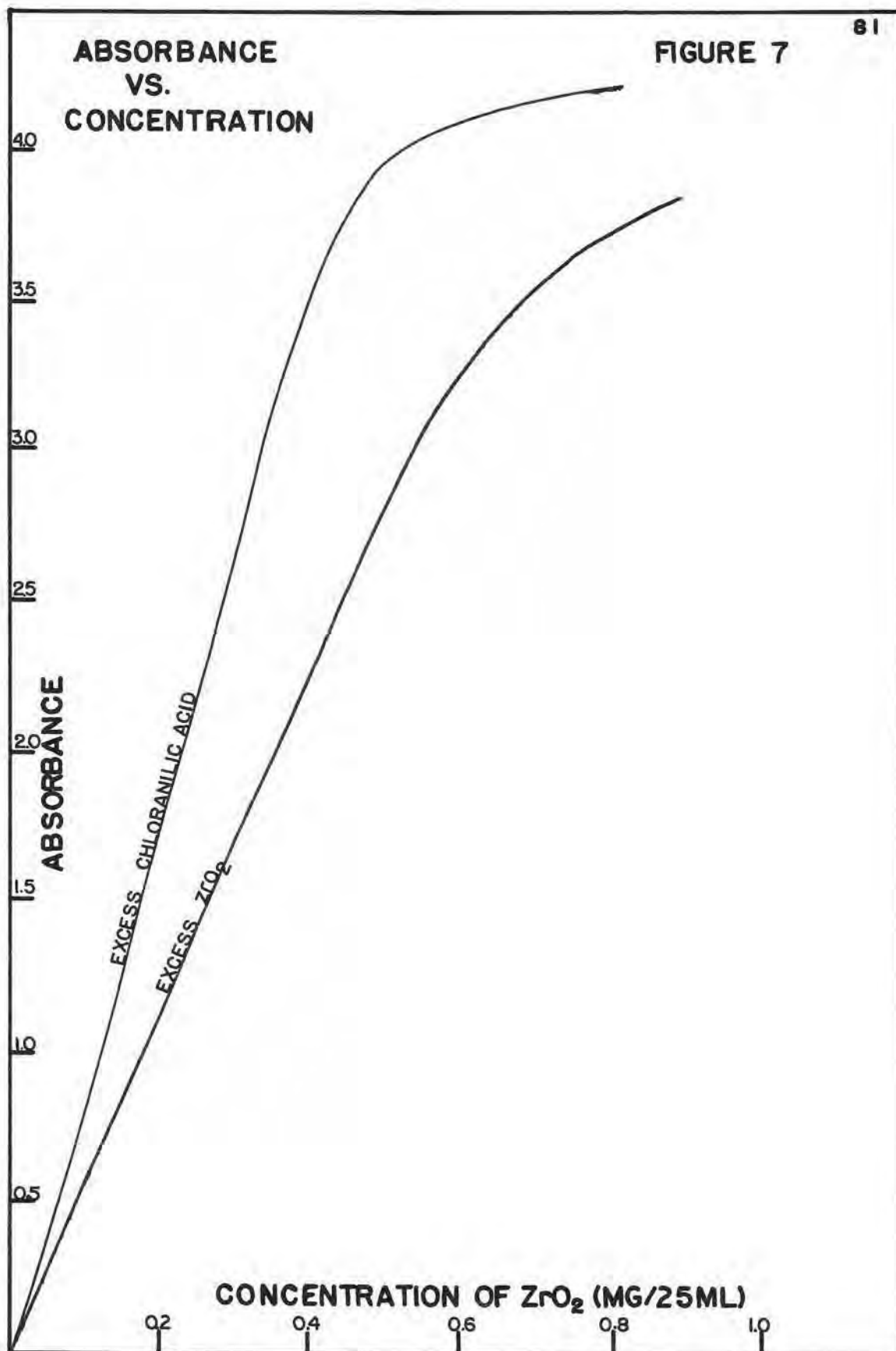
As seen from this table, the optimum concentration was 0.30 mg./25 ml. of ZrO_2 . When these data are used to plot absorbance vs. concentration, as in Figure 7, a slight positive deviation is observed for the first few points but beyond the optimum concentration, severe negative deviation is seen to occur. As previously noted, an examination of the absorption curves (Figures 5 and 6) for the zirconium chloranilate complex indicates the formation of a second complex of greater molar absorbance than the 1:1 complex, probably the 1:2 (Zr:Ch) complex. This could account for the initial positive deviation. The negative deviation probably resulted from excessive concentrations.

An optimum concentration determination was made using excess zirconium. With excess zirconium only the 1:1 complex should be present in the solution. This would, of course, have no practical application but is of interest in understanding the chemical system involved. Solutions containing tenfold concentrations of zirconium to chloranilic acid were used in making these measurements. The ZrO_2 concentrations ranged from 1.00 mg./25 ml. to 9.00 mg./25 ml. of ZrO_2 . Since these were in ten fold

TABLE XV

OPTIMUM CONCENTRATION
OF ZrO_2 WITH EXCESS
CHLORANILIC ACID

Solution ZrO_2 , mg/25 ml.		Slit (mm)	ΔA Diff. In Absorb.	Slope (S)	C	S x C
To Set Zero	To Obtain Reading					
water	0.05	0.015	0.378	7.56	-	-
0.05	0.10	0.020	0.422	8.44	0.05	0.42
0.10	0.15	0.025	0.448	9.97	0.10	0.88
0.15	0.20	0.040	0.489	9.78	0.15	1.47
0.20	0.25	0.070	0.520	10.4	0.20	2.08
0.25	0.30	0.120	0.502	10.1	0.25	2.51
0.30	0.40	0.220	0.840	8.40	0.30	2.52
0.40	0.50	0.560	0.389	3.89	0.40	1.56
0.50	0.60	0.900	0.104	1.04	0.50	0.52
0.60	0.70	1.025	0.063	0.63	0.60	0.38



excess, this means that only 0.100 mg./25 ml. to 0.900 mg./25 ml. were actually present as the 1:1 complex. The results of these measurements are shown in Table XVI.

An optimum concentration of 0.50 mg./25 ml. was obtained in this experiment. For comparison purposes, the absorbance vs. concentration was plotted in Figure 7. With the zirconium in excess, no positive deviation was noted which would seem to support the argument that a second more absorbing complex was present in the first case when excess chloranilic acid was present. In fact, this complete second curve is displaced from the first toward lower absorbance values. However, it should be noted that negative deviation starts to occur at approximately the same absorption value in both cases.

In order to further confirm the fact that the optimum concentration should be low, the experiment in the next section was carried out.

Determination of Difference in Absorbance (ΔA) of $f\text{HfO}_2 = 0$ and $f\text{HfO}_2 = 0.20$ at Different Total Oxide Levels

Several pairs of solutions containing 0 and 20% HfO_2 were prepared at different total oxide concentrations and ΔA between each pair was measured. The total oxide level varied from 0.250 mg. oxide/25 ml. to 1.250 mg. oxide/25 ml.. The results of this investigation are

TABLE XVI
OPTIMUM CONCENTRATION
OF EXCESS ZrO_2 IN
CHLORANILIC ACID

Solution
 ZrO_2 , mg/25 ml.

To Set Zero	To Obtain Reading	Slit (mm)	ΔA Diff. In Absorb.	Slope (S)	C (mg.)	S x C
water	1.00	0.0125	0.569	5.69	-	-
1.00	2.00	0.020	0.229	5.70	0.10	0.57
2.00	3.00	0.025	0.880	5.55	0.14	0.78
3.00	4.00	0.060	0.540	5.40	0.30	1.62
4.00	5.00	0.110	0.542	5.42	0.40	2.16
5.00	6.00	0.200	0.477	4.77	0.50	2.39
6.00	7.00	0.340	0.304	3.04	0.60	1.82
7.00	8.00	0.480	0.186	1.86	0.70	1.30
8.00	9.00	0.600	0.159	1.59	0.80	1.27

shown in Table XVII.

These data tend to confirm that the optimum concentration should be low since the greatest ΔA was observed at the lowest concentration.

Standard Curve for % HfO_2 in Presence of ZrO_2

A series of standard solutions containing 0 to 50% HfO_2 at optimum concentration of 0.30 mg./25 ml. of total oxide were prepared. A standard curve was then constructed by plotting difference in absorbance (ΔA) vs. % HfO_2 . Each standard solution was measured relative to the 50% HfO_2 solution as the reference. The results are summarized in Table XVIII and Figure 8.

A straight line calibration curve is obtained if the 1.00 % HfO_2 standard is disregarded. This point was probably out of line due to the difficulty of accurately preparing the low % HfO_2 standards.

Discussion

These data indicate that chloranilic acid is a suitable reagent for the determination of about 5 to 50% HfO_2 in ZrO_2 . It also seems likely that the range could be considerably narrowed to perhaps 0 to 20% HfO_2 and by very careful work possibly 0 to 10% HfO_2 could be determined by this method. However, it does not seem likely that

TABLE XVII

DIFFERENCE IN ABSORBANCE OF
0 AND 20% HfO₂ SOLUTIONS
WITH CHLORANILIC ACID

Solution %HfO₂

To Set Zero	To Obtain Reading	Total Oxide (mg/25 ml.)	Slit (mm)	ΔA
20	0	0.250	0.11	0.146
20	0	0.500	0.80	0.044
20	0	0.750	0.90	0.005
20	0	1.000	1.0	0.013
20	0	1.250	1.20	0.012

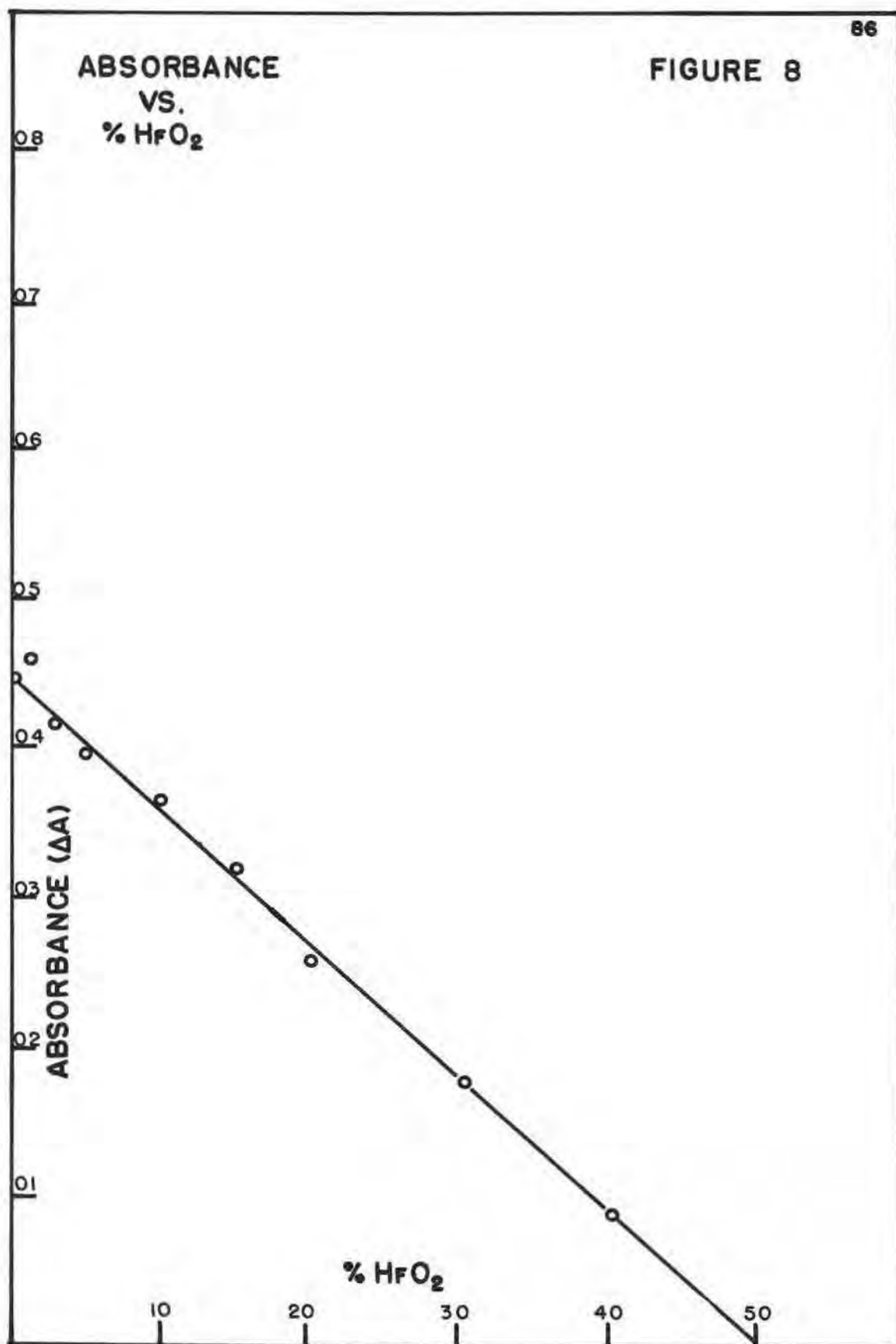
TABLE XVIII

STANDARDIZATION CURVE FOR
%HfO₂ IN PRESENCE OF ZrO₂

Solution %HfO₂

To Set Zero	To Obtain Reading	Absorbance (A)	Transmittance (T)
50.00	40.00	0.086	82.0
50.00	30.00	0.176	66.7
50.00	20.00	0.257	55.2
50.00	15.00	0.318	48.0
50.00	10.00	0.363	43.3
50.00	5.00	0.395	40.3
50.00	3.00	0.415	38.5
50.00	1.00	0.459	34.9
50.00	0.00	0.442	36.1

FIGURE 8



the 0 to 5% HfO_2 range could be used due to the small difference in absorbance between solutions in this region.

Since there seemed to be no probability of utilizing this method for the desired 0 to 5% range, a new reagent, quercetin, was investigated since it forms complexes with zirconium and hafnium of even higher molar absorptivities than does chloranilic acid.

INVESTIGATION USING QUERCETIN

It was hoped that quercetin with its very high molar absorptivity would have a sufficiently high optimum concentration to permit the determination of HfO_2 in the desired range. In view of this, a considerable amount of research was carried out in the determination of the optimum conditions to be used. The results of this research on quercetin are described in the following paragraphs.

Apparatus

The same apparatus was used in this investigation as was used for the mandelic acid and chloranilic acid work except that a tungsten lamp was used as the light source.

Reagents

1. ZrO_2 standard solutions. Prepared all solutions by dissolving high purity $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ in 6 N hydrochloric acid. These were standardized by the cupferron method.

2. HfO_2 standard solutions. Dissolved high purity $\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$ in 6 N hydrochloric acid and standardized with cupferron.

3. Quercetin solution, (tetrahydroxy flavanol, 5,7,3',4') 1.00 mg./ml. (3.31×10^{-3} M). Exactly 1.000 g.

of quercetin was dissolved and diluted to exactly 100 mls. with 95% ethanol.

Zirconium - Quercetin Absorption Curves

Absorbance vs. wavelength was determined and plotted for the following solutions:

1. 2.50×10^{-6} moles/50 mls. of quercetin.
2. 2.50×10^{-6} moles/50 mls. of quercetin and 2.50×10^{-5} moles/50 mls. of ZrO_2 .
3. 2.50×10^{-6} moles/50 mls. of quercetin and 2.50×10^{-6} moles/50 mls. of ZrO_2 .
4. 2.50×10^{-6} moles/50 mls. of quercetin and 2.50×10^{-7} moles/50 mls. of ZrO_2 .

Solutions 2, 3 and 4 were prepared according to the order of addition of reagents as recommended by Grimaldi and White (32). They suggested that the reagents be added in the following order: (Quantities are mine).

1. ZrO_2 solution. Added number of moles indicated above, using a 2.164 mg./ml. ZrO_2 solution.
2. Acid. Added just enough 6 N hydrochloric acid to adjust final acidity to 0.5 N.
3. Alcohol, 95%. Added 15.00 ml. to each solution.
4. Quercetin. Added 2.50×10^{-6} moles (in 95% alcohol) to each solution.
5. Water. Diluted to 50.00 mls. with distilled H_2O .

The absorbance of these solutions was then measured from 320 to 500 mμ using water as a reference. These curves are shown in Figure 9.

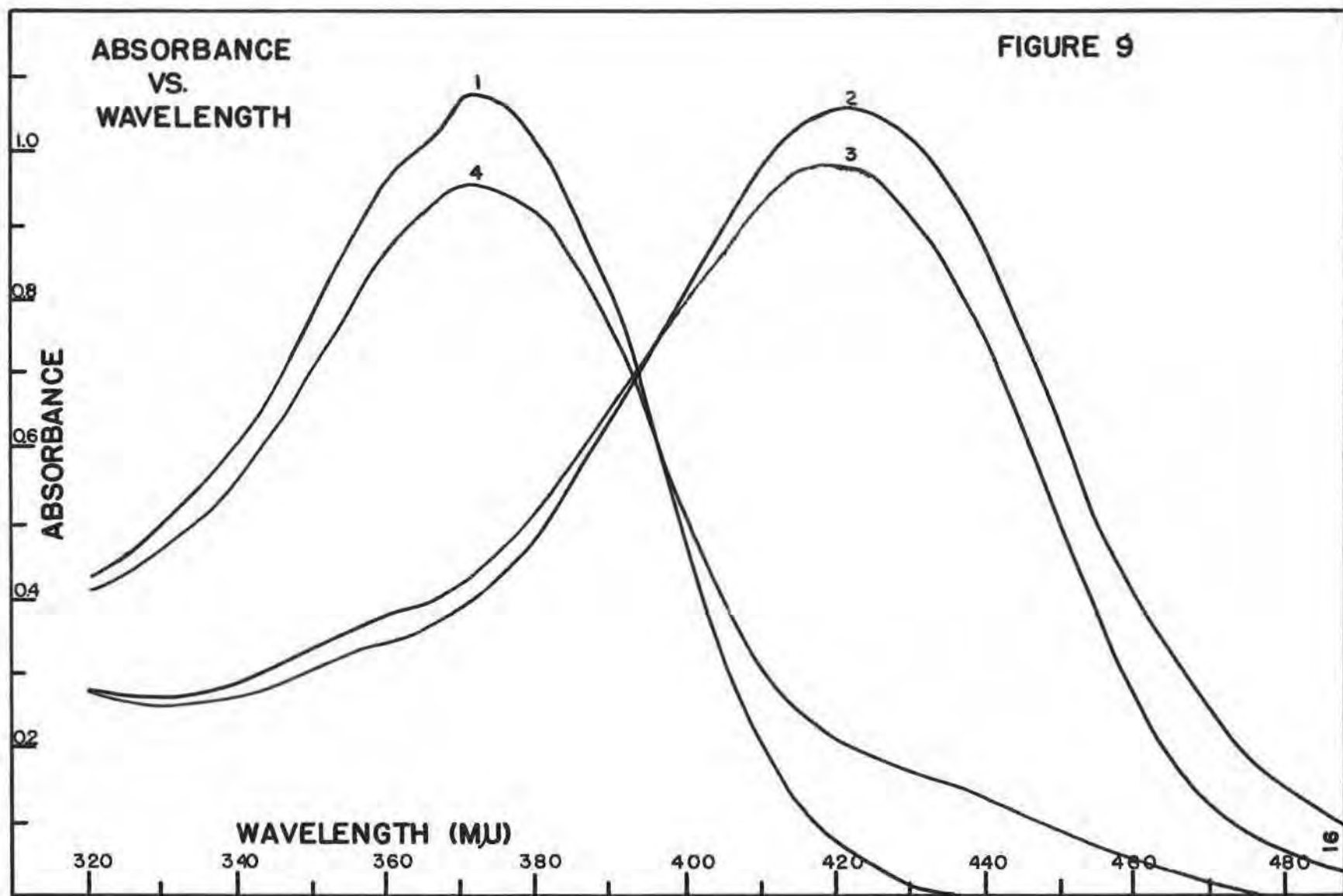
Hafnium - Quercetin Absorption Curves

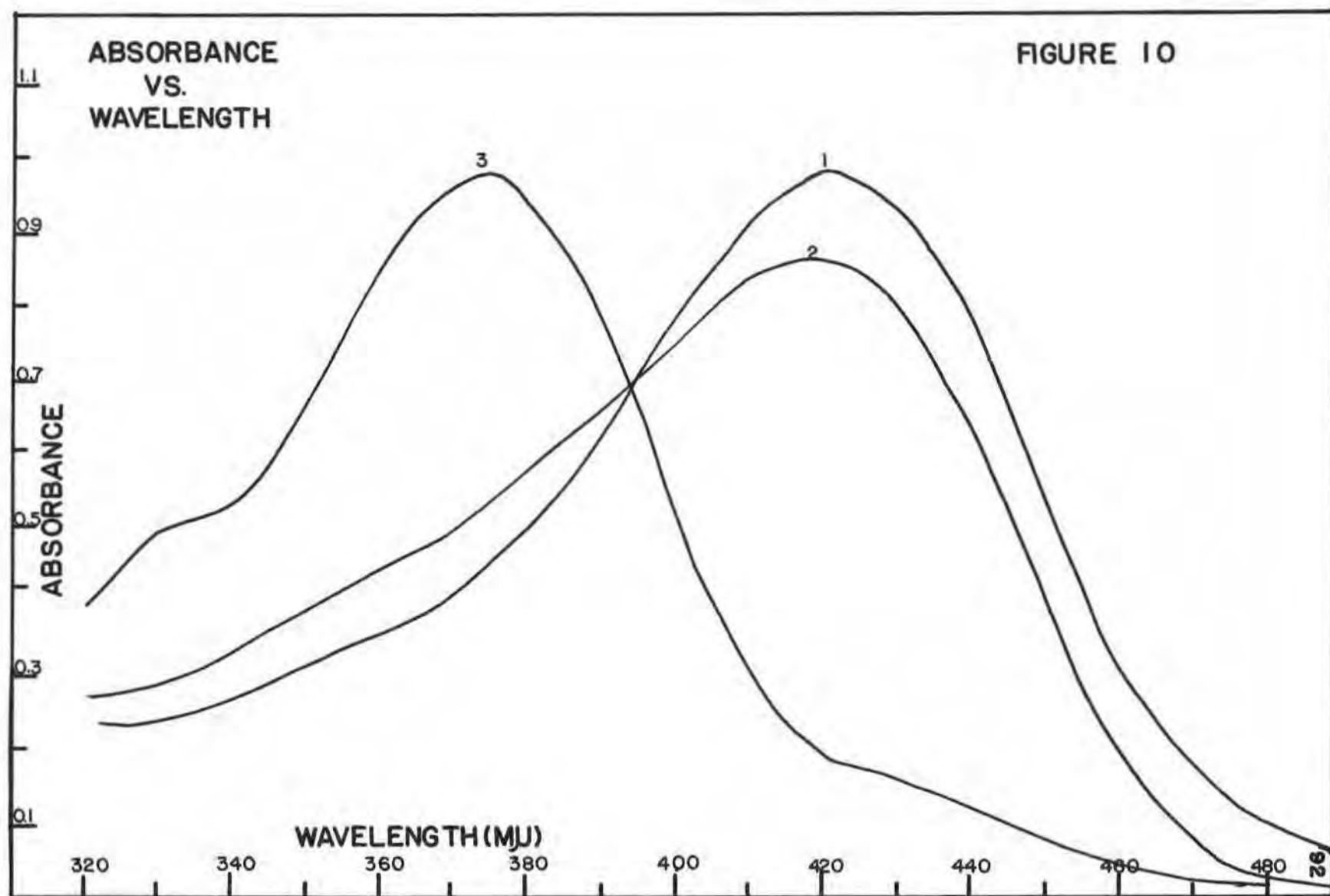
Absorbance vs. wavelength curves were determined for the following hafnium - quercetin solutions:

