Studies on the Organic Reagents for the Inorganic Analysis. I. Phenylfluorone as Sensitive Reagent for Colorimetric Determination of Zirconium

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Although many reagents and procedures are available for the determination of macro amounts of zirconium, the situation is far from satisfactory with respect to the determination of microgram amounts. Alizarin (or Alizarin Reds)[1-5] is the most general reagent for the colorimetric determination of zirconium, but its reaction is not too sensitive. The procedures using *p*-dimethylaminoazophenylarsonic acid[6,7] and the method using phosphomolybdic acid[8] are both indirect. Only quercetin has been recently reported as the sensitive reagent for the colorimetric determination of zirconium[9].

The purpose of this investigation was to find a colorimetric reagent sensitive to small concentrations of zirconium. The studies on the reaction between ortho diphenol derivatives and zirconium or other metals show that the ortho diphenol derivatives, having the mesomeric group at its para position, combine with metals and cause remarkable color change, which is larger in the case of zirconium than the other metals[10]. On the other hand the phenylfluorone (abbreviation of 2,3,7-trihydroxy-9-phenylfluorone), which is one of the ortho diphenol derivatives concerned, has been recently employed as the sensitive reagent for germanium[11]. These facts lead us to the expect that this reagent might be one of the most sensitive reagents for the colorimetric determination of zirconium.

1) H. A. Liebhafsky and E. H. Winslow, *J. Am. Chem. Soc.*, **60**, 1776 (1938).
2) J. F. Flagg, H. A. Liebhafsky and E. H. Winslow, ibid., **71**, 3630 (1949).
3) D. E. Green, *Anal. Chem.*, **20**, 370 (1948).
4) G. B. Wengert, ibid., **24**, 1449 (1952).
5) A. Mayer and G. Bradshaw, *Analyst*, **77**, 476 (1952).
6) V. A. Nazarenko, *Zhur, Priklad, Khim*, **10**, 1696 (1937).
7) W. G. Hayes and E. W. Jones, *Ind. Eng. Chem., Anal. Ed.*, **13**, 603 (1941).
8) E. W. Kiefer and D. F. Boltz, *Anal. Chem.*, **24**, 542 (1952).
9) F. S. Grimaldi and C. E. White, ibid., **25**, 1886 (1953).
10) F. Ihmura, H. Sano and M. Asada, Symposium on complex Chemistry, Osaka City Univ., Nov. 1955 : To be published shortly.

Experimental

Apparatus and Reagents.—The absorbancy measurements were made with a Beckman Model DU spectrophotometer and 1 cm. glass cell. The reference cell contained distilled water for all the measurements.

The alcoholic solution of phenylfluorone (1 ml. contain 0.6 mg. of phenylfluorone) was made up in the following way: 0.6 g. phenylfluorone, which was synthesized from hydroxyhydroquinone triacetate and benzaldehyde according to Cluley's prescription[11], was dissolved into 800 ml. of ethyl alcohol and 5 ml. of 0.1N hydrochloric acid and was diluted to 1 l. with ethyl alcohol.

Zirconyl chloride stock solution was prepared from reagent grade zirconium dioxide contained less than 0.2 per cent hafnium dioxide by spectrographic tests, and standardized gravimetrically using distilled ammonium hydroxide. The working zirconium chloride solution was prepared by dilution from the stock solution every time of experiment.

Distilled hydrochloric acid was used for all work.

Ethyl alcohol: Reagent grade 100 percent ethyl-alcohol.

Cyclohexanol: Reagent grade.

Fundamental Reaction.—The treatment of slightly acidic solution of zirconyl ions with an excess of a standard phenylfluorone solution results in the color change from yellow to red, and then the precipitation after being allowed to stand. This precipitation has the composition of four phenylfluorone to a zirconium atom quantitiatively. This shows, therefore, also the possibility of micro gravimetric analysis of zirconium. Various organic solvents, such as benzene, toluene, cyclohexanol, ethyl ether, isopropyl ether, acetone, ethyl isopropyl ketone, dioxane, methyl alcohol, ethyl alcohol, isopropyl alcohol, *n*-butyl alcohol, isobutyl alcohol, *n*-amyl alcohol, acetic acid, acetic anhydride, ethyl acetate, carbon tetrachloride, chloroform, petroleum ether, quinoline, carbon disulfide, etc., were tried to dissolve the red colored complex, but it was difficult. Then, it was alternatively tried to keep the complex in the colloidal solution with the addition of a suitable stabilizer. Among gum arabic, gelatin, soluble starch, cylohexanol, etc., tested, cyclohexanol was found as the most favorable stabilizer. In the experiments all the

11) H. J. Clueley, *Analyst*, **76**, 523 (1951).

solutions were made to a total volume of 50 ml. The order of addition of the reagents was always the same. The zirconium solution was added first; and acid, alcohol, cyclohexanol, and alcoholic solution of phenylfluorone were added in this order.

