

QUERCETIN AS A COLORIMETRIC REAGENT
FOR ZIRCONIUM

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INTRODUCTION

Zirconium has become an important metal in atomic energy technology because of its low neutron capture cross section and other desirable physical and chemical properties. One of the consequences has been an increased interest in the analytical chemistry of zirconium.

The literature contains numerous excellent reagents and procedures for the determination of macro amounts of zirconium. The situation, however, is far from satisfactory in regard to reagents and procedures suitable for the determination of microgram amounts of zirconium. This is largely because of the difficulties presented by the constancy of the valence state of zirconium, the colorless nature of the zirconium ion and of most zirconium complexes, and the similarity of zirconium to elements of its own and neighboring groups.

This study was undertaken with two objectives in mind. The first objective was to find a very sensitive organic reagent suitable for the colorimetric or fluorimetric determination of zirconium. High selectivity in the reagent would be desirable but not at the expense of high sensitivity. The second and main objective was to develop, with the reagent, a practical method of analysis for microgram amounts of zirconium in siliceous materials.

REVIEW OF THE LITERATURE ON THE ANALYTICAL CHEMISTRY OF ZIRCONIUM

The extraordinary ability of zirconium to form precipitates or chelate complexes in strongly acid medium is a property of paramount importance in the analytical chemistry of zirconium. Numerous reagents selectively precipitate zirconium in acid solution and such reactions form the bases of many excellent gravimetric procedures for the determination of zirconium.

The classical methods of zirconium analysis with phosphate (12) (45) and with selenite (9) (10) (65) (66) (67) are still important today. Willard's method (80) involves the precipitation of zirconium from homogeneous solution either with trimethyl phosphate or metaphosphoric acid to obtain denser precipitates. Schoeller introduced tannin as a precipitant for zirconium (56) (61). This reagent separates zirconium from sesquioxides, uranium, vanadium and thorium but titanium and tin are coprecipitated. Cupferron (46) (47) (48) (72) although not selective will always be valuable in separation procedures. The cupferrate of zirconium is soluble in organic solvents (21) and this property should prove valuable for purposes of concentrating zirconium.

The precipitation of zirconium as arsenate (5) (6) (13) (51) (59) (62) has received some attention lately.

In general the same separations are obtained as in the phosphate precipitation. Two precipitations are necessary when Bi, Be, Th, Sn, and Ti are present. On ignition arsenic is reduced (by the filter paper) and volatilized and the ignited precipitate can be weighed as ZrO_2 . Gump (30) obtains a more crystalline arsenate precipitate by forming arsenate ion in solution through oxidation of arsenite.

Like arsenic acid, organic derivatives of arsenic acid react with zirconium salts in acid solutions (2) (3) (8) (11) (15) (24) (36) (37) (58) (64). The ability of these compounds to precipitate zirconium is due to the salt forming group $-AsO(OH)_2$. The arsonic acids are capable of precipitating smaller amounts of zirconium, and for this reason are more useful, than arsenic acid. In general the arsonic acids are useful precipitants for Hf, Zr, Cb, and Ta. Titanium, Th, Sn, and W usually interfere, while Bi and Sb may interfere at low acidities. Propylarsonic acid (3) (24) is probably the best of the many arsonic acids proposed. Few zirconium reagents compare with propylarsonic acid in regard to specificity. This compound can be used to determine zirconium in the presence of Sn, Th, Ti, Mn, Ni, Fe, Al, Ce, V, Cr, Cu, Mg, Zn, U, Mo, Co, Be, W, and Cd. Kolthoff (39) uses m-nitrophenylarsonic acid and determines zirconium as well as U, Th, and Sn by amperometric titrations.

Colored zirconium precipitates are obtained by

using azo derivatives of benzenearsonic acid. The color of the zirconium salt usually differs from that of the azo arsonic acid and thus colorimetric procedures are possible.

In recent years considerable attention has been paid to the study of organic acids as precipitants for zirconium (55) (57) (60) (74) (75) (76) (77) (78). These reagents are very useful for separating zirconium from di and trivalent metals such as Mg, Fe, Al, and rare earths. Usually Ti, Th, Sn, Ce^{+4} interfere, although such interference for many acids (60) (74) (75) can be eliminated by double precipitation of zirconium. At lower acidities many of these reagents are useful precipitants for thorium and other quadrivalent elements. Mandelic acid and other glycolic acid derivatives (4) (23) (31) (32) (35) (40) (54) are especially important and have received much favorable attention because of their specificity toward zirconium. For example, in the mandelic acid procedure of Kumins (40) (54) Ti, Fe, V, Al, Cr, Th, Ce, Sn, Ba, Ca, Cu, Bi, Sb, or Cd do not interfere. The zirconium precipitating action of the (-CHOH-COOH) group is retained even after the introduction of an azo group into the mandelic acid molecule (53).

Sodium flavianate (18) is quite a specific reagent for precipitation of zirconium. Thorium, Ti, Y, La, Ce, Pr, Nd, Sm, Al, Fe, Cr, U, Be, Mn, Zn, Hf, Co, Cd, Cu, Sn, Bi, Mg, Ba, Ca, V, W, and Mo are not precipitated by this reagent.

The situation in regard to methods for the determination of small amounts of zirconium is not very satisfactory. Although numerous reagents have been proposed for the detection of zirconium only a few have been developed into quantitative methods. The hydroxyanthraquinones (17) form colored lakes with zirconium in acid solution. Liebhafsky and Winslow (19) (44) describe the use of alizarin, purpurin, and quinalizarin for the determination of small amounts of zirconium. The zirconium-alizarin lake is formed in alcoholic solution. Alizarin Red S (26) (29) (49) (69) (79) is probably the most important reagent for the colorimetric determination of zirconium. The zirconium lake with alizarin sulfonic acid is formed in aqueous medium generally in 0.1 to .2N HCl. Small amounts of ferric iron can be tolerated, but larger amounts must be removed or reduced to the ferrous state. One serious disadvantage of the Alizarin Red S color reaction is its relatively low sensitivity. The reagent 5-chlorobromamine acid (1-amino-5-chloro-4-bromo-2-anthraquinone sulfonic acid) was described by Yoe and Overholser (83) for detecting zirconium by the spot test technique. This reagent is not sensitive to small zirconium concentrations.

p-Dimethylaminoazophenylarsonic acid is second in importance to Alizarin Red S as a colorimetric reagent for zirconium (33) (52) (68). The procedures are indirect and involve precipitating zirconium with the arsono-azo dye, washing and decomposing the precipitate with ammonium

hydroxide and then measuring the absorption of the dye solution released. Stehney and Safranski (58) determined microgram amounts of zirconium in this manner. Titanium and tungsten interfere seriously and in spite of claims to the contrary, hydrogen peroxide cannot be used to eliminate the interferences because it destroys the reagent. Other elements such as U, Ta, Sn, Sb, Mo, and Sc interfere. Indirect procedures have obvious disadvantages. Also disturbing is the fact that the ratio of reagent to zirconium in the precipitate can be 1:1 or 2:1 depending on the concentration of zirconium.

Kuznetsov (41) has shown that o-hydroxyazo compounds having an arsono group ortho to the azo group, as in the structure $\text{AsO}(\text{OH})_2 - \text{N} = \text{N} - \text{C}_6\text{H}_3(\text{OH})$ react in acid medium with zirconium to yield a precipitate and simultaneous change in color. Thorium, Hf, Nb, Ta, Ti, and U interfere. These reagents lend themselves to direct colorimetric analysis and should be valuable for the determination of some of these elements. Kuznetsov (42) (43) describes 2-hydroxy-5-methylazobenzene-4'-sulfonic acid as a reagent for zirconium. No articles on this reagent have appeared since the original publications.

Various azo derivatives of mandelic acid were synthesized by Oesper and co-workers (53) in a search for a reagent producing a colored zirconium precipitate. m-Azo- β -naphtholmandelic acid was the best of those synthesized. The similarity of the color of the reagent to

its zirconium precipitate and the solubility characteristics of the m-azo- β -naphtholmandelic acid made it useful only with the Yagoda confined spot testing method.

Thamer, Voigt and others proposed chloranilic acid (2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone) (20) (70) (71) as a colorimetric reagent for zirconium. The reagent is not sensitive and U, Th, Sn, Sb, W, Mo, Cd, Ag, Tl, and Fe⁺³ interfere.

Only very few publications have appeared on the determination of zirconium by fluorescence reactions. Only one method useful for quantitative analysis has been developed. Flavonol (3-hydroxyflavone) (1) was found by Alford and co-workers to give a very sensitive fluorescence reaction with zirconium and the reagent was applied to the determination of zirconium in glass sands, clays, and refractories. Only hafnium and to a lesser extent aluminum fluoresce in .2N H₂SO₄ but iron and large concentrations of other elements may quench the fluorescence of zirconium. Microgram amounts of zirconium may be determined after the separation of zirconium from aluminum with sodium hydroxide and the removal of other possible interfering elements by electrolysis in a Melaven cell. Morin (25) and 8-hydroxyquinoline (25) are about the only other reagents reported to give fluorescent complexes with zirconium but no quantitative methods have been developed with these reagents.

QUERCETIN AND ITS ANALYTICAL APPLICATION

The difficulty of obtaining pure quercetin (3,3',4',5,7-pentahydroxyflavone) in the past has been a serious limitation to the study and use of quercetin as an analytical reagent. Today numerous chemical distributors can supply quercetin of such excellent quality that it requires no additional purification. Earlier workers have reported on the absorption spectrum of quercetin which can be used for its characterization (27) (28) (63). More recent data on the absorption spectrum of quercetin are given by Gage and co-workers (22), who also describe a method for the purification and quantitative estimation of micro amounts of quercetin by paper partition chromatography. Ice and Wender (34) have published a method for the separation of milligram amounts of closely related flavonoid compounds by adsorption onto magnesol from anhydrous acetone solution, and elution with a solution of ethyl acetate saturated with water. In a private communication Wender has disclosed that the method has been extended to the purification of gram amounts of commercial quercetin. Crude quercetin can be prepared from Lemon Flavin according to the general directions given by Morrow and Sandstrom (50).

The analytical applications of quercetin have been few in number. Kocsis (38) used quercetin for the detection of iron and uranium by the spot test technique.

Davydov and Devekki (16) used quercetin for the fluorimetric determination of a few micrograms of aluminum in solutions buffered at pH of 4.8. Willard and Horton (81) studied a number of reagents as possible indicators for detecting the end point in the titration of fluoride with thorium nitrate. Morin and quercetin were found to be the best fluorescent indicators. A procedure for the photo-fluorometric titration of fluoride with quercetin as the fluorescent indicator is also described by the same writers (82). In general, the same ions interfere in this photo-fluorometric method as in the visual Alizarin Red S method. Tomicek and Holecek (73) have used quercetin for gravimetric estimation of niobium and tantalum. Quercetin forms a red precipitate with niobium and an orange precipitate with tantalum in strongly acid solutions.

EXPERIMENTAL

INVESTIGATION OF ORGANIC REAGENTS FOR THE DETECTION OF ZIRCONIUM

The initial part of this research was concerned with the investigation of various organic compounds in search of a colorimetric or fluorimetric reagent for zirconium. In the course of this study over one hundred compounds were examined. A number of compounds are reported in the literature to give reactions with zirconium. These and their related compounds were tested first. Other compounds having different but characteristic structural and functional groups were then examined. When a reaction was obtained other compounds with the same reactive atomic groupings were studied in an attempt to improve on the results given by the parent compound. Several of these compounds were prepared specially by commercial firms and by the University of Maryland. The compounds tested are listed in Table 1. These include monoazo and diazo dyes, anthraquinones, quinones, quinolines, oximes, aromatic hydroxy-ketones, and various other compounds of interest.

Each compound was tested at 5 pH levels. The zirconium solution, 1 ml. = 2×10^{-4} ZrO₂, was prepared daily from a stronger stock solution by dilution with water. The stock solution was prepared by dissolving zirconyl nitrate in hot (1 + 1) HCl and diluting with water to form

a (1 + 49) HCl solution containing 1.0 mg. ZrO_2 per ml. The reagent was dissolved in water when possible, otherwise an alcoholic solution was used. In each case the concentration of the reagent was approximately 0.1%. The zirconium solution was added first, followed by the necessary reagents to give the desired acidity and then by the organic reagent solution. The final volume was always adjusted to 10 ml. in 30 ml. Pyrex test tubes. Usually 0.3 ml. of reagent solution was used although this was varied in the case of dyes when the resulting solution was too lightly or too deeply colored. Reagent blanks were run for each test condition. These were compared with the appropriate zirconium test solutions to establish whether or not a color or fluorescent reaction had occurred. Long wave ultraviolet light (3650A) was used to excite the fluorescence and observations were made in a view box. In order to attain the pH desired the specified amounts of the reagents indicated below were added in the test solutions:

1. pH 1 : 0.15 ml. (1 + 4) H_2SO_4
2. pH 1 : 0.45 ml. (1 + 4) HCl
3. pH 2.9: 0.50 ml. (1 + 9) acetic acid
4. pH 4.7, Buffered: 0.2 ml. of a solution
1M in NaOAc and 1M in HOAc
5. pH 11 : 1 ml. of a solution containing
10 g. K_2CO_3 and 5 g. Na_2SO_4 per 100 ml.
6. pH 13 : 1 ml. of 2.5N NaOH

Sulfuric acid was used in one of the test solutions in order to determine the effect of sulfate on the reaction. The mixed carbonate-sulfate solution was included because zirconium was found to be soluble in this medium.

Several compounds gave fluorescent tests with zirconium in acid medium. Benzoyl carbinol was the only reagent that reacted in alkaline solution, a slight fluorescence being obtained with zirconium from carbonate-sulfate medium. Resacetophenone, 2,4-dihydroxybenzaldehyde, o-hydroxyacetophenone, 2-carboxy-2'-hydroxy-3'-methylbenzophenone each gave a greenish blue fluorescence in acid media which was more intense at pH values of 3 to 5. The sensitivities of the reactions were not as high as were sought and the compounds were not studied further. These compounds all contain the grouping $\begin{array}{c} \text{OH} \quad \text{O} \\ \diagup \quad \diagdown \\ \text{C} \end{array}$ and this may be of theoretical importance in regard to zirconium specificity. It is interesting to note that 2,4 dihydroxybenzoic acid did not give a fluorescent reaction with zirconium. The carbonyl group in this compound is not free to react, probably because of resonance effects.