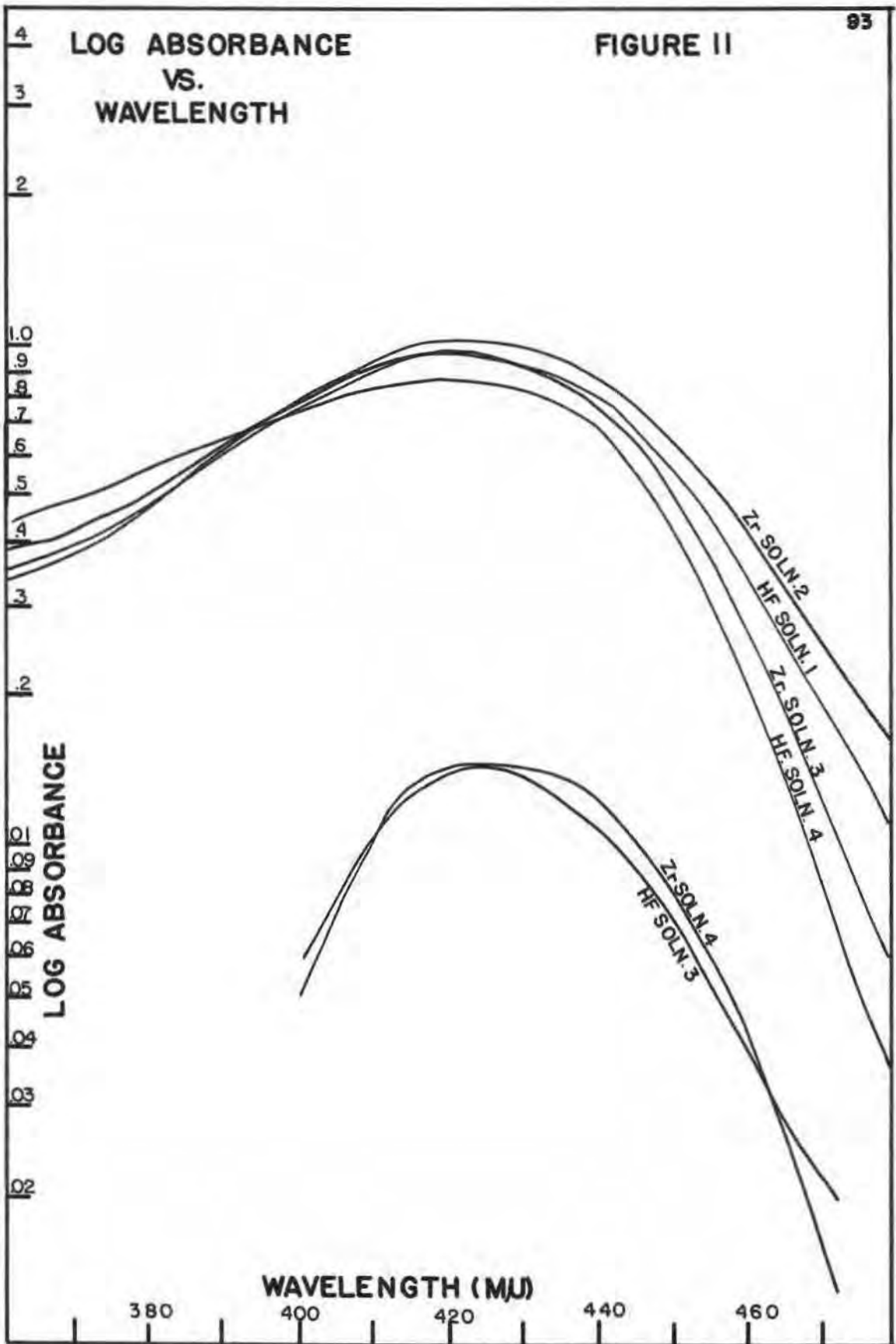
1. 2.50×10^{-6} moles/50 mls. of quercetin and 2.50×10^{-5} moles/50 mls. of HfO_2 .
2. 2.50×10^{-6} moles/50 mls. of quercetin and 2.50×10^{-6} moles/50 mls. of HfO_2 .
3. 2.50×10^{-6} moles/50 mls. of quercetin and 2.50×10^{-7} moles/50 mls. of HfO_2 .

These solutions were prepared in the same manner as the zirconium - quercetin except that a standard solution of 1.782 mg./ml. of HfO_2 was used. The resulting curves are found in Figure 10.

Upon examination of Figures 9 and 10, it appears that the absorption spectra of the quercetin complexes of zirconium and hafnium are essentially identical. However, the curves do seem to shift slightly depending upon whether the zirconium or hafnium ratio to quercetin is $<1:1$, $1:1$ or $>1:1$. This can be more readily observed when log absorbance vs. wavelength curves are plotted (Figure 11). From these curves there seems to be a small shift towards







higher wavelengths for the solutions in which quercetin is in a ten fold excess. The molar absorptivity is also greater under these conditions. These data seem to indicate the existence of more than one complex. Grimaldi and White (32) suggested that a 1:1 complex was first formed and as the ratio of quercetin to zirconium was increased, a mixture of 1:1 and 1:2 complex formed and finally only the 1:2 complex.

In view of the above findings a study of the relationships of absorbance to ratio of quercetin was made. First, however, the effect of time on color development of the zirconium and hafnium complexes of quercetin will be indicated and also the effect of acid concentration on absorbance.

Effect of Time on Color Development of Zirconium and Hafnium Complexes of Quercetin

The zirconium - quercetin solution contained 2.50×10^{-6} moles/50 mls. of ZrO_2 and 12.5×10^{-6} moles/50 mls. of quercetin and the hafnium - quercetin solution contained 2.50×10^{-7} moles/50 mls. of HfO_2 and 82.7×10^{-6} moles/50 mls. of quercetin. These solutions were prepared in the same manner as those for the absorption curves. A water reference was used and measurements were made at a wavelength of 440 m μ . These data are

found in Table XIX.

From these data it is obvious that measurements can be made within 15 minutes of preparation of complex solutions. Although the hafnium complex seems to fade slowly over a period of hours, this should cause no trouble.

Grimaldi and White found that the absorbance of the zirconium - quercetin complex was almost independent of hydrochloric acid concentration from 0.1 to 1 N (32). In the following section the effect of acidity on the hafnium complex will be discussed.

Effect of Acidity on Absorbance of Hafnium - Quercetin Complex

Hafnium solutions containing 0.0535 mg./50 mls. of HfO_2 at various hydrochloric acid normalities were prepared and the absorbancies determined as previously described. The results are recorded in Table XX.

For this complex, the acidity is nearly independent of acid concentrations from 0.10 N to about 0.90 N. Therefore, a 0.50 N acid concentration could be used for the hafnium as well as for the zirconium - quercetin complex.

Absorbance vs. Mole Ratio of Quercetin to Zirconium.

As previously stated, the effect of mole ratio of

TABLE XIX
EFFECT OF TIME ON ABSORPTION
OF ZIRCONIUM AND HAFNIUM
COMPLEXES OF QUERCETIN

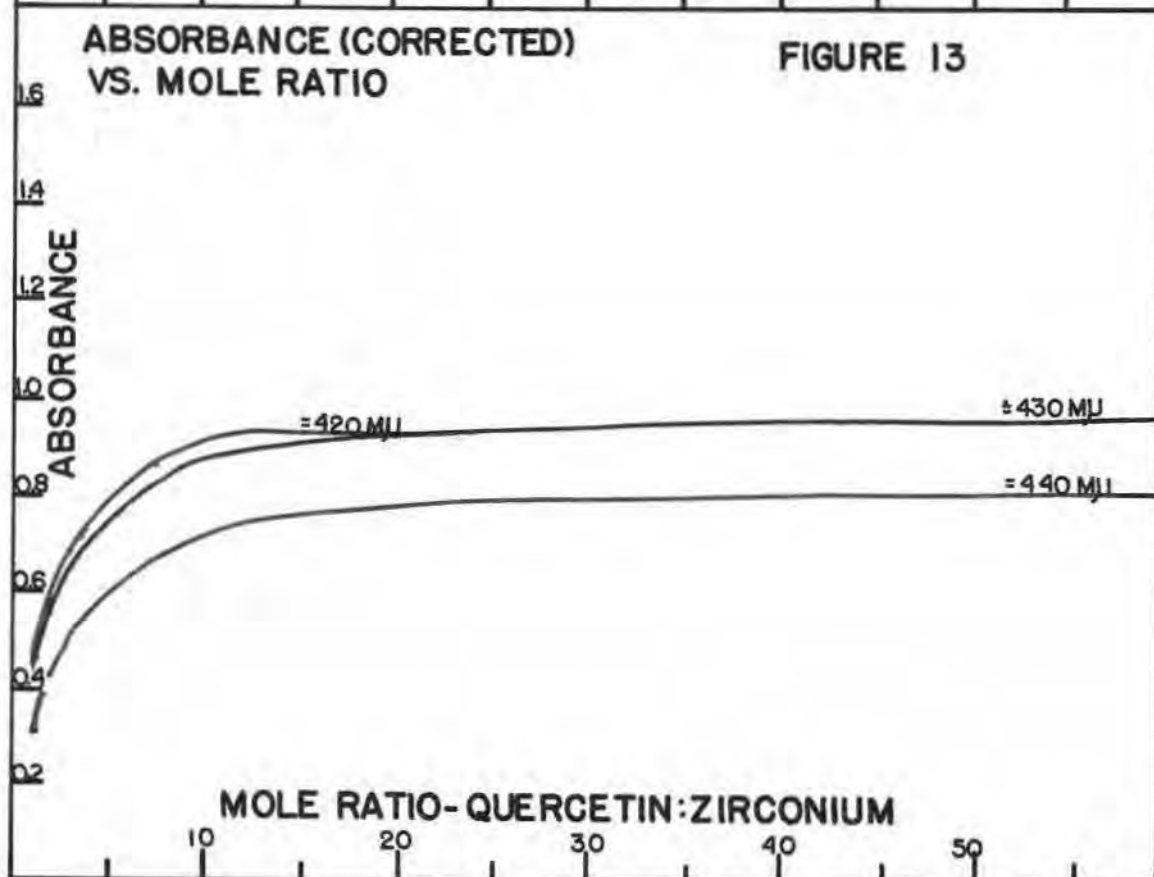
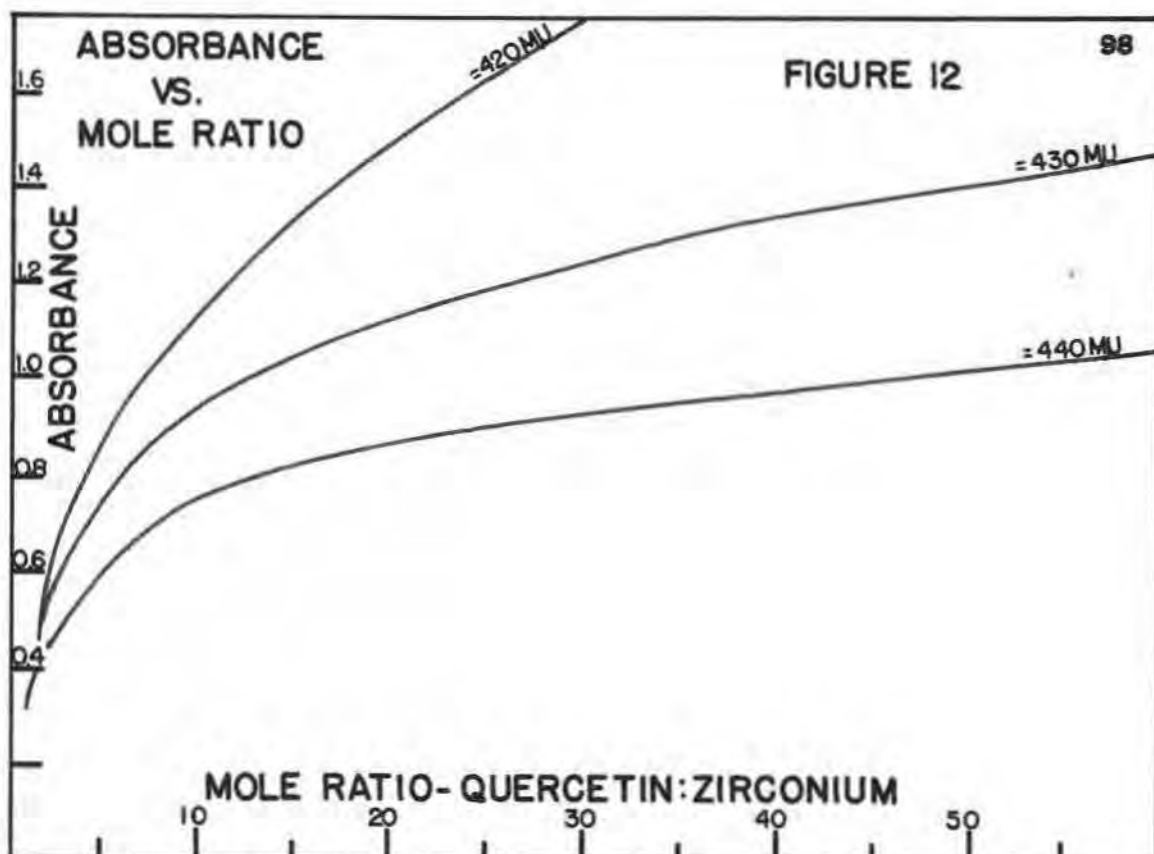
Time	Zirconium Complex	Hafnium Complex
	Absorbance	Absorbance
15 min.	1.29	0.322
30 min.	1.29	0.322
60 min.	1.29	0.321
120 min.	1.30	0.313
13.5 hrs.	-	0.305
20 hrs.	1.30	-

TABLE XX
ABSORBANCE OF THE HAFNIUM - QUERCETIN
COMPLEX AT VARIOUS ACIDITIES

Solution No.	Normality	A
1	0.10	0.322
2	0.30	0.309
3	0.50	0.312
4	0.70	0.323
5	0.90	0.334
6	1.1	0.340

quercetin to zirconium was determined. A series of solutions was prepared in which the zirconium concentration was held constant at $2.50 \times 10^{-5} \text{ M}$, and the quercetin was varied from $2.50 \times 10^{-5} \text{ M}$ to $1.50 \times 10^{-3} \text{ M}$ or from a ratio of 1:1 to 10:1. Figure 12 shows the results obtained at various wavelengths when water was used as the reference solution. When these absorbancies were corrected for absorbance of quercetin, the results summarized in Figure 13 were obtained. From these figures it is seen that the corrected absorbancies rise sharply from a mole ratio of 1:1 to 10:1 and then level off. A 10:1 or greater ratio of quercetin to zirconium should therefore be used. These data also seem to indicate, as previously suggested, that more than one complex is present in the system at low quercetin to zirconium ratios (1:1 to 10:1). The sharp rise in absorbancies from 1:1 to 10:1 ratios suggested the presence of more than one complex while the leveling off above the 10:1 ratio suggests the presence of only one complex.

It can be seen by examination of the uncorrected (Figure 12) and corrected (Figure 13) curves that the quercetin itself contributes considerably more to the absorbancies of these complexes at the lower wavelength of 420 m μ and 430 m μ than at 440 m μ . In view of these observations it seemed that measurements at 440 m μ , or



perhaps even higher, might be most advantageous since the effect of the quercetin would be the least at the higher wavelengths. Smaller slit widths should also be required for balancing the instrument when a highly absorbing reference solution is used to set the zero absorbance on the instrument.

The effect of wavelength on optimum concentration was investigated and is described in the next section.

Optimum Concentration of Zirconium - Quercetin Complex at Various Wavelengths

A series of zirconium solutions ranging in concentration from 0 to 0.90 mg./50 mls. of ZrO_2 were prepared and 25.00 mls. of quercetin solution (1.00 mg./ml. in 95% ethanol) was added to each. Hydrochloric acid was added to adjust the acidity to 0.5 N when solutions were diluted to 50.00 mls.

The optimum concentrations were then determined at 420 $m\mu$, 430 $m\mu$, 440 $m\mu$ and 450 $m\mu$, in the same manner as previously described. These data are summarized in Table XXI.

From these data it is apparent that the optimum concentration and product of $S \times C$ at the optimum concentration increases in going from a wavelength of 420 to 450 $m\mu$. This can be more readily visualized in Figure 14

TABLE XXI
OPTIMUM CONCENTRATION OF
ZIRCONIUM - QUERCETIN COMPLEX
AT VARIOUS WAVELENGTHS

$\lambda = 420 \text{ m}\mu$

Solution, ZrO_2 (mg./50 mls.)

To Set Zero	To Obtain Reading	Slit (mm.)	ΔA	C (mg/50ml)	S (Slope)	S x C
Blank	0.100	0.408	0.641	-	6.41	-
0.100	0.200	0.696	0.514	0.100	5.14	0.514
0.200	0.300	1.07	0.381	0.200	3.81	0.762
0.300	0.400	1.505	0.244	0.300	2.44	0.732
0.400	0.500	1.87	0.133	0.400	1.33	0.532
0.500	0.600	Solutions too absorbing to balance DU				

$\lambda = 430 \text{ m}\mu$

Solution, ZrO_2 (mg./50 mls.)

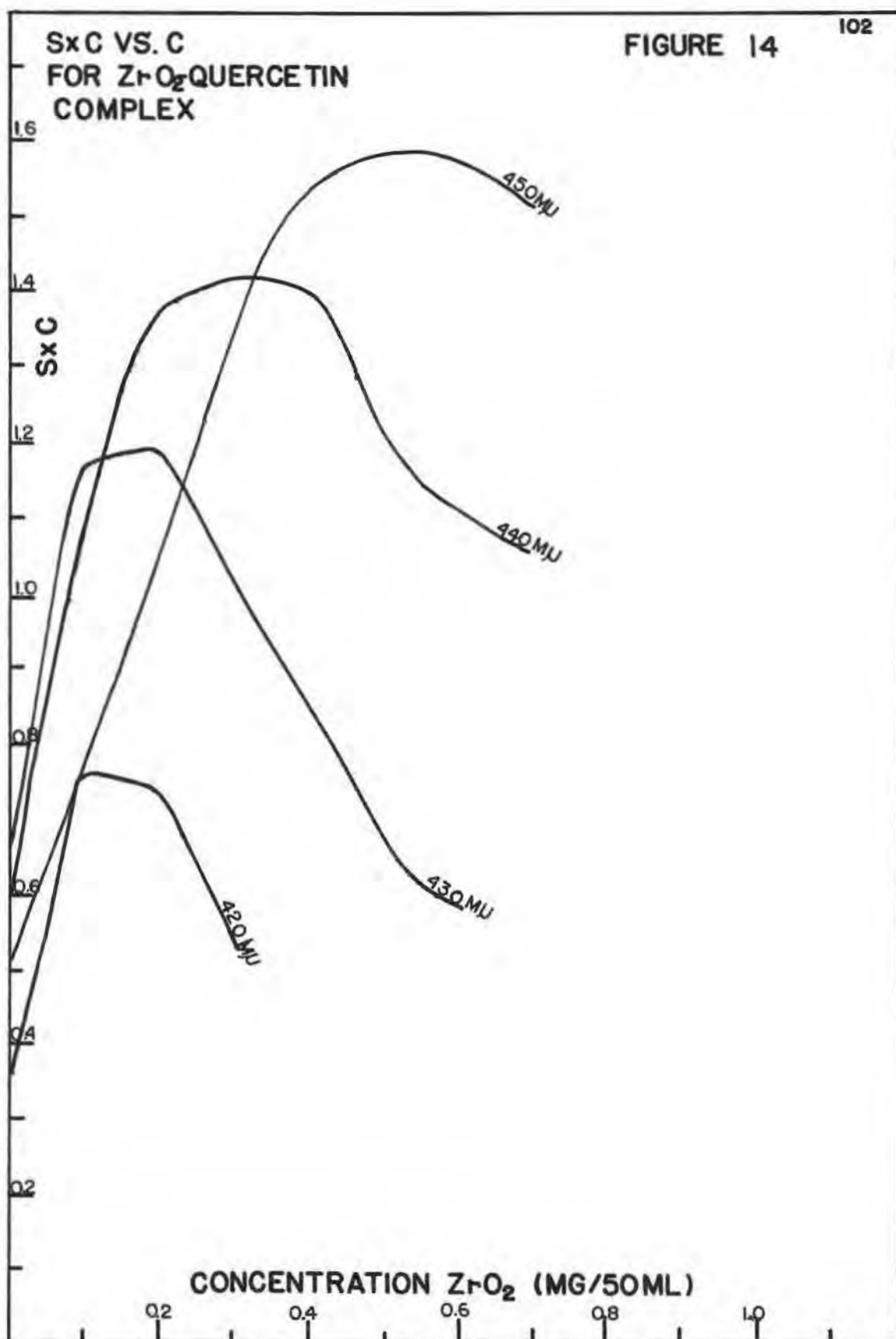
To Set Zero	To Obtain Reading	Slit (mm.)	ΔA	C (mg/50ml)	S (Slope)	S x C
Blank	0.100	0.100	0.731	-	7.31	-
0.100	0.200	0.222	0.674	0.100	6.74	0.674
0.200	0.300	0.466	0.586	0.200	5.86	1.18
0.300	0.400	0.905	0.396	0.300	3.96	1.19
0.400	0.500	1.29	0.251	0.400	2.51	1.00
0.500	0.600	1.575	0.169	0.500	1.69	0.845
0.600	0.700	1.82	0.109	0.600	1.09	0.654
0.700	0.800	1.94	0.084	0.700	0.84	0.588
0.800	0.900	Solution too absorbing to balance DU				

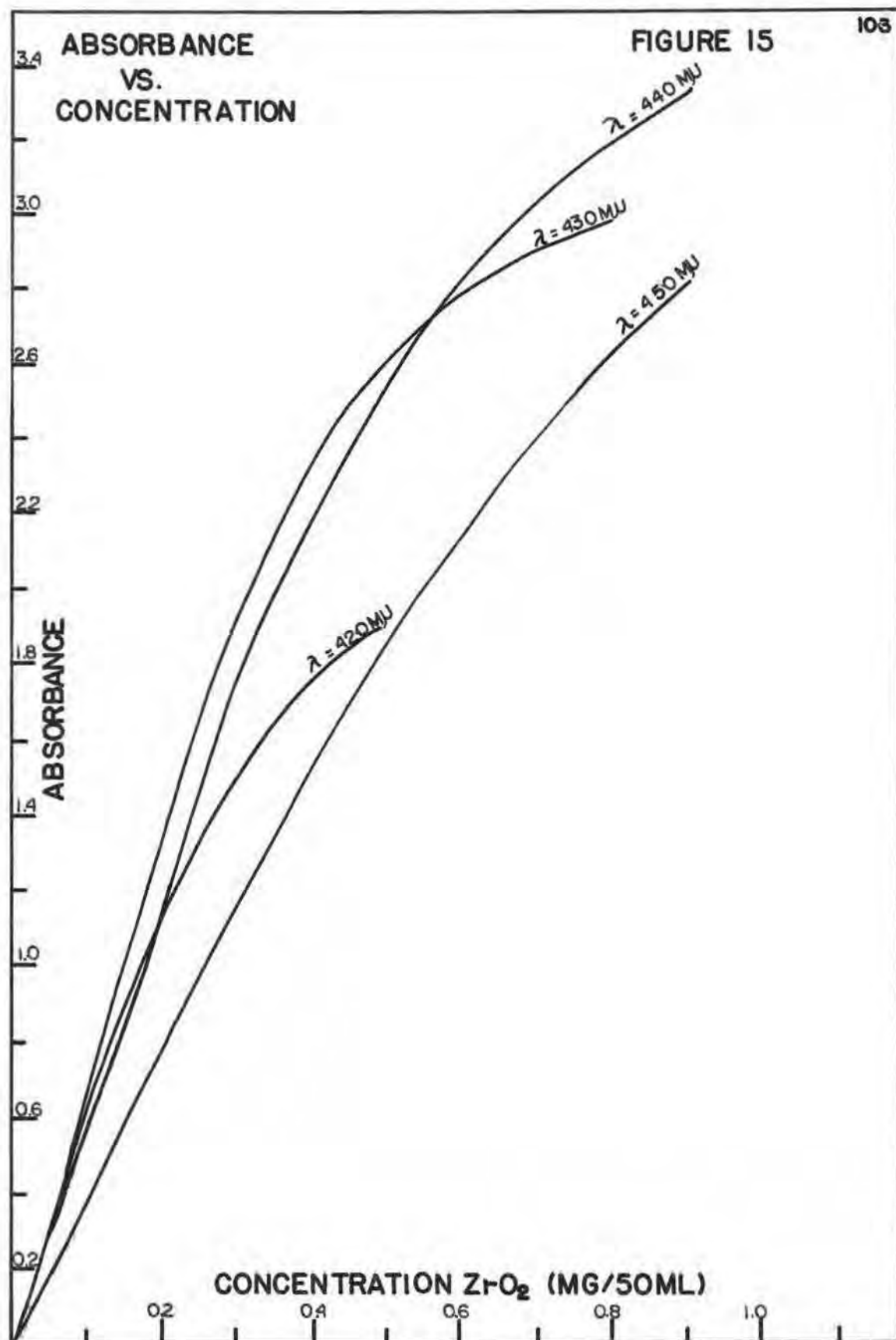
TABLE XXI
(continued) $\lambda = 440 \text{ m}\mu$ Solution, ZrO_2 (mg./50 mls.)

