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THE DETERMINATION OF ZIRCONIUM BY THE CHLORANILIC ACID METHOD

O. Menis

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THE DETERMINATION OF ZIRCONIUM BY THE CHLORANILIC ACID METHOD

O. Menis

ANALYTICAL CHEMISTRY DIVISION

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April 7, 1954

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THE DETERMINATION OF ZIRCONIUM BY THE CHLORANILIC ACID METHOD

ABSTRACT

The use of the zirconium chloranilate complex, of Thamer and Voigt,[7] for the estimation of zirconium in low concentrations, of the order of micrograms, was investigated. The optimum conditions, including acid concentration, wavelength, temperature, quantity of reagent, stability and tolerance for interfering ions have been established.

The additive properties of a multicomponent system, consisting of zirconium complex, uranium complex and excess reagent were studied and a method was developed for determining zirconium in the presence of relatively high concentrations of uranium.

Procedures for eliminating some of the most seriously interfering ions such as F^- and Fe^{+++} were developed.

The range of zirconium concentration and the degree of precision for this method under optimum conditions are given.

THE DETERMINATION OF ZIRCONIUM BY THE CHLORANILIC ACID METHOD

INTRODUCTION

Until recently there has been a dearth of reliable methods for the determination of zirconium in microgram amounts. Of the methods which have been published recently, the p-dimethyl aminoazophenylarsonic acid method[5] is time-consuming and requires that separations be made from a large number of interfering elements, while methods based on the formation of lakes with alizarine and alizarine S[2, 9] require careful control of pH, and suffer from a number of interferences, especially sulfate. In addition, the sensitivity of the last two methods is relatively low, the optimum range being from 100 to 300 μg of zirconium. Another method which was recently published involves the indirect determination of zirconium based on a colorimetric method for the determination of phosphate[4]. A method in which the thoron reagent was used by Horton[3] was published while this report was in preparation. Thamer and Voigt[7] in their study of complexes of chloranilic acid and zirconium, showed that the absorbancy of the complex obeys Beer's law and indicated its advantages for analytical purposes. Their study was carried out in solutions of one and two molar perchloric acid and covered a number of interferences only qualitatively.

An extensive study has been conducted to evaluate the effect of certain conditions on the sensitivity and precision of a method based on the use of the chloranilate complex for the determination of zirconium in microgram amounts. This study involved the determination of the effects

of acid concentration and reagent concentration, and their relationship to other ionic interferences. Because the separation of small amounts of zirconium from a uranyl solution is at best a long and difficult process[6], special consideration has been given to the determination of zirconium in solutions of uranyl sulfate and fluoride without benefit of prior chemical separations.

In the determination of zirconium in uranyl solutions, the effect of excess chloranilic acid reagent, concentration of perchloric acid, effect of other ions, and the effect of wavelength selection on the three component system were studied with regard to sensitivity and precision.

EXPERIMENTAL WORK

Wavelength Selection

The absorption spectra of the zirconium chloranilate complex, and of the reagent in a 1 M perchloric acid solution are shown in Figure 1. The adherence of the complex to Beer's absorbancy law was tested in the region of constant slope, between 335 mμ and 355 mμ. See Table 1 and Figure 2.

In Figure 2 the data are plotted according to the method of Ringbom[1], the inflection point of the slope occurs at 0.368 transmittancy, a characteristic typical of solutions which obey Beer's law. At the higher wavelengths the interference of other ions and the absorbancy of the reagent is least, while at the lower wavelengths the sensitivity is greatest. The selection of the proper wavelength for absorbancy measurements depends on the presence of other ions and is described in subsequent sections.

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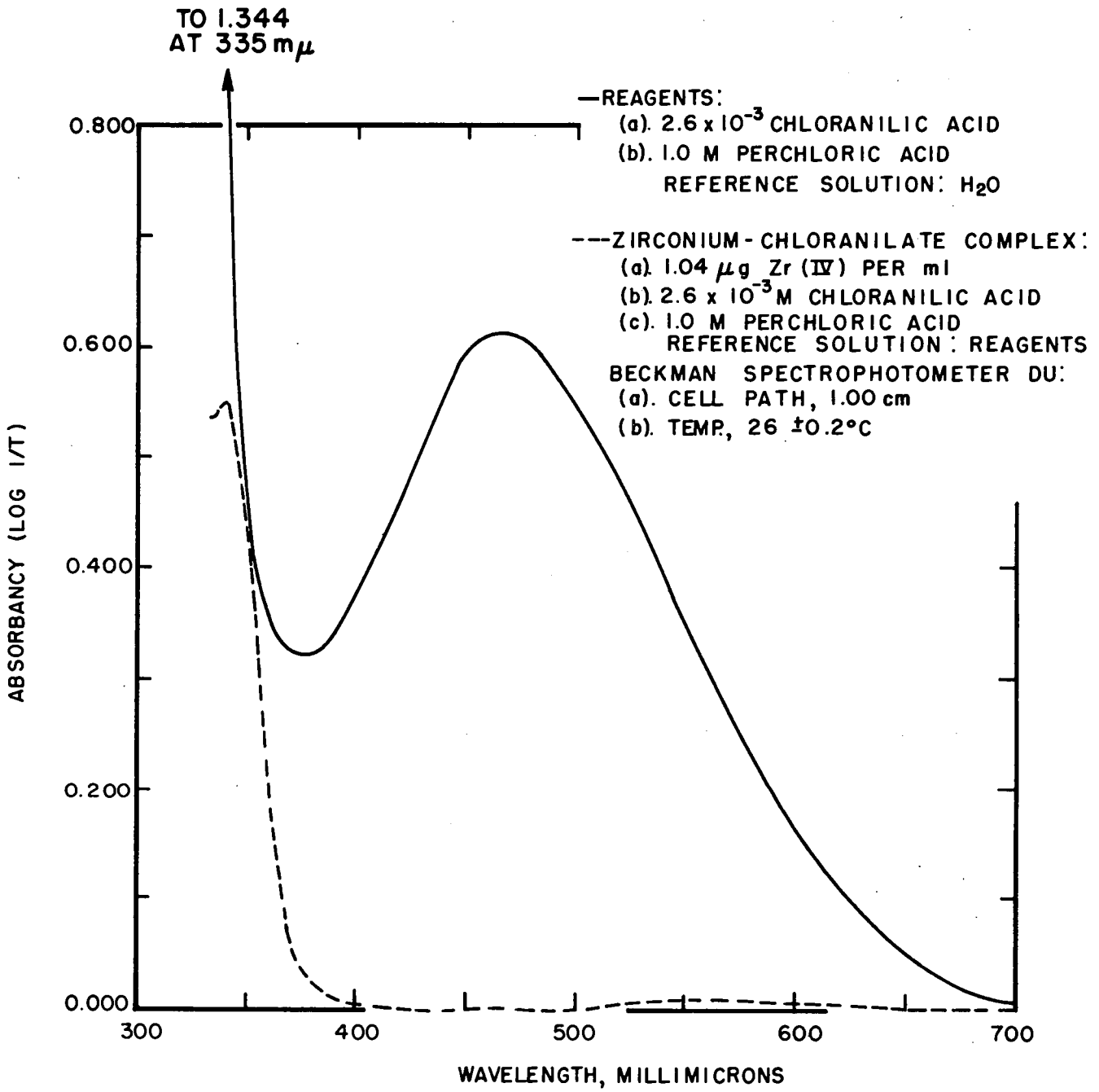

ABSORBANCY-WAVELENGTH CURVES FOR SOLUTIONS OF CHLORANILIC ACID AND ZIRCONIUM CHLORANILATE

FIGURE 1.