8-Hydroxyquinoline gave a fluorescent reaction in acetic acid and buffered solutions. Quercetin and morin gave a green fluorescence with zirconium at acidities greater than 0.1N but the sensitivity for quercetin is too low to be of analytical importance. The fluorescence with morin was very sensitive, especially in 2N HCl and

0.5N H_2SO_4 . Chrome Fast Garnet RF gave a good red fluorescence, especially in 0.5N HCl and in 0.1N H_2SO_4 . Calco-dur GL Conc. gave best fluorescence in buffered acetate solution but the intensity was less than that given by either morin or Chrome Fast Garnet RF.

Numerous compounds gave color reactions with zirconium in the various acid test conditions but none reacted in alkaline medium. The following anthraquinones produced color compounds with zirconium: Quinizarin, anthrarufin, chrysazin, sodium alizarin sulfonate, purpurin, quinalizarin, and quinizarin-2-sulfonic acid. All were about as sensitive toward zirconium as sodium alizarin sulfonate with the possible exception of quinalizarin which was slightly more sensitive. Among the other anthraquinones that reacted it is doubtful whether any would be much of an improvement over the alizarin sulfonate. The other anthraquinones, Table 1, gave no reaction, although zirconium caused a decrease in the intensity of the original color of several of these dyes.

The following monoazo dyes reacted: Lithosol Claret B, 2-hydroxy-3,5-dinitrobenzene-azo-p-cresol, Chrome Fast Garnet R, Alizarine Black, Pontacyl Fast Red Extra Conc., Comacid Fast Red A, FD & C Red No. 2, 2-hydroxy-3,5-dinitrobenzene-azo-p-nitrophenol, 2-hydroxy-3,5-dinitrobenzene-azo-p-cresol, 2-hydroxy-3,5-dinitrobenzene-azo-beta-naphthol, and 2-hydroxy-5-nitrobenzene-azo-beta-naphthol.

Alizarine Black and Chrome Fast Garnet R appeared to be the most sensitive of the reagents in this group and possibly could be useful analytical reagents for zirconium.

Calcodur Orange GL Conc. and Alizarine Black SAE were the only diazo dyes giving color tests with zirconium. The sensitivity of each of these dyes was best in buffered solution but too low to be of value.

Gallein, gallocyanine, hematoxylin, aurintricarboxylic acid, quercetin, and morin were the only other reagents to give color reactions with zirconium. The reactions with gallein and gallocyanine were best at lower acidities (pH 3-5) while those for morin and quercetin were better at higher acidities (0.1N for H_2SO_4 and 0.1N to 1N for HCl). Quercetin appeared to be the most sensitive of all the reagents tested.

At the conclusion of this preliminary work, the search for a zirconium reagent narrowed down to the following: morin by fluorescence or color; Chrome Fast Garnet R; Alizarine Black; and quercetin by color. After further studies on these reagents it was decided to concentrate on quercetin as a colorimetric reagent for zirconium. Quercetin is the only reagent combining the most desirable properties for a colorimetric reagent: High sensitivity, a nearly colorless blank, stable color over a wide acidity range, and availability in a pure state.

Table 1
Compounds Tested for Zirconium Reactivity

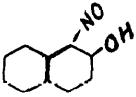
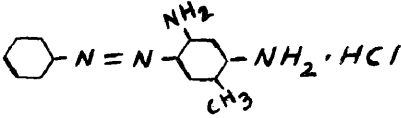
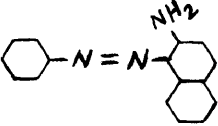
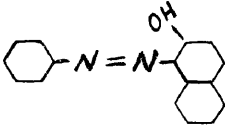
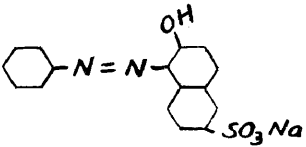
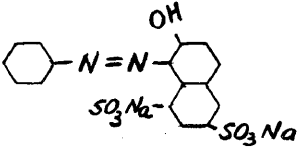
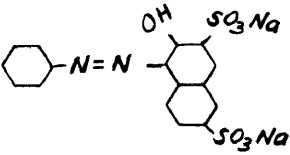
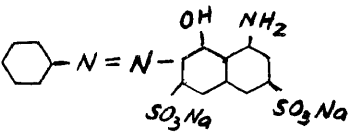
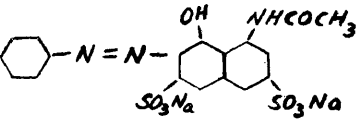
Color Index	Name	Formula
2	α -Nitroso- β -Naphthol	
21	Dupont Chrysoidene R	
22	F D and C Yellow No. 3	
24	Oil Orange 7078V	
26	Croceine Orange Y Conc.	
27	Dupont Orange G	
29	Fast Fuchsine G	
30	D and C Red No. 33	
31	Pontacyl Carmine 2 G Conc. 150%	

Table 1 (Cont.)

Compounds Tested for Zirconium Reactivity

Color Index	Name	Formula
35	Brilliant Lake Red N	
40	Pontachrome Yellow 3RN	
44	p-nitrobenzene-azo-β-naphthol	
53	Pontacyl Violet 4BSN	
68	Hiltonil Fast Scarlet G Base	
69	D and C Red No. 35	
73	Brilliant Oil Scarlet B Conc.	
79	Calcocid Scarlet 2R	
80	F D and C Red No.1	

Table 1 (Cont.)

Compounds Tested for Zirconium Reactivity

Color Index	Name	Formula
88	Lithosol Claret B	
90	Pontacyl Violet 6R Conc. 150%	
104	2-hydroxy-3,5-dinitrobenzene-azo-p-cresol	
118	Hiltosal Fast Scarlet R Salt	
148	Tropaeoline O	
151	D and C Orange No. 4	
153	Azo Fuchsine GA	
163	Lithosol Rubine B Powder	
165	D and C Red No. 8	

Table 1 (Cont.)

Compounds Tested for Zirconium Reactivity

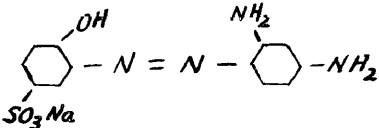
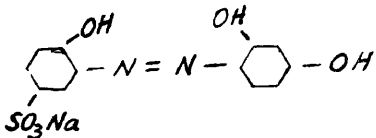
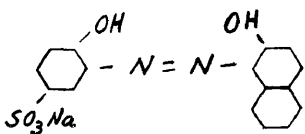
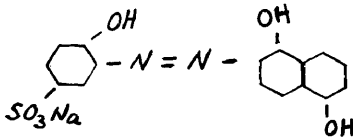
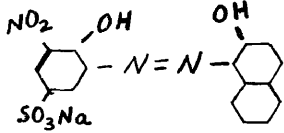
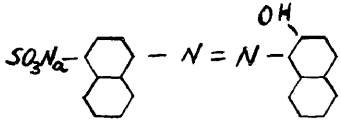
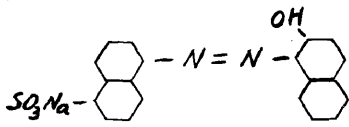
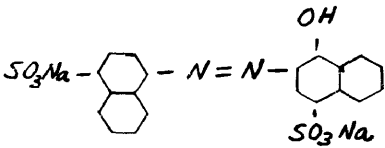
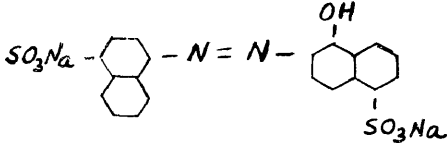
Color Index	Name	Formula
167	Calchochrome Brown 2R	
168	Chrome Fast Garnet R	
169	Superchrome Violet B	
170	Diamond Black	
172	Alizarine Black	
176	Pontacyl Fast Red Extra Conc.	
177	Comacid Fast Red A	
179	Calcocid Rubine XX Conc.	
180	Calcochrome Blue F4B	

Table 1 (Cont.)

Compounds Tested for Zirconium Reactivity

Color Index	Name	Formula
183	Calcocid Scarlet 4RN	
184	F D and C Red No.2	
185	Comacid Brilliant Scarlet 3R	
189	D and C Red No. 11	
201	Superchrome Blue B Extra Conc.	
202	Pontachrome Blue Black R	
208	Pontacyl Fast Blue R	
209	Calcocid Wool Blue B Conc.	
214	Barium Salt of Red Lake D	

Table 1 (Cont.)
Compounds Tested for Zirconium Reactivity

Color Index	Name	Formula
216	Pontachrome Red B	
225	Calcomine Brilliant Pink SX Double Cond	
234	Calcocid Brown Y	
275	Calcocid Milling Red 3R Conc.	
336	Alizarine Black SEA	
376	Direct Rubine Conc.	
394	Erie Violet 3R	
420	Erie Fast Brown 3RB	
640	F D and C Yellow No. 5	

Table 1 (Cont.)

Compounds Tested for Zirconium Reactivity

Color Index	Name	Formula
653	Calcodur Orange GL. Conc.	
	p-nitrobenzene-azo-orcinol	
	p-nitrobenzene-azo-resorcinol	
	2-hydroxy-3,5-dinitrobenzene-azo-p-nitrophenol	
	2-hydroxy-3,5-dinitrobenzene-azo-α-naphthol	
	2-hydroxy-5-nitrobenzene-azo-α-naphthol	
	2-hydroxy-5-sodium sulfonatebenzene-azo-α-naphthol	
	2-hydroxy-3,5-dinitrobenzene-azo-β-naphthol	
	2-hydroxy-5-nitrobenzene-azo-β-naphthol	

Table I (Cont.)

Compounds Tested for Zirconium Reactivity

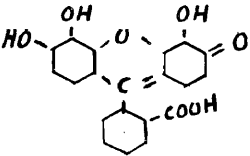
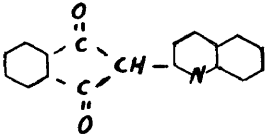
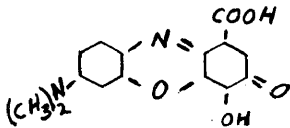
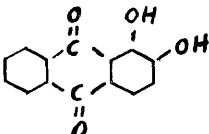
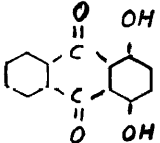
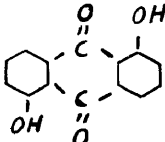
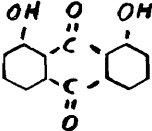
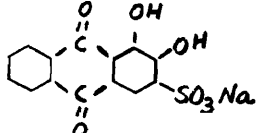
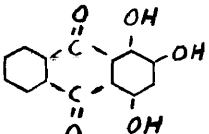
Color Index	Name	Formula
781	Gallein	
801	Quinoline Yellow Conc.	
883	Gallocyanine	
1027	Alizarin	
1028	Quinizarin	
1029	Anthrarufin	
1030	Chrysazin	
1034	Sodium Alizarin Sulfonate	
1037	Purpurin	

Table 1 (Cont.)

Compounds Tested for Zirconium Reactivity

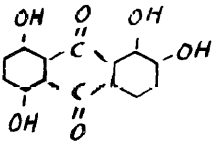
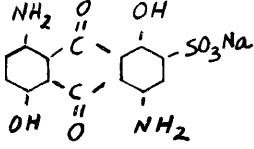
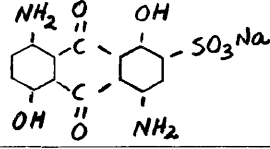
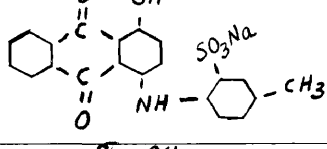
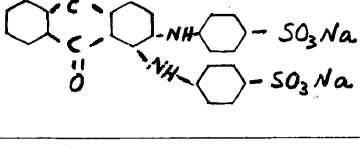
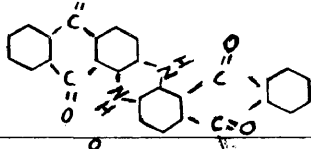
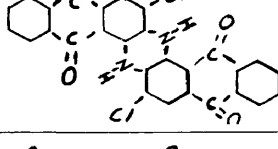
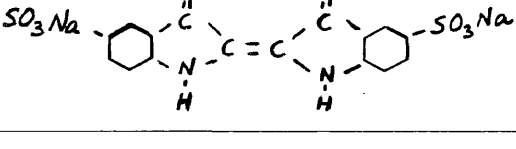
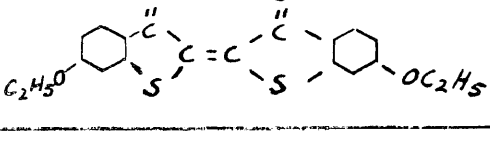
Color Index	Name	Formula
1045	Quinalizarin	
1053	Alizarine Blue WSA	
1054	Alizarine Blue SAP Conc.	
1073	Hastings Light Fast Violet IRS	
1085	Du Pont Alizarine Blue Black B	
1106	Ponsol. Blue RP Triple Powder	
1113	Cibanone Blue GL. Powder	
1180	F D and C Blue No.2	
1217	Algol Orange RFA Powder	

Table 1 (Cont.)
Compounds Tested for Zirconium Reactivity

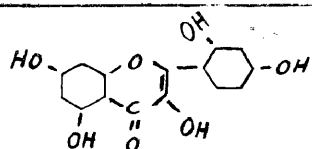
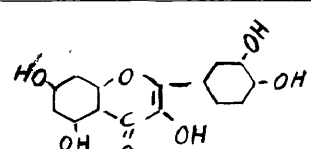
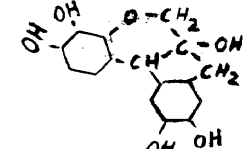
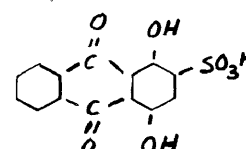
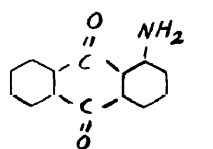
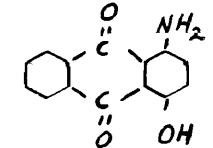
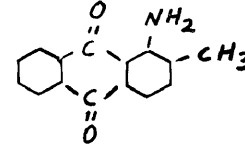
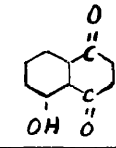
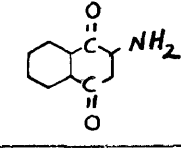
Color Index	Name	Formula
1232	Morin	
1233	Quercetin	
1246	Hematoxylin	
	Quinizarin-2-sulfonic acid	
	1-Amino-anthraquinone	
	1-Amino-4-hydroxy-anthraquinone	
	1-Amino-2-methyl-anthraquinone	
	5-hydroxy-1,4-naphthoquinone	
	2-Amino-1,4-naphthoquinone	

Table 1 (Cont.)