To Set Zero	To Obtain Reading	Slit (mm)	ΔA	C (mg/50ml)	S (Slope)	S x C
Blank	0.100	0.066	0.620	-	6.20	-
0.100	0.200	0.127	0.589	0.100	5.89	0.589
0.200	0.300	0.240	0.556	0.200	5.56	1.11
0.300	0.400	0.466	0.459	0.300	4.59	1.38
0.400	0.500	0.729	0.356	0.400	3.56	1.42
0.500	0.600	0.972	0.280	0.500	2.80	1.40
0.600	0.700	1.18	0.200	0.600	2.00	1.20
0.700	0.800	1.325	0.159	0.700	1.59	1.11
0.800	0.900	1.45	0.133	0.800	1.33	1.06

 $\lambda = 450 \text{ m}\mu$ Solution, ZrO_2 (mg./50 mls)

To set Zero	To Obtain Reading	Slit (mm)	ΔA	C (mg/50ml)	S (Slope)	S x C
Blank	0.100	0.056	0.405	-	4.05	-
0.100	0.200	0.087	0.387	0.100	3.87	0.387
0.200	0.300	0.130	0.384	0.200	3.84	0.768
0.300	0.400	0.219	0.333	0.300	3.33	0.999
0.400	0.500	0.310	0.336	0.400	3.36	1.344
0.500	0.600	0.434	0.324	0.500	3.24	1.620
0.600	0.700	0.590	0.255	0.600	2.55	1.530
0.700	0.800	0.711	0.226	0.700	2.26	1.582





where $S \times C$ vs. C is plotted. The optimum concentration at 450 $m\mu$ was rather uncertain as the points at the higher concentrations were scattered. There is no doubt however, but that the optimum concentration is higher than for the lower wavelengths. This shift was probably due in part to the much greater absorbance of excess quercetin at the lower wavelengths which made excessively large slit widths necessary to set the instrument for the more highly concentrated solutions. At 440 $m\mu$ and 450 $m\mu$ the absorption of the quercetin was very small. This plus the increased sensitivity of the instrument at the higher wavelengths permitted all of the solutions to be measured.

Here again it is of interest to plot absorption vs. concentration of ZrO_2 (Figure 15) and to compare the optimum concentration which might be predicted on the basis of the negative deviation with those found in the $S \times C$ vs. C plots. The predictions based on the 420, 430 and 440 $m\mu$ curves seem to agree as expected but there is still some doubt about the 450 $m\mu$ curves. This was, however, resolved in the next series of experiments.

Optimum Concentration and Wavelength Using 0 and 20% HfO_2 Solutions

In order to help determine both the optimum

concentration and wavelength, a series of 0 and 20% HfO_2 solutions were prepared at 0.300 to 1.500 mg./50 mls. of total oxide content. Hydrochloric acid, quercetin and water were then added as in the preceding paragraph. The difference in absorbance was then measured between each pair of solutions at the same total oxide concentration. This seemed to be a realistic approach since this was the type of measurement which would eventually be made in running standards and unknowns. The 0 and 20% HfO_2 levels were selected for convenience. 0 and 10% HfO_2 or even 0 and 5% HfO_2 etc. could have been used but these lower % HfO_2 solutions were more difficult to accurately prepare. It was felt that what was true for the 0 to 20% HfO_2 solutions would also be true for the 0 to 5% HfO_2 . Measurements were made at several wavelengths. The results of this series of measurements are summarized in Table XXII.

Examination of this table shows an optimum concentration of 0.800 mg./50 mls. of total oxides at 450 m μ . This essentially agrees with data in the preceding section. Subsequent measurements were therefore made under these conditions.

The variation of ΔA with wavelength at the various oxide levels is more readily seen in Figure 16. Figure 17 shows the curves of $S \times C$ vs λ . On comparing these

TABLE XXII

OPTIMUM CONCENTRATION AND WAVELENGTH
USING 0 AND 20% HfO₂ SOLUTIONS

Solution, %HfO₂

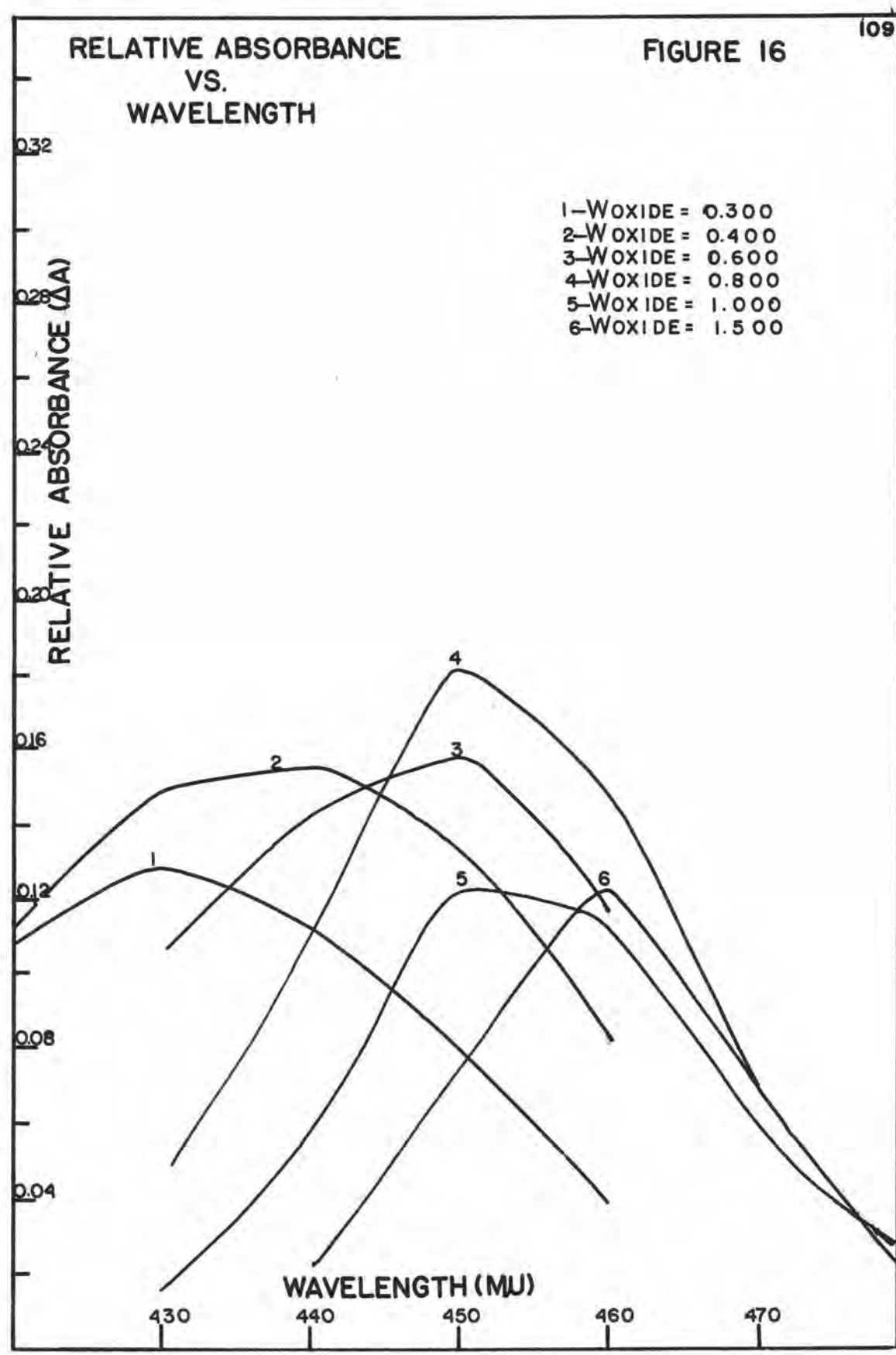
To Set Zero	To Ob- tain Reading	Total Oxide mg/50mls.	λ (m μ)	Slit (mm)	A	S	CzrO ₂ mg/ml (calc)	S x C
20	0	0.300	420	0.82	0.1075	4.32	0.2751	1.19
			430	0.44	0.129	5.18		1.43
			440	0.26	0.1125	4.52		1.24
			450	0.13	0.081	3.25		0.89
			460	0.08	0.040	1.61		0.44
20	0	0.400	420	1.45	0.109	3.28	0.3668	1.20
			430	0.92	0.149	4.49		1.65
			440	0.52	0.156	4.70		1.72
			450	0.24	0.134	4.03		1.48
			460	0.11	0.084	2.53		0.93
20	0	0.500	420	1.875	0.085	2.05	0.4585	0.94
			430	1.30	0.126	3.04		1.39
			440	0.76	0.156	3.76		1.72
			450	0.34	0.145	3.50		1.60
			460	0.13	0.097	2.34		1.07
20	0	0.600	420	Could not balance			0.5502	-
			430	1.60	0.105	2.11		1.16
			440	1.00	0.142	2.85		1.57

			450	0.116	0.1575	3.16	1.74
			460	0.17	0.116	2.33	1.28
20	0	0.700	420	Could not balance 0.6420 -			
			430	1.825	0.095	1.64	1.05
			440	1.175	0.1375	2.37	1.52
			450	0.58	0.168	2.90	1.86
			460	0.21	0.1375	2.37	1.52
20	0	0.800	430	1.525	0.043	0.65 0.7337	0.48
			440	0.960	0.108	1.63	1.20
			450	0.460	0.181	2.74	2.01
			460	0.140	0.146	2.20	1.61
			470	0.060	0.70	1.06	0.78
20	0	0.900	430	1.400	0.019	0.25 0.8254	0.21
			440	1.05	0.064	0.86	0.71
			450	0.56	0.134	1.80	1.49
			460	0.18	0.116	1.56	1.29
			470	0.075	0.059	0.79	0.65
20	0	1.000	430	1.475	0.015	0.18 0.9171	0.17
			440	1.15	0.057	0.69	0.63
			450	0.64	0.124	1.50	1.38
			460	0.20	0.114	1.50	1.27
			470	0.075	0.060	0.72	0.66
			480	0.050	0.028	0.34	0.31

20	0	1.500	430	1.70	0.002	0.016	1.3756	0.022
			440	1.475	0.0225	0.18		0.25
			450	1.00	0.0775	0.62		0.85
			460	0.48	0.124	1.00		1.38
			470	0.16	0.068	0.55		0.76
			480	0.090	0.018	0.145		0.20

Note: The C_{ZrO_2} is the weight concentration of the 20% HfO_2 solution expressed as ZrO_2 only:

$$C_{ZrO_2} = W_{ZrO_2} + W_{HfO_2} \times \frac{ZrO_2}{HfO_2}$$

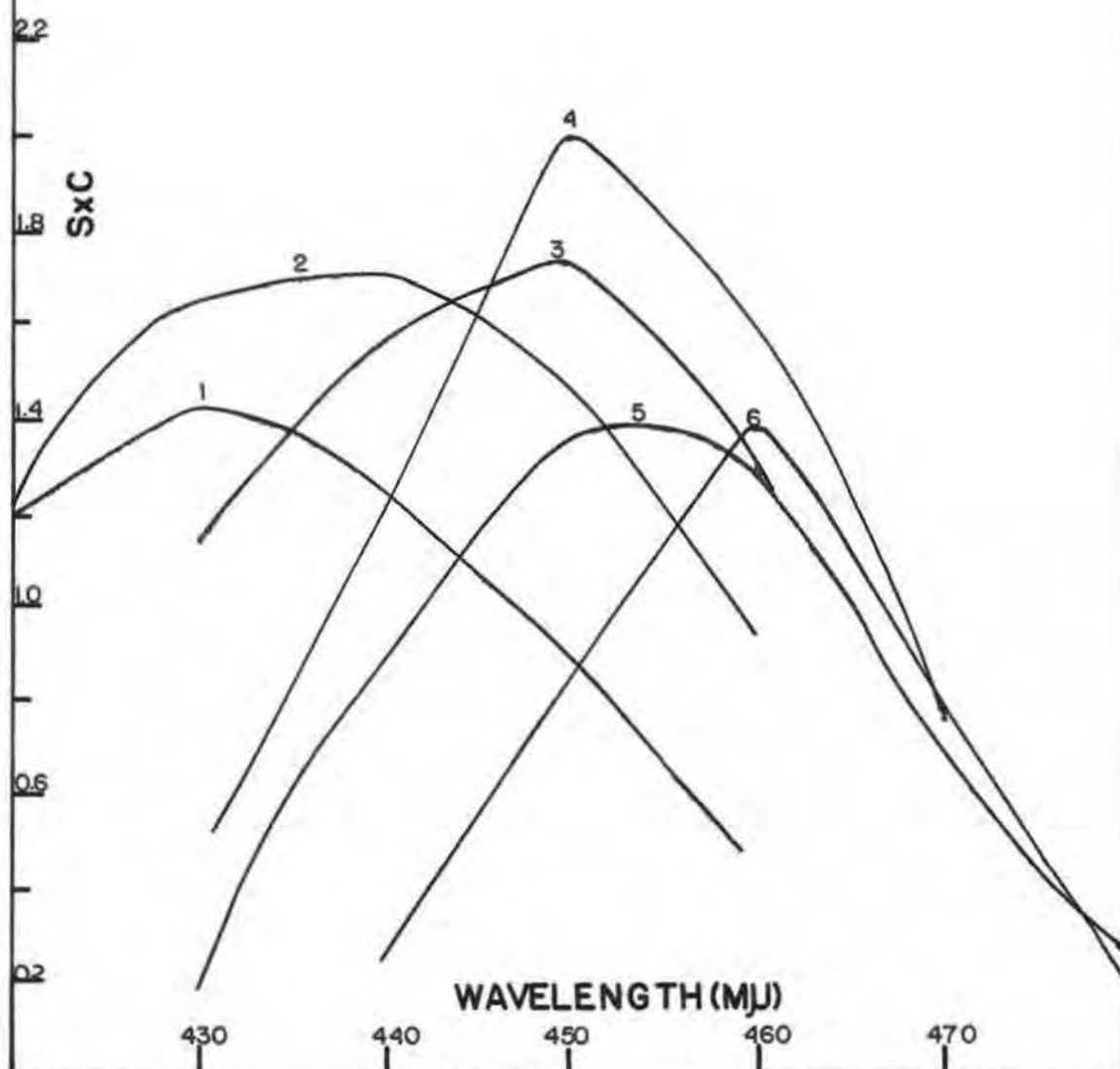


**Sx C VS. WAVELENGTH
FOR Zr-Hf-QUERCETIN
COMPLEX**

FIGURE 17

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- 1-WOXIDE = 0.300
- 2-WOXIDE = 0.400
- 3-WOXIDE = 0.600
- 4-WOXIDE = 0.800
- 5-WOXIDE = 1.000
- 6-WOXIDE = 1.500



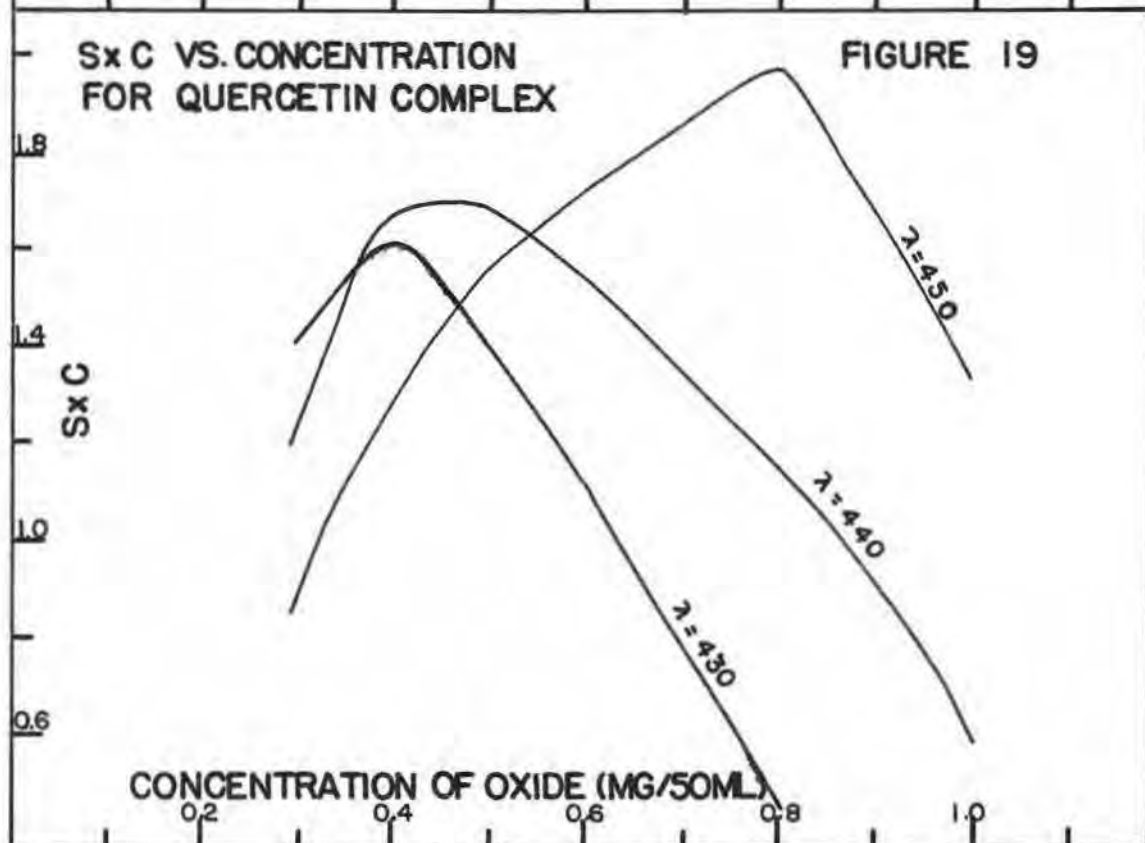
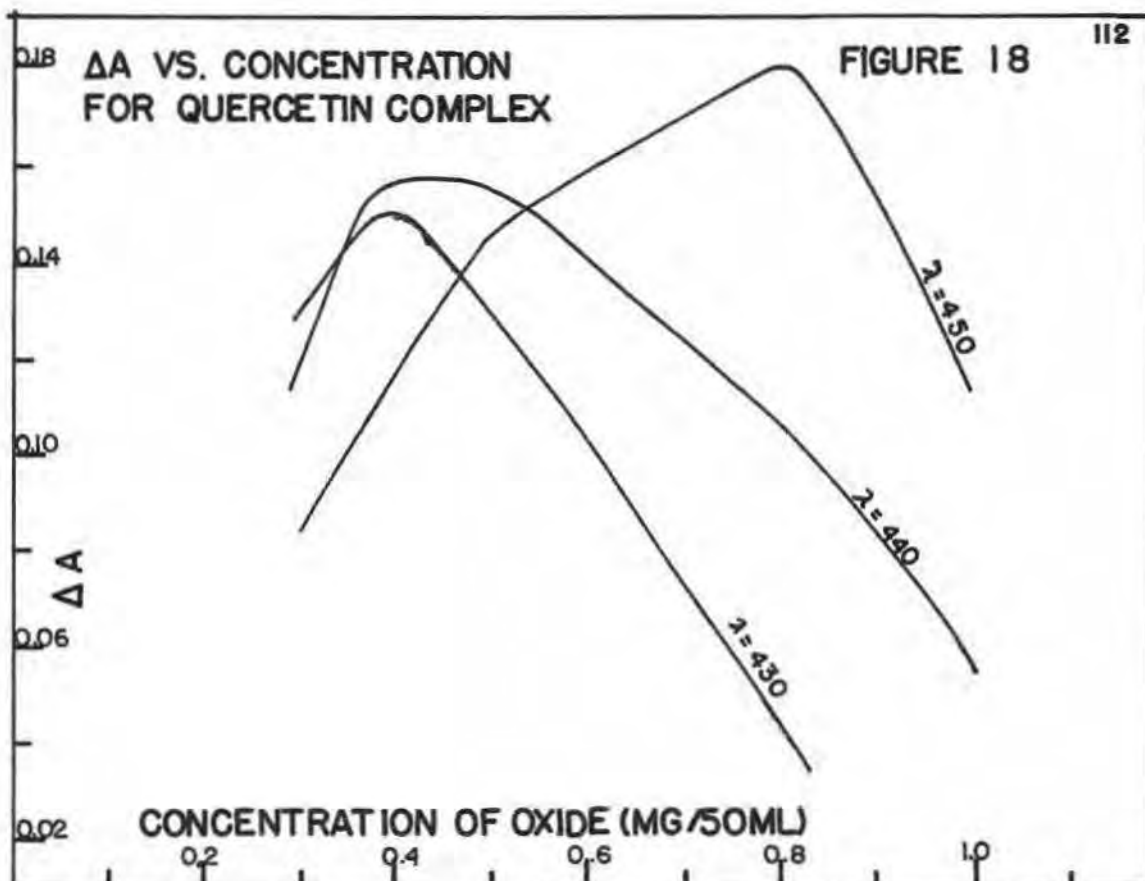
curves it is noted that the curves for ΔA vs λ and $S \times C$ vs. λ are of the same shape and the optimum wavelength at various oxide levels are found to be exactly the same.

When ΔA vs. concentration and $S \times C$ vs. concentration are compared as in Figure 18 and 19, the same shape curves are again observed and with identical optimum concentrations. This leads to the conclusion that for this approach ΔA vs. C_{oxide} at a given wavelength can be plotted directly to determine the optimum concentration at that wavelength. In a like manner, ΔA vs λ can be used directly to find the optimum wavelength for a given oxide concentration.

A calibration curve for % HfO_2 in ZrO_2 was determined next using the optimum conditions found above.

Standard Curve for the Determination of % HfO_2 in the Presence of ZrO_2

Several sets of standard solutions containing from 0 to 10% HfO_2 in ZrO_2 at a total oxide concentration of 0.800 mg./50 mls. were prepared and run. The acidity was adjusted to 0.5 N with hydrochloric acid and 25.00 mls. of quercetin (1.00 mg./ml. in 95% ethanol) were added to each solution and the solutions diluted to 50.00 mls. with distilled water.



A standard curve for 0 to 10% HfO_2 was run first and ΔA vs. % HfO_2 was plotted. The 10% HfO_2 solution was used as the reference and all other standards were measured against it. The standard curve is shown in Figure 20.

Standard curves for 0 to 5% HfO_2 were run on different days. The resulting calibration curves are found in Figure 21. There seems to be a considerable shift in the curves and also a scattering of points. These data indicate that it would certainly be necessary to run a new calibration curve for each set of unknowns.