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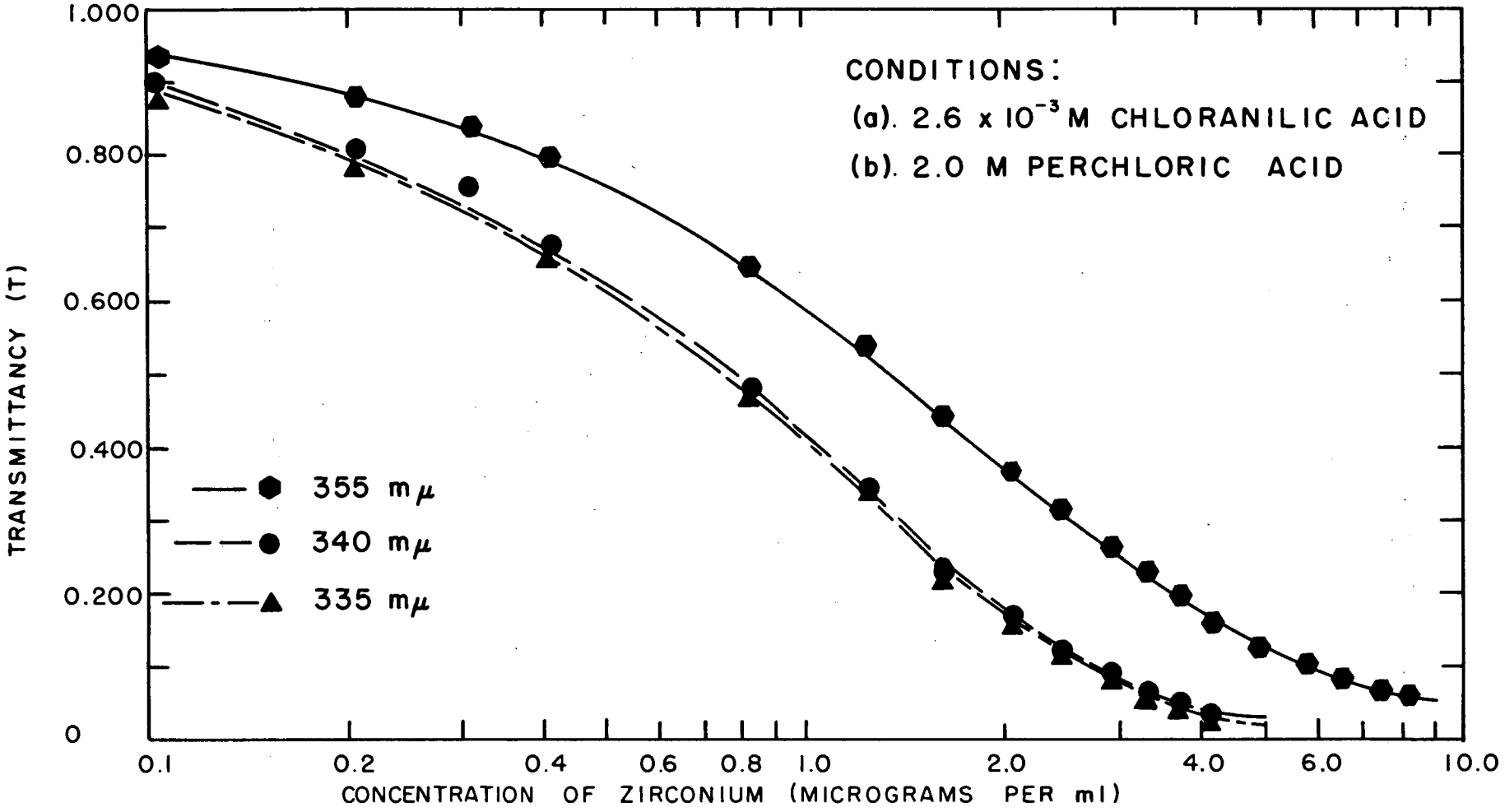

RINGBOM PLOT OF CALIBRATION DATA AT THREE WAVELENGTHS
FIGURE 2.

Table 1

Absorbancy of Zirconium Chloranilate at Several Wavelengths

Solution - 2 M $HClO_4$
Reagent - 3.4×10^{-3} M Chloranilic Acid
Zr Concentration Range - 1.2 to 3.2 μg/ml

Wavelength mμ	Number of Determinations	Absorbancy Coefficient[1] $cm^{-1} \times 1000$	Coefficient of Variation, V_c[2] Per Cent
335	6	0.362	1
340	12	0.353	1
350	24	0.282	2
355	18	0.214	2

(1) $K_s = \log_{10} \frac{1/T_s}{b}$

where: K_s = absorbancy coefficient
T_s = transmittancy
b = cell thickness in cm

(2) $V_c = \frac{100S}{c}$

where: V_c = coefficient of variation
S = standard deviation, μg/ml
c = concentration of zirconium, μg/ml

Excess Reagent

Thamer and Voigt[4] used 10^{-4} molar chloranilic acid reagent for concentrations of Zr(IV) from 2×10^{-5} molar. Figure 3 indicates that the sensitivity increases as the concentration of the reagent is increased. In 1.7×10^{-3} to 2.9×10^{-3} molar chloranilic acid, shown in the plot by the region of 140 to 250 reagent to zirconium molar ratio, the slope of the curve is less steep, and suggest the optimum range of reagent concentration to use. When the concentration of the reagent is increased to 3.4×10^{-3} molar, precipitation occurs. At higher temperatures the reagent solubility increases and the greater concentrations of reagent may be used.