Compounds Tested for Zirconium Reactivity

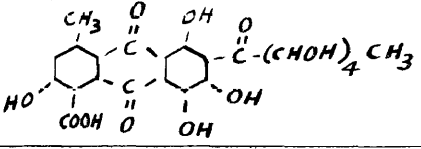
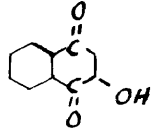
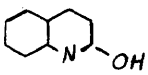
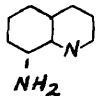
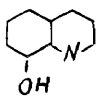
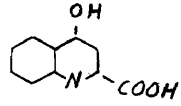
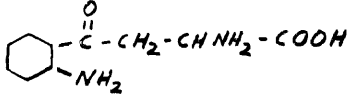
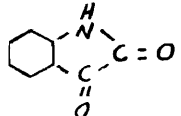
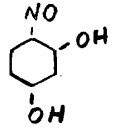
Color Index	Name	Formula
	Carminic acid	
	Phthiocol	
	2-Hydroxyquinoline	
	8-Aminoquinoline	
	8-Hydroxyquinoline	
	Kynurenic acid	
	Kynurenine sulfate	
	Isatin	
	Nitrosoresorcinol	

Table 1 (Cont.)

Compounds Tested for Zirconium Reactivity

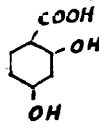
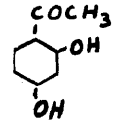
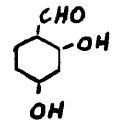
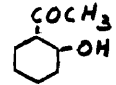
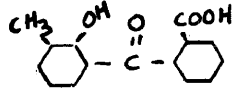
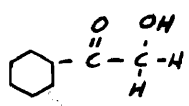
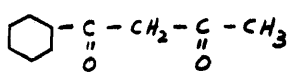
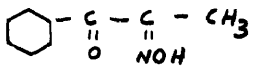
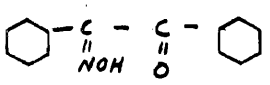
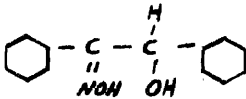
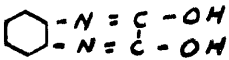
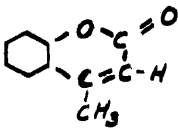
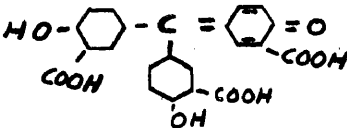
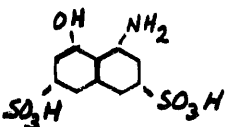
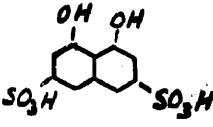
Color Index	Name	Formula
	2-4-dihydroxy-benzoic acid	
	Resacetophenone	
	2,4-dihydroxy-benzaldehyde	
	o-Hydroxyaceto-phenone	
	2-Carboxy- 2'hydroxy- β'-methylbenzo-phenone	
	Benzoyl carbinol	
	Benzoyl acetone	
	α-Iso-nitroso-propio-phenone	
	α-Benzilmcnoxime	

Table 1 (Cont.)

Compounds Tested for Zirconium Reactivity

Color Index	Name	Formula
	α -Benzoinoxime	
	2,3-Dihydroxy-quinoxaline	
	β -Methyl Umbelliferone	
	Aurintricarboxylic acid	
	1-Amino-8-naphthol-3,6-disulfonic acid	
	1,8-Dihydroxy-naphthalene-3,6-disulfonic acid	

FACTORS AFFECTING THE ZIRCONIUM-QUERCETIN COLOR SYSTEM

Various factors affecting the zirconium-quercetin color system were studied to establish optimum working conditions. Preliminary experiments indicated that a certain amount of alcohol was necessary to prevent the precipitation of quercetin and this variable was included in the study. In the experiments, the solutions were always made to a total volume of 25 ml. The order of addition of the reagents was always the same. The zirconium solution was added first, acid second, alcohol third, and an alcoholic solution of quercetin last. Optical densities were determined with a Beckman Spectrophotometer, Model DU, using one centimeter cells and distilled water as reference solution. The slit width was always 0.05 mm. except for the spectral transmittancy data below 420 m μ where 0.1 mm. was used.

The spectral transmittancy data for the reagent blank and 30 micrograms of ZrO_2 are given in Fig. 1. The solutions used were 0.5N in HCl and contained 3 mg. of quercetin and 8 ml. of alcohol. The optimum wave length was taken as 440 m μ because here the absorption given by the blank is small and that by zirconium still large. In the work that follows, all optical densities were measured at 440 m μ .

Fig. 2 illustrates the effect of alcohol concentration on the optical density of 54.4 μ ZrO_2 . The solutions were 0.5N in HCl and contained 3 mg. of quercetin.

The optical density increases slightly with increase in alcohol concentration.

A precipitate of quercetin was obtained almost immediately from solutions containing less than 6 ml. of alcohol; with 6 ml. of alcohol some quercetin precipitated after ten hours. It is desirable to keep the alcohol concentration to a minimum because of the smaller solubility of salts in alcoholic media. For this reason 8 ml. of alcohol in 25 ml. of solution was taken as optimum and maintained in subsequent work.

The effect of acid concentration on the zirconium-quercetin color system is illustrated in Fig. 3. Each 25 ml. of solution contained 54.4% ZrO_2 , 8 ml. of alcohol, 3 mg. of quercetin and different amounts of hydrochloric acid. The color is almost independent of acid concentration in the region from 0.1N to 1N. The density of the reagent blank increases slightly with increase in acidity while a slight increase and then decrease in density is noted for the zirconium solution. The reagent blank increases sharply in density for acid concentrations above 1N and reaches a value of over 0.2 density units at 3N. On the basis of the foregoing the optimum acidity was taken as 0.5N.

The reaction can also be carried out in nitric or perchloric acid solution as comparable data are obtained. Hydrochloric acid is preferable to perchloric acid because of the greater stability of zirconium in hydrochloric acid solution (14). For example it was found that standard

perchloric acid solutions of zirconium "lose" strength rapidly if the acid concentration is below 20% by volume. Nitric acid is inferior to hydrochloric acid because of its tendency to oxidize quercetin. This effect is serious at elevated temperatures for solutions of greater acidity than 0.5N. The sensitivity of the zirconium-quercetin color system is greatly diminished in sulfuric acid medium probably because of the complexing action of sulfate with zirconium.

The data in Fig. 4 and Tables 2 and 3 were obtained by keeping the zirconium concentration fixed at two levels (20% and 54.4% ZrO_2) and varying quercetin concentration in each series. The densities shown are corrected for the densities of blanks containing the same amounts of quercetin. Three mg. of quercetin for 25 ml. of solution was taken as the optimum concentration of quercetin. In Fig. 5 and Tables 4 and 5 the quercetin concentration was kept fixed at two levels (150% and 300% of quercetin) and the zirconium concentration was varied. This same general procedure was used in obtaining the data for Fig. 6 and Table 6 except that the quercetin was maintained constant at 3 mg. Interpretation of the nature of these curves is given later.

Data for the working curve are given in Fig. 7 and Table 7. These data were obtained using the optimum conditions previously established. The solutions were 0.5N in HCl and contained 8 ml. of alcohol, and 3 mg. of quercetin in a total volume of 25 ml. A straight line relationship

between optical density and micrograms of ZrO_2 is shown up to 60 micrograms of ZrO_2 . Solutions containing from 60 to 150 micrograms of ZrO_2 deviated slightly from the Beer-Lambert-Bouguer Law but their optical densities are reproducible. The region from 0 to 10 micrograms of ZrO_2 was examined in great detail for any deviation from the straight line relationship but none was found.

The solutions, containing up to 150 γ ZrO_2 , were allowed to stand for 24 hours after which time the densities were redetermined. The maximum change in density was found to be 0.003. The sensitivity of the zirconium-quercetin color reaction is 0.004 γ ZrO_2/cm^2 .

Table 2

Effect of Quercetin Concentration

(Zirconium fixed at 0.163 microgram mol ZrO_2)

Quercetin \times Mols	Mol Ratio Q/Zr	Optical Density	Corrected Density
0.0326	0.200	0.008	0.008
0.0652	0.400	0.018	0.018
0.0978	0.600	0.028	0.028
0.130	0.800	0.034	0.034
0.163	1.00	0.042	0.042
0.196	1.20	0.051	0.051
0.228	1.40	0.057	0.057
0.261	1.60	0.062	0.062
0.326	2.00	0.069	0.068
0.652	4.00	0.098	0.096
1.30	8.00	0.136	0.131
1.96	12.00	0.158	0.151
3.26	20.0	0.184	0.172
6.52	40.0	0.219	0.195
9.78	60.0	0.242	0.206

Table 3

Effect of Quercetin Concentration

(Zirconium fixed at 0.442 microgram mol ZrO_2)

Quercetin γ Mols	Mol Ratio Q/Zr	Optical Density	Corrected Density
0.0980	0.217	0.048	0.048
0.192	0.434	0.096	0.096
0.288	0.651	0.144	0.144
0.384	0.870	0.176	0.176
0.470	1.06	0.207	0.207
0.576	1.30	0.233	0.233
0.768	1.74	0.276	0.276
0.960	2.17	0.302	0.302
1.15	2.61	0.324	0.323
2.30	5.22	0.417	0.409
3.84	8.70	0.478	0.465
7.68	17.4	0.548	0.525
11.5	26.1	0.596	0.554
17.3	39.2	0.638	0.575

Table 4

Effect of Zirconium Concentration

(Quercetin fixed at 0.497 microgram mol)

ZrO ₂ × Mols	Mol Ratio Q/Zr	Optical Density
0.0441	11.3	0.026
0.0883	5.63	0.057
0.114	4.36	0.072
0.145	3.42	0.087
0.177	2.81	0.106
0.221	2.25	0.129
0.265	1.88	0.148
0.309	1.61	0.170
0.354	1.40	0.188
0.396	1.25	0.202
0.442	1.13	0.220
0.617	0.805	0.261
0.883	0.563	0.283
1.33	0.375	0.298

Table 5

Effect of Zirconium Concentration
(Quercetin fixed at 0.994 microgram mol)

ZrO ₂ % Mols	Mol Ratio Q/Zr	Optical Density
0.0441	22.5	0.038
0.0883	11.2	0.065
0.177	5.61	0.134
0.265	3.75	0.198
0.354	2.81	0.247
0.442	2.25	0.308
0.529	1.88	0.357
0.617	1.61	0.398
0.794	1.25	0.472
0.969	1.03	0.522
1.15	0.867	0.552
1.33	0.750	0.572
1.50	0.663	0.588
1.77	0.562	0.595

Table 6

Effect of Zirconium Concentration
(Quercetin fixed at 9.94 microgram mols)

ZrO ₂ γ Mols	Mol Ratio Q/Zr	Optical Density	Corrected Density
0.081	123	0.137	0.104
0.162	61.4	0.248	0.215
0.243	40.9	0.347	0.314
0.324	30.7	0.450	0.417
0.406	24.5	0.545	0.512
0.487	20.4	0.644	0.611
0.526	18.9	0.692	0.659
0.567	17.5	0.740	0.707
0.608	16.3	0.778	0.745
0.689	14.4	0.870	0.837
0.770	12.9	0.975	0.942
0.812	12.2	1.010	0.977
1.015	9.80	1.220	1.187
1.216	8.18	1.430	1.397

Table 7
Working Curve

ZrO ₂ δ	Optical Density
0.00	0.033
0.20	0.035
0.50	0.037
1.00	0.046
2.00	0.057
3.00	0.064
4.00	0.078
5.00	0.090
10.00	0.137
20.00	0.245
30.00	0.347
40.00	0.450
50.00	0.545
60.00	0.644
65.00	0.692
70.00	0.740
75.00	0.778
85.00	0.870
95.00	0.975
100.0	1.010
125.0	1.220
150.0	1.430