Discussion

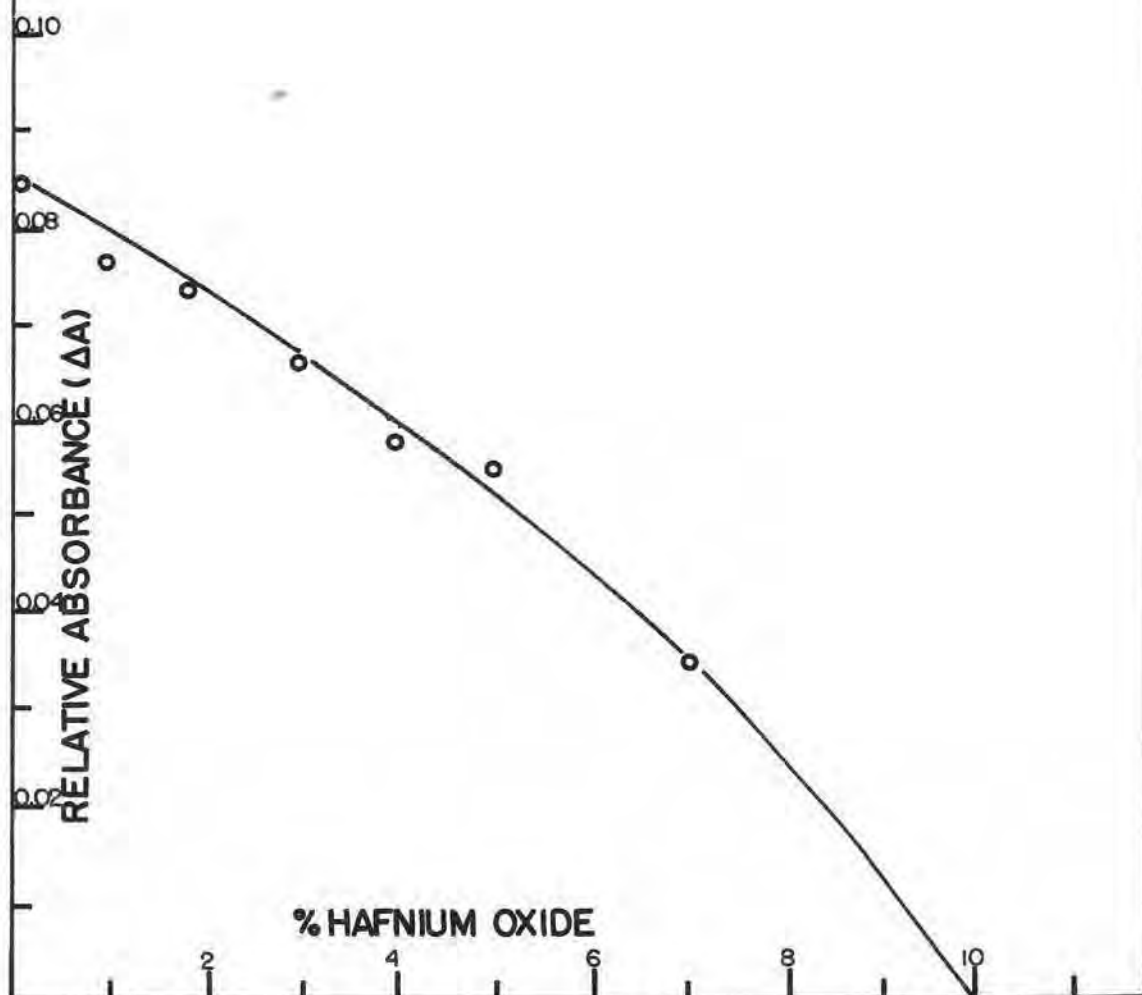
The findings in this study using quercetin seem to indicate that it would be of potential use for the determination of 0 to 5% HfO_2 in ZrO_2 if no better method could be developed. No doubt this procedure could be further refined to eliminate most of the scattering of points. Perhaps if a permanent standard, which was roughly equivalent to the 5% HfO_2 colored solution could be found then the shift in calibration curve might also be eliminated.

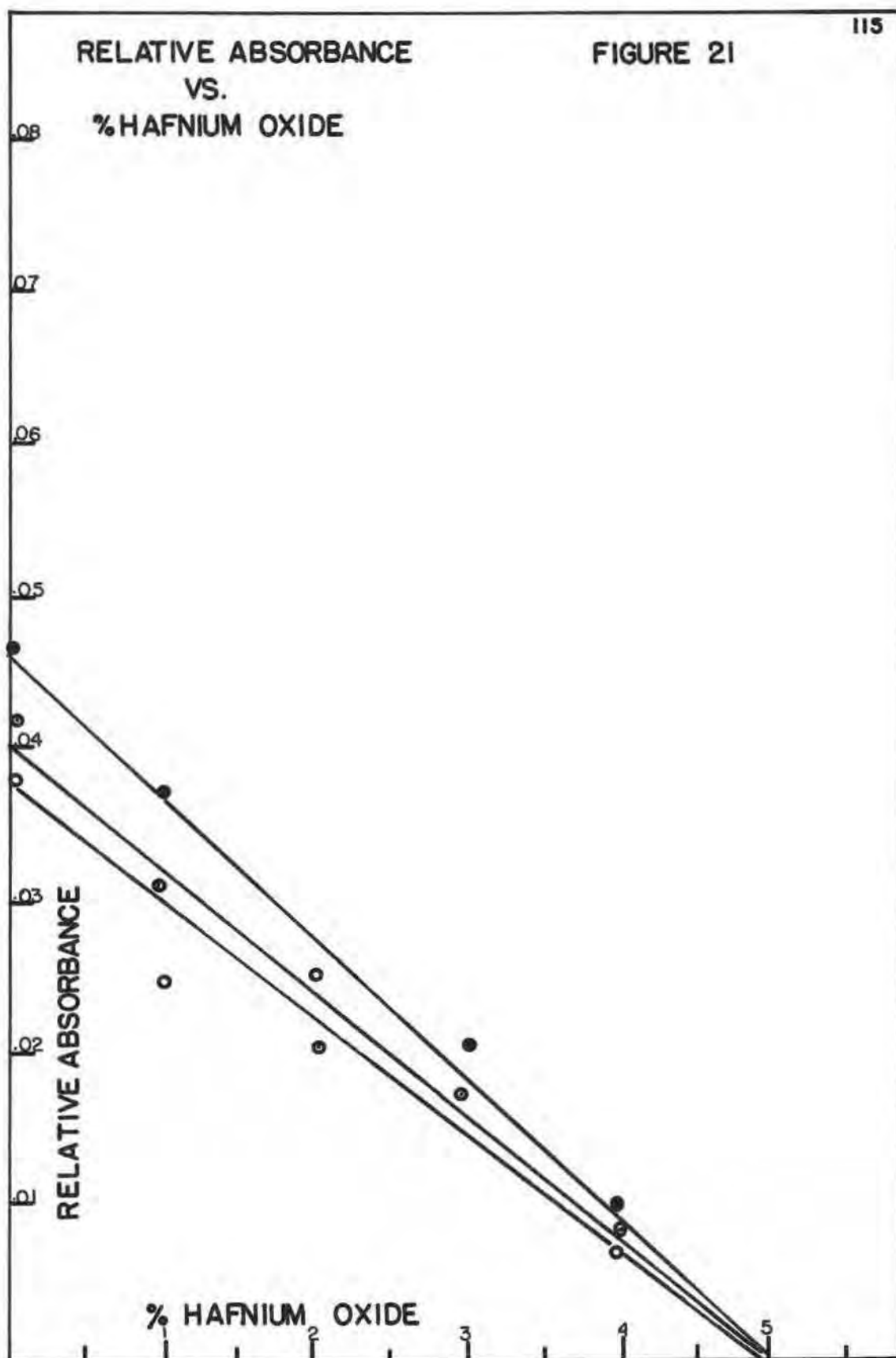
More research would have been devoted to this system if a more promising method using Xylenol Orange had not been suggested by Cheng (36). This new method

RELATIVE ABSORBANCE (ΔA)
VS.
% HAFNIUM OXIDE

FIGURE 20

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seemed to offer the possibility of actually measuring the absorbance of the hafnium complex formed with Xylenol Orange, rather than just the difference due to differences in atomic weights of hafnium and zirconium. Details of this work will be discussed next.

INVESTIGATION USING XYLENOL ORANGE

The investigation of Xylenol Orange differed from the preceding methods in that it was an indirect differential method while the direct differential approach was used on the mandelic acid, chloranilic acid and quercetin.

A small fraction of this work was carried out to confirm the findings of Cheng (12; 13; 14; 15; 16), but since his work was principally with perchloric acid solutions and this work was with hydrochloric acid solutions, there was little overlap.

In this investigation advantage was taken of the fact that H_2O_2 almost completely bleaches the zirconium - Xylenol Orange complex while it only bleaches the hafnium - Xylenol Orange to a slight extent. In this case then, while holding the weight of oxides constant as before, the 0% HfO_2 solution was the reference used to set the instrument and the absorbance of the other standard solutions were measured relative to it.

Apparatus

The same apparatus as previously used was utilized in this investigation.

Reagents

1. ZrO_2 solutions. Used high purity $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ for most of this work. High purity ZrO_2 was used in preparing some of the standards for the unknown sample calibration curves. These solutions were made up in 6 N hydrochloric acid (standardized) and were analyzed using the cupferron method.

2. HfO_2 solutions. $\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$ was used for preparation of all standard solutions. They were made up in standard 6 N hydrochloric acid and were standardized by the cupferron method.

3. Xylenol Orange, 0.05% and 0.50% solutions. Weighed out exactly 0.0500 g. and 0.5000 g. respectively of Xylenol Orange (sodium salt), dissolved in distilled water and diluted to volume in a 100 ml. volumetric flask. Xylenol Orange may be obtained from Lamont Laboratories, 5002 West Mockingbird Lane, Dallas 9, Texas.

4. Hydrochloric acid, 6.000 N. Diluted about 1250 mls. of concentrated hydrochloric acid to about 2500 mls. with distilled water. Standardized with standard sodium hydroxide solution using phenolphthalein.

Absorption Spectra of Xylenol Orange

Absorption curves of 5.8×10^{-5} M Xylenol Orange

solutions in distilled water, 0.3 N, 0.8 N and 1.6 N hydrochloric acid were determined using a distilled water reference solution. These curves are found in Figure 22. It can be seen from these curves that the acidity has a pronounced effect on the absorption of this dye.

Absorption Spectra of the Zirconium - Xylenol Orange Complex

Solutions containing 1.31×10^{-5} M zirconium and 5.8×10^{-5} M Xylenol Orange, were prepared at 0.3 N, 0.8 N and 1.2 N hydrochloric acid concentrations and the absorption curves, using a water reference were determined as shown in Figure 23. Here again the acidity produced a pronounced effect on the absorption curves. The wavelength for maximum absorbance tends to shift towards lower wavelengths as the acidity is increased. The absorbance also increases in going from 0.3 N acid solution to 0.8 N and decreases at 1.2 N.

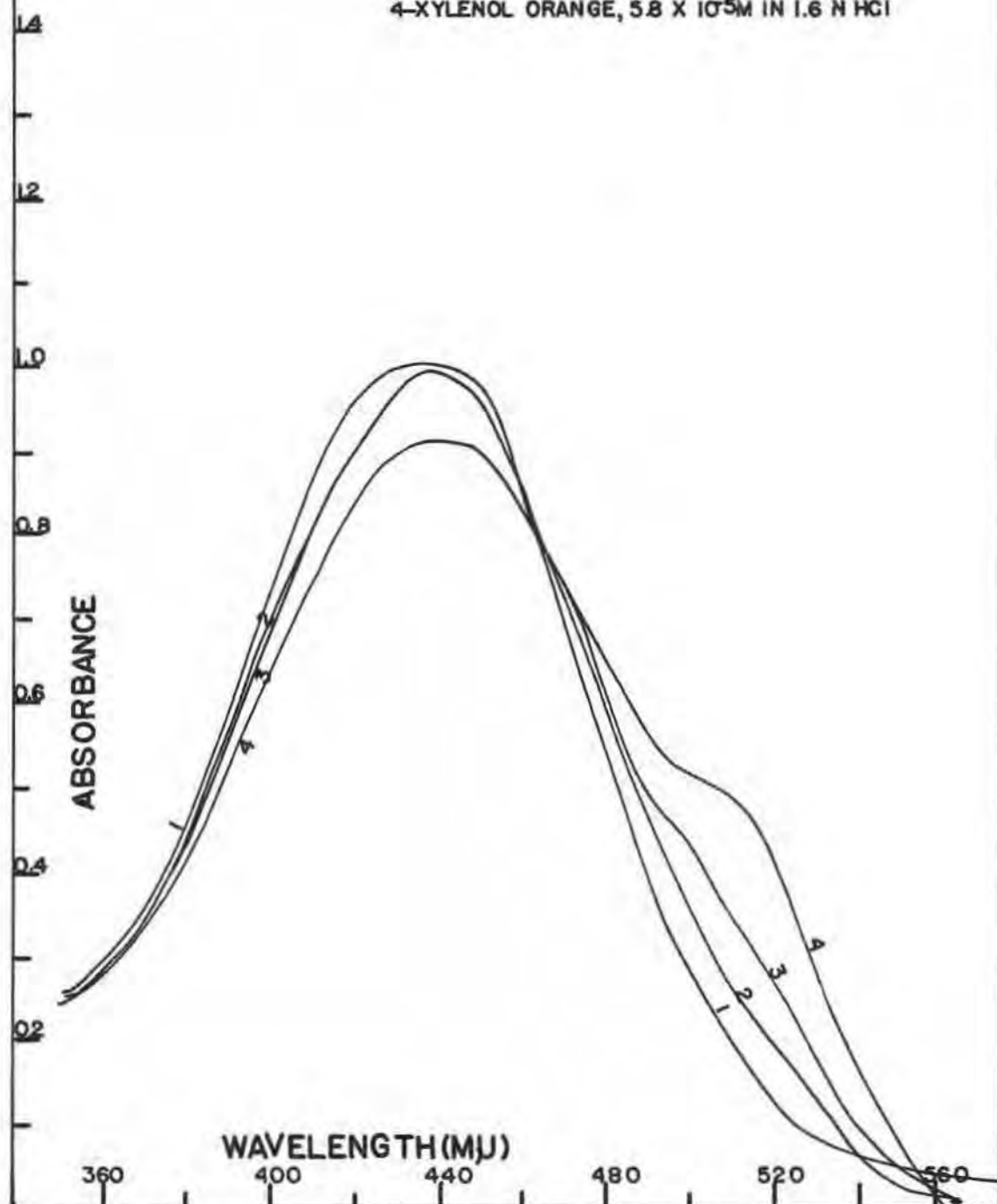
Absorption Spectra of the Hafnium - Xylenol Orange Complex

Absorbance curves were run on solutions of 1.25×10^{-5} M hafnium and 5.8×10^{-5} M Xylenol Orange at 0.3 N, 0.8 N and 1.0 N hydrochloric acid. A water reference

ABSORBANCE OF XYLENOL
ORANGE VS.
WAVELENGTH

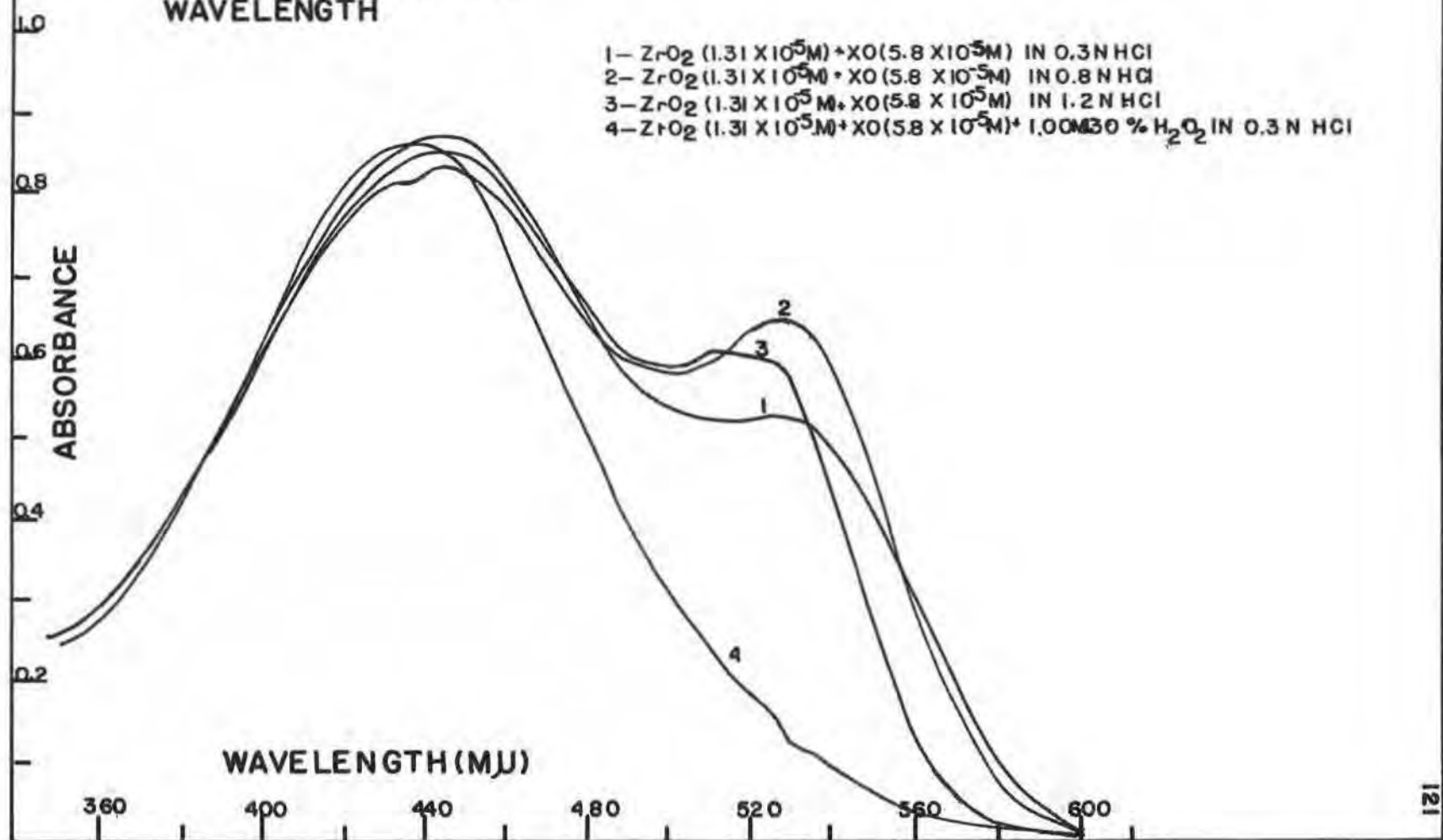
FIGURE 22

- 1—XYLENOL ORANGE (NO ACID) $5.8 \times 10^{-5} \text{M}$
2—XYLENOL ORANGE, $5.8 \times 10^{-5} \text{M}$ IN 0.3 N HCl
3—XYLENOL ORANGE, $5.8 \times 10^{-5} \text{M}$ IN 0.8 N HCl
4—XYLENOL ORANGE, $5.8 \times 10^{-5} \text{M}$ IN 1.6 N HCl



ABSORBANCE OF Zr-XYLENOL
ORANGE COMPLEX VS.
WAVELENGTH

FIGURE 23



was used. These results are found in Figure 24. The same general trend as that noted for zirconium is observed.

Absorption Spectra of Zirconium and Hafnium - Xylenol Orange Complexes in Presence of Hydrogen Peroxide

In order to observe the masking effect of hydrogen peroxide on these complexes, 0.3 N solutions identical to those above were prepared except that 1.00 ml. of 30% hydrogen peroxide was added just before the Xylenol Orange, as suggested by Cheng (12). The effect on the zirconium complex is seen in Figure 23 and for the hafnium in Figure 24. It is observed that the masking effect of the hydrogen peroxide on the zirconium - Xylenol Orange is considerably greater than on the hafnium. On the basis of Cheng's work, this was expected.

Effect of Time on Absorbance

The absorbances of solutions containing 1.31×10^{-5} M zirconium and hafnium and 5.8×10^{-5} M Xylenol Orange at 0.5 hydrochloric acid concentration were determined at various times against a water reference. The results are shown in Table XXIII.

These data indicate that the color of these complexes under the above conditions has fully developed

ABSORBANCE OF HF-XYLENOL
ORANGE COMPLEX VS.
WAVELENGTH

FIGURE 24

- 1- $\text{HFO}_2 (1.31 \times 10^{-5} \text{ M}) + \text{XO} (5.8 \times 10^{-5} \text{ M})$ IN 0.3 N HCl
- 2- $\text{HFO}_2 (1.31 \times 10^{-5} \text{ M}) + \text{XO} (5.8 \times 10^{-5} \text{ M})$ IN 0.8 N HCl
- 3- $\text{HFO}_2 (1.31 \times 10^{-5} \text{ M}) + \text{XO} (5.8 \times 10^{-5} \text{ M})$ IN 1.0 N HCl
- 4- $\text{HFO}_2 (1.31 \times 10^{-5} \text{ M}) + \text{XO} (5.8 \times 10^{-5} \text{ M}) + 1.00 \text{ ML } 30\% \text{ H}_2\text{O}_2$ IN 0.3 N HCl

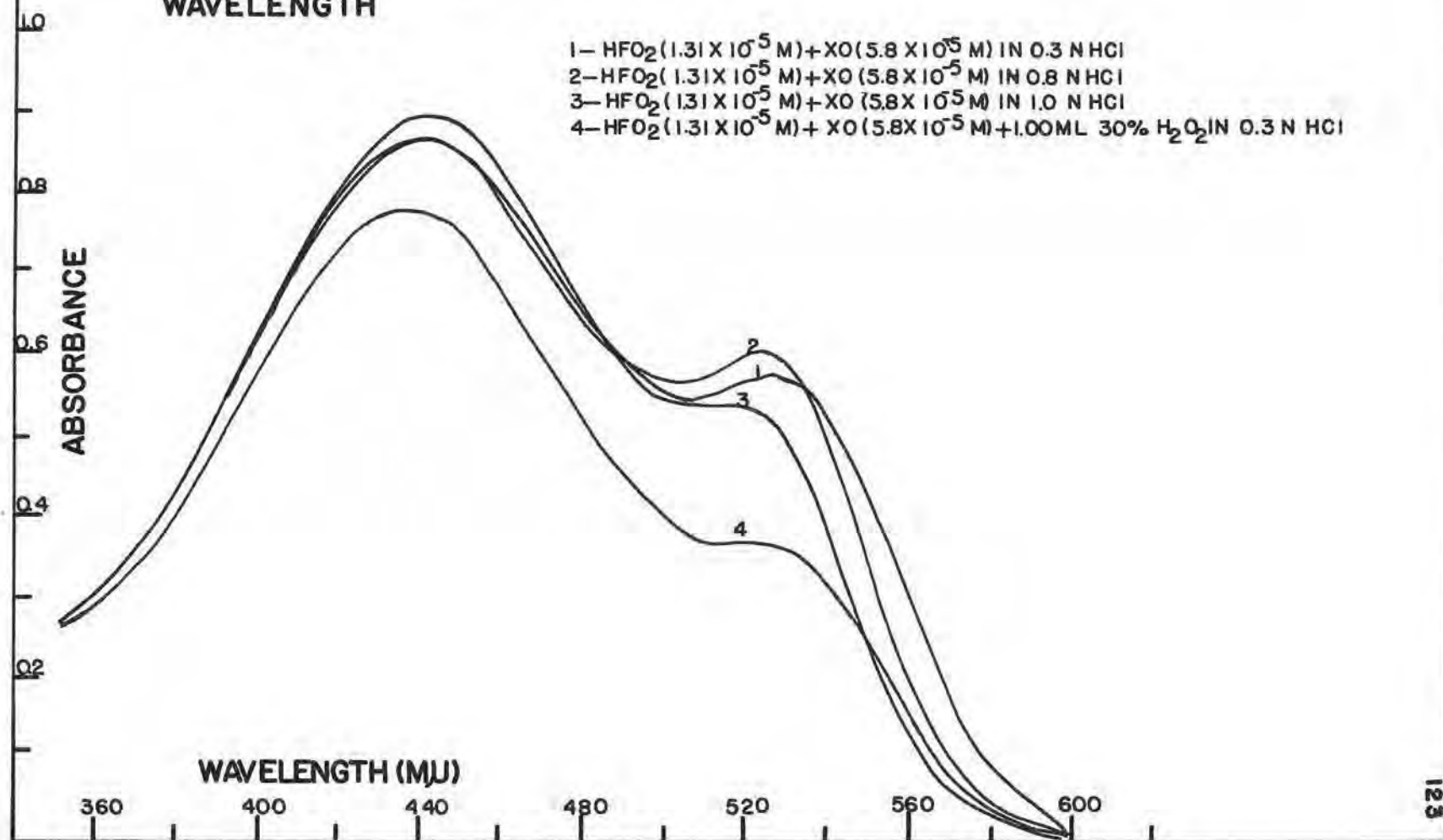


TABLE XXIII

ABSORBANCE VS. TIME FOR
COLOR DEVELOPMENT OF
ZIRCONIUM AND HAFNIUM-
XYLENOL ORANGE COMPLEXES

Time Hours	Zirconium Complex Absorbance	Hafnium Complex Absorbance
0.25	0.590	0.621
0.50	0.589	0.620
1.0	0.589	0.619
2.5	0.586	0.616
12.0	0.580	0.614
24.0	0.588	0.618
48.0	0.588	0.620
72.0	0.539	0.565

after 15 minutes and that they are stable for at least 48 hours.