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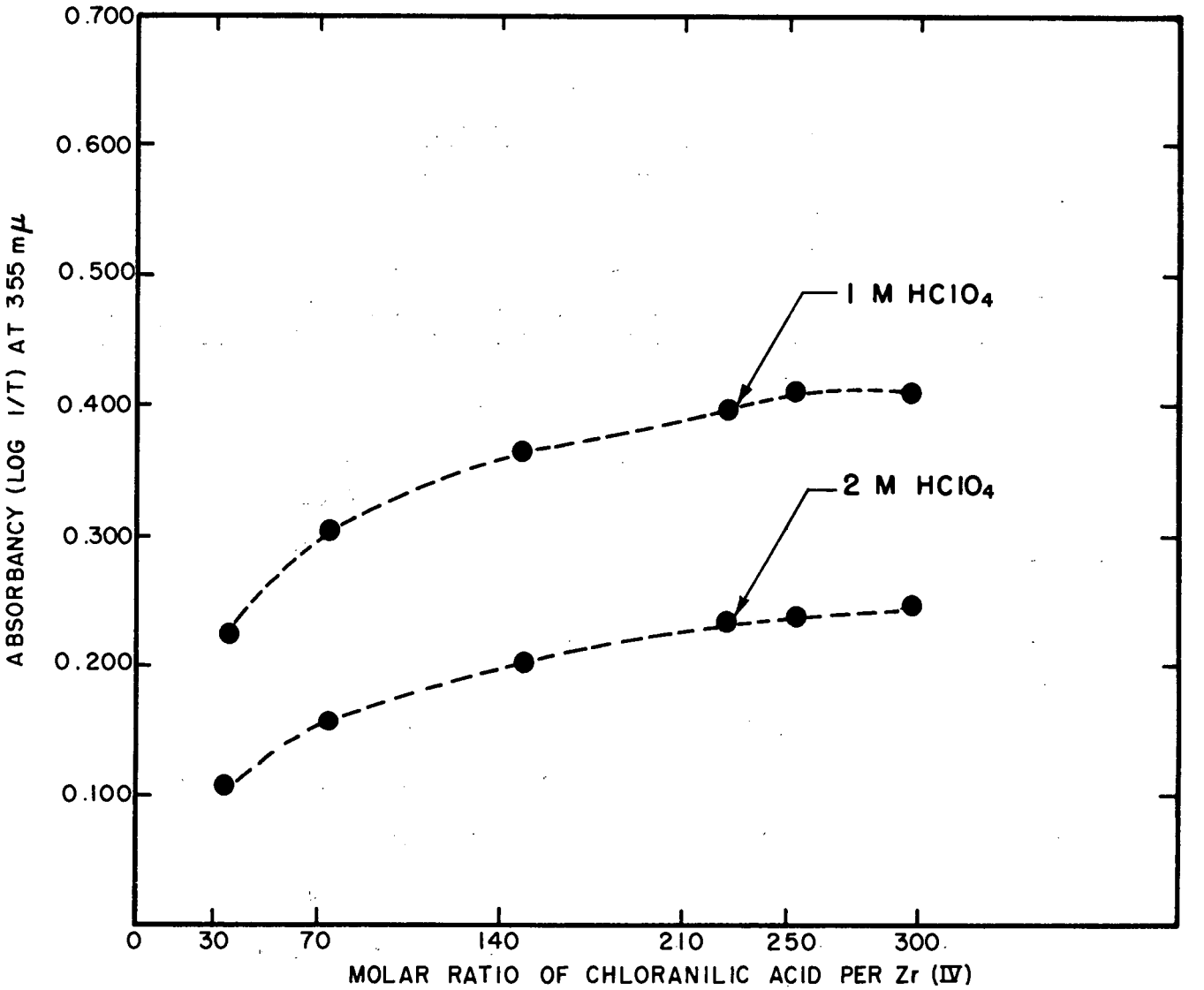


ABSORBANCY OF ZIRCONIUM (IV) CHLORANILATE SOLUTIONS WITH EXCESS CHLORANILIC ACID AT TWO PERCHLORIC ACID CONCENTRATIONS
FIGURE 3.

The Effect of Temperature

The absorbancy of the complex is not sensitive to moderate temperature variation; the effect, as shown in Table 2, is within the experimental error for the two temperatures of 25° and 37° C. The absorbancy of the complex is not affected when the solution is heated to 90° C and then cooled to within the above temperature range.

Table 2

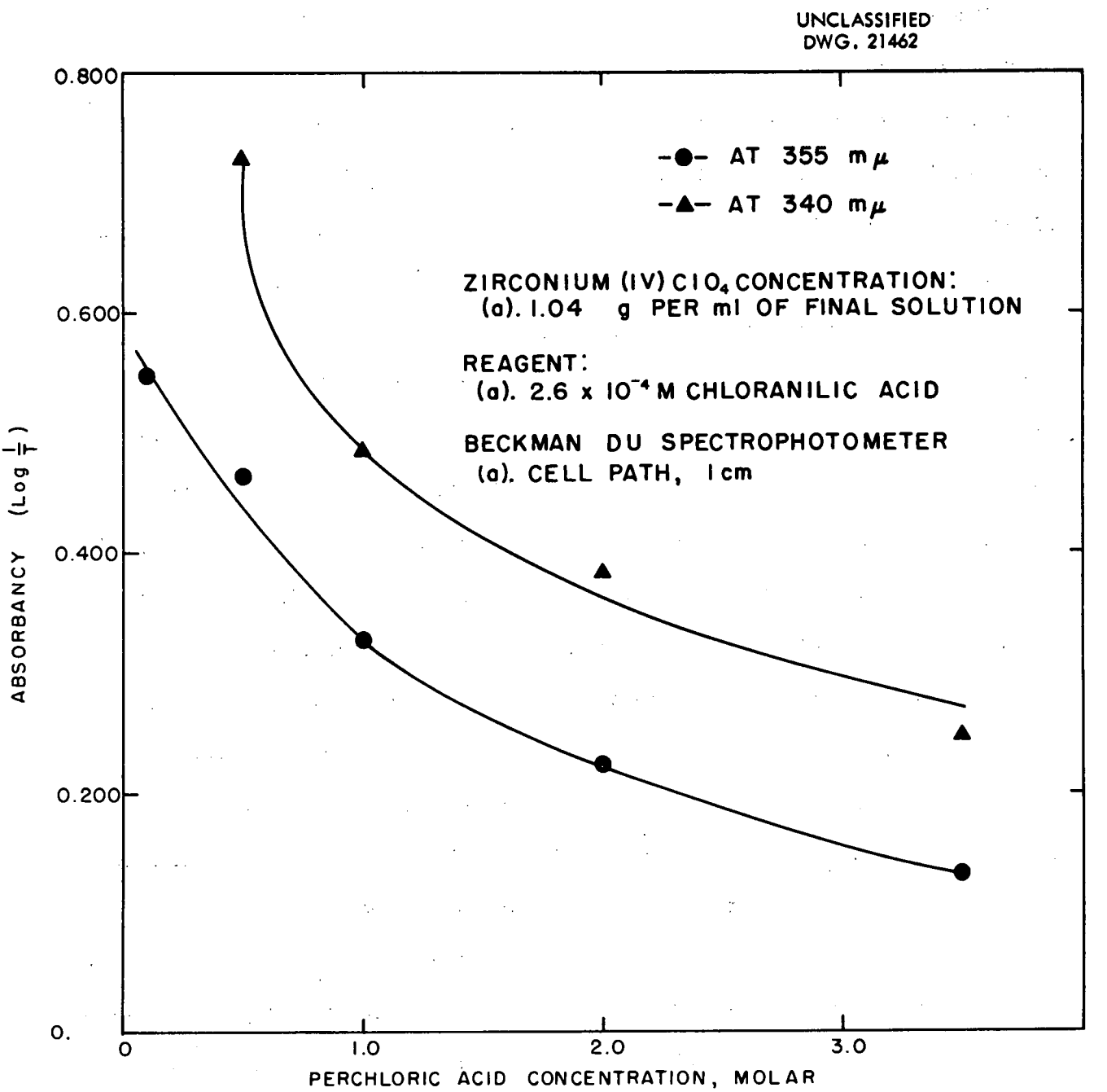
Effect of Temperature on the Absorbancy of Zirconium Chloranilate