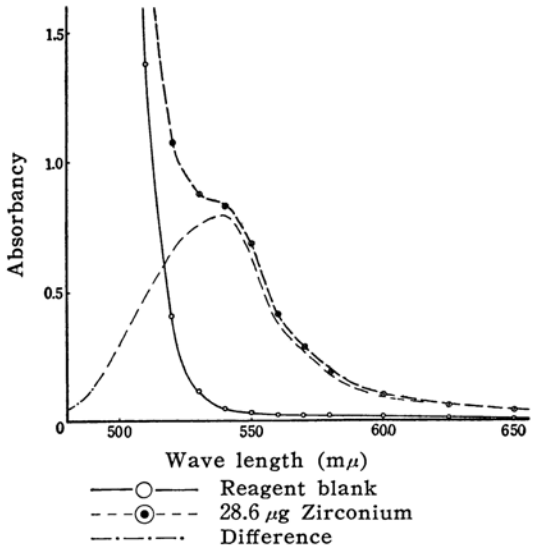

Fig. 1. Absorption spectra.

Spectral absorbancy data for the reagent blank and 28.6 μg. of zirconium (following the standard procedure mentioned later) are given in Fig. 1. The optimum wave length was taken as 530-550 mμ because at this range the absorption given by the blank is small and that by zirconium sufficiently large.

Effect of Alcohol and Cylohexanol Concentration.—A precipitate of zirconium phenylfluoronate is obtained after a while from solutions containing no cyclohexanol and less than 10ml. of alcohol. Although the colored solution becomes stable with increase in the amount of cyclohexanol added, cyclohexanol layer separates from alcoholic water layer in above a certain amount of cyclohexanol to the amount of alcohol added. The solution shows no differece in its absorbancy with the variation of the amount of alcohol or cyclohexanol added. From these results 5 ml. of cyclohexanol, 10 ml. alcohol and 10ml. alcoholic solution of phenylfluorone was taken as optimum.

Effect of Acidity and Digestion Time.— The effect of acid concentration and digestion time on the absorbancy given by 17.2 μg. of zirconium and 3 mg. phenylfluorone is illustrated in Table I. A precipitate of zirconium phenylfluoronate is obtained after it is allowed to stand for a day, but the stable suspension is able to regenerate with short shaking by hand. The absorbancy given by this procedure was shown as the data after a day. The absorbancy in 0.05 N hydrochloric acid solution is nearly constant but that in 0.10 N hydrochloric acid solution increases slowly by time. These data show that the increase of acidity causes the decrease of its absorbancy and that it means the decrease of the velocity to reach its equilibrium.

From these results it would be expected that the increase of the amount of phenylfluorone is available for obtaining the stable absorbancy in higher acidity, because the reaction should be the competition of hydrogen ion concentration with reagent concentration. The data given by 17.2 μg. of zirconium and 6 mg. of phenylfluorone are shown in Table I, too.

The stability in this condition is more favorable particularly in 0.10N HCl, than the case of 3 mg. reagent. The reagent blank shows no variation in absorbancy at 540 mμ or more, for increasing its acidity, though the decrease in absorbancy occurs at below 530 mμ.

The stability of absorbancy for the time in the acid concentrations above 0.15 N is not so suitable as below 0.10 N for the practical procedure, probably because of its slow velocity to reach the equilibrium.

Standard Procedure.—The following was recommended as the optimum procedure from the results above mentined.

Transfer the sample solution (less than 20ml.) to a 50 ml. volumetric flask. If the sample is known to contain more than 40 to 50 μg. zirconium, an aliquot portion of the sample solution containing the desired amount of zirconium in a final volume is pipetted into a 50 ml. volumetric flask. Additional acid will then be required to bring the acidity up to 0.10 N hydrochloric acid used in the determination of zirconium with phenylfluorone. Adjust the volume to about 20 ml. with distilled water. Add 10 ml. of alcohol, 5 ml. of cyclohexanol, and 10 ml. of alcoholic solution containing 6 mg. of phenylfluorone in this order using pipettes. Make the solution to the mark, mix with shaking by hand, allow to stand for about two hours, and obtain the absorbancy of the solution in the spectrophotometer

TABLE I

ABSORBANCY IN DIGESTION TIME (min.)

Amount of Phenylfluorone	30	50	75	90	120	180	240	1500	Concn. of HCl
3 mg.	0.410	0.450	0.448	0.448	0.447	0.445	0.444	0.443	0.05N
	0.226	0.260	0.295	0.317	0.349	0.389	0.418	0.432	0.10N
	0.507	0.520	0.528	0.535	0.542	0.557	0.565	0.574	0.05N
6 mg.	0.442	0.470	0.486	0.496	0.510	0.523	0.530	0.540	0.10N
	0.359	0.400	0.430	0.445	0.463	0.492	0.501	0.518	0.15N

at 540 mμ using a 1 cm. glass cells and distilled water as a control solution. Determine the amount of zirconium by reference to a standard working curve.