Effect of Acidity on the Absorbance of Xylenol Orange, and its Zirconium and Hafnium Complexes at Various Wavelengths

A series of 5.8×10^{-5} M Xylenol Orange solutions were prepared at 0.1 N to 1.6 N hydrochloric acid concentration. The absorbancies of these solutions were measured at wavelengths of 525, 530, 535 and 540 m μ using a water reference. The results are shown in Figure 25.

The above procedure was repeated for solutions containing 1.31×10^{-5} M zirconium and also for solutions containing 1.25×10^{-5} M hafnium. These results are also shown in Figure 25. Corrections for the absorbance of Xylenol Orange have been made on these curves.

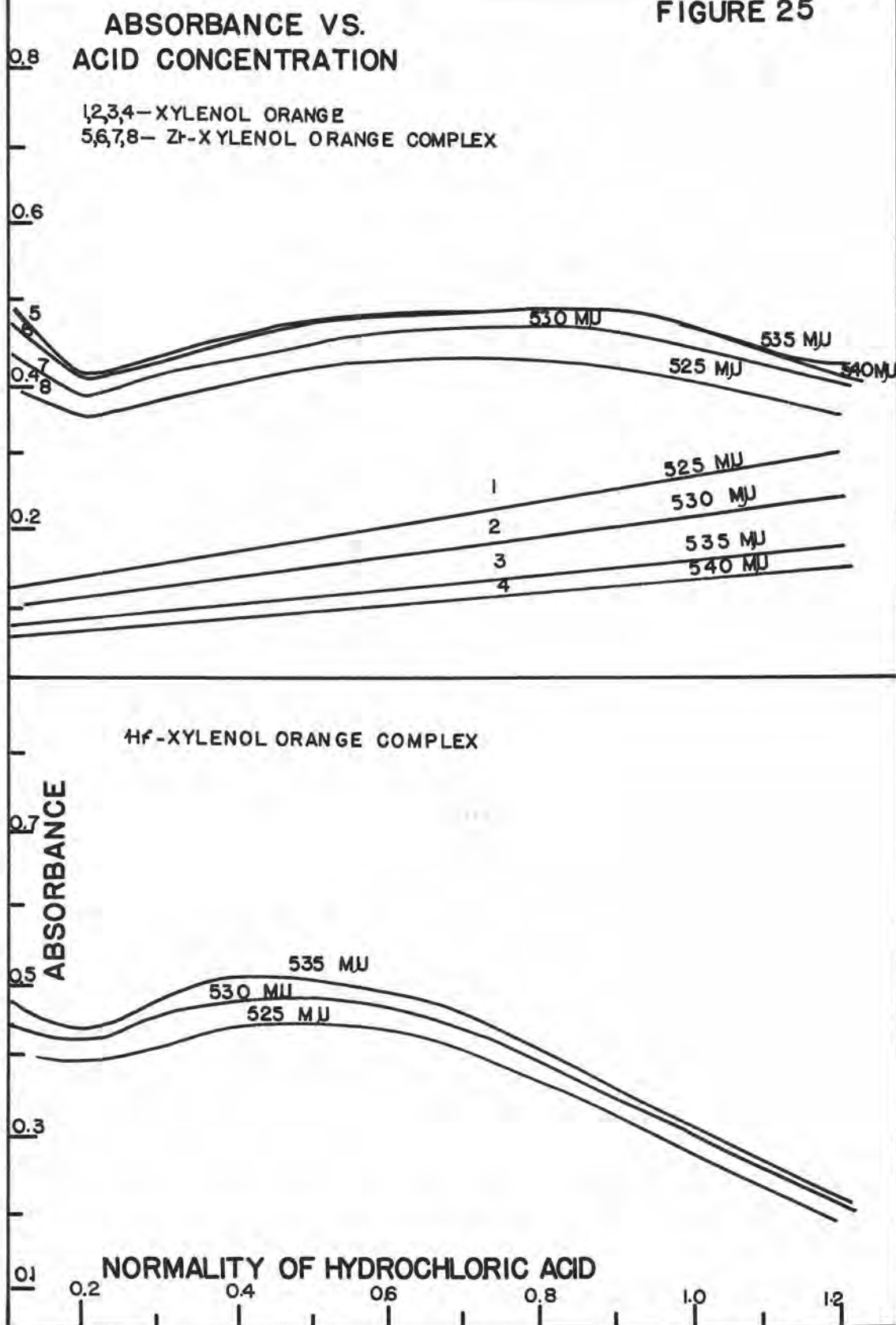
These Xylenol Orange curves indicate that the absorbance increases with increasing acidity but that the effect is less pronounced at the higher wavelengths.

The zirconium complex curves indicate that its maximum absorbance occurs at an acidity of 0.7 to 0.9 N and at a wavelength of 535 or 540 m μ .

In the case of hafnium, the maximum absorbance occurs at an acid concentration of 0.4 N and at 535 m μ .

The effect on absorbance of the ratio of Xylenol Orange to zirconium was next determined.

FIGURE 25

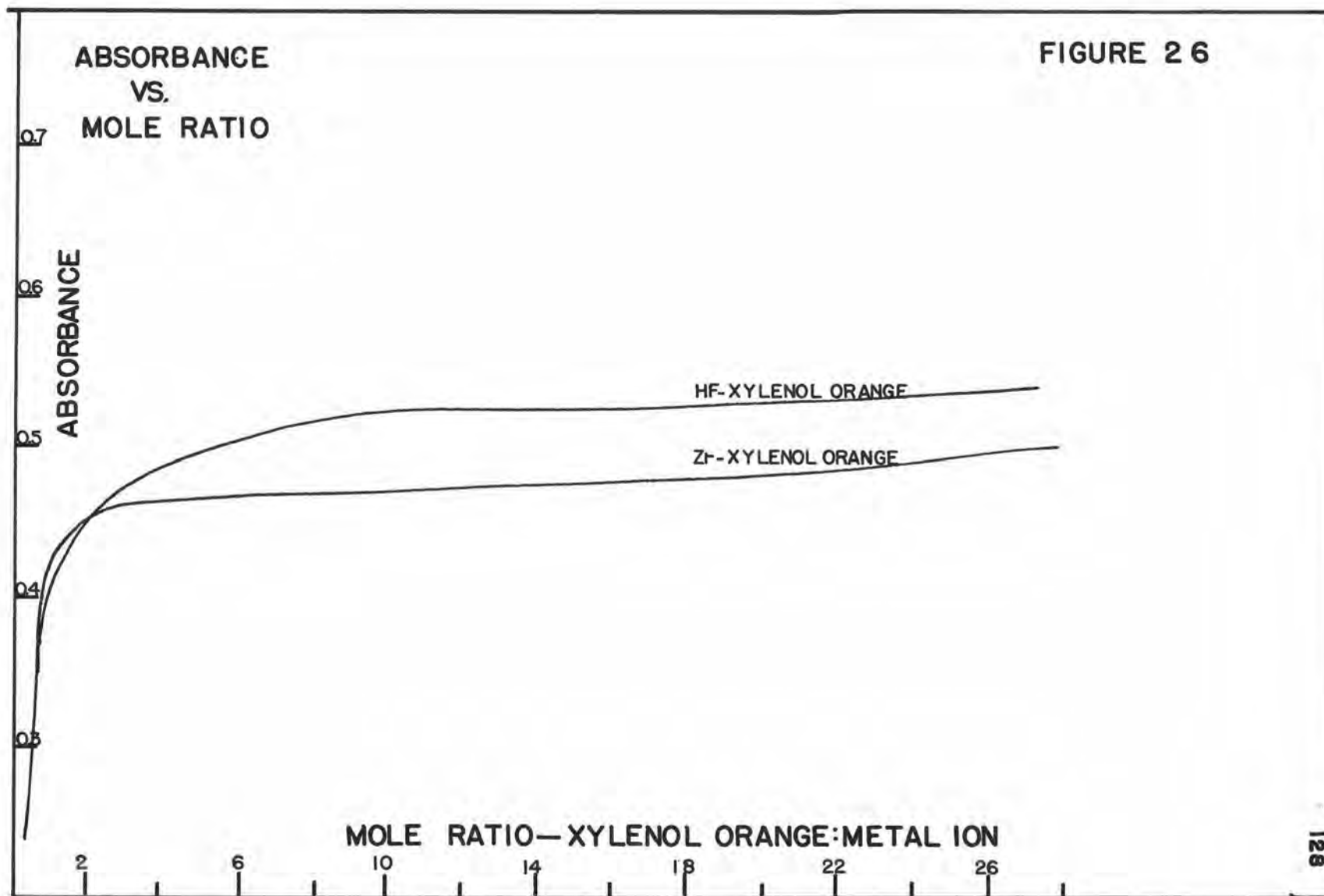


Absorbance vs. Mole Ratio of Xylenol Orange to Zirconium and Hafnium

Solutions containing from 0.45 to 27 mole ratio of Xylenol Orange to zirconium and hafnium were prepared and the absorbance determined at 535.m μ . The acid concentration was 0.4 N in both cases. This acidity was used since the conditions eventually desired are those which will give a maximum absorbance for the hafnium complex and a minimum absorbance for the zirconium complex. Figure 26 shows these curves which have been corrected for the absorbance of Xylenol Orange.

These curves are seen to rise sharply from a mole ratio of 0.45 to about 3 and then they taper off and become essentially constant from a mole ratio of about 3.0 to 27 for the zirconium and about 10 to 27 for the hafnium. It therefore appears that a mole ratio of about 5.0 or greater should give the maximum absorbance but that not much sensitivity would be lost by using a 3 to 1 mole ratio of Xylenol Orange to zirconium and hafnium, if necessary.

After the optimum acidity, wavelength and mole ratio had been determined, the masking effect of hydrogen peroxide on the zirconium and hafnium - Xylenol Orange complexes was studied.



Effect of Time on Absorbance of Zirconium and Hafnium -
Xylenol Orange Complexes in Presence of Hydrogen Peroxide

A series of zirconium - Xylenol Orange complexes containing 1.31×10^{-5} M zirconium and 7.2×10^{-5} M Xylenol Orange at an hydrochloric acid concentration of 0.4 N was prepared. Various amounts of 30% hydrogen peroxide were added. The hydrogen peroxide was added after the dye. All measurements were made at 535 m μ over a period of several hours using a water reference. All curves, shown in Figure 27, have not been corrected for the absorbance of Xylenol Orange in order to better indicate the changing nature of these solutions. Figure 28 shows these same curves plus some additional ones which have been corrected for the absorbance of Xylenol Orange.

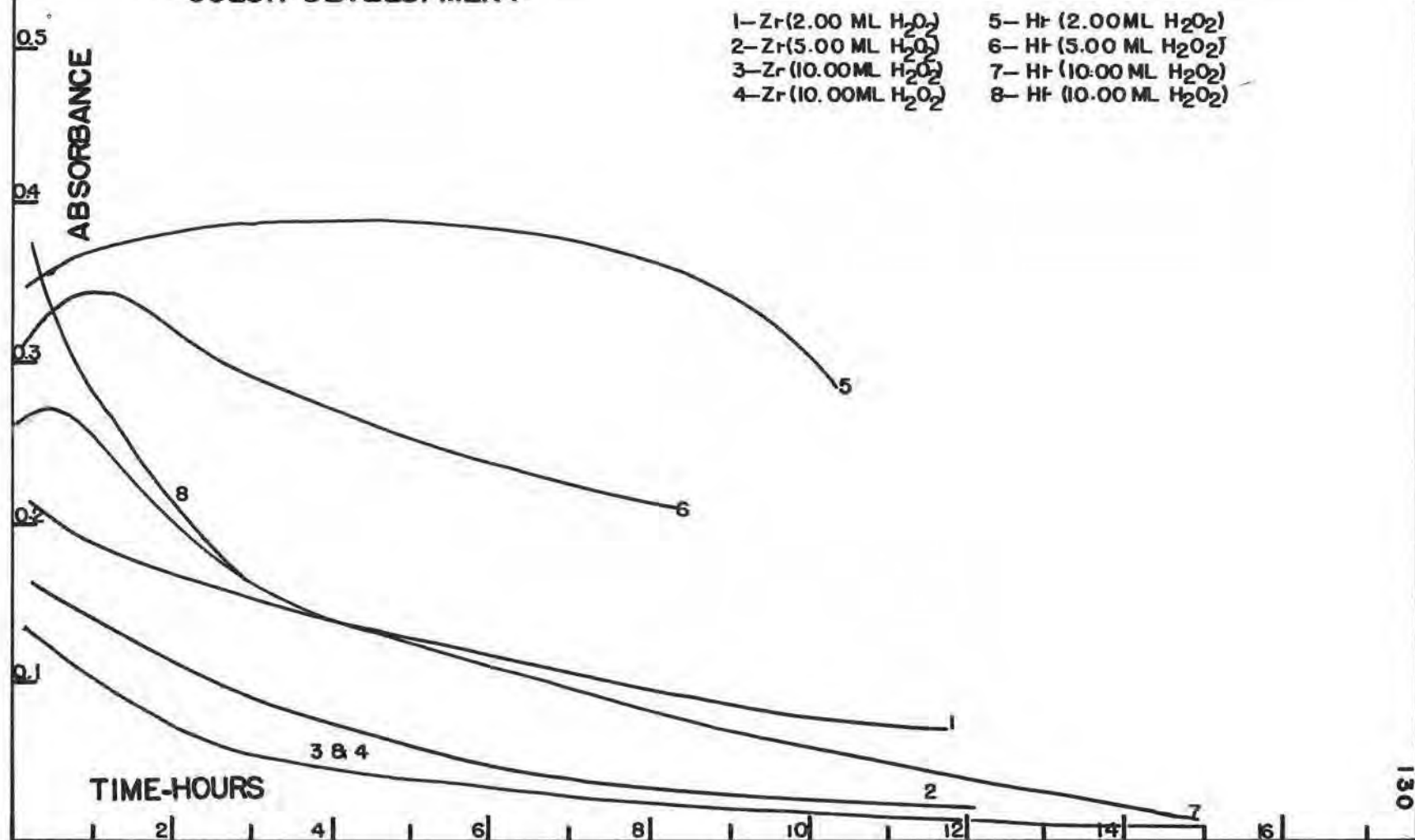
The above procedure was repeated except that 1.31×10^{-5} M hafnium was used. These results are also shown in Figure 27 and 28.

Examination of the corrected curves in Figure 28 indicate that the zirconium - Xylenol Orange is bleached within about 15 minutes after preparation and the absorbances decreases only slightly over a period of two to three hours. No apparent difference was noted regardless of whether the hydrogen peroxide was added before or

ABSORBANCE VS. TIME OF COLOR DEVELOPMENT

FIGURE 27

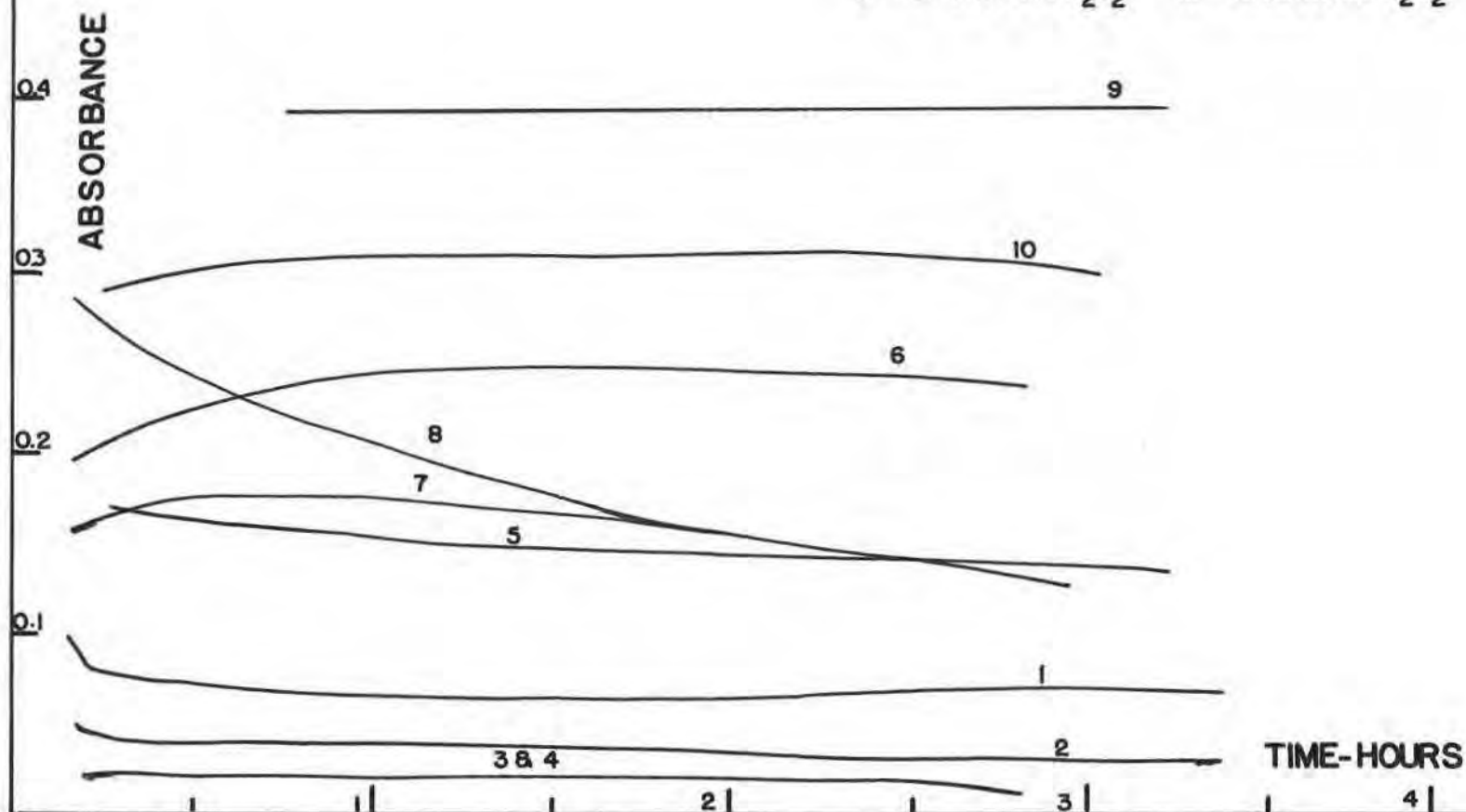
- | | |
|---------------------------|----------------------------|
| 1- Zr (2.00 ML H_2O_2) | 5- Hf (2.00ML H_2O_2) |
| 2- Zr (5.00 ML H_2O_2) | 6- Hf (5.00 ML H_2O_2) |
| 3- Zr (10.00ML H_2O_2) | 7- Hf (10.00 ML H_2O_2) |
| 4- Zr (10.00ML H_2O_2) | 8- Hf (10.00 ML H_2O_2) |



ABSORBANCE (CORRECTED)
VS. TIME OF
COLOR DEVELOPMENT

FIGURE 28

- | | |
|---------------------------|---------------------------|
| 1—Zr (2.00 ML H_2O_2) | 6—Hf (5.00 ML H_2O_2) |
| 2—Zr (5.00 ML H_2O_2) | 7—Hf (10.00 ML H_2O_2) |
| 3—Zr (10.00 ML H_2O_2) | 8—Hf (10.00 ML H_2O_2) |
| 4—Zr (10.00 ML H_2O_2) | 9—Hf (1.00 ML H_2O_2) |
| 5—Zr (1.00 ML H_2O_2) | 10—Hf (3.00 ML H_2O_2) |



after the Xylenol Orange.

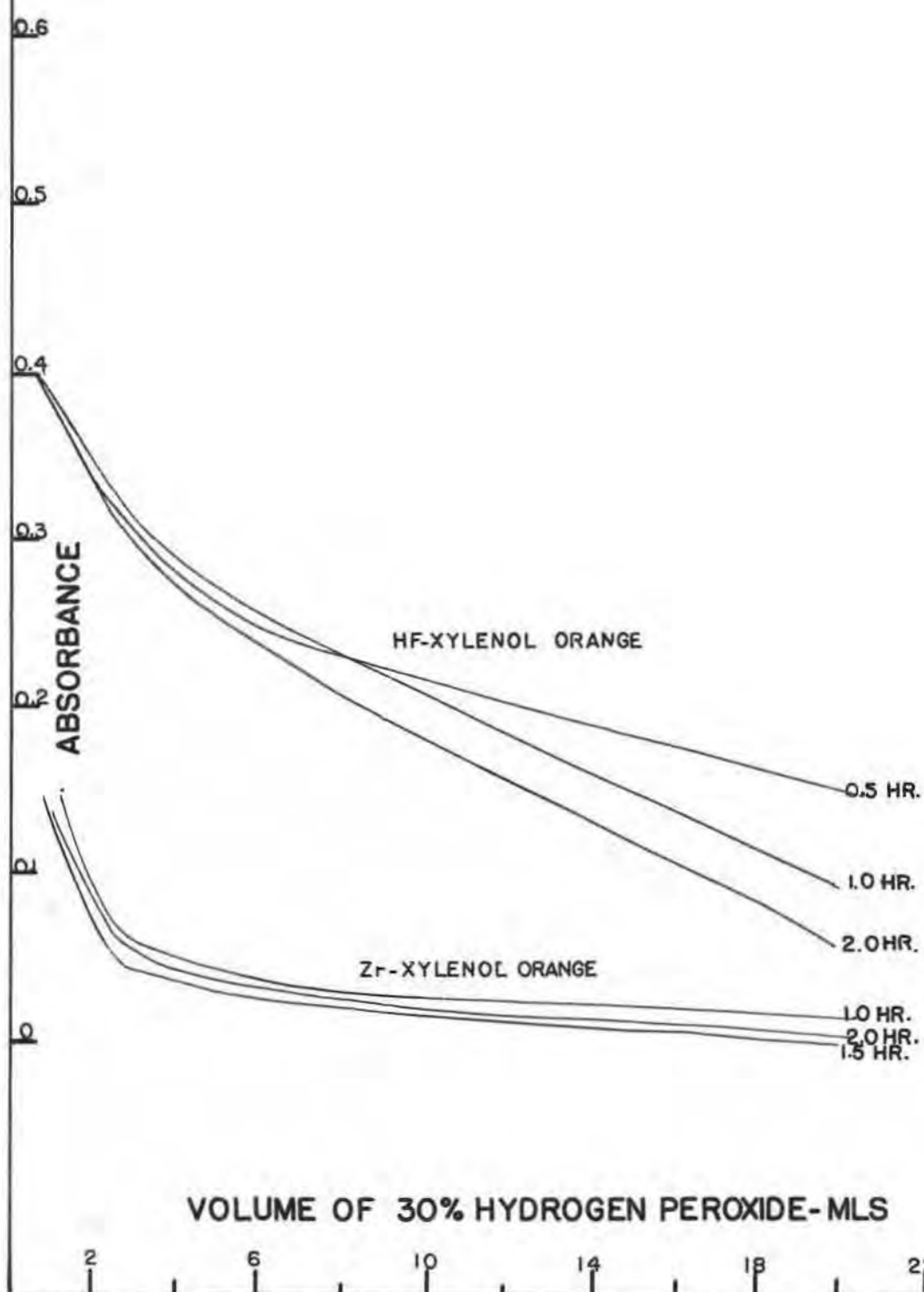
In the case of the hafnium complex, the absorbance generally rose to a maximum within half an hour and then slowly decreased although for all practical purposes it was essentially constant for a period of 1-2 hours. As expected from Cheng's work (12), the behavior was much different when the hydrogen peroxide was added after the Xylenol Orange. Under this condition, the absorbance was initially at a maximum and continually decreased over a period of hours until it finally merged with the identical solution to which the hydrogen peroxide had been added before the dye.