Solution - 2 M $HClO_4$
Reagent - 2.6×10^{-3} M Chloranilic Acid

Temperature °C	Zirconium µg/ml	Absorbancy, log 1/T			
		355 mµ	Difference	335 mµ	Difference
25	1.04	0.248		0.408	
37	1.04	0.247	0.001	0.406	0.002
25	1.66	0.383		0.640	
37	1.66	0.374	0.009	0.628	0.012
25	2.08	0.462		0.786	
37	2.08	0.463	0.001	0.786	0.000

Acid Concentration

Throughout the major part of this study, perchloric acid was used. Effects of other acids will be discussed in the section on anion interferences. As is shown in Figure 4, it was observed that the sensitivity decreases as the concentration of perchloric acid is increased from 0.1 to 3.5 molar. The sensitivity decreases most rapidly in the range of 0.1 to 1 M perchloric acid solution. For best precision, the quantity of acid has to be controlled carefully. The selection of final acid concentration depends also on the presence of other interfering ions.



SENSITIVITY - ABSORBANCY OF ZIRCONIUM CHLORANILATE AS A FUNCTION OF PERCHLORIC ACID CONCENTRATION, AT TWO WAVELENGTHS.

FIGURE 4.

Interference of Uranium(VI)

Tests were made to determine the interference of uranyl ion in both sulfate and perchlorate solutions. It was observed that the uranyl ion also forms a complex with chloranilic acid as shown in Figure 5b. The possibility of determining zirconium in the presence of this complex without the benefit of prior separation was investigated. The determination of zirconium was thus carried out in a three-component system, containing the zirconium complex, uranyl chloranilate and excess reagent. The absorption spectra of the zirconium complex is shown in Figure 5a, that of the uranyl complex is shown in Figure 5b, and that of both complexes measured together is shown in Figure 5c. The smooth curves in Figure 5 a,b,c, were drawn from data secured from the readings of the absorbancy of the complex versus water. The readings were corrected for reagent absorbancy. The points indicated specifically on the smooth curves are those of the respective complexes when the absorbancy was read versus a reference solution containing the other component or components. The close agreement between the points and the smooth curves, as well as the algebraic sum of the two components in the last curve (Figure 5) reveals that the mixture has additive properties at the several wavelengths tested*.

To establish whether zirconium and uranium chloranilate complexes show additive properties over a wide range of uranium concentration, known mixtures were prepared and the additivity of the absorbancy coefficient was tested.

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* To avoid possible complications from the use of wide slit widths, a photomultiplier attachment to the Beckman instrument was used in the studies of the multicomponent systems. A discussion of this attachment is given in greater detail in the appendix.

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ABSORPTION SPECTRA
THE ADDITIVE ABSORBANCIES OF A THREE-COMPONENT SYSTEM

I. Zr CHLORANILATE COMPLEX

1.04 μg Zr per ml

II. U-VI CHLORANILATE COMPLEX

1.0 mg U-VI (as UO_2SO_4) per ml

REAGENTS:
2.6×10^{-3} M CHLORANILIC ACID
2.0 M $HClO_4$

III. Zr & U-VI CHLORANILATE COMPLEX

1.04 μg Zr per ml
1.0 mg U-VI (as UO_2SO_4) per ml

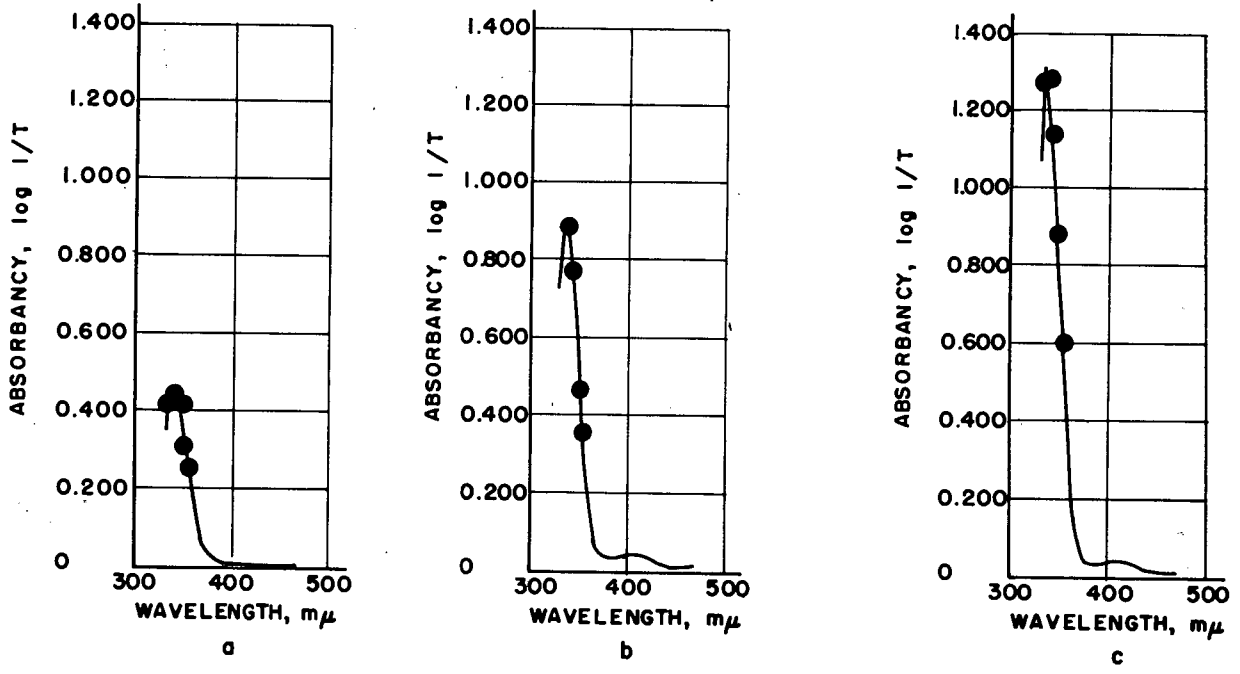

FIGURE 5.