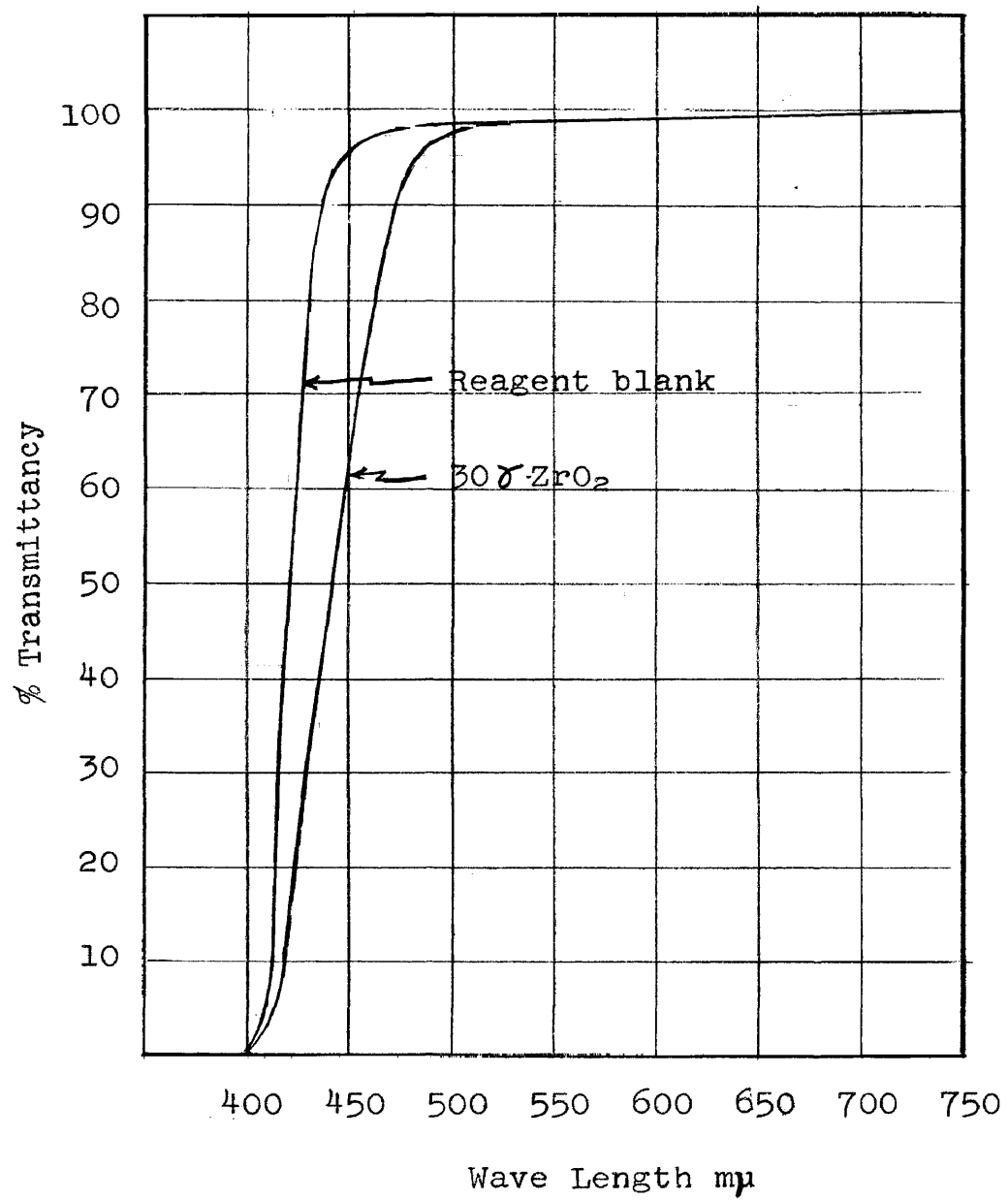


Fig.1. Spectral transmittancy curve

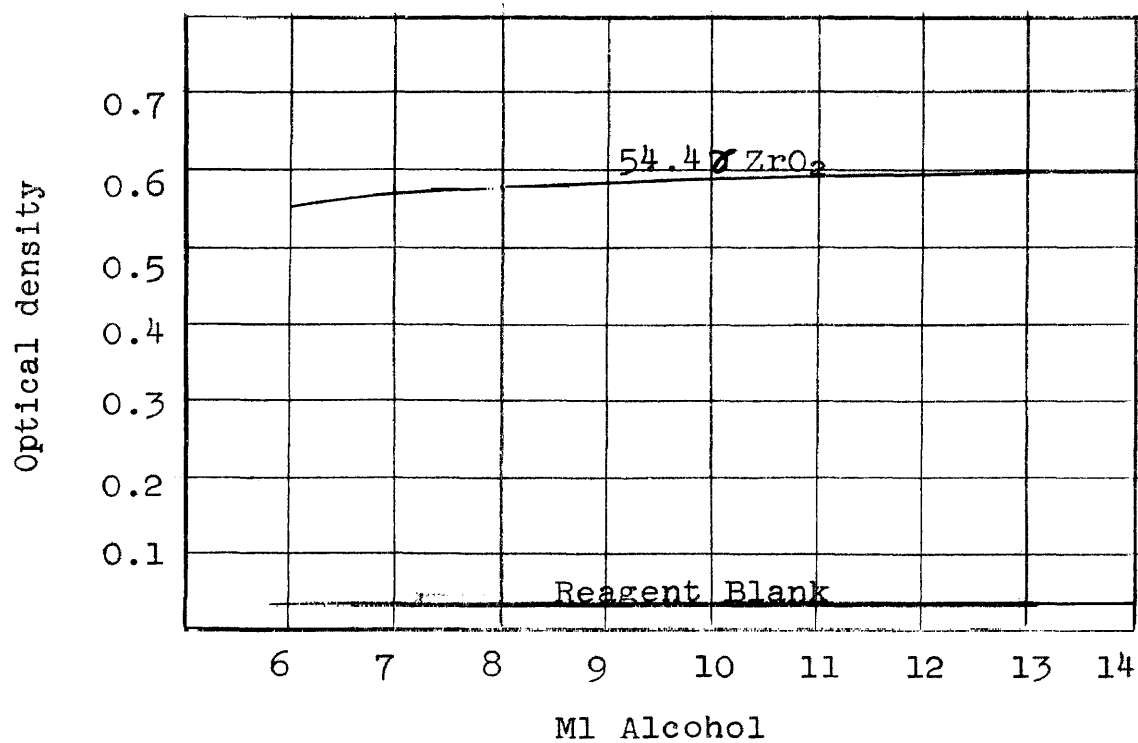


Fig. 2. Effect of Alcohol Concentration

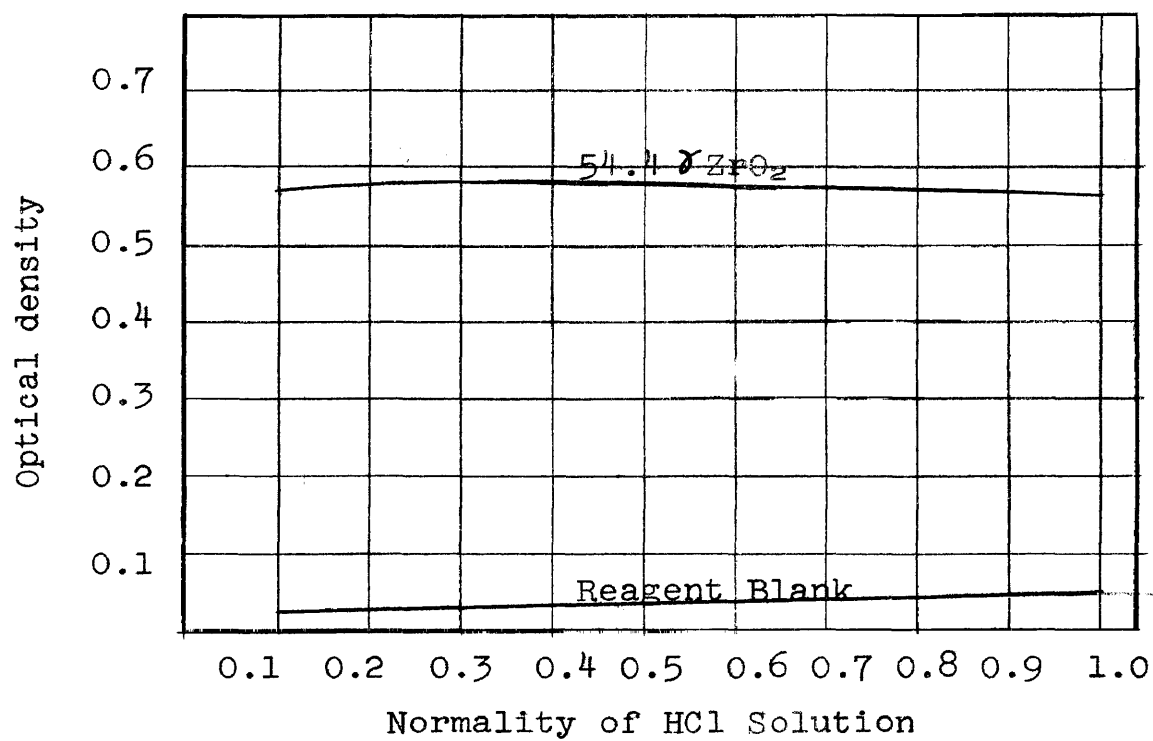


Fig. 3. Effect of Acidity

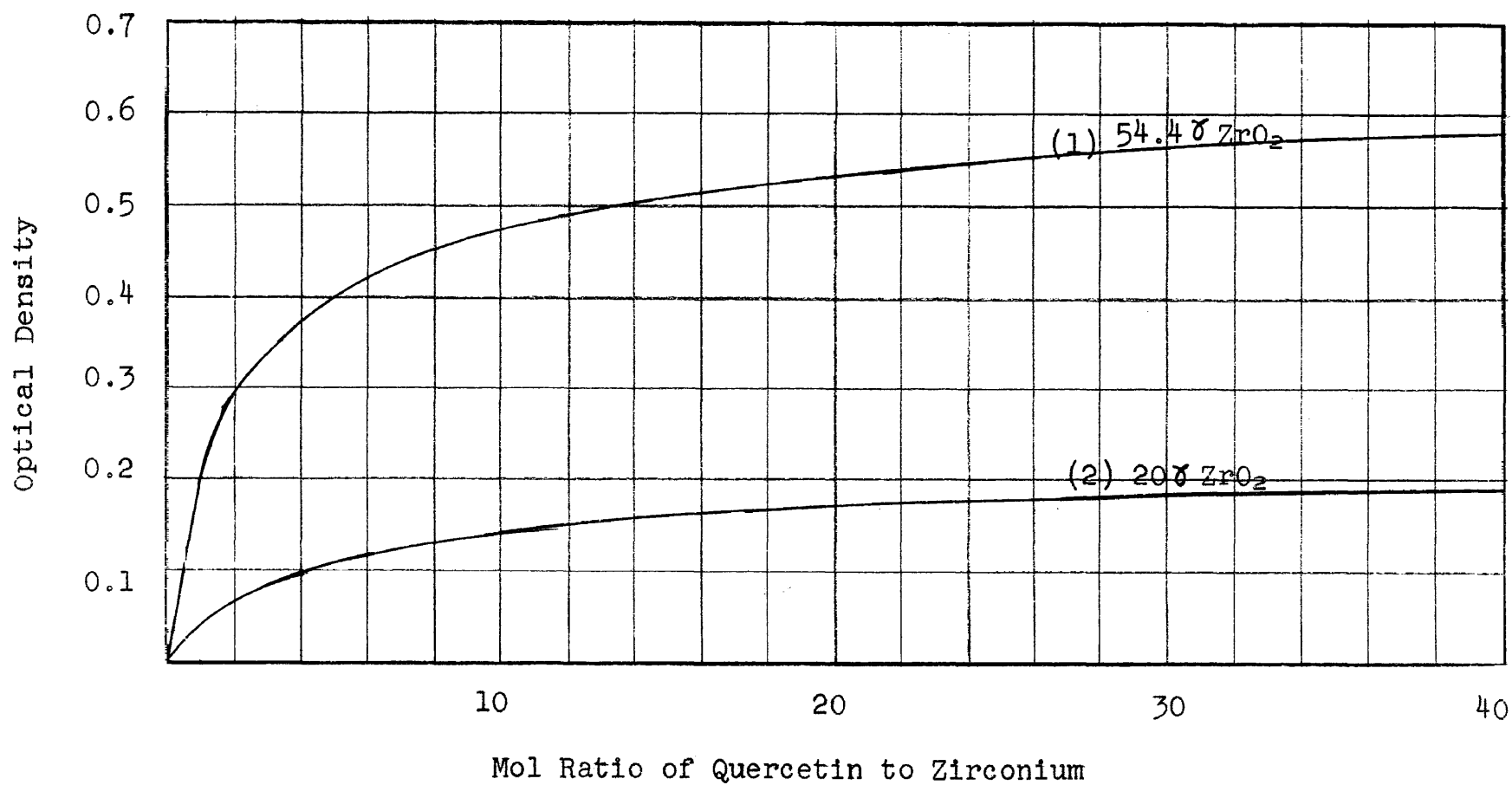


Fig. 4. Effect of Quercetin Concentration (Zirconium Conc. Fixed)

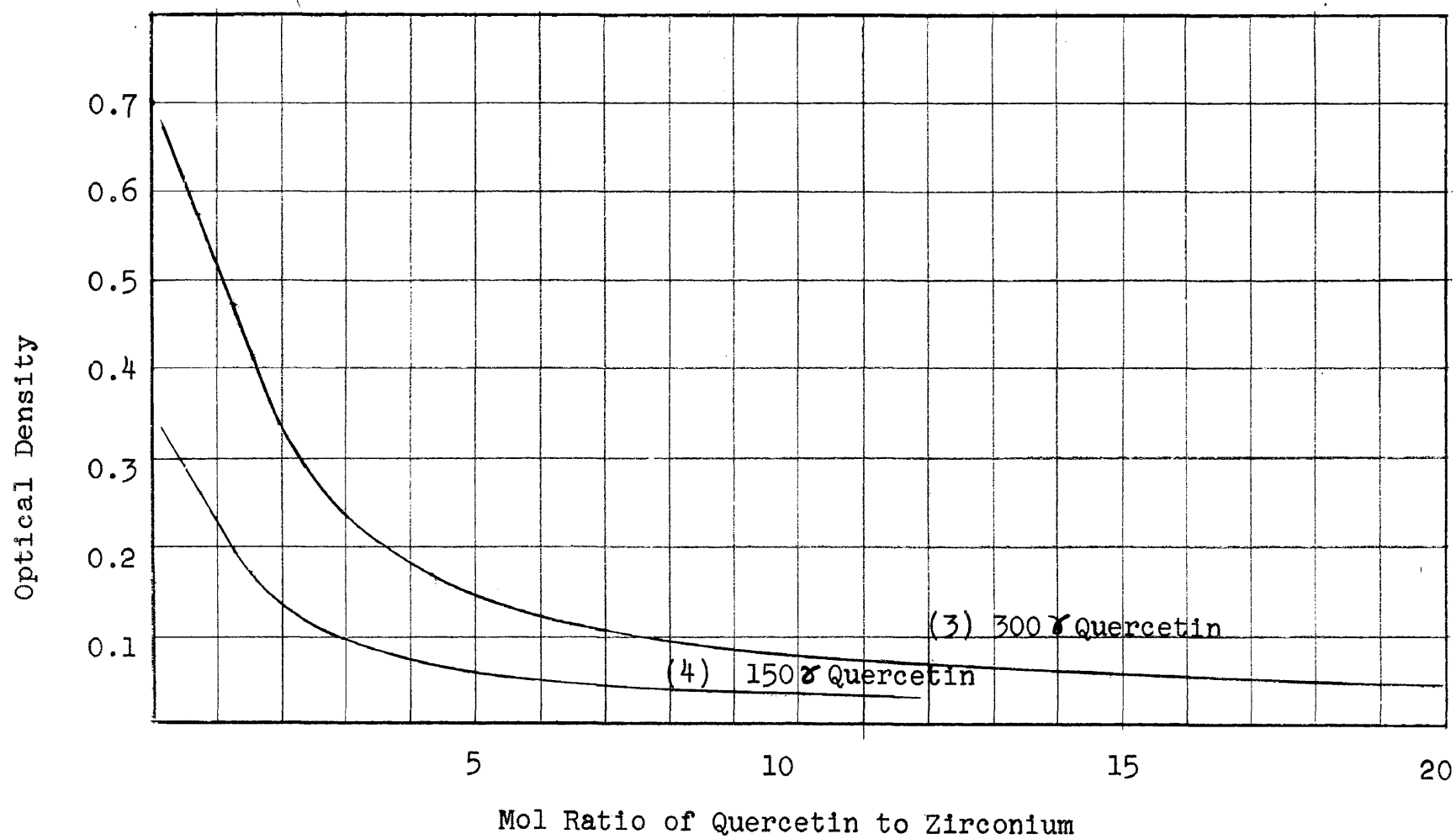


Fig. 5. Effect of Zirconium Concentration (Quercetin Conc. Fixed) (I)