It is also noted that both complexes decrease in absorbance with the addition of increasing amounts of hydrogen peroxide.

The effect of volume of 30% hydrogen peroxide on absorbance can be seen in Figure 29 where absorbance is plotted against the volume of 30% H_2O_2 added to solutions containing 1.31×10^{-5} M zirconium and hafnium and 10.00 mls. of 0.05% Xylenol Orange. The final acid concentration was 0.4 N in a total volume of 100 mls. The H_2O_2 was added before the Xylenol Orange. From this figure it is observed that the maximum difference in absorbance occurs where 1 to 4 mls. of hydrogen peroxide were added. It is also noted that in this range the effect of

ABSORBANCE VS. VOLUME
OF 30% HYDROGEN PEROXIDE

FIGURE 29 133



time on absorbance is at a minimum.

Judging from Figures 28 and 29, it seems that under the above conditions, a volume of about 2 to 4 mls. of 30% hydrogen peroxide would be optimum.

Determination of Optimum Conditions for the Differential Measurement of 0 to 5% HfO₂ in ZrO₂

The study of the Xylenol Orange system up to this time has been concerned with a study of optimum conditions for a non - differential system. Using the information found from the non - differential studies, it was therefore necessary to investigate the optimum conditions for the differential system which was eventually used. This proved somewhat more difficult than for the investigation of the previous systems. This was due to the nature of the indirect approach used to examine this system.

The wavelength selected for making differential absorbance measurements was 535 mμ, based on the absorbance curves earlier determined for the zirconium and hafnium complexes and on the measurement of ΔA at various wavelengths. This is shown in Table XXIV. It should be recalled that for this approach, the total weights of oxides are held constant. Four different pairs of solutions containing 0 and 5% HfO₂ in ZrO₂ at different total weights of oxides were run under the conditions

TABLE XXIV

RELATIVE ABSORBANCE (ΔA) VS.
WAVELENGTH OF 0 AND 5%
HfO₂-XYLENOL ORANGE SOLUTIONS

W Oxide (mg/25mls)	XO(0.5%) (mls)	H ₂ O ₂ (30%) (mls)	Wavelength (m μ)	Slit (mm)	ΔA
0.200	2.00	1.00	510	0.115	0.0251
			515	0.10	0.030
			520	0.085	0.034
			525	0.07	0.037
			530	0.06	0.0395
			535	0.06	0.038
			540	0.06	0.036
0.400	4.00	2.00	510	1.125	0.073
			515	0.90	0.0765
			520	0.68	0.0805
			525	0.49	0.0815
			530	0.33	0.0815
			535	0.23	0.078
			540	0.14	0.0715
0.800	8.00	4.00	510	1.50	0.0675
			520	1.025	0.0725
			525	0.85	0.074
			530	0.64	0.075
			535	0.47	0.075
			540	0.29	0.0745

TABLE XXIV
(continued)

1.000	10.00	5.00	510	1.65	0.110
			520	1.20	0.116
			525	0.98	0.1175
			530	0.77	0.120
			535	0.63	0.120
			540	0.40	0.121
			545	0.14	0.1125

indicated in the table. Measurements were made at full sensitivity after about an hour. The 5% HfO_2 (95% ZrO_2) solutions were measured relative to the 0% HfO_2 (100% ZrO_2).

From this table it appears that most any wavelength from 520 to 540 could be used without any significant loss in sensitivity. However, it is also noted that the slit widths required to balance the instrument are much smaller at the higher wavelengths, thus resulting in more monochromatic light. The optimum wavelength therefore seems to be about 535 μ . Thus, this wavelength was used for all subsequent absorbance measurements.

After the optimum wavelength had been determined, it was next attempted to determine the optimum initial temperature for color development or bleaching, concentration of oxides, volume of 0.5% Xylenol Orange and 30% hydrogen peroxide.

In addition it was also necessary to determine the best time interval before making measurements.

As already mentioned, the initial temperature for color development or bleaching was investigated as it seemed to be of importance. Consequently, this effect was studied briefly. It was found that most any initial temperature up to about 60°C could actually be used as long as it was the same for each solution being run.

For the maximum relative absorbance reading in a minimum of time, an initial temperature of 50°C for 10 to 20 minutes was selected. A temperature of 60°C gives a slightly greater absorbance reading, however, bubble formation from decomposition of the hydrogen peroxide seems to be much greater thus making it more difficult to make readings. The temperature effect was determined on several pairs of 0 and 5% HfO_2 solutions containing 1.200 mg. of oxide per 25 mls, 6.00 mls. of 0.5% Xylenol Orange and 2.00 mls. of 30% hydrogen peroxide. Both solutions in each pair were treated in exactly the same manner before making measurements. These solutions were immediately cooled to 25°C after the initial heating. The results are shown in Figure 30 where relative absorbance vs. time is plotted for various initial temperatures. In order to help determine the optimum concentration of mixed oxides, Xylenol Orange and hydrogen peroxide, the solutions shown in Table XXV were prepared.

The relative absorbance vs. time of the solutions in Table XXIV were run and the results are shown in Figure 31. The maximum ΔA occurs at a concentration of 6.000 mg. of oxide per 25.00 mls. However, these were not run at exactly identical conditions. It seemed that many possible combinations of oxide concentration, Xylenol Orange and hydrogen peroxide concentrations might

RELATIVE ABSORBANCE
VS. TIME
(AT VARIOUS INITIAL TEMPERATURES)

FIGURE 30

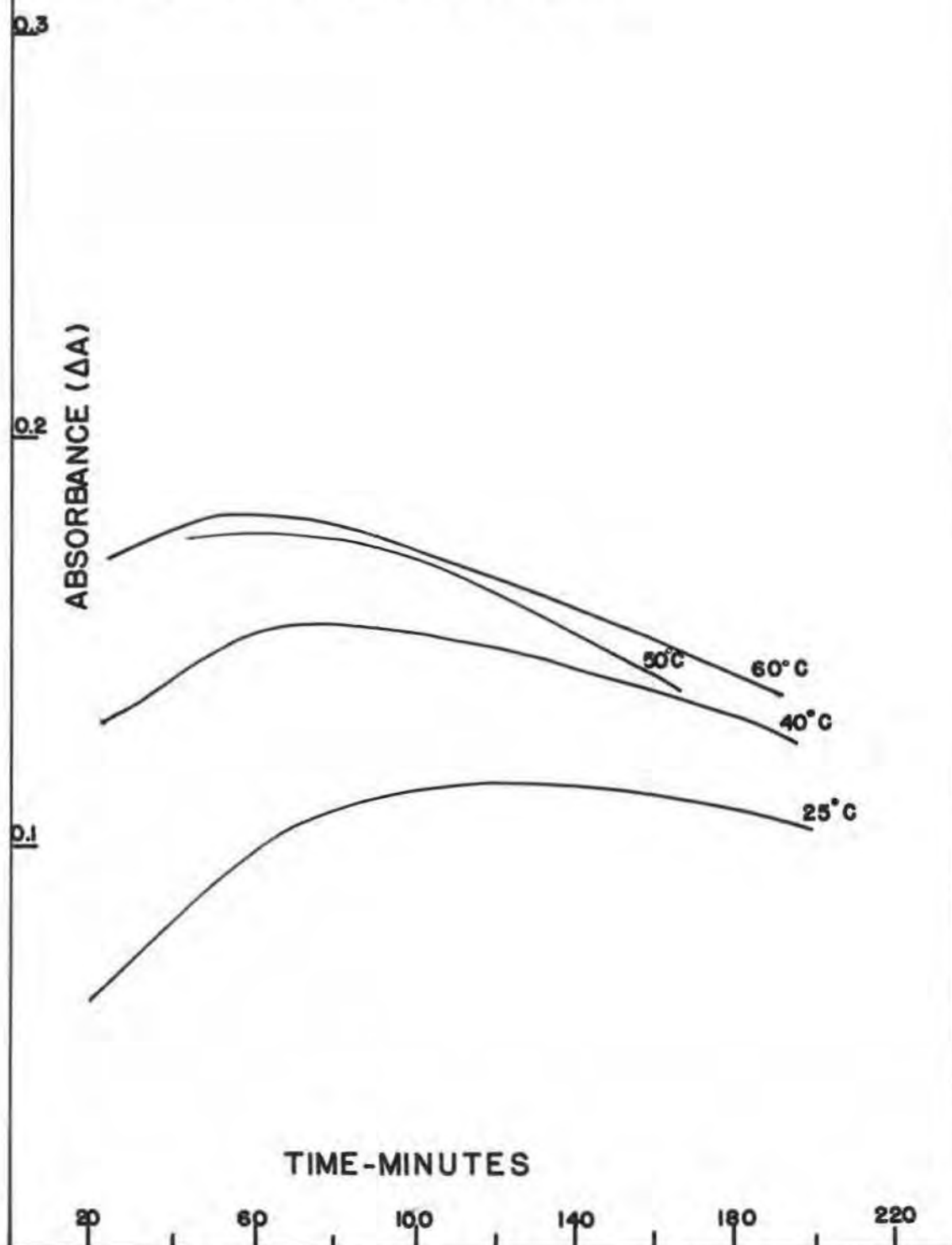
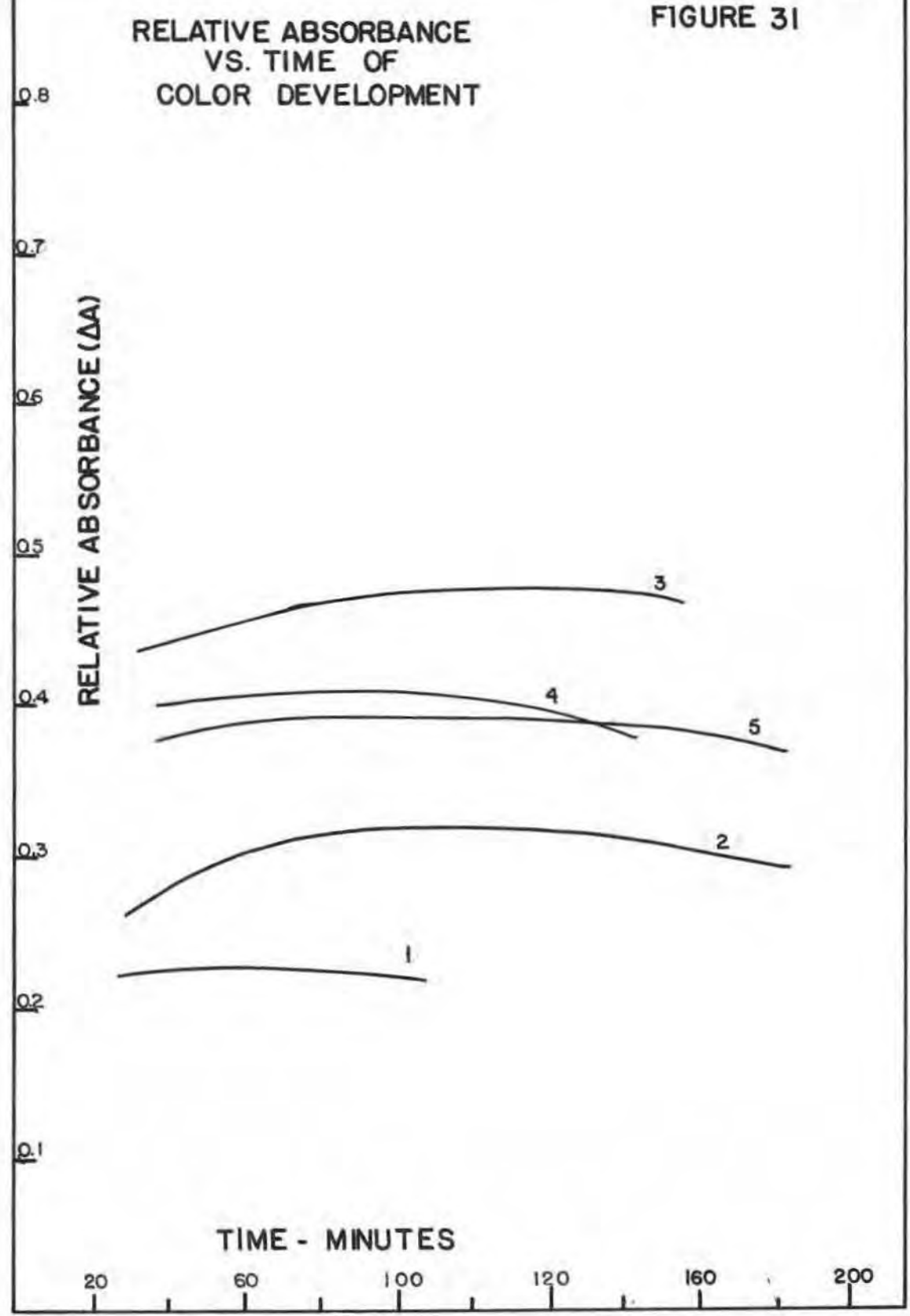


TABLE XXV

SOLUTIONS USED IN STUDY
OF OPTIMUM CONDITIONSSolution, HfO_2

Solution No.		W Oxide (mg/25ml)	Xylenol Orange (0.5%)(mls)	Hydrogen Peroxide (mls)	Temp. (°C)	Time (min.)
0%	5%					
1	1a	2.000	6.00	2.00	50°	10
2	2a	4.000	10.00	2.00	50°	10
3	3a	6.000	10.00	2.00	50°	15
4	4a	8.000	10.00	2.00	50°	20
5	5a	10.00	12.00	2.00	50°	20

FIGURE 31

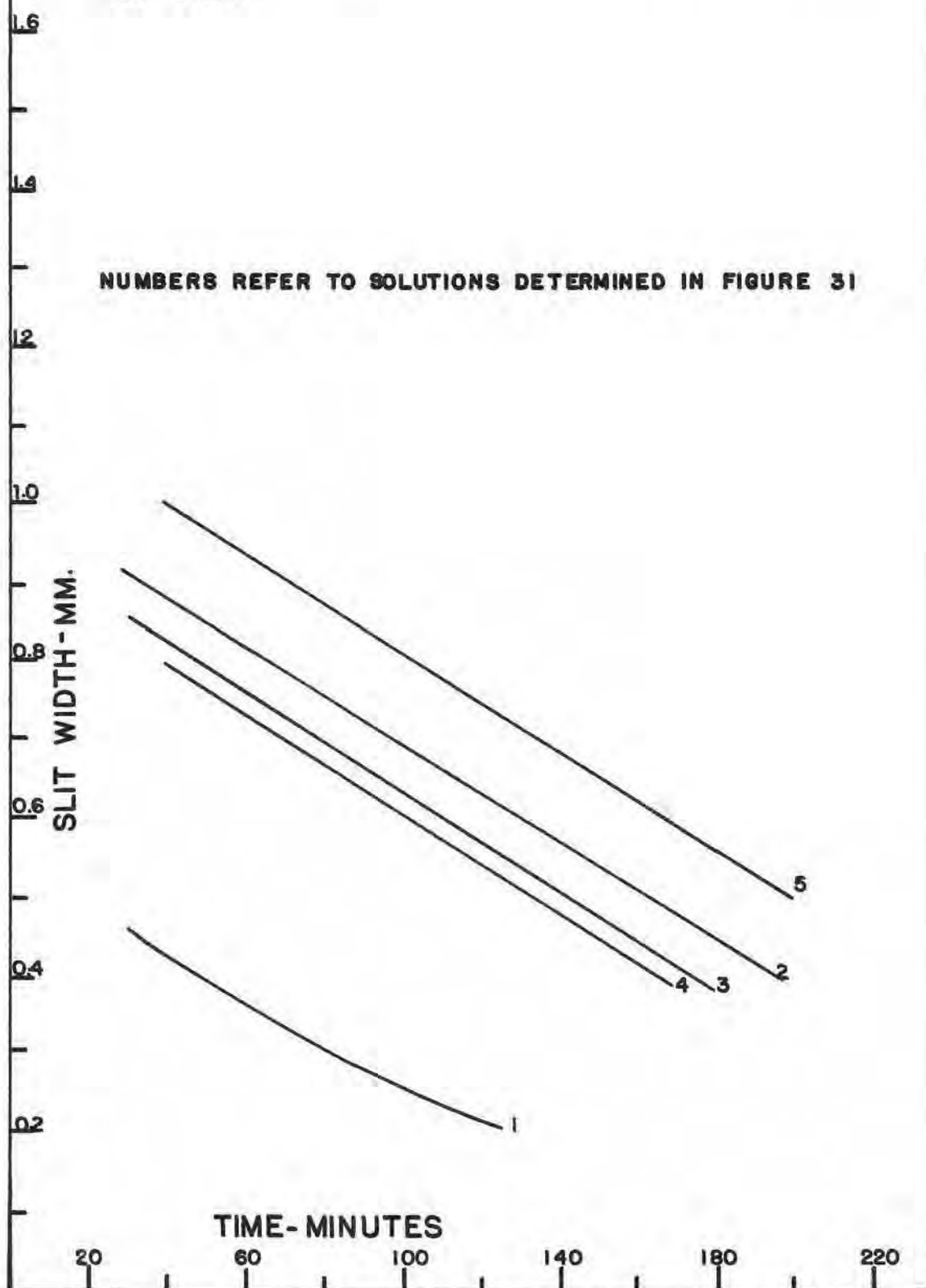


be possible depending on temperature used to develop the color etc. These solutions were observed to be changing rather rapidly as can be seen from the large changes in slit width required to set the instrument after short time intervals. Fortunately, both solutions seemed to be changing at essentially the same rate for a period of one to two hours since constant relative absorbance readings were obtained during these intervals. Figure 32 shows the slit necessary to balance the instrument for the above several sets of solutions over a period of about three hours.

It can be seen from Figure 32 that the rate of change of slit width with time is essentially constant for all of the curves plotted. This seems to imply that the reference solutions were changing at a fairly constant rate over the time interval investigated.

Although it has been noted that under the conditions used, the concentration for maximum ΔA was 6.000 mg. of oxide per 25 mls., a concentration of 5.000 mgs. oxide/25 mls. was finally selected as the concentration to be used. This lower concentration was used because of a slight precipitate formation at the higher concentrations, after one to three hours. These higher concentrations would probably be usable if measurements were made before precipitation occurred.

FIGURE 32

SLIT WIDTH
VS. TIME

In selecting the concentration of 0.5% Xylenol Orange to be used, the physical limitations were considered. This was selected on the basis of a 10.00 ml. aliquot of oxide solution per 25 mls. being used (4.00 mls. oxide/10 mls.). 8.00 mls. (or 3.00 mls.) of 0.5% Xylenol Orange was therefore considered to be an adequate compromise concentration of dye. This then allowed an unused volume of 7.00 mls. (or 3.00 mls.) for hydrogen peroxide, acid and rinsing.

The amount of 30% hydrogen peroxide to be used was next determined. On the basis of previous data, it seemed likely that a rather small volume would be suitable. In order to determine the effect of 30% hydrogen peroxide, a series of the complex solutions containing 2.000 mg. of oxide (0 and 5% HfO_2), 3.00 mls. of 0.5% Xylenol Orange and several peroxide concentrations were run. The results are shown in Table XXVI. The final volume was 10.00 mls. and the acidity was 0.4 N at an initial reaction temperature of 50°C. The 5% HfO_2 solutions were measured relative to the 0% HfO_2 solutions.

From this table it can be seen that any of these volumes could be used without any great loss in sensitivity. However, for convenience, the 0.40 ml./10 ml. volume was adopted for subsequent work since this is equivalent to 1.00 ml./25 mls. and can easily be measured

TABLE XXVI

EFFECT OF VOLUME OF 30% HYDROGEN PEROXIDE ON
RELATIVE ABSORBANCE OF ZIRCONIUM AND
HAFNIUM-XYLENOL ORANGE COMPLEXES

Run No.	Slit (mm)	Volume 30% Hydrogen Peroxide (mls)	Maximum Relative Absorbance (ΔA)
1	1.20	0.30	0.384
2	0.80	0.40	0.410
3	0.70	0.50	0.424
4	0.70	0.60	0.404
5	0.60	0.70	0.380

with a volumetric pipet.

Since all conditions have been defined for running differential solutions of 0 to 5% HfO_2 in ZrO_2 , calibration curves were constructed next.

Standard Curves for the Determination of 0 to 5% HfO_2 in Presence of ZrO_2

As concluded from the preceeding section, the concentrations of reagents which were used in the preparation of standard curves were:

$W(\text{total oxide}) = 5.00 \text{ mg./25 mls. (2.00 mg./10 mls.)}$

$V(\text{H}_2\text{O}_2) = 1.00 \text{ ml. of 30\% H}_2\text{O}_2/25 \text{ mls. (0.40 mls./10 mls.)}$

$V(\text{XO}) = 8.00 \text{ mls. of 0.5\% Xylenol Orange/25 mls. (3.00 mls./10 mls.)}$

Acid Concentration = 0.40 N hydrochloric acid.