The additive properties of the two complexes at various concentrations of perchloric acid are shown in Figure 6. Examination of this graph shows that in 1.0 M perchloric acid the absorbancy curves of uranium alone and uranium plus zirconium are parallel from 0.5 to 2 mg of uranium per ml indicating that in that range of uranium concentrations the absorbancy of these two ions are additive. Similarly this additivity is shown in 2 M and 3.5 M perchloric acid for uranium concentrations ranging from 0.5 through 3 mg per ml and 0.5 through 6 mg per ml, respectively. Also, in a procedure in which the absorbancy of the zirconium complex is measured versus the other components in the reference cell, the absorbancy coefficient of a range of concentrations of zirconium in a uranyl sulfate solution containing 0 to 6 mg uranium per ml of final volume is shown in Table 3. In the presence of up to 2 mg of uranium per ml of final volume the absorbancy coefficient remains fairly constant. At higher concentrations of uranium the wider slit widths which are required to zero the reference solution produce a variation of absorbancy coefficient.

Table 3

Absorbancy Coefficient of Zirconium as a Function of Uranium Concentration and Slit Width

Solution - 2 M $HClO_4$
Reagent - 3.4×10^{-3} M Chloranilic Acid
Zr Conc. Range - 1.2 to 3.2 μg/ml
Reference Solution - Reagents plus UO_2SO_4
Wavelength - 355 mμ

Uranium(VI) mg/ml	No. of Determinations	Slit Width mm	Absorbancy Coefficient $cm^{-1} \times 1000$	Coefficient of Variation Per Cent
0.00	6	0.192	0.216	2
1.00	6	0.319	0.211	4
1.25	6	0.394	0.208	4
2.00	6	0.482	0.207	3
4.00	6	0.855	0.180	1
6.00	6	1.370	0.149	4

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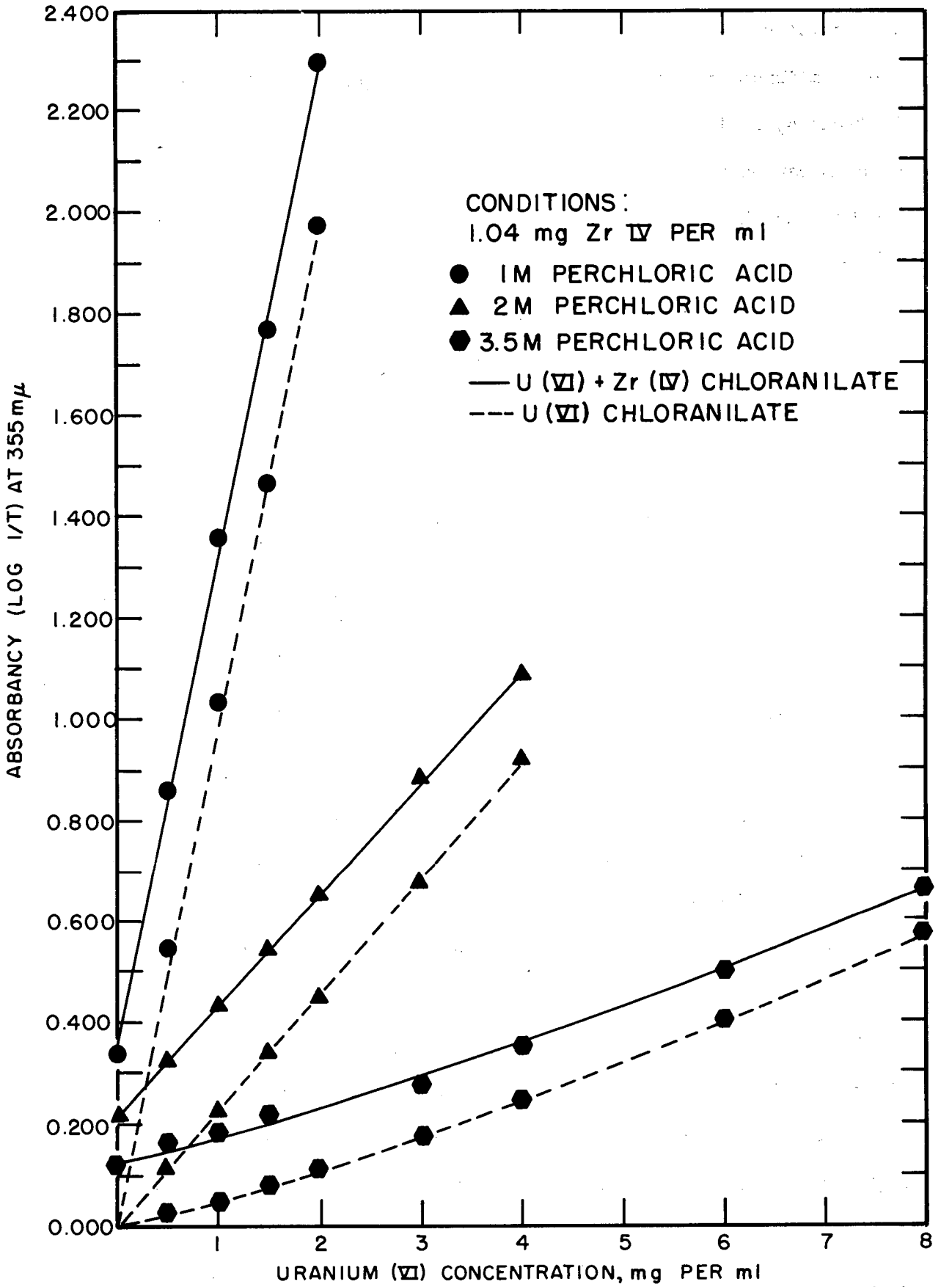


ADDITIVE ABSORBANCIES OF URANIUM (VI) AND ZIRCONIUM (IV) CHLORANILATE AT THREE ACID CONCENTRATIONS

FIGURE 6.

With solutions having higher concentrations of uranium, it is best to use a calibration curve for the determination of zirconium. As is shown in Table 4, at the higher wavelength, 355 mμ, higher concentrations of uranium can be tolerated. At 335 mμ the absorbancy contribution of the reagent and the uranium complex is too great to allow for a three-component-system measurement. There is, however, an approximately threefold loss in sensitivity at this higher wavelength.