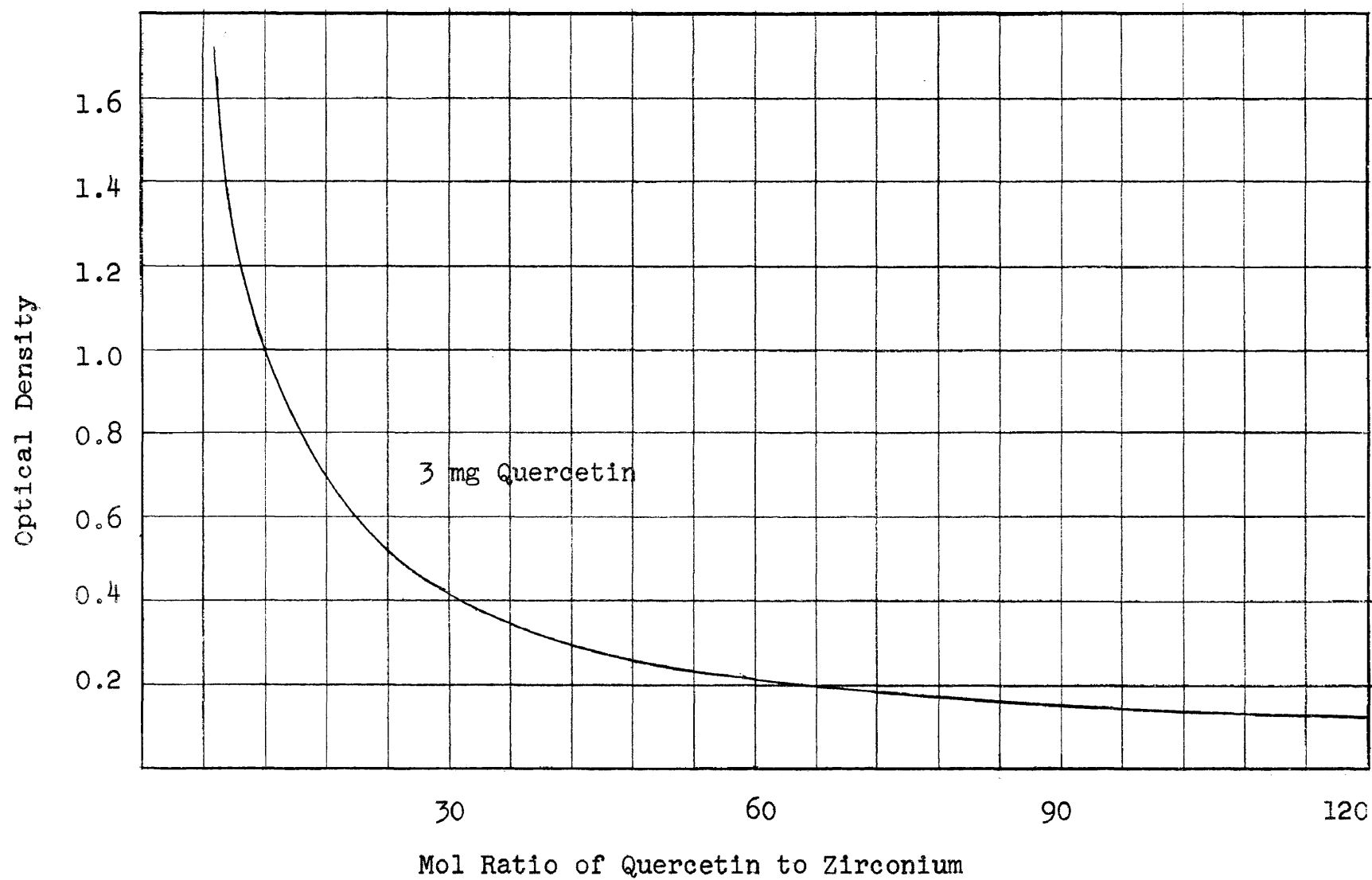


Fig. 6. Effect of Zirconium Concentration (Quercetin Conc. Fixed) (II)

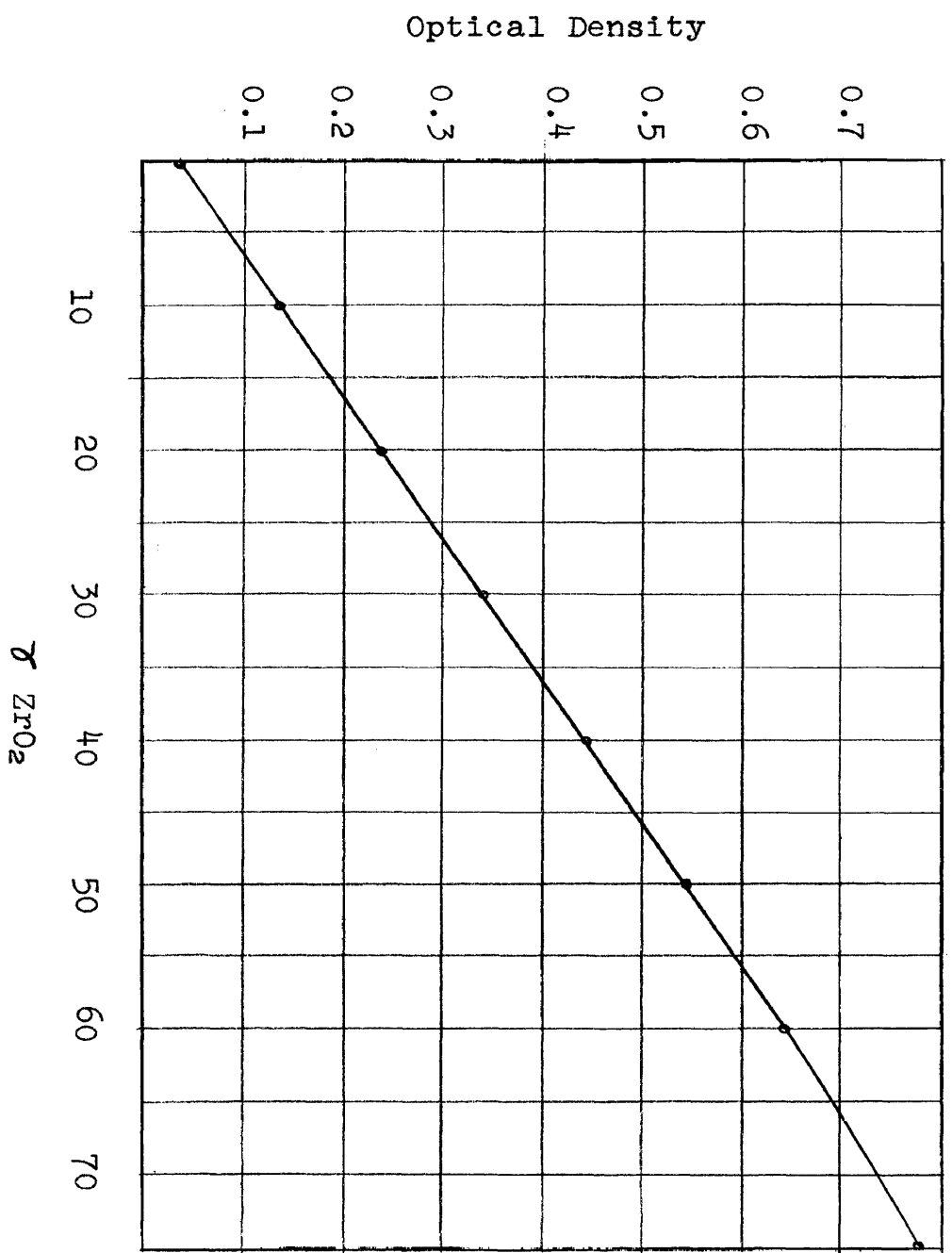


Fig.7. Working Curve

THEORETICAL ANALYSIS OF THE ZIRCONIUM-QUERCETIN REACTION

The relationship between optical density and mol ratio of quercetin to zirconium, Curves 1 and 2, Fig. 4, is linear up to a mol ratio of 1:1. At ratios where the molar concentration of the quercetin is greater than that of the zirconium the optical density increases in a non-linear fashion with increase in quercetin (zirconium concentration fixed) and reaches a nearly constant value for very high mol ratios.

There are three possible explanations for the nature of the curves plotted from these data. The first explanation is based on the hypothesis that two zirconium-quercetin complexes can coexist in the solutions. The second explanation is based on the hypothesis that only a 1:1 complex is involved and the equilibrium allows zirconium, quercetin and the complex to coexist in various solutions. The third explanation is based on the hypothesis that only a 2:1 complex is formed and the equilibrium involved allows zirconium, quercetin and the 2:1 complex to coexist in various solutions. These hypotheses are now to be tested.

Hypothesis 1: Two zirconium complexes may coexist.

In the dilute regions it is reasonable to assume that the zirconium forms only the 1:1 complex. The fraction of the zirconium present in the form of 1:1 complex in these dilute solutions would depend on the equilibrium involved.

As the quercetin concentration is increased (zirconium concentration fixed) a greater fraction of the zirconium forms the 1:1 complex. As the quercetin concentration is increased still further a point is reached where nearly all the zirconium is in the form of 1:1 complex and the 2:1 complex makes its appearance. The relative amount of the 2:1 complex increases as more quercetin is added until all the zirconium is present in the form of 2:1 complex. At this point the density of the solution should remain constant unless a third complex is formed with still more quercetin. The curves of Fig. 4 show little evidence of a third complex.

In order to test these hypotheses it may be profitable to calculate the extinction coefficient of the zirconium-quercetin complex from Curves 1 and 2, Fig. 4, in the region up to and including mol ratios of 1:1:

From Curve 1

ZrO_2 fixed at 54.4 %

Original conc. of $\text{ZrO}_2 = 1.77 \times 10^{-5}$ moles/liter

Density at 1:1 = 0.205

Assuming all Zr in form of Zr-quercetin complex
(ZrQ)

Conc. of ZrQ = 1.77×10^{-5}

$d = k_1 c l$ $l = 1 \text{ cm.}$

$k_1 = \frac{d}{c l} = \frac{0.205}{1.77 \times 10^{-5}} = 11,600$

From Curve 2

ZrO_2 fixed at 20.0 %

Original conc. of $\text{ZrO}_2 = 0.65 \times 10^{-5}$ moles/liter

Density at 1:1 = 0.042

Conc. of $\text{ZrQ} = 0.65 \times 10^{-5}$ moles/liter

$$k_1 = \frac{d}{c} = \frac{0.042}{0.65 \times 10^{-5}} = 6,500$$

The differing values of k can be taken as indication that the zirconium-quercetin complex is unstable and that mass action effects determine the proportion of the total zirconium that can be present in the form of 1:1 zirconium-quercetin complex.

The equilibria involved for the 1:1 complex and the 2:1 complex follow:

For the 1:1 complex



$$\frac{(\text{ZrO}^{++}) (\text{Cl}^-) (\text{QH})}{(\text{H}^+) (\text{ZrOClQ})} = K_1$$

$(\text{H}^+) = (\text{Cl}^-)$ since HCl is in great excess

$$\text{Thus } \frac{(\text{ZrO}^{++}) (\text{QH})}{(\text{ZrOClQ})} = K_1$$

Or using simplified notation

$$\frac{(\text{Zr}) (\text{Q})}{(\text{ZrQ})} = K_1$$

For the 2:1 complex



$$\frac{(\text{ZrO}^{++}) (\text{QH})^2}{(\text{ZrOQ}_2) (\text{H}^+)^2} = K_2'$$

At constant (H^+) this reduces to

$$\frac{(\text{ZrO}^{++}) (\text{QH})^2}{(\text{ZrOQ}_2)} = K_2 \quad \text{where } K_2 = K_2' (\text{H}^+)^2$$

Or using simplified notation

$$\frac{(Zr)(Q)^2}{(ZrQ_2)} = K_2$$

For both complexes coexisting in equilibrium

$$\frac{(ZrQ)(Q)}{(ZrQ_2)} = \frac{K_2}{K_1} = k \quad (1)$$

The first hypothesis is to be tested by calculating k for various test solutions in which both complexes coexist and noting if these values are reasonably constant. It is assumed that in solutions where both complexes coexist the concentration of uncombined zirconium is negligible and that no complexes of zirconium other than the quercetin complexes are formed.

For the calculations the values of the extinction coefficients of ZrQ and ZrQ_2 are required. It is reasonable to assume that if the quercetin concentration is kept constant and the zirconium concentration is made infinitely large, the quercetin should be used up completely to form the 1:1 complex. These conditions would be obtained if the curves in Fig. 5 (quercetin concentration fixed) were extrapolated to zero mol ratio. The densities thus obtained could be used to calculate the extinction coefficient of the pure 1:1 complex ZrQ . For Curve 3 the extrapolated density equals 0.700. The concentration of the pure complex is equal to the original concentration of quercetin.

Thus $(ZrQ) = 3.98 \times 10^{-5}$ moles/liter

$$k_{1:1} = \frac{d}{cl} = \frac{0.700}{3.98 \times 10^{-5} \times 1} = 17,600$$

The same value of $k_{1:1}$ is obtained if Curve 4 is used.

The extinction coefficient of the 2:1 complex could be calculated if Curves 1 and 2, Fig. 4, were extrapolated to infinite mol ratio of quercetin to zirconium. This cannot be done, but an approximation can be made. For Curve 1 the limiting optical density is about 0.584 and for Curve 2, 0.200.

From Curve 1

Original conc. of $ZrQ_2 = 0.0000177$ moles/liter

If the Zr is completely in the form of 2:1
complex ZrQ_2

Then $(ZrQ_2) = 1.77 \times 10^{-5}$ moles/liter

$$k_{2:1} = \frac{d}{c} = \frac{0.584}{1.77 \times 10^{-5}} = 33,000$$

From Curve 2

$$k_{2:1} = 30,800$$

$$\text{Average } k_{2:1} = 32,300$$

It is now possible to test the hypothesis by calculating k (equation 1).

$$\text{From Curve 1} \quad \textcircled{a} \quad \frac{(Q)}{(Zr)} = 5:1$$

$$d = 0.402$$

Original $(Zr) = 1.77 \times 10^{-5}$ moles/liter

Original $(Q) = 8.85 \times 10^{-5}$ moles/liter

$$(ZrQ) = \frac{d_{ZrQ}}{17,600}$$

$$(ZrQ_2) = \frac{d_{ZrQ_2}}{32,300}$$

$$\frac{d_{ZrQ}}{17,600} + \frac{d_{ZrQ_2}}{32,300} = 1.77 \times 10^{-5}$$

$$1.84d_{ZrQ} + d_{ZrQ_2} = 0.572$$

$$\text{Also} \quad d_{ZrQ} + d_{ZrQ_2} = 0.402$$

$$\text{And} \quad 0.84d_{ZrQ} = 0.170$$

$$d_{ZrQ} = .202$$

$$d_{ZrQ_2} = .200$$

$$(ZrQ) = \frac{0.202}{17,600} = 1.15 \times 10^{-5} \text{ moles/liter}$$

$$(ZrQ_2) = 0.62 \times 10^{-5} \text{ moles/liter}$$

$$\text{Uncombined (Q)} = (8.85 - 1.15 - 2 \times 0.62) \times 10^{-5}$$

$$\text{Uncombined (Q)} = 6.46 \times 10^{-5} \text{ moles/liter}$$

$$k = \frac{(ZrQ)(Q)}{(ZrQ_2)} = \frac{1.15 \times 10^{-5} \times 6.46 \times 10^{-5}}{0.62 \times 10^{-5}}$$

$$k = 1.2 \times 10^{-4}$$

The "k" was calculated also for several points in Figs. 4, 5 and 6. The results are given in Table 8.