All measurements were made under the following conditions:

Sensitivity of Photomultiplier - Full

Light Source - Tungsten lamp

Cells - Silica (Pyrex could have been used)

Wavelength - 535 μ

Temperature of measurements - 25°C

A series of standard solutions containing 0, 0.50, 1.00, 2.00, 3.00, 4.00 and 5.00% HfO_2 in ZrO_2 were prepared such that the stock standard solutions contained

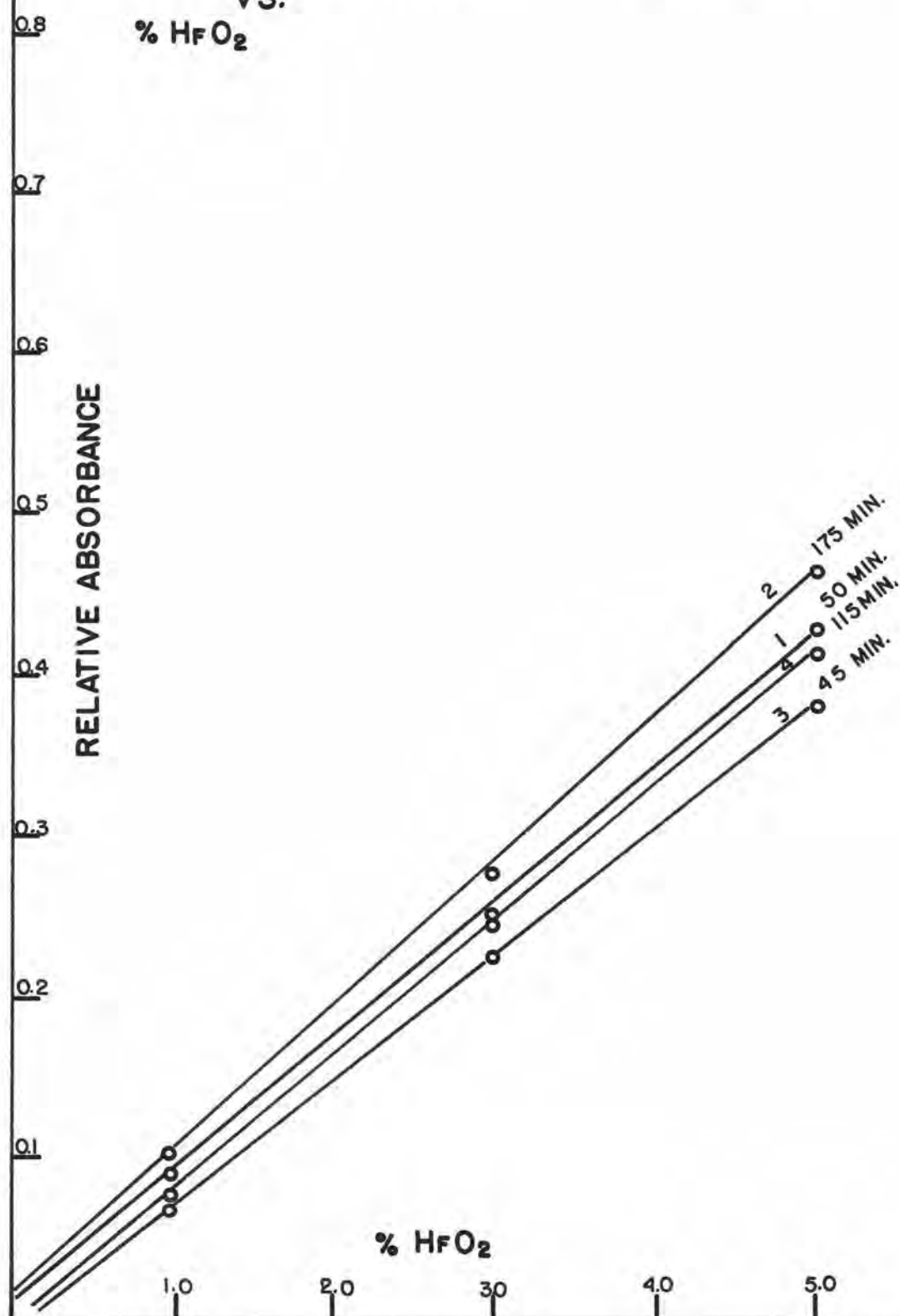
100 mgs. of oxide/100 mls. at an hydrochloric acid concentration of 1.00 N. When preparing standard curves, 2.00 ml. aliquots were measured into 10.00 ml. volumetric flasks and 1.00 ml. of 2.00 N hydrochloric acid was added to each solution. When finally diluted to 10 mls. the complex solutions were at the proper acid concentrations. Exactly 0.40 mls. of 30% hydrogen peroxide were added to each solution and then 0.5% Xylenol Orange. The solutions were then diluted to volume with distilled water. The Xylenol Orange was added as rapidly as possible to each solution so that they were prepared at as nearly the same time as possible.

All solutions were simultaneously shaken 50 times. They were then placed in a water bath at 50°C for 20 minutes after which time they were removed and cooled to 25°C before making measurements.

The effect of time on the calibration curves was determined by running the 0, 1.00, 3.00 and 5.00% HfO_2 solutions. The absorbance of the 1.00, 3.00 and 5.00% HfO_2 complex solutions were measured relative to the 0% HfO_2 solution at various times. Several of these curves are shown in Figure 33. Curves 1 and 2 are from the same solutions at different times and 3 and 4 from a second set of solutions. Although these three point calibration curves shift with time, a straight line curve was obtained

RELATIVE ABSORBANCE
VS.
% HfO_2

FIGURE 33

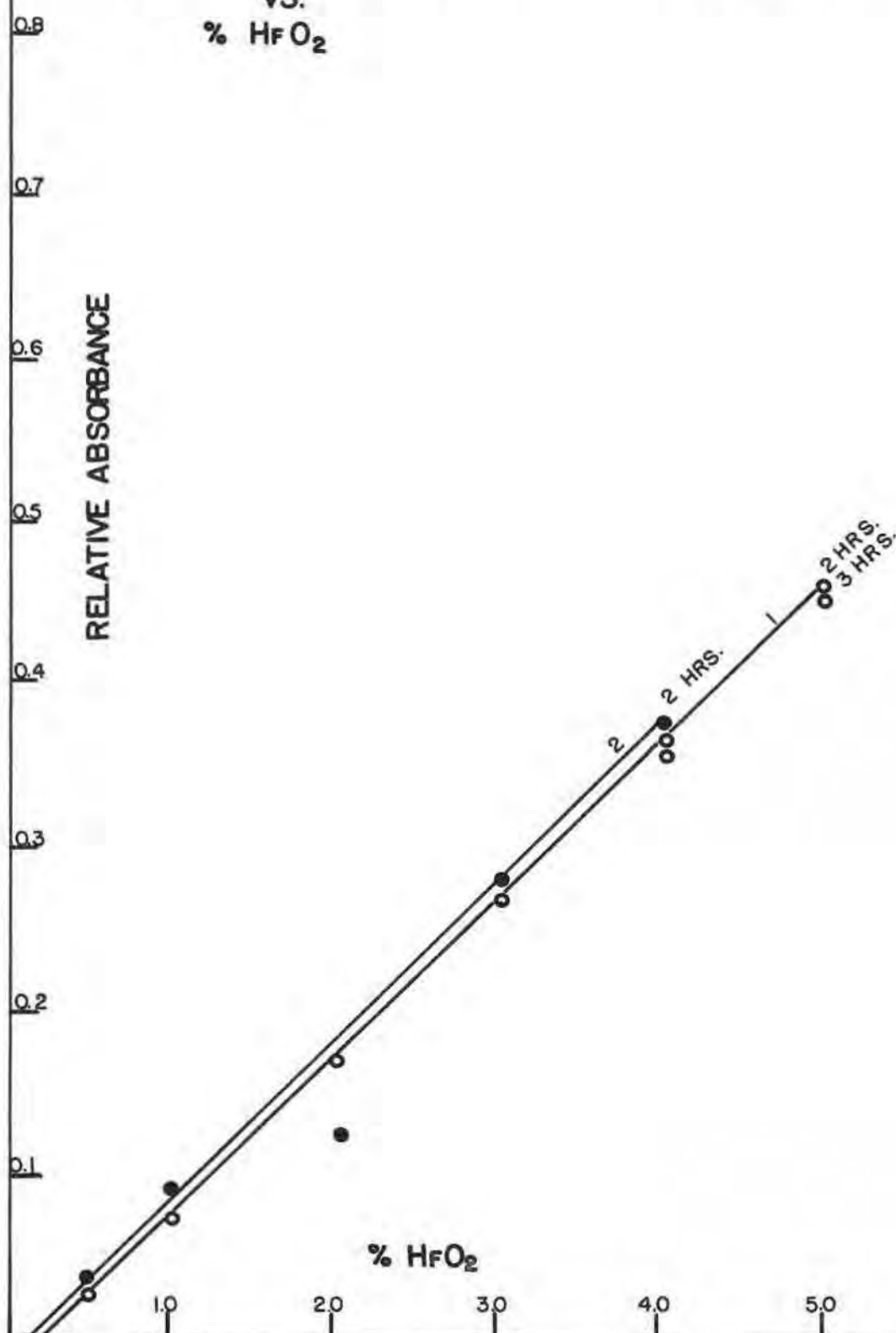


in each case. This seemed to indicate that the calibration curve could be run after almost any time interval that would give a straight line just as long as the samples being determined were measured at approximately the same time.

Calibration curves for all standard solutions on two different days were run next. Measurements for curve 1 were made after both 2 and 3 hours and was essentially identical for each time. These are found in Figure 34. Examination of these standard curves certainly indicates that this method should be applicable to the determination of unknown samples of ores or mixed oxides. The next section will therefore include details for these applications.

RELATIVE ABSORBANCE
VS.
% HfO_2

FIGURE 34



PROCEDURE FOR DETERMINATION OF HAFNIUM
IN THE PRESENCE OF ZIRCONIUM
USING XYLENOL ORANGE

Details for the determination of hafnium in the presence of zirconium are included in this section. The analysis of three different zirconium - hafnium ores, using the Xylenol Orange method, are included. These results are compared to those obtained by the X-ray fluorescence method.

Apparatus

The Beckman Model DU Spectrophotometer with photomultiplier was used for all absorbance measurements. A tungsten lamp was used for the light source. Matched silica cells were used in all absorbance measurements (Pyrex could have been used).

Reagents

1. HfO_2 standard, 1.068 mg. $\text{HfO}_2/\text{ml.}$ in 2.940 N HCl . Dissolved about 1 g. of high purity $\text{HfOCl}_2 \cdot 8\text{H}_2\text{O}$ in 250 mls. of 5.880 N hydrochloric acid and diluted to 500 ml. with distilled water. 50.00 ml. aliquots were used for standardization by the cupferron method.

2. ZrO_2 standard, 2.732 mg. $\text{ZrO}_2/\text{ml.}$ in 2.940 N HCl . Fused about 3 g. of high purity ZrO_2 with 40 g. of

potassium pyrosulfate until a clear melt was obtained. Dissolved melt in dilute hydrochloric acid and filtered. The hydrous oxide was precipitated with 28% ammonia and washed with distilled water, until no test for sulfate was obtained in the wash solution. The precipitate was then dissolved in 500 mls. of 5.880 N hydrochloric acid and diluted to 1 liter with distilled water. 25.00 ml. aliquots were used for standardization by the cupferron method.

3. Xylenol Orange, 0.5% aqueous solution. Dissolved 0.5000 g. of Xylenol Orange (sodium salt) in distilled water and diluted to 100 mls.

Calibration Curves

Using the conditions previously determined for the Xylenol Orange method (Investigation Using Xylenol Orange), a series of standard solutions containing from 0 to 8 and 10% HfO_2 in ZrO_2 were prepared by accurately measuring the standard ZrO_2 and HfO_2 solutions into a 250 ml. volumetric flask and adding a quantity of hydrochloric acid which resulted in a 1.000 N acid solution upon dilution to volume with water. The same volumetric flask was used for all dilutions. The total oxide concentration for each solution was made up to be 125 mg. of oxide per 250 ml. of solution or 0.500 mg. oxide/ml. A 10.00 ml. aliquot was

therefore used to give 5.00 mg. oxide/25 ml. or 4.00 mls. to give 2.00 mg. oxide/10 ml. Since the stock standards were made to have a 1.000 N hydrochloric acid concentration, the aliquots above resulted in 0.40 N acid solutions when diluted to volume.

One milliliter of 30% hydrogen peroxide was added to each standard for a 25 ml. volume of 0.40 ml. for a 10 ml. volume. 8.00 ml./25 ml. or 3.00 ml./10 ml. of 0.5% Xylenol Orange was added and each solution diluted to volume with distilled water. All solutions were simultaneously shaken 50 times and placed in a 50° C water bath for 20 minutes after which they were removed, shaken 10 more times and cooled to 25°C.

Absorbance measurements were made from one to two hours from initial time of preparation. The 0% HfO_2 solution was used for the reference solution and all measurements were made relative to it. A standard curve was then drawn. The % HfO_2 in unknowns were determined from this curve. A calibration curve was prepared each time a new analysis was carried out. Typical calibration curves are shown in Figure 35 and 36.

Determination of HfO_2 in Cyrtolite and Nigerian Zircon Ores Using Sulfuric Acid Treatment

Cyrtolite and Nigerian Zircon Ores - Five gram

samples of Cyrtolite and Nigerian ores were weighed into evaporating dishes and 10 g. of concentrated sulfuric acid was added to each, as suggested by Larsen, Fernelius and Quill (49) for cyrtolite ores. These samples were placed on a hot sand bath. The cyrtolite was heated until a thick mud was produced and the Nigerian ore was digested for about an hour. They were then rinsed into beakers of water and evaporated to fumes of SO_3 . Water was then added to dissolve salts and the mixtures were filtered. 28% ammonia solution was added to these filtrates until basic and the resulting hydrous oxides of zirconium and hafnium were filtered and washed with water until all sulfates were eliminated. The precipitates were then dissolved with hot dilute hydrochloric acid. (6N). Portions of these cool solutions were treated with 50 mls. of 16% mandelic acid and the temperature slowly raised to about 85-90°C. The precipitates which formed were allowed to digest for half an hour and then cooled and filtered through sintered glass crucibles. The precipitates were washed with a saturated zirconium tetramandelate solution and then dissolved in 5% sodium hydroxide solution plus hot water. The precipitates which almost immediately formed were re-dissolved in dilute hydrochloric acid and a second mandelic acid precipitation made with subsequent treatment with 5% sodium hydroxide solution. The

resulting hydrous oxides were washed several times with water. Both precipitates were dissolved by adding them to 127.5 mls. of 5.880 N hydrochloric acid. These solutions were filtered into 250 ml. volumetric flasks and the beakers and filter papers were washed several times with water. The final acid concentration was then 3.00 N. These solutions were then analyzed for total oxide concentration by the cupferron method.

The Nigerian Zircon (N-1) was found to contain 1.536 mg. oxide/ml. and the cyrtolite (C-2) 2.642 mg. oxide/ml. Stock solutions of the unknowns containing 125 mg. oxide/250 mls. and of 1.00 N hydrochloric acid concentration were prepared from the above solutions.

A standard curve was run and the % HfO_2 in the total oxides determined. 4.00 ml. aliquots (2.00 mg.) of each standard oxide and unknown were pipetted into 10.00 ml. volumetric flasks and 0.40 ml. of 30% hydrogen peroxide were added to each. 3.00 mls. of 0.5% Xylenol Orange was then added and the solutions diluted to volume with distilled water. All solutions were simultaneously shaken 50 times and placed in a 50°C water bath for 20 minutes. They were then cooled to 25°C and absorbance measurements were made at 535 mμ after one hour from the time of initial preparation. The analytical results for sample N-1 (#1 and #2) and C-2 (#1 and #2) are shown in Table XXVII.

TABLE XXVII

Analysis of HfO_2 in Mixed Oxides
From Zirconium - Hafnium Ores

Ore	Sample No.	% HfO_2 (X-ray Method)	% HfO_2 (Xylenol Orange Method)
Cyrtolite	C-2(1)	-	6.70
	C-2(2)	-	6.44
	C-2(3)	-	6.75
	C-2(4)	-	6.75
(Oxide Used For X-ray Analysis)	X-134(C)-1c	6.35	6.33
	X-134(C)-1d		6.10
	X-134(C)-1e		6.03
Nigerian Zircon	N-1(1)	-	6.74
	N-1(2)	-	6.54
	N-1(3)	-	6.55
	N-1(4)	-	6.90
(Oxide Used For X-ray Analysis)	X-133(N)-1c	6.17	6.65
	X-133(N)-1d		6.40
	X-133(N)-1e		6.73
Australian Zircon			
(Oxide Used For X-ray Analysis)	X-132(A)-1c	2.19	2.42
	X-132(A)-1d		2.18
	X-132(A)-1e		2.32

Typical calibration curves are shown in Figures 35 and 36 for subsequent samples.

The above determination was repeated except that 10.00 ml. aliquots of standards and unknowns were transferred to 25.00 ml. volumetric flasks. 1.00 ml. of 30% hydrogen peroxide and 8.00 ml. of 0.5 % Xylenol Orange were added and solutions diluted to volume with distilled water. The remainder of this procedure was the same as that above. Results for sample N-1 (#3 and #4) and C-2 (#3 and #4) are also found in Table XXVII.

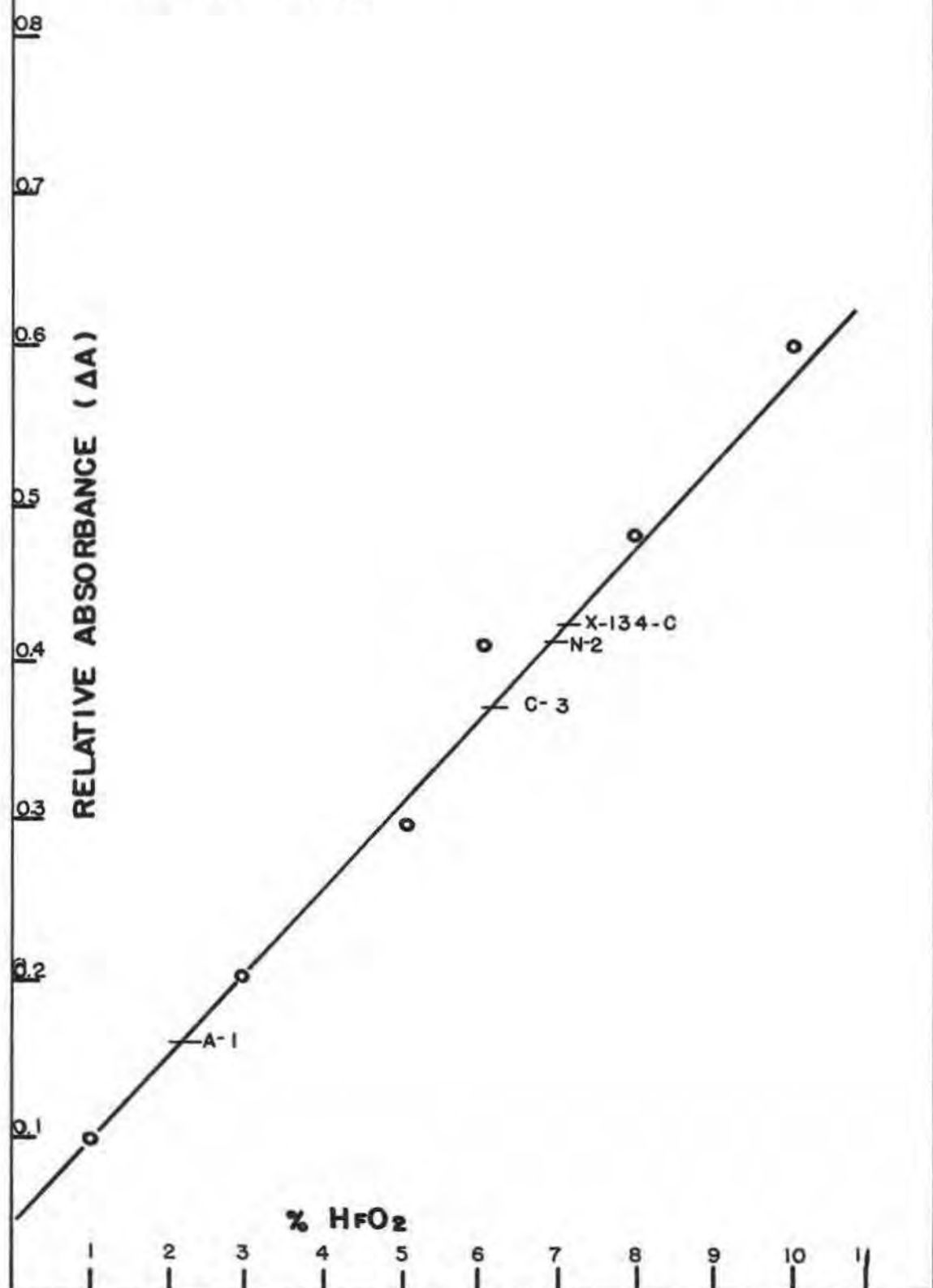
These oxides above, had been previously analyzed for hafnium by Wah Chang Corporation, Albany, Oregon, using the X-ray fluorescence method. In order to compare results, the oxides used for the X-ray analysis were analyzed using Xylenol Orange.

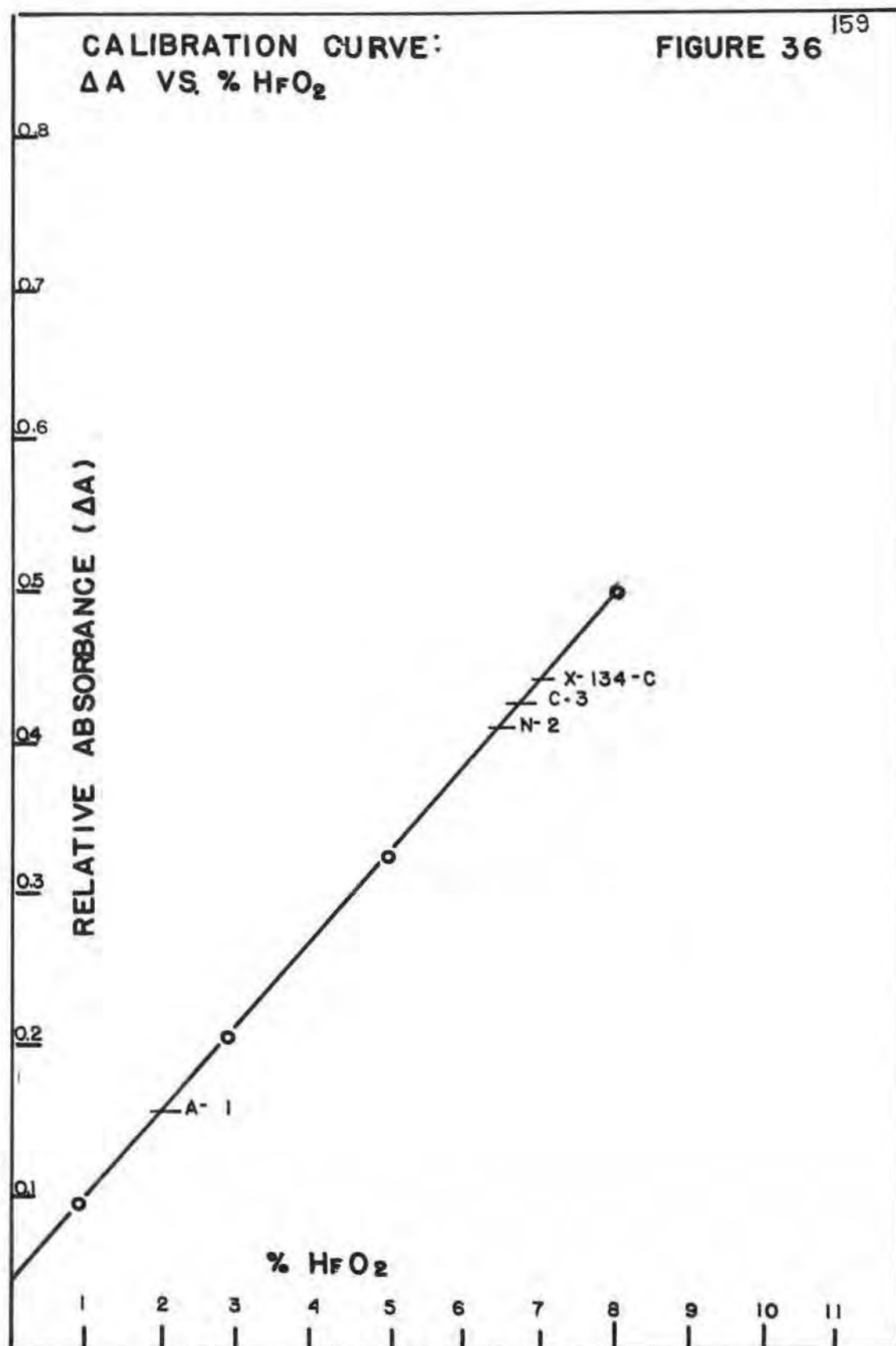
Determination of HfO_2 in X-ray Oxide Samples

X-ray samples - Fifty milligrams of the X-ray oxide samples, X-132, X-133(N) and X-134(C) were weighed into porcelain crucibles and 2 g. of potassium pyrosulfate was added. The samples were then fused to a clear melt (about 15 minutes). The melts were cooled and dissolved in dilute hydrochloric acid, then 28% ammonia was added until basic. The hydrous oxides were filtered and washed with water until no test for sulfate was obtained in the

CALIBRATION CURVE:
 ΔA VS. % HfO_2

FIGURE 35 158





wash water. They were then dissolved from the filter paper into 100 ml. volumetric flasks using 17.00 ml. of 5.880 N hydrochloric acid which had been diluted to about 50 mls. with water. The filter paper was washed several times with water and the solutions were diluted to volume. These solutions then contained 0.500 mg. oxide/ ml. at a 1.00 N acid concentration.