Table 4

Maximum Permissable Uranium Concentration in the Determination of Zirconium as a Function of Wavelength

Solution - 2 M $HClO_4$
Reagent - 3.4×10^{-3} M Chloranilic Acid
Zr Conc. Range - 1.2 to 3.2 μg/ml

Wavelength mμ	Uranium(VI) mg/ml	Slit Width mm	Absorbancy Coefficient $cm^{-1} \times 1000$	Coefficient of Variation Per Cent
335	0.0	0.662	0.362	1
340	1.5	1.920	0.325	4
350	4.0	1.700	0.190	2
355	6.0	1.370	0.149	4

Interference of Anions

The effect of various anions on the zirconium complex was investigated. Since the main objective of this study was the determination of zirconium in an uranyl sulfate solution, the effect of the SO_4^- anion which is known to form a stable complex with zirconium was investigated in a perchlorate medium. The data shown in Table 5 show that sulfate ions when present in concentrations equivalent to those of the maximum concentration of uranium do not affect the results. The effect of sulfate ion when present in much higher concentrations was determined at various acid concentrations and at

several wavelengths (see Table 6). At higher acid concentrations, 3.5 M $HClO_4$ and .024 M $SO_4^=$ solutions, the interference with the absorbancy of zirconium complex becomes noticeable. In the 1 M perchloric acid solutions a 0.20M $SO_4^=$ solution produced only significant changes in the absorbancy when measured at 355 mμ. The interference of other anions is summarized in Table 7.

In an acetate medium, the absorbancy of the complex is much greater, more than doubling the sensitivity, the absorption curve shows a broad maximum around 340 mμ. The complex obeys Beer's absorbancy law as shown in Table 8; however, the absorbancy of the uranyl complex in the presence of acetate is greatly increased, thus making it an unsuitable medium in a multicomponent system. However, in the absence of interfering ions this medium may be used when increased sensitivity is desired. Of the other elements shown in Table 7, fluoride ions interfere most seriously. The bleaching effect is more pronounced as the ratio of F^- to Zr(IV) becomes greater than 0.003 mg/gram. The interference of the fluoride ion can best be removed by simply heating to dryness with perchloric acid as described in the appendix.

Table 5

Effect of Sulfate Ion on the Absorbancy of the Zirconium Complex in a Uranyl Perchlorate Zirconium Perchlorate System

Solution - 2 M $HClO_4$
Reagent - 2.6 x 10^{-3} M Chloranilic Acid
Beckman Spectrophotometer Model DU with Photomultiplier Tube Attachment
Corning Filter No. 5880
Reference Solution - Contains all components except sulfate

Concentration, x 10^3 M			Absorbancy Coefficient, cm^{-1} x 1000		
Uranium(VI)	SO_4	Zirconium		Average	Difference
2.1	-	0.0137	0.236		
2.1	-	0.0182	0.227	0.231	
2.1	2.1	0.0137	0.249		
2.1	2.1	0.0182	0.240	0.244	+0.013
4.2	-	0.0137	0.247		
4.2	-	0.0182	0.241	0.244	
4.2	4.2	0.0137	0.235		
4.2	4.2	0.0182	0.235	0.235	-0.009
8.4	-	0.0137	0.235		
8.4	-	0.0182	0.236	0.236	
8.4	8.4	0.0137	0.246		
8.4	8.4	0.0138	0.246	0.246	+0.010
12.6	-	0.0182	0.237		
12.6	-	0.0137	0.242	0.239	
12.6	12.6	0.0137	0.231		
12.6	12.6	0.0182	0.233	0.232	+0.007
20.1	-	0.0137	0.211		
20.1	-	0.0182	0.217	0.214	
20.1	20.1	0.0137	0.212		
20.1	20.1	0.0182	0.217	0.215	+0.001

Table 6

Effect of Perchloric Acid Concentration on the Interference of Sulfate as a Function of the Absorbancy of Zirconium Chloranilate

Zirconium Concentration - 1.04 μg/ml

Sulfate M x 10^5	Absorbancy, log 1/T					
	1 M $HClO_4$		2 M $HClO_4$		3.5 M $HClO_4$	
	355 mμ	340 mμ	355 mμ	340 mμ	355 mμ	340 mμ
0.042	0.312	0.522	0.187	0.342	0.094	0.193
.084	.307	.513	.193	.349	.095	.194
.126	.300	.508	.193	.349	.096	.196
.168	.309	.512	.191	.346	.094	.194
.210	.307	.512	.193	.349	.097	.196
.81	.310	.530	-	-	.094	.196
1.62	.309	.528	-	-	.085	.181
2.43	.310	.530	-	-	.079	.173
3.34	.310	.530	-	-	.076	.169
20.0	.286	.529	-	-	.031	.091

Table 7

Interference of Anions on the Absorbancy of Zirconium Chloranilate

Sodium Salt of Anions
Zirconium Conc. - 1.04 μg/ml

Anion	Ion to Zr Wt. Ratio mg/μg	Absorbancy, log 1/T			
		355 mμ		340 mμ	
			Change Per Cent		Change Per Cent
None	-	0.320	-	0.520	-
NO_3	10	.329	+3	.551	+6
	20	.340	+6	.587	+13
	30	.227	-29	.447	-14
Cl^-	10	.329	+3	.541	+4
	20	.333	+4	.572	+10
	30	.336	+5	.562	+8
$SO_4^=$	2	.320	0	.520	0
	20	.288	-10	.529	+2
ClO_4	20	.321	-2	.490	-6
F	0.003	.311	-3	-	-

Table 8

Absorbancy of Zirconium Chloranilate Complex in an Acetate Medium

Test of Beer's Absorbancy Law

Solution - 0.1 M Acetic Acid
Reagent - 4×10^{-4} M Chloranilic Acid

Zirconium	Absorbancy Coefficient, $cm^{-1} \times 1000$	
µg/ml	340 mµ	350 mµ
0.6	0.662	0.546
1.0	0.658	0.541
2.0	0.649	0.541

Interference of Cations

The interference of some of the cations has been investigated, and the relative error caused by their presence is shown in Table 9 at two wavelengths and at two acid concentrations. Of these, Sn(II), Sn(IV) and Fe(III) interfere most seriously. The effect of the Fe(III) interference is linear in the lower concentration range of Fe(III) tested. If the concentration falls within that range and is determined independently a correction can be readily applied. The interferences of Fe(III), Sn(II) and Sn(IV) are also reduced at higher perchloric acid concentrations. (See Table 9).

Attempts were made to eliminate the interference of ferric iron by the use of the reducing agents, thiosulfate, thioglycolic acid and hydrazine hydrochloride. Thiosulfate is troublesome because of the formation of colloidal sulfur under the conditions of the test. Thioglycolic acid interferes by increasing the absorbancy of the reagent. Hydrazine hydrochloride under special conditions readily reduces the iron to the ferrous state without interfering in the determination of the zirconium complex.