The values are seen to be reasonably constant and lend some weight to the foregoing interpretation. Curve 4, Fig. 5, could not be used for similar calculations since the levels of concentrations used indicated that only the 1:1 complex could exist in these solutions.

Table
Equilibrium

Reference	Mol Ratio Q/Zr	Optical Density	Original
			(Zr) $\times 10^5$
Fig. 4, Curve 1	5:1	0.402	1.77
" " " "	10:1	0.476	1.77
" " " "	15:1	0.512	1.77
Fig. 4, Curve 2	10:1	0.142	0.65
" " " "	15:1	0.158	0.65
Fig. 5, Curve 3	5:1	0.151	0.80
" " " "	10:1	0.076	0.40
" " " "	15:1	0.054	0.27
Fig. 6	10:1	1.16	4.00
" "	20:1	0.620	2.00

¹ The assumption that no ZrO^{++} ions exist in these solutions is evidently not valid. These values were omitted from the average.

8

Constants (I)

Original	(Q)			$k = \frac{(Q)(ZrQ)}{(ZrQ_2)}$
(Q)	(ZrQ)	(ZrQ ₂)	Uncombined	
$\times 10^5$	$\times 10^5$	$\times 10^5$	$\times 10^5$	$\times 10^4$
8.85	1.15	0.62	6.46	1.2
17.7	0.65	1.12	14.8	0.86
26.6	0.41	1.36	23.5	0.71
6.5	0.46	0.19	5.7	1.3
9.75	0.35	0.30	8.8	1.0
3.98	0.70	0.10	3.1	2.1 ¹
3.98	0.35	0.04	3.54	3.0 ¹
3.98	0.22	0.049	3.67	1.6
40.0	0.68	3.12	32.9	0.92
40.0	0.17	1.82	36.2	0.38

Ave = 1.0×10^{-4}

Before proceeding to the second possible explanation, it would not be out of place here to calculate the values of the equilibrium constants K_1 and K_2 of the two complexes. For a 1:1 complex the extinction coefficient value obtained above was 17,600.

$$K_1 = \frac{(Zr)(Q)}{(ZrQ)}$$

From Curve 1 © Mol Ratio $\frac{(Q)}{(Zr)} = 1$

$$d = 0.205$$

$$(ZrQ) = \frac{d}{k} = \frac{0.205}{17,600} = 1.17 \times 10^{-5} \text{ moles/liter}$$

$$\text{Original } (Zr) = 1.77 \times 10^{-5} \text{ moles/liter}$$

$$\begin{aligned} \text{Uncombined } (Zr) &= (1.77 - 1.17) \times 10^{-5} = \\ &0.60 \times 10^{-5} \text{ moles/liter} \end{aligned}$$

$$\text{Uncombined } (Q) = 0.60 \times 10^{-5} \text{ moles/liter}$$

$$K_1 = \frac{0.60 \times 10^{-5} \times 0.60 \times 10^{-5}}{1.17 \times 10^{-5}} = 0.31 \times 10^{-5}$$

From Curve 3 © $\frac{(Q)}{(Zr)} = 1$

$$d = 0.522$$

$$(ZrQ) = \frac{0.522}{17,600} = 2.97 \times 10^{-5} \text{ moles/liter}$$

$$\text{Original } (Q) = 3.98 \times 10^{-5} \text{ moles/liter}$$

$$\text{Uncombined } (Q) = 1.01 \times 10^{-5} \text{ moles/liter}$$

$$\text{Uncombined } (Zr) = 1.01 \times 10^{-5} \text{ moles/liter}$$

$$K_1 = \frac{1.01 \times 10^{-5} \times 1.01 \times 10^{-5}}{2.97 \times 10^{-5}} = 0.34 \times 10^{-5}$$

From Curve 4 \odot $\frac{(Q)}{(Zr)} = 1$

$$d = .232$$

$$(ZrQ) = \frac{0.232}{17,600} = 1.32 \times 10^{-5} \text{ moles/liter}$$

$$\text{Original } (Q) = 1.99 \times 10^{-5}$$

$$\text{Uncombined } (Q) = 0.67 \times 10^{-5}$$

$$\text{Uncombined } (Zr) = 0.67 \times 10^{-5}$$

$$K_1 = \frac{0.67 \times 10^{-5} \times 0.67 \times 10^{-5}}{1.32 \times 10^{-5}} = 0.34 \times 10^{-5}$$

$$\text{Average } K_1 = 0.33 \times 10^{-5}$$

The equilibrium constant K_2' for the 2:1 complex may be evaluated from the relationships $\frac{K_2}{K_1} = k$, and

$$K_2' = \frac{K_2}{(H^+)^2}.$$

$$K_2' = \frac{k \times K_1}{(H^+)^2}$$

$$K_2 = \frac{1.0 \times 10^{-4} \times 0.33 \times 10^{-5}}{0.5 \times 0.5} = 1.3 \times 10^{-9}$$

Hypothesis 2: Only the 1:1 zirconium complex is formed. In the second explanation it is assumed that the zirconium-quercetin complex is relatively weak and that quercetin, zirconium and complex coexist in the various solutions. A further postulate is made that the molar ratio of zirconium to quercetin in the complex for the solutions studied is always 1:1. The evidence for a 1:1 complex is supported by chemical analysis and is discussed in a later section.

The constancy of optical density at very high mol ratios is taken to mean that in these regions the zirconium complex is completely in the 1:1 form and the fraction of the complex present at smaller mole ratios may then be calculated. Equilibrium constants for the reaction $ZrQ \rightleftharpoons Zr + Q$ are then calculated for various solutions studied. If the values are relatively constant the foregoing assumptions may be considered valid. Curves 1 and 2, Fig. 4; Curves 3 and 4, Fig. 5; and Fig. 6 are used to obtain the data. A sample calculation follows:

1. Extinction Coefficient

From Curve 1

Original conc. of $ZrO_2 = 54.4 \text{ g}/25 \text{ ml.} =$

$0.0000177 \text{ moles/liter}$

If Zr is completely in form of complex

Then $(ZrQ) = 1.77 \times 10^{-5} \text{ moles/liter}$

Optical density = 0.584

$$k = \frac{d}{c} = \frac{0.584}{1.77 \times 10^{-5}} = 33,000$$

From Curve 2

Original conc. of $ZrO_2 = 20 \text{ g}/25 \text{ ml.} =$

$0.65 \times 10^{-5} \text{ moles/liter}$

Optical density = 0.200

$$k = \frac{d}{c} = \frac{0.200}{0.65 \times 10^{-5}} = 30,800$$

Average $k = 32,300$

2. Equilibrium Constant

From Curve 1 @ $\frac{(Q)}{(Zr)} = 5$

$$d = 0.400$$

$$(ZrQ) = C = \frac{d}{k} = \frac{0.400}{32,360} = 1.24 \times 10^{-5}$$

moles/liter

Original (Zr) = 1.77×10^{-5} moles/liter

Uncombined (Zr) = $(1.77 - 1.24) \times 10^{-5} =$

$$0.53 \times 10^{-5} \text{ moles/liter}$$

Original (Q) = 8.85×10^{-5} moles/liter

Uncombined (Q) = $(8.85 - 1.24) \times 10^{-5} =$

$$7.61 \times 10^{-5} \text{ moles/liter}$$

$$K_1 = \frac{(Zr)(Q)}{(ZrQ)} = \frac{0.53 \times 10^{-5} \times 7.61 \times 10^{-5}}{1.24 \times 10^{-5}}$$

$$K_1 = 3.2 \times 10^{-5}$$

The results of the calculations are given in

Table 9.

9

Constants (II)

(Zr) Uncombined $\times 10^5$	Original (Q) $\times 10^5$	(Q) Uncombined $\times 10^5$	Equil. Constant $K_1 \times 10^5$
1.13	1.77	1.13	2.0
0.53	8.85	7.61	3.2
0.30	17.7	16.3	3.3
0.18	26.6	25.0	2.8
0.52	0.65	0.52	2.1
0.32	3.25	2.92	2.9
0.21	6.5	6.06	2.9
0.16	9.75	9.26	3.0
2.36	3.98	2.36	3.4
0.33	3.98	3.51	2.5
0.163	3.98	3.75	2.2
0.098	3.98	3.81	2.2
1.27	1.99	1.27	2.2
0.20	1.99	1.79	1.8
0.10	1.99	1.89	1.9
0.39	40.0	36.4	3.9
0.19	40	37.5	2.8

Ave $K_1 = 2.7 \times 10^{-5}$

The constancy of K_1 , Table 9, indicates that there is some substance in the explanation that only a 1:1 complex forms. Chemical analysis also indicates a 1:1 ratio and there would be a tendency to accept this idea as being quite valid. However, experience in attempting to isolate the complex by solvent extraction (discussed later) gave incontrovertible evidence that in certain instances the solvents can strip quercetin from the complex. If the second explanation were valid it would be expected that the value of the extinction coefficient calculated for the region where zirconium was in considerable excess should be the same as that obtained for the region where quercetin was in considerable excess. This is not the case for in the high zirconium end the value of 17,600 was obtained compared to 32,300 for the high quercetin end. On the basis of this, the first explanation seems more logical.

Hypothesis 3: Only the 2:1 zirconium complex is formed. The equilibrium constant involved in this instance is given by

$$K_{2:1} = \frac{(Zr) (Q)^2}{(ZrQ_2)}$$

The extinction coefficient for the 2:1 complex is first calculated:

For Curve 3 the extrapolated density = 0.700

The conc. of the pure complex is equal to one-half
the original conc. of quercetin

$$(ZrQ_2) = \frac{3.98 \times 10^{-5}}{2} = 1.99 \times 10^{-5} \text{ moles/liter}$$

$$K_{2:1} = \frac{d}{cl} = \frac{0.700}{1.99 \times 10^{-5}} = 35,200$$

The same value of $K_{2:1}$ is obtained if Curve 4 is used.

The values of the equilibrium constant may now be calculated:

$$\text{From Curve 1} \quad \odot \quad \frac{(Q)}{(Zr)} = 1$$

$$d = .206$$

$$(ZrQ_2) = \frac{.206}{35,200} = 0.59 \times 10^{-5} \text{ moles/liter}$$

$$\text{Original (Zr)} = 1.77 \times 10^{-5} \text{ moles/liter}$$

$$\text{Original (Q)} = 1.77 \times 10^{-5} \text{ moles/liter}$$

$$\text{Uncombined (Zr)} = 1.18 \times 10^{-5} \text{ moles/liter}$$

$$\text{Uncombined (Q)} = 0.59 \times 10^{-5} \text{ moles/liter}$$

$$K_{2:1} = 0.70 \times 10^{-10}$$

$$\text{From Curve 1} \quad \odot \quad \frac{(Q)}{(Zr)} = 5:1$$

$$d = 0.400$$

$$(ZrQ_2) = \frac{0.400}{35,200} = 1.14 \times 10^{-5} \text{ moles/liter}$$

$$\text{Original (Zr)} = 1.77 \times 10^{-5} \text{ moles/liter}$$

$$\text{Uncombined (Zr)} = 0.63 \times 10^{-5} \text{ moles/liter}$$

$$\text{Original (Q)} = 8.85 \times 10^{-5} \text{ moles/liter}$$

$$\text{Uncombined (Q)} = 8.85 \times 10^{-5} - 2.28 \times 10^{-5} =$$

$$6.57 \times 10^{-5} \text{ moles/liter}$$

$$K_{2:1} = 43 \times 10^{-10}$$

From Curve 2 $\frac{(Q)}{(Zr)} = 10:1$

$$d = .142$$

$$(ZrQ_2) = \frac{0.142}{35,200} = 0.40 \times 10^{-5} \text{ moles/liter}$$

$$\text{Original } (Zr) = 0.65 \times 10^{-5} \text{ moles/liter}$$

$$\text{Uncombined } (Zr) = 0.25 \times 10^{-5} \text{ moles/liter}$$

$$\text{Original } (Q) = 6.5 \times 10^{-5} \text{ moles/liter}$$

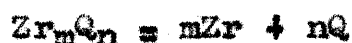
$$\begin{aligned} \text{Uncombined } (Q) &= 6.5 \times 10^{-5} - 0.8 \times 10^{-5} = \\ &5.7 \times 10^{-5} \text{ moles/liter} \end{aligned}$$

$$K_{2:1} = 20 \times 10^{-10}$$

These three calculations of $K_{2:1}$ are sufficient to show that the third hypothesis is untenable.

Bent and French (7) have described a method especially applicable to the determination of formulas of dissociable complexes.

For the general reaction



the expression for the equilibrium constant becomes

$$K = \frac{(Zr)^m (Q)^n}{(Zr_m Q_n)}$$

Taking the logarithm of both sides it follows that

$$\log (Zr_m Q_n) = m \log (Zr) + n \log (Q) - \log K$$

If the concentration of one of the ions is kept constant a straight line is obtained by a plot of the log of the optical density, which is proportioned to the concentration of the complex, against the logarithm of the concentration of the other ion. The slope of this straight line

then gives the value of n or m . In practice the logarithm of the total concentration of the ion is plotted instead of the logarithm of the equilibrium concentration of the ion. In dilute solution where the colored complex is largely dissociated a straight line is obtained, but deviations will occur as soon as an appreciable fraction of the ion is present in the form of the complex.

The data necessary for the method of Bent and French are given in Tables 2, 4, 10 and 11. This method indicates that in the dilute region the mol ratio of quercetin to zirconium in the complex is 1:1. If dissociation is appreciable, it can be shown that the degree of dissociation can be constant only if the limiting slope is unity. The degree of dissociation was calculated for each of several points in the dilute region (Fig. 4, Curve 2, and Table 10). The values obtained were found to be constant at 62%. The constancy of α is also indicated by the linear relationship between optical density and total concentration of quercetin added (dilute region, Curves 1 and 2).