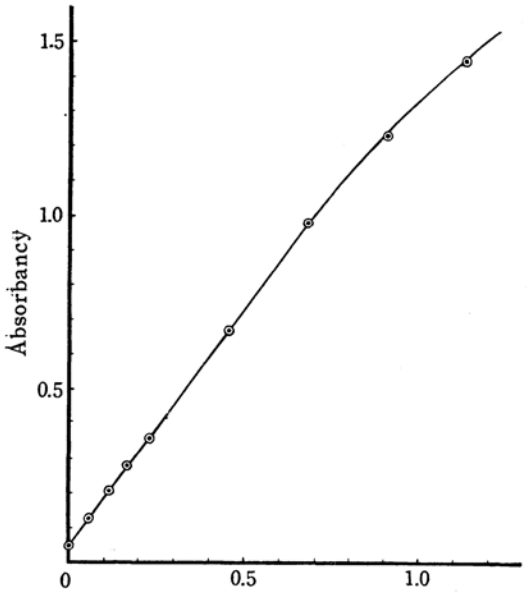

Fig. 2. Working curve

Working Curve.—Data for the working curve are given in Fig. 2. These data were obtained following the standard procedure. The solution was 0.10 N in hydrochloric acid and contained 10 ml. of alcohol, 5 ml. of cyclohexanol, and 10 ml. alcoholic solution of phenylfluorone in a total volume of 50 ml. The absorbancy was measured after allowing it to stand for about two hours. A straight line relationship between absorbancy and micrograms of zirconium is shown up to 0.7 p. p. m. Solutions containing from 0.7 to 1.0 p. p. m. deviate from the Beer's law but their absorbancies are reproducible.

The sensitivity of this method, given by the inclination of the working curve, is about forty or fifty times for Alizaline Red S method, and several times for quercetin method reported as the sensitive method for the determination of zirconium.

Effect of Diverse Ions.—The effect of various ions was studied using 0.3 p. p. m. of zirconium. The standard procedure was employed, with the exception that the desired amount of the diverse ion was added prior to the zirconium solution. In present of iron (III) or titanium (IV) a precipitation occurs, so the solution was allowed to stand for about two hours in a cell and the absorbancy was measured after they precipitated. The concentration of zirconium and diverse ion are expressed on the basis of the final volume 50 ml. The change in absorbancy was then measured at 540 mμ. Errors of less than 2 per cent of the zirconium present were considered negligible. A negligible error was obtained with the following maximum about:

2000 p. p. m. of: sodium, potassium, ammonium, magnesium, calcium, barium, strontium, zinc, cadmium, mercurous and mercuric.

500 p. p. m. of: lanthanum, neodymium, cerrous, silver and lead.

100 p. p. m. of: aluminium, thorium and uranyl. Chloride, bromide, nitrate, acetate (2000 p. p. m.) and sulfate (1000 p. p. m.) ions do not interfere.

Some elements interfere by decreasing the color intensity given by zirconium. Some elements produce colors with phenylfluorone. Table II lists the interfering ions and their effect.

TABLE II

INTERFERING DIVERS IONS

Ion	Amount added p. p. m.	Error, %	Permissible Amount, p. p. m.
Fe^{3+}	1.5	10	0.3
Ti^{4+}	0.5	20	0.05
Ge^{4+}	0.1	10	0.02
Sn^{4+}	0.1	10	0.02
As^{3+}	10	2	10
Sb^{3+}	1	5	0.4
F^-	2	25	0.1
$C_2O_4^{2-}$	55	20	0.5
HPO_4^{2-}	5	10	1

Serious interference is given by the following ions: oxalate, fluoride, phosphate, titanium, germanium, tin, iron (III) and antimony tested.

Some additional observations are to be noted. Phenylfluorone is useful as a colorimetric reagent for fluorine (by quenching of the zirconium phenylfluoronate color)[12] and may prove effective for tin (IV) or hafnium. These color reactions are being investigated.

Summary and Discussion

Methods reported in the literature for the determination of zirconium are generally designed for relatively large amounts of this element, in spite of the fact that a procedure using colorimetric reagent for the determination of trace amounts is desirable. The systematic studies on the organic reagents for the spectrophotometric determination of several metals led us the phenylfluorone as one of the most sensitive reagents for the colorimetric determination of zirconium. The phenylflurone method recommended here, which is carried out in 0.1 N hydrochloric acid solution, shows the about forty or fifty times sensitivity of Alizarine Red S method and the several times of Quercetin method reported later as a sensitive reagent for zirconium. The solution becomes stable enough to carry on the colorimetric determination by adding some cyclohexanol and

12) H. Sano, *Japan Analyst*, **5**, 289 (1956).

ethyl alcohol, although it is not true solution but colloidal.

On the other hand the investigation to find a phenylfluorone derivative to make a soluble complex with metals has succeeded recently[13]. The new reagent, 2,3,7-trihydroxyl-9-(4-dimethylaminophenyl)-fluorone, synthesized by the authors and Miss M. Asada give a soluble colored complex with germanium and make colorimetric procedure very convenient. This new reagent also forms a soluble intense colored complex with zirconium. This detailed investigation will be published before long.

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13) K. Kimura, H. Sano, and M. Asada, *Bull. Chem. Soc. Japan*, **29**, 640 (1956).