Table 9

Interference of Cations on the Absorbancy of Zirconium Chloranilate

Reagent - 1.7×10^{-3} M Chloranilic Acid
Zr Conc. - 1.04 µg/ml

Cation	Ion to Zr Weight Ratio	Per Cent Change in Absorbancy: 1 M $HClO_4$ 355 mµ	1 M $HClO_4$ 340 mµ	3.5 M $HClO_4$ 355 mµ	3.5 M $HClO_4$ 340 mµ
NH_4^+	10	-3	-4		
	100	-2	-1		
Cu^{++}	10	+3	10		
	100	+39	+95		
Ni^{++}	10	-1	-0		
	100	+6	+25		
Fe^{++}	4	+2	0		
	12	+1	0		
	20	+2	0		
Fe^{+++}	0.2	+4	+3	+2	+2
	1.0	+25	+13	+3	+2
	3.0	+77	+46	+12	+8
Sn^{++}	1.0	+3	+11	+4	+5
	3.0	+18	+40	+10	+18
	20.0	+200	+300	+50	+81
Sn^{++++}	1.0	-1	+2	+0	+2
	3.0	+6	+16	+7	+15
	20.0	+120	+185	+75	+120
Cr^{+++}	10	0	-2		
	100	0	0		
Ce^{++++}	10	0	-4		
Ti	10	0	+5		
Th	1	+3	+5		
	2	+8	+14		
	10	+25	+74		
UO^{++}	1	+13	+20		
	5	+68	+100		
	10	+140	+200		

Ferric iron is reduced by heating the acid test solution after the addition of hydrazine hydrochloride, then cooling and developing the colored complex at room temperature. See procedure in Appendix C. It is to be noted that at temperatures of the order of 80° C, the reductant reacts with the chloranilic acid reagent. The solutions must be cooled before the addition of the reagent to avoid the occurrence of this reaction. As much as 0.5 mg of Fe(III) in a 50-ml volume is readily reduced with 200 mg of hydrazine hydrochloride. When 1 to 5 mg of Fe(III) are present in solution, greater concentrations of hydrazine hydrochloride are required.

Stability

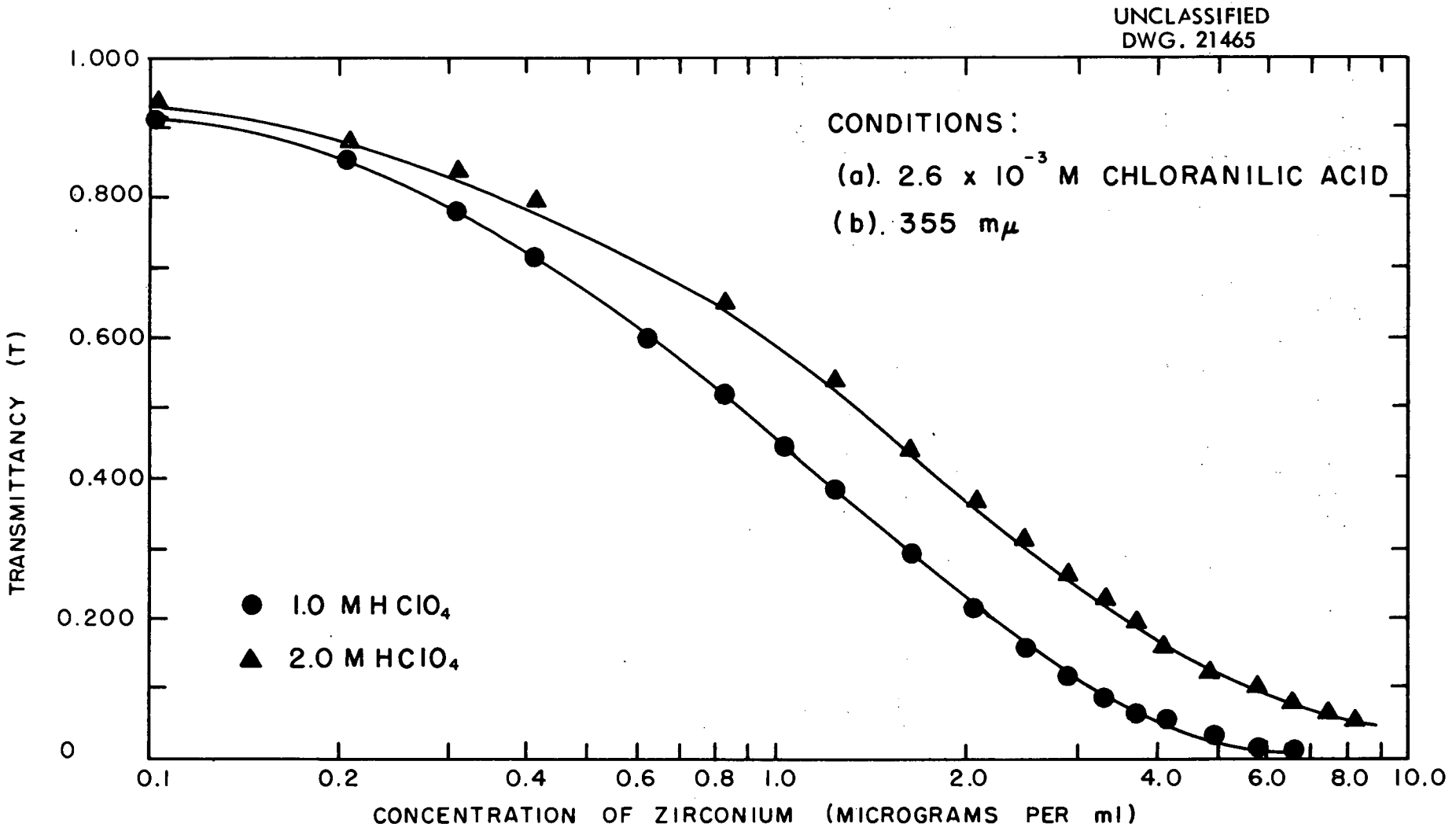
The zirconium chloranilate complex is stable in 1.7×10^{-3} to 2.9×10^{-3} M chloranilic acid, and 1 to 3.5 M perchloric acid solutions for at least 24 hours, without any detectable change in absorbancy.

Range and Precision

The concentration range over which zirconium can be determined at optimum precision was established by the use of the Ringbom plot[1] at several wavelengths (see Figure 2) and at two different acid concentrations (see Figure 7). In using this method, the relative error is calculated from the slope of the line (see Table 10).

$$\text{Slope of the line} = \frac{\text{Relative error, per cent}}{\text{one per cent instrumental error}} = \frac{230\ d \log C}{d\ I}$$

where: C = concentration
I = 1 per cent instrumental error



RINGBOM PLOT OF CALIBRATION DATA AT TWO ACID CONCENTRATIONS
FIGURE 7.