Table 10

Data for the Evaluation of the
Formula of the Complex

(Zirconium concentration fixed at
 0.65×10^{-5} moles/liter)

(Q) $\times 10^6$	$\log (Q)$	d	$\log d$
1.30	-5.886	0.008	-2.097
2.60	-5.585	0.018	-1.745
3.90	-5.409	0.028	-1.553
5.20	-5.284	0.034	-1.469
6.50	-5.187	0.042	-1.377
7.80	-5.108	0.051	-1.292
9.10	-5.041	0.056	-1.252
10.4	-4.983	0.062	-1.208
13.0	-4.886	0.068	-1.167
26.0	-4.585	0.096	-1.018
52.0	-4.284	0.151	-0.883

Table 11

Data for the Evaluation of the
Formula of the Complex

(Quercetin concentration fixed at
 1.99×10^{-5} moles/liter)

(ZrO ₂)			
$\times 10^6$	log (ZrO ₂)	d	log d
1.77	-5.752	0.026	-1.585
3.54	-5.451	0.057	-1.244
4.56	-5.341	0.072	-1.143
5.80	-5.237	0.087	-1.060
7.08	-5.150	0.106	-0.975
8.85	-5.053	0.129	-0.890
10.6	-4.975	0.148	-0.830
12.4	-4.908	0.170	-0.770
14.2	-4.848	0.188	-0.726
15.8	-4.799	0.202	-0.695
17.7	-4.752	0.220	-0.658
24.7	-4.608	0.261	-0.583
35.3	-4.452	0.283	-0.548
53.0	-4.276	0.298	-0.526

COMPOSITION OF THE ZIRCONIUM-QUERCETIN COMPLEX

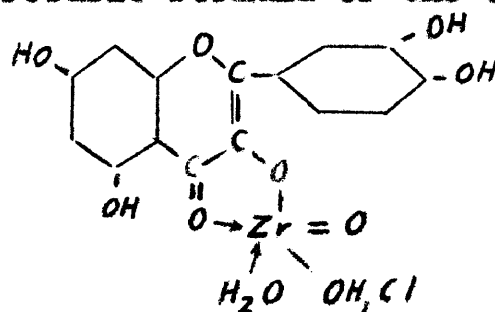
The isolation of the zirconium-quercetin complex presented some difficulties because of the high solubility of the complex in water and the insolubility in organic solvents. The complex was found to be insoluble in ether, n-butyl ether, toluene, tetralin, carbon tetrachloride, chloroform, ethyl acetate, amyl acetate, isoamyl alcohol, benzyl alcohol, cyclohexanol, cyclohexanone, p-methyl cyclohexanone and 4-methyl-2-pentanone. Isolation of the complex by solvent extraction was therefore abandoned.

It was found that ether was able to extract quercetin from solutions containing about 32% by volume of alcohol and 0.5N in HCl. This offered a means of isolating the complex by crystallization from solutions in which the excess quercetin had been removed by extraction. Accordingly, 100 ml. of 0.5N HCl solution was made containing 21.8 mg. ZrO_2 , 267 mg. quercetin, and 32 ml. of alcohol. The mol ratio of quercetin to zirconium in the solution was 5:1. The solution was extracted with several 100 ml. portions of ethyl ether until the ether layer remained colorless. The aqueous layer was then heated gently at about 40° C to remove the ether and the solution was then allowed to cool in a refrigerator overnight. The crystals which formed were filtered, washed with water and dried under vacuum at 70° C in an Abderhalden pistol drier. The yield of the complex was 11 mg. Robert Meyrowitz of the U. S.

Geological Survey analyzed the complex for C, H, Zr, and Cl by micro-chemical techniques. His analysis follows:

	%	G. Atoms	Atomic Ratios
C	41.2	3.44	14.5
H	2.8	2.8	11.8
ZrO ₂	29.1	0.237	1
Cl	3.1	0.087	0.37

A 1:1 complex is indicated on the basis of the analysis. The probable formula of the complex is



The evidence for a 1:1 complex is not conclusive however. For example in attempting to isolate the complex by solvent extraction it was found that cyclohexanol stripped the quercetin completely away from the zirconium. Possibly ether acts in a similar manner but not to the same extent as cyclohexanol.

THE REACTIONS OF QUERCETIN WITH OTHER ELEMENTS

Nearly all of the elements were tested to determine their behavior with quercetin under the optimum conditions used for the zirconium-quercetin color system. Generally the cations were introduced in the form of chloride or nitrate salts and the anions in the form of sodium salts. Reagent grade chemicals were used for the common elements while special high purity chemicals (99.8% or better) were used for the less commonly available elements such as hafnium and the rare earths.

Each element was tested in the absence of zirconium and at two levels (5% ZrO_2 and 25% ZrO_2) of zirconium. The solutions were always made to 25 ml. volume before measuring their optical densities. Elements forming colored ions were tested in the absence of both quercetin and zirconium to determine the extent of the absorption at 440 m μ produced by the natural color of these ions. If an element gave indications of a color change, different concentrations of the element were tested. The data (density vs. concentration) were plotted to determine the minimum amount of the element which produces no effect. A density difference of 0.003 units (equivalent to 0.3% ZrO_2) was taken as the cut off for reporting interference. The elements not tested include Fr, Ra, Tb, Ho, Er, Tm, Lu, Ac, Pa, Tc, Os, Ir, Po, At, and the inert gases.

The following cations do not interfere in the

maximum amounts (expressed as oxides) indicated:

0.5 g. - Na, K, and NH_4

0.1 g. - Rb, Cs, Mg, Ca, Ba, Sr,
Zn, Cd, Hg^{++} , Ag, Pb,
 Tl^+ , Mn^{++} , and As^{+++}

0.05 g. - La and Y

0.004 g. - Eu, Yb, Gd, and Dy

Acetate (0.5 g.) and bromide (0.2 g.) ions do not interfere.

Some elements interfere by decreasing the color intensity given by zirconium. These elements probably consume reagent or their anions react with zirconium. Some elements interfere because of the natural color of their ions in hydrochloric acid solution. Some elements produce unstable colors with quercetin while other elements react to increase the color intensity of the solution. The minimum amount of each element that can be tolerated and the nature of the interference are given in Table 12. It is interesting to note that at low concentrations of zirconium ($5 \times \text{ZrO}_2$ per 25 ml.) larger amounts of some interfering ions can be tolerated than at higher concentrations ($25 \times \text{ZrO}_2$ per 25 ml.) of zirconium. Serious interference is given by the following ions: Oxalate, fluoride, phosphate, scandium, gallium, mercurous mercury, titanium, hafnium, thorium, germanium, tin, vanadium, chromium, molybdenum, tungsten, iron, antimony, niobium, tantalum, and the platinum metals tested. The only elements that would interfere after a potassium hydroxide separation of zirconium (under oxidizing

conditions) would be scandium, titanium, hafnium, thorium, iron, and possibly antimony, niobium and tantalum.

Some additional observations are to be noted. Tungsten, antimony, niobium and tantalum form precipitates with quercetin. Since quercetin does not precipitate titanium and zirconium it may prove a valuable reagent for the separation of niobium and tantalum from titanium and zirconium.

The very sensitive color reaction given by tin with quercetin should be investigated for the colorimetric determination of tin. Quercetin may also prove useful as a colorimetric reagent for fluorine (by quenching of the Zr-quercetin color), and for hafnium, molybdenum, antimony and hexavalent chromium.

Table 12

Maximum Permissible Amounts
of Various Anions and Cations

(Amounts calculated as oxides unless otherwise indicated)

Compound Tested	Max. Amount At 5 % ZrO ₂ Level	Max. Amount At 25 % ZrO ₂ Level	Nature of Interference
Citric Acid	10 mg. acid	1 mg. acid	Negative (i.e. quenches)
Tartaric Acid	10 mg. acid	1 mg. acid	Negative
(NH ₄) ₂ HPO ₄	> 100 % P ₂ O ₅	65 % P ₂ O ₅	Negative
NaF	10 % F	5 % F	Negative
Na ₂ SO ₄	13 mg. SO ₃	3.5 mg. SO ₃	Negative
LiCl	> 50 mg.	16 mg.	Negative
HAuCl ₄	0.25 mg.	0.25 mg.	Pos., colored ion
CuCl ₂	5 mg.	5 mg.	Unstable soln.
Be(NO ₃) ₂	3 mg.	3 mg.	Positive
Ce(NO ₃) ₃	25 mg.	5 mg.	Negative
Sm(NO ₃) ₃	10 mg.	10 mg.	Positive
Pr(NO ₃) ₃	10 mg.	10 mg.	Pos., colored ion
Nd(NO ₃) ₃	25 mg.	25 mg.	Positive
Sc(NO ₃) ₃	20 %	20 %	Positive
H ₃ BO ₃	8 mg.	8 mg.	Positive
AlCl ₃	0.6 mg.	0.6 mg.	Positive
Ga(NO ₃) ₃	15 %	15 %	Positive
In(NO ₃) ₃	7 mg.	7 mg.	Positive
HgNO ₃	150 %	150 %	Unstable soln.
TiCl ₂ (OAc) ₂	15 %	15 %	Positive

Table 12 (Cont.)

Maximum Permissible Amounts
of Various Anions and Cations

(Amounts calculated as oxides unless otherwise indicated)

Compound Tested	Max. Amount At 5 % ZrO_2 Level	Max. Amount At 25 % ZrO_2 Level	Nature of Interference
$HfOCl_2$	0.75 %	0.75 %	Positive
$Th(NO_3)_4$	40 %	40 %	Positive
$GeCl_4$	75 %	75 %	Positive
$SnCl_4$	0.4 %	0.4 %	Positive
NH_4VO_3	200 %	200 %	Unstable soln.
$BiCl_3$	5 mg.	5 mg.	Positive
$CrCl_3$	250 %	250 %	Pos., colored ion
$K_2Cr_2O_7$	1 % Cr_2O_3	1 % Cr_2O_3	Positive
$(NH_4)_6Mo_7O_{24}$	0.2 %	0.2 %	Positive
Na_2WO_4	0.5 %	0.5 %	Positive
$FeCl_3$	6 %	6 %	Pos., unstable soln.
$Fe(NH_4)_2(SO_4)_2$	50 %	50 %	Pos., unstable soln.
$CoCl_2$	5 mg.	5 mg.	Pos., colored ion
NaI	5 mg. I^-	5 mg. I^-	Pos., I_2
Na_2HASO_4	-	3 mg. As_2O_5	Negative
H_2SeO_3	> 0.2g SeO_2	50 mg. SeO_2	Negative
H_2TeO_3	10 mg. TeO_2	10 mg. TeO_2	Positive
$NiCl_2$	8 mg.	8 mg.	Pos., colored ion
$UO_2(NO_3)_2$	3 mg.	3 mg.	Positive

Table 12 (Cont.)

Maximum Permissible Amounts
of Various Anions and Cations

(Amounts calculated as oxides unless otherwise indicated)

Compound Tested	Max. Amount At 5 % ZrO ₂ Level	Max. Amount At 25 % ZrO ₂ Level	Nature of Interference
Na ₂ SiO ₃	-	40 mg.	Negative
SbCl ₃	3 %	3 %	Positive
Nb ₂ O ₅ in H ₂ SO ₄	1 %	1 %	Positive
Ta ₂ O ₅ in H ₂ SO ₄	2 %	2 %	Positive
H ₂ PdCl ₄	60 % Pd	60 % Pd	Pos., colored ion
H ₂ RhCl ₅	100 % Rh	100 % Rh	Pos., colored ion
H ₂ RuCl ₅	4 % Ru	4 % Ru	Pos., colored ion
H ₂ PtCl ₆	500 % Pt	500 % Pt	Pos., colored ion

THE COLORIMETRIC DETERMINATION OF ZIRCONIUM BY MEANS OF QUERCETIN

DISCUSSION OF PROCEDURE

In the determination of zirconium by means of quercetin provisions must be made for the removal of interfering ions, especially iron and titanium which are common constituents in most naturally occurring materials. Precipitation of zirconium by means of either propylarsonic acid or mandelic acid would be an effective means of accomplishing this but no carrier for zirconium could be found that would be precipitated by these reagents. At this point it seemed that the best approach was to find a zirconium reagent which would quantitatively precipitate microgram amounts ($5 \gamma \text{ZrO}_2$) of this element without carrier and which would at the same time separate zirconium from interfering elements. The reagent p-dimethylaminoazophenylarsonic acid offered a means of accomplishing this if it were possible to prevent the precipitation of titanium with hydrogen peroxide. Preliminary experiments indicated that hydrogen peroxide could not be used because of its rapid and complete oxidation of the azo-arsonic acid. Attempts to prevent the precipitation of titanium with the azo-arsono dye by employing media of high acidity were not completely successful. At the same time it was observed that the titanium formed no precipitate when the solutions were hot, a precipitate being obtained

only during the cooling process. Experiments indicated that only a few micrograms of titanium coprecipitated with zirconium if the zirconium precipitate was formed in (15+85) HCl solution and the solution was filtered hot (70 - 90° C). In this manner microgram amounts of zirconium could be separated from at least 10 mg. TiO_2 (See Experiments, 1, page 82). Other elements usually precipitated by the azo-arsono dye were found to be more soluble under these conditions. Of the elements that would interfere seriously in the determination of zirconium by means of quercetin only W, Ta, Nb, and Sc were found to be precipitated by the azo-arsono dye in hot (15+85) HCl solution (See Experiments, 2, page 82). The amount of scandium precipitated is small and possibly 0.5 mg. Sc_2O_3 can be tolerated in the solution used for precipitating zirconium. Vanadium and other strong oxidizing agents oxidize and destroy the azo-arsonic acid and should be absent.

The precipitation of zirconium in microgram amounts by p-dimethylaminoazophenylarsonic acid is very sensitive to fluoride. Even microgram amounts of fluoride ion hinder the precipitation of zirconium. Fluoride in any form should not be used in the preparation of the solution for analysis because it cannot be completely removed even by prolonged fuming with perchloric acid (See Experiments, 3, page 83). Small amounts of sulfate (70 mg. SO_3 maximum tested) do not interfere. Phosphate in amounts under 0.6 mg. P_2O_5 (maximum tested) was also without effect.