The % HfO_2 in the above solutions was determined using 4.00 ml. aliquots of standards and unknowns. 1.00 ml. of 30% hydrogen peroxide was added to each solution by mistake (should have been 0.40 ml.) and 3.00 ml. of 0.5% Xylenol Orange. The remainder of the procedure was the same as previously described. Although the above error was made, the analysis was completed and the results for samples X-132(A)-1c, X-133(N)-1c and X-134(C)-1c are shown in Table XXVII. It can be seen from the table that these results are comparable to the others included. The X-132(A), X-133(N) and X-134(C) refer to the X-ray oxides prepared from the Australian Zircon, Nigerian Zircon and cyrtolite respectively. The last number and letter refer to the run number.

The above determination was repeated twice except that 0.40 mls. of 30% hydrogen peroxide was used. A new standard curve was run for each set of samples. These results for samples X-132(A)-1d, X-133(N)-1d, X-134(C)-1d

and X-132(A)-1e, X-133(N)-1c, X-134(C)-1e are also shown in Table XXVII.

In order to check the standards used for the Xylenol Orange procedure, they were precipitated with ammonia, filtered, washed and ignited to the oxides and subsequently used as standards for the X-ray fluorescence analysis of X-132(A), X-133(N), X-134(C), N-1 and C-2 oxide samples. These results shown in Table XXVIII indicate that the standards were satisfactory. The second column in this table shows the results obtained on the samples using the X-ray method and X-ray standards. The third column shows the results obtained using the X-ray method and the standards used for the Xylenol Orange method. The fourth column shows the results using the Xylenol Orange method and the Xylenol Orange Method standards.

Up to this point the determinations carried out were concerned principally with testing the method and comparison of the Xylenol Orange and X-ray fluorescence methods. The next section will therefore describe the complete procedure for the analysis of total hafnium in the ores.

Procedure for Analysis of Hafnium in Ores

The ores analyzed were the Nigerian Zircon (N) and cyrtolite (C) previously used and in addition an Australian Zircon(A).

TABLE XXVIII

X-RAY ANALYSIS OF MIXED OXIDES
USING THE XYLENOL ORANGE
OXIDE STANDARDS

Sample No.	% HfO ₂ (X-ray Method) (X-ray Standards)	% HfO ₂ (X-ray Method) (XO Standards)	% HfO ₂ (XO Method) (XO Standards)	
X-132(A)	2.19	2.02	2.31	} ave. three runs
X-133(N)	6.17	6.23	6.59	
X-134(C)	6.35	6.56	6.15	
N-1	-	6.03	6.68	
C-2	-	5.76	6.66	

Due to typist's error page 163 was omitted.

Two 0.300 g. samples of ore (A) and (N) and two 0.5000 g. samples of (C) were weighed into nickel crucibles. About 1 - 2 teaspoonfuls of sodium peroxide were added to each sample and fused until all of each sample went into solution. When cool, the samples and crucibles were removed and rinsed. Hydrochloric acid was added to the solutions until acid (green solution). When acid, 60 ml. of 1:1 sulfuric acid was added and samples evaporated to heavy fumes of SO_3 to drop out the silica. Water was added to dissolve salts and the solutions filtered. The residues and filter papers were washed with hot dilute hydrochloric acid.

These solutions were made basic with 28% ammonia and the precipitates washed with water until all sulfate was eliminated. Precipitates on filter papers were dissolved with hot dilute hydrochloric acid (6N) and the filter paper was thoroughly washed with this solution. These samples were allowed to cool and 50 ml. of 16% mandelic acid was added to each and the temperature was slowly raised to 85-90°C and allowed to remain for 30 minutes. The resulting precipitates were then filtered and washed with hot 5% mandelic acid containing 2% hydrochloric acid. The filter papers and precipitates were dried, and the paper burned off at a low temperature. The oxides were finally ignited at 900°C for an hour to convert to oxides.

They were cooled, weighed and the % total oxide calculated. Results are shown in Table XXIX.

Fifty milligram samples of the oxides from above were weighed into porcelain crucibles, fused with potassium pyrosulfate etc., as previously described for the X-ray oxide samples X-132(A), X-133(N) and X-134(C). The final solutions then contained 0.500 mg./ml. in 1.00 N acid solution.

4.00 ml. aliquots of standards and unknowns were used for a total volume of 10 ml. 0.40 mls. of 30% hydrogen peroxide and 3.00 ml. of 0.5% Xylenol Orange were used as previously described. The remainder of the procedure was also carried out as before giving the resulting %HfO₂ values shown in Table XXIX.

In Table XXIX, the first column lists the samples analyzed. The samples X-132(A), X-133(N), and X-134(C) were the X-ray oxides from the Australian Zircon, Nigerian Zircon and Cyrtolite, respectively. The A-1 sample was the oxide prepared from the Australian Zircon by peroxide fusion. Sample N-1 was the oxide prepared from Nigerian Zircon by sulfuric acid digestion and N-2 was the oxide prepared by peroxide fusion. C-2 was the oxide prepared from the cyrtolite by sulfuric acid digestion and C-3 was prepared by peroxide fusion. Sample X-134-C was the X-ray oxide re-run from the same cyrtolite sample

TABLE XXIX

ANALYSIS OF HfO_2 IN ZIRCONIUM - HAFNIUM
ORES BY THE XYLENOL ORANGE METHOD

Sample	% Total Oxide	% HfO_2 in Total Oxide	% HfO_2 in Ore	Average Deviation (%)
Australian Zircon X-132(A)	63.3	2.42 2.18 2.32	1.53 1.37 1.46	1.45
A-1	64.1 63.9	640 2.22 2.28 2.28	1.42 1.46 1.46	1.45
Nigerian Zircon X-133(N)	55.1	6.65 6.40 6.73	3.66 3.53 3.71	3.63
N-1	55.1 56.0	555 6.74 6.54 6.55 6.90	3.74 3.63 3.63 3.83	3.71
N-2		6.90 6.52	3.83 3.62	10.09
Cyrtolite X-134(C)	29.8	6.33 6.10 6.03	1.89 1.82 1.80	1.84
X-134-C	28.9	6.96 7.05	2.01 2.04	2.03
C-2	30.8 30.8	308 6.70 6.44 6.75 6.75 6.12 6.87	2.06 1.98 2.08 2.08 1.88 2.12	2.03

X-134(C). In column two is shown the percent total oxide in the ore. The total oxide values for samples X-132(A), X-133(N), X-134(C) and X-134-C are those reported by Wah Chang Corporation. The other values shown were those determined by peroxide fusion for this thesis research. Column three indicates the percent HfO_2 found by the Xylenol Orange Method, in the total oxide. In column four the percent HfO_2 in the ore has been calculated from the percent HfO_2 (column 3) in the total oxide and from the percent total oxide in the ore (column 2). Column five shows the average deviation in the values of percent HfO_2 in the ore (column 4).

A summary of the X-ray analysis is found in Table XXX and a summary of both the X-ray and Xylenol Orange methods is found in Table XXXI.

TABLE XXX

ANALYSIS OF HfO_2 IN ZIRCONIUM - HAFNIUM
BY X-RAY METHOD (WAH CHANG)

Sample	% Total Oxide (Wah Chang)	% HfO_2 in Total Oxide	% HfO_2 in Ore
Australian Zircon			
X-132(A)	63.3	2.19	1.39
Nigerian Zircon			
X-133(N)	55.1	6.17	3.40
Cyrtolite			
X-134(C)	29.8	6.35	1.89
X-134-C	28.9	8.83	2.55

TABLE XXXI
SUMMARY OF ANALYTICAL DATA
% HfO₂ IN ORES

Sample	% HfO ₂ (X-ray)	% HfO ₂ (ave.) (Xylenol Orange)	Difference (%)
X-132(A)	1.39	1.45	0.06
A-1	-	1.45	-
X-133(N)	3.40	3.63	0.23
N-1	-	3.71	-
N-2	-	3.73	-
X-134(C)	1.89	1.84	0.05
X-134-C	2.55	2.03	0.52
C-2	-	2.05	-
C-3	-	2.00	-

SUMMARY AND
CONCLUSIONS

The application of differential spectrophotometry to the determination of hafnium in the presence of zirconium was investigated using the mandelic acid, chloranilic acid, quercetin and Xylenol Orange methods.

A literature search was made in which the chemical and physical methods presently available for the determination of hafnium and zirconium and of hafnium and zirconium in the presence of each other were extensively reviewed.

It was then possible to select systems which appeared to be promising for the application of the differential spectrophotometric Method II ("transmittance-ratio") to the determination of hafnium in the presence of zirconium.

A theoretical discussion of the application of Method II spectrophotometry to the problem is included. Some possible chemical and instrumental limitations for the differential approach were discussed with particular emphasis on the characteristics of phototubes and photomultipliers.

The equation, $\frac{\Delta C}{C} = \frac{\Delta A}{Sx C}$, which is the basis for the determination of the optimum concentration of oxides to be used, was derived starting with the fundamental relationship suggested by Beilley. In order to facilitate

the study of the several differential systems which were investigated an equation,

$$\log R = 2.000 - \epsilon f_0 W_t \times 3.365 \times 10^{-3}$$

was derived, relating the log of the instrument scale reading, R , to the weight of total oxide, W_t , fraction of HfO_2 , f_0 , molar absorptivity, ϵ , of complex and the molecular weights of ZrO_2 and HfO_2 .

It can be concluded from this preceding research that the approach outlined in "Approach to the Problem" was sound and its application did lead to the development of methods for the determination of hafnium in the presence of zirconium.

Actually four methods, using different complex systems were developed. Only the Xylenol Orange method, however, was found to be suitable for the determination of 0 to 5% HfO_2 in ZrO_2 . The other three methods are, however, of potential value for the determination of a wider range of HfO_2 in ZrO_2 . This should then make it possible to determine from 0 to 100% HfO_2 in ZrO_2 by using the Xylenol Orange for the 0 to 10% HfO_2 range and one of the other reagents for the higher percentages.

Mandelic Acid

The mandelic acid system should be ideally suited for the determination of HfO_2 in ZrO_2 at relatively high

percentages of HfO_2 . It was confirmed that zirconium and hafnium could be quantitatively precipitated from strong hydrochloric acid and weighed directly as the tetramandelates. It was then found that these tetramandelates could be dissolved in 1 M ammonia and their absorbancies measured at 258 μ .

By holding the total weights of tetramandelates constant (2.400 g/l) and varying the $\%\text{Hf(M)}_4$ it was found that a standard curve could be run. This curve seemed to indicate that this procedure should be applicable to the determination of 5 to 50% Hf(M)_4 in a mixture of pure zirconium and hafnium tetramandelates. There is no reason to believe that this range could not be narrowed or broadened somewhat.

One of the most attractive features of this method is that mandelic acid can be used for the separation of zirconium and hafnium from practically every other element, as well as for the subsequent differential determination of Hf(M)_4 in 1 M ammonia solution.

Unfortunately, the mandelic acid procedure was not found to be sufficiently sensitive to determine the 0 to 5% HfO_2 range that was desired. This was due to the small molar absorptivity and the low optimum concentration.

Chloranillic Acid

It was found that the chloranillic acid system had certain desirable characteristics and that it could be used for the differential spectrophotometric determination of about 5 to 50% HfO_2 . It also seems probable that the range could be narrowed so that 5 to 20% HfO_2 could be determined.

Although this complex system had a very high molar absorptivity, the optimum concentration was so small that it is not likely that the 0 to 5% HfO_2 range could be determined with any accuracy. The optimum concentration was found to be 0.30 mg. ZrO_2 /25 mls. or 0.012 g. ZrO_2 /l. in 1 M perchloric acid solution. Absorbance measurements were made at 330 mu.

This particular complex system does make it possible to work in an aqueous acid system which is quite stable for a long period of time.

Quercetin

Quercetin seemed to offer some possibilities for the determination of small amounts of HfO_2 in ZrO_2 . It was found that, as in the case of the zirconium complex, the absorbance of the hafnium complex was almost independent of hydrochloric acid concentration from 0.1 to 1 N. It

was observed in the course of this work that the optimum concentration varied with wavelength. The optimum concentration of oxides was found to be 0.800 mg./50 mls. at the optimum wavelength of 450 mμ. This wavelength was found to be considerably shifted from the maximum wavelength found in the original absorption curves.

It was also found that when the relative absorbance was plotted against concentration of oxide, it gave exactly the same shape curve and optimum concentration as when the slope times concentrations was plotted against concentration of oxide. This seemed to indicate that the optimum concentration could be found by plotting A vs. concentration as well as by plotting $S \times C$ vs. concentration.

Standard curves were run for solutions from 0 to 10% HfO_2 and from 0 to 5% HfO_2 in ZrO_2 . It appeared that this system offered the possibility of determining HfO_2 in these ranges although a scattering of points and shifting of standard curves were observed. Nevertheless with additional refinement this method could probably be used at least for 0 to 10% HfO_2 in ZrO_2 . Additional time was not spent in refining this procedure because of the possibilities offered by the indirect "transmittance-Approach" using Xylenol Orange.

Xylenol Orange

The application of Xylenol Orange to the determination of small amounts of hafnium in the presence of zirconium was found to be by far the most promising of the procedures investigated.

It was confirmed that hydrogen peroxide will bleach the zirconium - Xylenol Orange complex to a much greater extent than it will the hafnium complex. It was found that this selective bleaching action can be applied to the determination of hafnium in the presence of zirconium.

The approach used for this complex system differed from the other three only in that it utilized the indirect "transmittance-ratio" method whereas in the other three procedures the ordinary "transmittance-ratio" method was used. In the ordinary "transmittance-ratio" method the reference solution used to set the 100 end of the instrument scale contained the highest percentage of Hf whereas in the indirect approach, the solution containing no hafnium was the reference solution.

After preliminary non-differential investigations on the zirconium and hafnium complexes were completed, the differential solutions were studied. The preliminary non-differential work helped to establish the proper conditions for differential operation. It was found that the zirconium complex has its maximum absorbance at

an acidity of 0.7 to 0.9 N hydrochloric acid at a wavelength of 535 to 540 $m\mu$ while the hafnium complex shows a maximum absorbance when the acid concentration is 0.4 N and at 535 $m\mu$.

The effect of hydrogen peroxide and the time of color development (or bleaching) was investigated and it was observed that the zirconium - Xylenol Orange complex was mostly bleached within about 15 minutes after preparation and the absorbance decreased only slightly over a period of three hours. No apparent difference was noted regardless of whether the hydrogen peroxide was added before or after the Xylenol Orange.

In the case of the hafnium complex, it was found that the absorbance generally rose to a maximum within half an hour to an hour and then slowly decreased, although for all practical purposes it was essentially constant for a period of one to two hours. However, when the hydrogen peroxide was added after the Xylenol Orange, the absorbance was initially at a maximum and it continually decreased over a period of several hours and finally merged with the curve of the solution to which the hydrogen peroxide had been added first.

A considerable amount of research was carried out with the purpose of determining the optimum conditions for the differential determination of hafnium in the

presence of zirconium. It was not possible to determine any one set of conditions which could be said to be optimum as it seemed that many combinations were possible. The conditions used were therefore based to a certain extent upon such factors as solubilities of complexes, the size of the volumetric flasks to be used for making up the complex solutions, etc.

It was found that the initial temperature for color development (or bleaching) had a great effect on the relative absorbance measurements which were finally made. Although it was observed that the reference and standard solutions were continually changing, they were evidently doing so at about the same rate as there was a period of about two hours when the relative absorbance was essentially constant. During this time it was possible to construct a standard curve.

Several three point calibration curves were constructed after various times of color development. They were found to shift with time but a straight line curve was obtained in each case. This seemed to indicate that a standard curve and unknowns could be run after most any time interval just as long as they were measured at approximately the same time.

Standard curves were determined for the 0 to 10% HfO_2 and the 0 to 5% HfO_2 range. Since these showed

straight line curves it seemed very likely that this method could be used to determine the % HfO_2 in an unknown oxide or ore.

This method was tested using three zirconium - hafnium ore samples. These were analyzed for both the total oxide content and for the % HfO_2 in the total oxide. These results were compared with those obtained by Wah Chang Corporation, using the X-ray fluorescence method. The Xylenol Orange method results were found to compare very favorably with the X-ray results.

This procedure was, therefore, found to be applicable to the determination of 0 to 5% HfO_2 starting with either a mixture of pure oxides of hafnium and zirconium or with zirconium - hafnium ores.

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APPENDIXES

APPENDIX A

DETERMINATION OF ZIRCONIUM
AND HAFNIUM WITH CUPFERRON

Details of the cupferron method as used for standardization of the zirconium and hafnium solutions used for the preceeding work are included below. Hillebrand, Lundell, Bright and Hoffman (17, p. 572-3) and Scott (18, p. 1099-1100) also give detailed directions for the use of cupferron.

Solutions

1. Cupferron solution, 6%. Dissolved 6 g. of cupferron in 100 mls. of distilled water.
2. Cupferron - sulfuric acid wash solution. Dissolved 0.6 g. of cupferron in 500 mls. of distilled water containing 5 mls. of concentrated sulfuric acid.

Procedure

In most cases 25.00 or 50.00 ml. aliquots of the stock zirconium and hafnium solutions were used for analysis depending on the estimated oxide content. These aliquots were diluted to about 175 mls. with distilled water, cooled to 10°C and precipitated with 15 mls. of 6% cupferron solution. These precipitates were then filtered and washed several times with the cupferron

sulfuric acid solution. The filter papers and precipitates were placed in previously weighed platinum crucibles, dried in the oven and the paper burned off at a low temperature with a final ignition at 900°C for one hour. The crucibles were cooled, weighed and the concentration of oxide in mg./ml. calculated.

APPENDIX B

PREPARATION OF ZIRCONIUM
OXYCHLORIDE

Fused 5 g. of ZrO_2 with potassium pyrosulfate until a clear melt was obtained. The melt was dissolved in 1 M hydrochloric acid. The resulting solution was filtered into a beaker and treated with ammonia until basic. The resulting precipitate was thoroughly washed, filtered, and then dissolved in hydrochloric acid. A second precipitation was made with ammonia and the precipitate was again filtered, washed and finally dissolved in concentrated hydrochloric acid. This solution was again filtered and evaporated to near dryness. The crystals of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ which separated out were filtered through a sintered glass funnel and washed with a small amount of ice cold concentrated hydrochloric acid. Air was drawn through the funnel until the crystals were dry.

APPENDIX C

PURIFICATION OF CHLORANILIC ACID

The procedure used to purify the chloranilic acid was the one suggested by Thamer and Voigt (75).

Eight grams of practical grade chloranilic acid were dissolved in a liter of distilled water at the boiling point and filtered. The filtrate was extracted with two 200 ml. portions of benzene in a separatory funnel at 50°C. The benzene phases were discarded since they contained only a slight amount of chloranilic acid. The aqueous phase was cooled in an ice bath yielding bright red crystals of chloranilic acid which were filtered off and washed with three 10 ml. portions of water. The crystals were dried in an oven at 115°C in order to expel the water of hydration. The overall yield of chloranilic acid was approximately 50%

APPENDIX D

DERIVATION OF FORMULA
FOR CALCULATING
RELATIVE ABSORBANCE

A different approach was made in the following derivation from that in the "Approach to the Problem" section.

ΔA or $\Delta(\log R)$ can be estimated between any two solutions using Method II when $f_{HfO_2} = 0$ and $f_{HfO_2} = n$ ($n = 0.05, 0.10, 0.25$ etc.) at constant of total oxide.

(1) $\Delta A = A_1 - A_0$ and assuming Beer's law is valid

$$A = \epsilon b c \text{ and}$$

$$A_0 = \epsilon_{ZrO_2} \times b(W_t - W_{tf_0}) \times \frac{1}{ZrO_2} + \epsilon_{HfO_2} \times b \times W_{tf_0} \times \frac{1}{HfO_2}$$

$$A_1 = \epsilon_{ZrO_2} \times b \times W_t \times \frac{1}{ZrO_2}$$

where

A_0 = absorbance of reference solution ($ZrO_2 + HfO_2$)

A_1 = absorbance of pure ZrO_2 complex solution

ϵ_{ZrO_2} = molar absorptivity of zirconium complex

ϵ_{HfO_2} = molar absorptivity of hafnium complex

$W_t = W_{ZrO_2} + W_{HfO_2} = \text{constant} = g/l$

f_0 = fraction of HfO_2 in reference solution

Substituting into equation (1) gives

$$(2) \quad \Delta A = \epsilon_{ZrO_2} \times b \times W_t \times \frac{1}{ZrO_2} - \left[\epsilon_{ZrO_2} \times b(W_t - \right.$$

$$W_{tfo}) \times \frac{1}{ZrO_2} + HfO_2 \times b \times W_{tfo} \times \frac{1}{HfO_2} \Big]$$

$$\Delta A = \epsilon_{ZrO_2} \times b \times W_t \times \frac{1}{ZrO_2} - \epsilon_{ZrO_2} \times b \times W_t \times \frac{1}{ZrO_2} + \epsilon_{ZrO_2} \times b \times W_{tfo} \times \frac{1}{ZrO_2} - \epsilon_{HfO_2} \times b \times W_{tfo} \times \frac{1}{HfO_2}$$

$$\Delta A = \epsilon_{ZrO_2} \times b \times W_{tfo} \times \frac{1}{ZrO_2} - \epsilon_{HfO_2} \times b \times W_{tfo} \times \frac{1}{HfO_2}$$

and simplifying,

$$(3) \quad \Delta A = b \times W_{tfo} \left(\frac{\epsilon_{ZrO_2}}{ZrO_2} - \frac{\epsilon_{HfO_2}}{HfO_2} \right) \text{ and since } \epsilon_{ZrO_2} =$$

$$\epsilon_{HfO_2} = \epsilon \text{ and if } b = 1 \text{ cm then}$$

$$(4) \quad \Delta A = \epsilon \times W_{tfo} \left(\frac{1}{ZrO_2} - \frac{1}{HfO_2} \right)$$

$$\Delta A = \epsilon \times W_{tfo} \left(\frac{1}{123.2} - \frac{1}{210.6} \right)$$

$$\Delta A = \epsilon \times W_{tfo} \times 3.365 \times 10^{-3}$$

$$\text{and since } A_0 = \log \frac{1}{R_0} \text{ and } A_1 = \log \frac{1}{R_1}$$

$$(5) \quad \Delta A = \log \frac{1}{R_1} - \log \frac{1}{R_0}$$

then

$$\log R_0 - \log R_1 = \epsilon \times W_{tfo} \times 3.365 \times 10^{-3}$$

and

$$\Delta(\log R) = \epsilon \times W_{tfo} \times 3.365 \times 10^{-3}$$

and since $R_0 = 100$ for the Method II reference solution, then

$$(6) \quad \log 100 - \log R_1 = \epsilon \times W_{ZrO_2 f_o} \times 3.365 \times 10^{-3}$$

and therefore

$$\log R_1 = 2.000 - x W_{ZrO_2} f_o \times 3.365 \times 10^{-3}$$

It can be seen that this derivation confirms the validity of the previous one.