Table 10

Optimum Range and Precision for the Determination of Zirconium at Two Acid Concentrations

(Data from Figure 2)

$HClO_4$ M	Optimum Range µg Zr(IV)/ml	Per Cent Relative Analysis Error per 1 Per Cent Absolute Photometric Error
1	0.4 to 3.5	3
2	0.8 to 4.0	3

CONCLUSION

The modified zirconium chloranilate method, in addition to being much less time-consuming, is more reliable than other methods. Many troublesome separations can be avoided by this procedure. A perchloric acid medium offers a more sensitive method for the determination of microgram quantities of zirconium. In the absence of interfering ions an acetate medium offers enhanced sensitivity.

APPENDIXES

A. RECOMMENDED PROCEDURE FOR THE DETERMINATION OF ZIRCONIUM IN THE PRESENCE OF URANIUM

1. Pipet a suitable portion of the sample into a 50-ml volumetric flask. Solution should contain less than 6 mg uranium per ml of final volume.
2. Add 8.6 ml of 72 per cent perchloric acid. (Final solution 2 N with respect to $HClO_4$).
3. Add 20 ml of chloranilic acid reagent (900 mg chloranilic acid per liter of water).
4. Adjust volume to mark with water.
5. Let solutions stand for 15 to 30 minutes.
   (a) For solutions containing 0 to 2 mg of uranium per ml of final volume, determine the absorbancy versus the reference solution, prepared as directed below, with a Beckman DU spectrophotometer at 355 mu.
   (b) For solutions containing 2 to 6 mg of uranium, determine the absorbancy of the solution from Step 5 versus water. Determine the concentration of uranium in sample. From a uranyl chloranilate calibration curve, obtain the value of absorbancy of the uranium complex and subtract from the above reading.

Reference Solution

From a standard solution of uranium, pipet a volume sufficient to yield an amount of uranium approximately equivalent to that contained in the samples being analyzed.

The reference solution is processed in accordance with the steps outlined in the procedure and at the same time that samples are being analyzed.

If water is used as the reference solution (sample solutions containing 2 to 6 mg of uranium per ml) proceed as above except that uranium is not added.

B. MODIFIED PROCEDURE

(Solutions Which Contain Fluoride Ion)

1. Pipet sample or portion of sample into 300-ml, tall-form beaker.
2. Add 5 ml of 72 per cent $HClO_4$.
3. Evaporate to dryness on a hot plate.
4. Place in a muffle furnace at 300° C for 30 minutes.
5. Cool and wash down sides of beaker with 2 ml of 72 per cent $HClO_4$ and 5 ml water.
6. Heat to dissolve cake.
7. Transfer into a 50-ml volumetric flask.
8. Wash beaker with 2 ml of 72 per cent $HClO_4$ and 5 ml of water.
9. Repeat washing - Step 8.
10. Combine washings with solution from Step 7.
11. Add 2.6 ml 72 per cent $HClO_4$.
12. Proceed as stated in the recommended procedure starting with Step 3.

Note: If the sample contains ferric ion, in addition to fluoride, proceed from Step 6 of the procedure after the addition of 2.3 ml of 72 per cent $HClO_4$ to Step 3 of the iron procedure and continue as stated therein. (see next page).

C. MODIFIED PROCEDURE

(Solutions Which Contain Ferric Ion)

1. Pipette sample into 50-ml beaker.
2. Add 4.3 ml of 72 per cent $HClO_4$.
3. Add 0.2 g hydrazine hydrochloride (Note A).
4. Add 10 ml of water and cover with watch glass.
5. Heat on hot plate for 10 minutes.
6. Cool in ice bath to room temperature.
7. Transfer to 50-ml volumetric flask.
8. Add 4.3 ml of 72 per cent $HClO_4$.
9. Continue as stated in the recommended procedure with Step 3.

Note A: Up to 0.5 mg of Fe(III) are readily reduced by 0.2 g of hydrazine hydrochloride. One to 5 mg Fe(III) require 0.4 g of hydrazine reagent.

D. PREPARATION OF STANDARD SOLUTION OF ZIRCONIUM

Dissolve 400 mg of zirconium metal in 4 ml of 48 per cent HF and 10 ml of 72 per cent $HClO_4$ by heating in a platinum dish to fumes of $HClO_4$. Add 10 ml $HClO_4$ and heat again to fumes of $HClO_4$. Transfer to a 2-liter volumetric flask, add 20 ml of 72 per cent $HClO_4$ and dilute to two liters with water. This solution is approximately 0.2 N with respect to $HClO_4$. Standardize gravimetrically by precipitating as the hydroxide and weighing the oxide.

E. CHLORANILIC ACID REAGENT

Chloranilic acid "practical grade" (Eastman Kodak Co.) is purified in the following manner[8]: Dissolve 8 g of the reagent in 1 liter of boiling water and filter while hot. Extract the filtrate at 50° C, in a 2-liter separatory funnel with two 200-ml portions of benzene. Discard the benzene phase. Cool the aqueous phase in an ice bath until crystallization begins. Filter off the red crystals of the reagent and wash the crystals with 3 to 10-ml portions of water. Dry the crystals at 115° C. An aqueous solution of this reagent is stable for two to three days. In the presence of perchloric acid it is stable for several weeks.

F. USE OF PHOTOMULTIPLIER ATTACHMENT

A photomultiplier attachment, specifically recommended for use in flame photometric analyses (obtained from the Beckman Instrument Inc. and described in Bulletin 282) may be used to increase the sensitivity of the Beckman DU spectrophotometer. This addition permits narrow slit widths (0.05 to 0.1 mm) with highly absorbing solutions.

In the application of this attachment three additions were found to be useful or necessary. One, a voltage tap-switch was added which made it simpler to control the voltage applied to the phototube. Previously the voltage could be adapted only by opening the box that houses the series of dry batteries and disconnecting some of the batteries. Second, an additional phototube band resistor (20 megohms resistor in parallel with 0.01 μF capacitor) was installed to reduce the galvanometer fluctuations which are experienced when the phototube is used at the maximum sensitivity. This band resistor slows down the fluctuation of the galvanometer needle, making it easier to balance the instrument and obtain a reading. Third, the most essential, was

the addition of a filter adapter in front of the tungsten light source.

The photomultiplier phototube when used at its highest sensitivity becomes also very sensitive to stray radiation. To improve the monochromaticity of the instrument, filters may be introduced which cut off most of the undesired stray radiation. As an example, in the absence of a filter, a solution of potassium dichromate showed large deviations from the linearity expected for Beer's law adherence, when measured at 353 mμ. The use of a Corning Filter No. 5970 restored this linearity.

In the study of the zirconium complexes and the additive properties of the multicomponent system a Corning Filter No. 5850 was used.

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