A procedure was developed for the colorimetric determination of zirconium in glass sands, clays, and burnt refractories. The sample, 0.2 g., is fused with a mixture of potassium carbonate and borax. The melt is digested with water and the precipitate is filtered to separate zirconium from fluoride, phosphate and other anions. The residue is dissolved in hot HCl, and zirconium is precipitated with p-dimethylaminoazophenylarsonic acid from 50 ml. of (15+85) HCl solution. The zirconium precipitate is filtered hot with the aid of paper pulp and washed with a hot acid solution of the azo dye. The precipitate is ignited at 500° C and dissolved in H₂SO₄. Excess acid is fumed off and the zirconium is then dissolved in HCl solution for the determination with quercetin.

A few details of the procedure need to be examined. It is common knowledge that zirconium is insoluble in water after fusing with a carbonate flux. This holds for milligram or larger amounts of zirconium but does not always hold for microgram amounts of zirconium in the absence of specific carriers such as iron and titanium. For example it was found that in samples with insignificant amounts of iron or titanium nearly all the zirconium was soluble after fusion with carbonate. The zirconium probably forms a soluble complex carbonate in these instances. The complex carbonate of zirconium can be destroyed at alkalinities higher than given by carbonate solutions. Thus for samples containing very small amounts of iron or titanium the

detailed procedure calls for the addition of ferric iron (equivalent to 5 mg. Fe_2O_3) to the leach of the carbonate melt and sufficient KOH solution to increase the alkalinity prior to the filtration of the solution.

The precipitate of zirconium with the pararsonic acid tends to leak through the filter unless a very tight filter, such as Whatman No. 42, and paper pulp are used in the filtration. The precipitate should be heated slowly and in the absence of drafts to prevent dusting losses. The ignition should be made in a small muffle furnace and the temperature must not be allowed to exceed 500°C else the residue becomes difficult to dissolve in sulfuric acid. After solution in sulfuric acid, the excess sulfuric is removed because sulfate quenches the zirconium-quercetin color.

REAGENTS AND APPARATUS

Standard stock solution of zirconium in (1+1)HCl, 1 ml. = approximately 2 mg. ZrO_2 : Add 100 ml. (1+1)HCl to 2.17 g. $\text{ZrO}(\text{NO}_3)_2 \cdot 2\text{H}_2\text{O}$ ² and boil gently until 75 ml. remain. Make to 500 ml. in a volumetric flask with (1+1)HCl. Standardize by taking 20 ml. portions and precipitating with redistilled NH_4OH and igniting to oxide.

² ZrO_2 prepared from zirconyl nitrate obtained from Fisher Scientific Co. contained less than 0.3% HfO_2 by spectrographic tests.

Standard zirconium solution in (1+4)HCl, 1 ml. = 10 γ ZrO₂:

Take 5 ml. (or appropriate amount) of stock solution, add 395 ml. (1+1)HCl and make to 1 liter with distilled water. Tests indicated that zirconium solutions containing more than two percent by volume of HCl are stable for at least six months.

p-Dimethylaminoazophenylarsonic acid solution, 0.3% in

(1+1)HCl: Powder the pararsonic acid in an agate mortar and dissolve 3 g. in hot (50° C) (1+1)HCl and make to 1 liter with (1+1)HCl.

Alcoholic solution of quercetin³, 1 ml. = 1.00 mg. quercetin:

Dissolve 0.500 g. quercetin in 300 ml. of 95% alcohol, warming if necessary. Make to 500 ml. with alcohol.

The solution should be filtered if necessary.

Potassium hydroxide solution: Dissolve 10 g. KOH in 100 ml. of distilled water.

Ferric chloride solution, 1 ml. = 1 mg. Fe₂O₃: Dissolve 0.1 g. pure iron wire in HCl using a small amount of H₂O₂ to oxidize the iron. Evaporate the solution to dryness on the steam bath. Add 1 ml. of (1+1)HCl and 20 ml. of water, digest the solution, cool and make to 100 ml.

³The quercetin used was obtained from Delta Chemical Co., 23 West 60th St., N. Y. S. B. Penick Co., 50 Church St., N. Y., and T. Schuchardt Ltd., Leopoldstrasse 4, Munchen 23, Germany, also supply quercetin of excellent quality.

Carbonate-borate flux: Mix 3 parts of anhydrous K_2CO_3 with 1 part of borax.

Hydrochloric acid: Use redistilled acid for all work including the preparation of reagents.

Sulfuric acid: Reagent grade.

Spectrophotometer: The Beckman Spectrophotometer, Model DU was used. Presumably other good spectrophotometers may be substituted.

PROCEDURE

1. Weigh 0.200 gram of sample, ground to an impalpable powder, into a platinum crucible. Burn off organic matter if present in the sample.

2. Add 3 g. of the carbonate-borate flux and mix thoroughly. Cover the crucible and heat gently at first and then fuse the sample at high heat over a burner for 30 minutes. The fusion period can be greatly shortened for samples that are not refractory. Cool.

3. Leach the melt with about 50 ml. of water. Remove crucible and cover, scrubbing and rinsing them before setting them aside. The total volume at this point should be about 70 ml.

4. If the sample is known to contain iron or titanium proceed to Step 5. If the sample contains negligible amounts of iron or titanium add 5 ml. of ferric chloride solution and stir. Add 10 ml. of KOH solution, stir, and digest the solution on the steam bath for at least one hour.

5. Filter the solution on Whatman No. 40 paper and wash the precipitate with 1% KOH solution. Drain the paper and stem of the funnel thoroughly.

6. Dissolve the precipitate with 10 ml. of hot (1+1)HCl (use pipette), collecting the filtrate in a 100 ml. beaker. Wash the paper with water.

7. Add 5 ml. of p-dimethylaminoazophenylarsonic acid solution and adjust the volume to 50 ml. and digest the solution on the steam bath for at least one hour.

8. Add a generous amount of paper pulp and filter the precipitate of zirconium hot. In order to prevent precipitation of titanium the solution must not be allowed to cool below 70° C during the filtration.

9. Wash the precipitate thoroughly with a hot wash solution of the dye (made by taking 10 ml. of the azo-arsenic acid solution, 70 ml. of conc. HCl and diluting to 500 ml. with water).

10. Transfer the paper and precipitate to a platinum crucible and remove most of the water by drying in an oven for about an hour. Then gently ignite the precipitate in a small muffle furnace at 500° C starting with a cold furnace.

11. Add 10 drops of H₂SO₄, cover the crucible and heat on the hot plate for about one-half hour to dissolve the zirconium residue. A small amount of silica

usually follows zirconium up to this point so that a complete solution of the residue may not result. However the zirconium is dissolved by this treatment.

12. Remove the cover and allow the sulfuric acid to evaporate on the hot plate until no more fumes of acid appear.

13. Holding the crucible with platinum tipped tongs, remove the last traces of sulfuric by gently heating below 500°C over a low burner.

14. Add 5.2 ml. of (1+4)HCl by a pipette. Cover the crucible and warm the solution a few minutes to dissolve the zirconium. Rinse the cover with water adding the washings to the crucible. Transfer the solution to a 25 ml. volumetric flask.

15. Adjust the volume to about 15 ml. with water. Cool. Add 5 ml. of alcohol and 3 ml. of quercetin using pipettes. Make the solution to the mark, mix and obtain the density of the solution in a spectrophotometer at 440 m μ .

16. Determine the amount of zirconium by reference to a standard curve.

Note 1: An aliquot of the solution should be taken at Step 14 if the sample is known to contain more than 25-50% ZrO_2 . Additional acid will then be required to bring the acidity up to 0.5N HCl used in determination of zirconium with quercetin.

Note 2: A blank should be run in the procedure.

For example 1.8 ZrO₂ was found in the combined residue of the filter paper and pulp used for the filtration of the azo-arseno precipitate.

TEST OF THE PROCEDURE

The procedure was applied to the determination of zirconium in glass sands, clays, and refractories. Bureau of Standards standard samples were used. The composition of the samples is given in Table 13. The results obtained for zirconium by the quercetin procedure are compared to certificate values in Table 14. The agreement is satisfactory.

Table 13
Composition of Standard Samples

	B.S. 76 (Burnt Refrac- tory)	B.S. 77 (Burnt Refrac- tory)	B.S. 78 (Burnt Refrac- tory)	B.S. 97 (Flint Clay)	B.S. 98 (Clay)
SiO ₂	54.68	32.38	20.69	42.87	59.11
Al ₂ O ₃	37.67	59.39	69.97	38.77	25.54
Fe ₂ O ₃	2.38	.90	.79	.98	2.05
TiO ₂	2.21	2.93	3.37	2.38	1.43
ZrO ₂	.07	.09	.12	.25	.041
P ₂ O ₅	.069	.45	.62	.08	.08
V ₂ O ₅	.021	.032	.047	.040	.025
Cr ₂ O ₃	-	-	-	.079	.021
CaO	.27	.26	.38	.10	.21
MgO	.58	.50	.51	.26	.72
K ₂ O	1.37	2.11	2.83	.54	3.17
Na ₂ O	.38	.86	.53	.33	.28
SO ₃	-	-	-	.042	.07
MnO	-	-	-	.002	.005
CuO	-	-	-	.003	.009
Ign. Loss	.22	.21	.26	13.35	7.28

Table 13 (Cont.)

Composition of Standard Samples

	B.S. 81 (Glass Sand)	B.S. 91 (Opal Glass)
SiO_2	-	67.53
MgO	.016	-
CaO	.029	10.48
Na_2O	-	8.48
K_2O	-	3.25
Al_2O_3	.265	6.01
F	-	5.72
As_2O_3		.091
As_2O_5	-	.102
Fe_2O_3	.0732	.081
PbO	-	.097
ZnO		.08
P_2O_5	-	.022
TiO_2	.095	.019
ZrO_2	.031	.0095
Cl	-	.014
Ign. Loss	.23	

Table 14

Comparison of Results
Of Zirconium Analysis

Sample No.	% ZrO ₂ Certified Analysis (Average)	% ZrO ₂ Quercetin Procedure
B. S. 76	0.07	0.072
B. S. 77	0.09	0.089
B. S. 78	0.12	0.112, 0.114
B. S. 81	0.031	0.033, 0.029
B. S. 91	0.0095	0.0100, 0.0104
B. S. 97 .	0.25	0.245
B. S. 98	0.041	0.0409

EXPERIMENTS

1. Separation of Microgram Amounts of Zirconium from Milligram Amounts of Titanium. In these experiments zirconium was precipitated hot with 5 ml. of the pararsonic acid solution from a total volume of 50 ml. of (15+85)HCl solution and containing various amounts of titanium. The titanium was added as a dilute hydrochloric acid solution of the salt $Ti(OAc)_2Cl_2$. The zirconium precipitate was filtered hot after one hour and washed with a hot wash solution of the dye (See Procedure). The precipitate was ignited in porcelain and fused with a small amount of $K_2S_2O_7$. The cooled melt was leached with 10 ml. of (1+9) HNO_3 , a few drops of H_2O_2 were added and the titanium color was compared with a series of titanium standards. Table 15 illustrates the combinations used and the amount of TiO_2 coprecipitated under these conditions. The maximum amount of TiO_2 coprecipitated was $25\% TiO_2$ when $500\% ZrO_2$ was used. Because quercetin is capable of determining just a few micrograms of ZrO_2 even this slight interference of TiO_2 is removed by dilution.

2. Behavior of Various Elements under the Conditions of Precipitation of Zirconium with Pararsonic Acid. Various elements were tested to determine the precipitating action of pararsonic acid in hot (15+85)HCl solution. The solutions were made to 50 ml. volume and contained 5 ml. of the pararsonic acid solution. Each solution was kept on steam bath for at least one hour. The solutions were then

examined while still hot for any precipitate that might be present. An estimate of the amount of each element precipitated was made from the size of the precipitation obtained. The results are given in Table 16.

3. Incomplete Removal of Fluoride by Prolonged Fuming with Perchloric Acid. Five milliliters of hydrofluoric acid and one ml. of perchloric acid were added to a chloride solution in a 30 ml. platinum crucible containing 0.1 g. Al_2O_3 and 0.250 mg. ZrO_2 . The resulting solution was evaporated on the steam bath and then on a hot plate to remove the perchloric acid. One ml. HClO_4 solution was added and fumed dry on the hot plate. This was repeated twice more with 1 ml. portions of HClO_4 . The residue was dissolved in 10 ml. of (1+1) HCl by warming and the solution transferred to a small beaker. Water was added to 30 ml. and 5 ml. of the pararsonic acid solution was added. The volume was adjusted to 50 ml. with water and the solution heated on the steam bath for one hour. No precipitate of zirconium formed. This experiment was repeated several times with the same result. When the experiment was repeated in the absence of aluminum only 80% of the zirconium was precipitated.

Table 15

Coprecipitation of Titanium

Combination Taken		TiO ₂ Coprecipitated
7	mg. TiO ₂	
0.5	mg. ZrO ₂	0.025 mg. TiO ₂
7	mg. TiO ₂	
0.25	mg. ZrO ₂	0.020 mg. TiO ₂
7	mg. TiO ₂	
0.15	mg. ZrO ₂	0.020 mg. TiO ₂
10	mg. TiO ₂	
0.10	mg. ZrO ₂	0.015 mg. TiO ₂
10	mg. TiO ₂	
0.05	mg. ZrO ₂	0.015 mg. TiO ₂
0.2	mg. TiO ₂	
0.05	mg. ZrO ₂	not detected
0.05	mg. TiO ₂	
0.02	mg. ZrO ₂	not detected

Table 16

Elements Precipitated by Pararsonic
Acid in Hot (15-85)HCl Solution

Element Taken	Amount Tested As Oxide (Mg.)	Observations
Sc	20	Large ppt; about 3 mg.
Sc	1	Small ppt; about 0.4 mg.
Sc	0.5	Small ppt; about 0.02 mg.
W	1	Ppt; prob. quantitative
Mo	50	No ppt.
Sb	50	No ppt.
Th	40	Small ppt; about 0.03 mg.
Th	10	Small ppt; about 0.005 mg.
Bi	50	No ppt.
Nb	1	Ppt; prob. quantitative
Ta	1	Ppt; prob. quantitative
Au	5	No ppt.
Be	50	No ppt.
Ga	50	No ppt.
Ge	15	No ppt.
V ⁺⁵	50; 5	No ppt; destroys dye
Cr ⁺³	50	No ppt.
U	50	No ppt.
Pt	50 mg. Pt	No ppt.
Sn ⁺⁴	50	No ppt.
Ce ⁺³	20	No ppt.

Table 16 (Cont.)

Elements Precipitated by Pararsonic
Acid in Hot (15+85)HCl Solution

Element Taken	Amount Tested As Oxide (Mg.)	Observations
Y	20	No ppt.
Pr	20	No ppt.
Gd	20	No ppt.

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