Studies on Organic Reagents for Inorganic Analysis. V. m-Nitrophenylfluorone for the Spectrophotometric Determination of Zirconium

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For the determination of zirconium, the phenylfluorone (abbreviation for 2,3,7-trihydroxy-9-phenylfluorone) method was recommended previously by the present author and Kimura(1). The reactions between phenylfluorone and several metals were also studied(2,3). The method, which is about forty times more sensitive than the alizarin red S method(4), is the most sensitive method for the colorimetric determination of zirconium, but the absorbance of the chelate decreases with increasing acidity in the solution. On the other hand, several derivatives of phenylfluorone were synthesized by the author, and the effect of the substituent on the utility of the derivative as a spectrophotometric reagent was studied(5,6). The results suggested that *m*-nitrophenylfluorone (abbreviation for 2,3,7-trihydroxy-9-(3′-nitrophenyl)fluorone) was one of the most excellent reagents in view of the sensitivity, stability, and other characteristics. In this paper, detailed procedure for the spectrophotometric determination of zirconium using this reagent is described.

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1) K. Kimura and H. Sano, This Bulletin, **30**, 80 (1957).

2) H. Sano, ibid., **30**, 790 (1957).

3) H. Sano, *Japan Analyst* (*Bunseki Kagaku*), 7, 235 (1958).

4) E. B. Sandell, "Colorimetric Determination of Traces of Metals", 2nd Ed., (1950), Interscience Publishers Inc., New York.

5) H. Sano, This Bulletin, **30**, 672 (1958).

6) H. Sano, ibid., **30**, 974 (1958).

Experimental and Results

Apparatus and Reagents Used. — The absorbance measurements were made with a UVISPEK spectrophotometer using a 10 mm. glass cell. The reference cell contained distilled water for all the measurements, except for the measurement of the absorption spectrum of the chelate, in which the blank solution was used as a reference solution.

Ethanolic solution of m-nitrophenylfluorone was made up in the following way: *m*-nitrophenylfluorone was synthesized from hydroxyhydroquinone triacetate and *m*-nitrobenzaldehyde according to the prescription reported previously[2,3], and 0.120 g. of this reagent was dissolved in 150 ml. of ethanol and 1 ml. of 5 N hydrochloric acid by warming. After being cooled, the solution was diluted to 200 ml. with ethanol.

Ethanolic solution of phenylfluorone was prepared dy dissolving 120 mg. of phenylfluorone in 150 ml. and 1 ml. of 5 N hydrochloric acid, and diluting to 200 ml. with ethanol.

Zirconyl chloride stock solution was prepared by dissolving analytical grade zirconyl chloride octahydrate in 1 N hydrochloric acid, and standardized gravimetrically using distilled aducous ammona. This solution contains 2.07 mg. of zirconium per ml. A working solution was prepared from the stock solution by dilution with dilute hydrochloric acid, every time an experiment was made,

Cyclohexanol.—Reagent grade cyclohexanol was used without further purification.

Ethanol: Reagent grade 99% ethanol was used.

Fundamental Reaction.—The treatment of slightly acidic solution of zirconyl ions with an excess of a standard *m*-nitrophenylfluorone solution results in a color change from yellow to red; an orange-red colored precipitate appears, aftar it is allowed to stand. Various organic solvents, such as acetic acid anhydride, acetone, benzene, carbon disulfide, carbon tetrachloride, chloroform, cyclohexane, cyclohexanol, dioxane, ethanol, ethyl acetate, diethyl ether, ethyl *iso*propyl ketone, *iso*butanol, *iso*propanol, di*iso*propyl ether, methanol, *n*-pentanol, *n*-butanol and petroleum ether were tried to dissolve the precipitate of zirconium *m*-nitrophenylfluoronate, with little success. Then an attempt was made to keep the complex in the supersaturated or colloidal solution with the addition of a suitable stabilizer. A cyclohexanol-ethanol mixed solution was found to be the most favorable stabilizer. In the experiments described below, all the solutions were made to a total volume of 25 ml. The order of the addition of the reagents was always the same. The zirconium solution was added first; and acid, ethanol, cyclohexanol, and ethanolic solution of *m*-nitrophenylfluorone were added in this order.

Spectral absorbance data for the reagent blank and 20.7 μg. of zirconium (following the standard procedure mentioned later) are given in Fig. 1. The absorption maximum of the dye and the chelate was found at 475 mμ and 550 mμ, respectively. The optimum wavelength was taken as 550 mμ because at this point the absorption caused by the blank solution is small and that by zirconium *m*-nitrophenylfluoronate is the greatest.

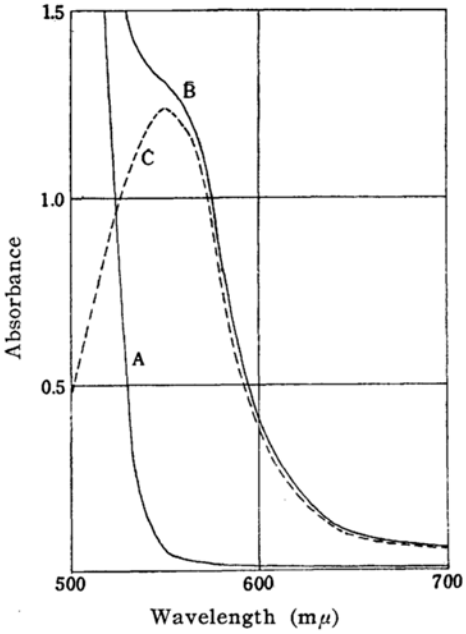


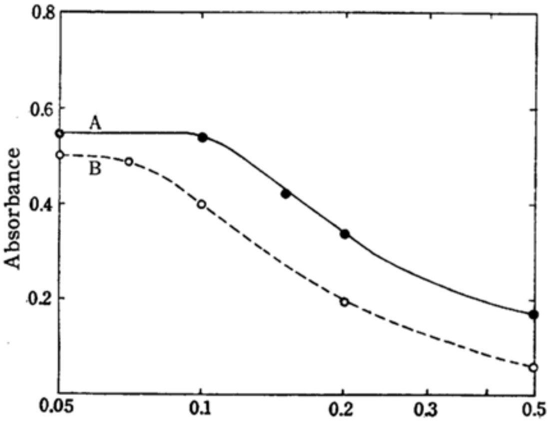
Fig. 1. Absorption spectra.

Curve A: Reagent blank (Reference solution: water)
Curve B: 20.7 μg. Zirconium (Reference solution: water)
Curve C: 20.7 μg. Zirconium (Reference solution: reagent blank solution)

Effect of Cyclohexanol and Ethanol Concentration.—A precipitate of zirconium *m*-nitrophenylfluoronate is obtained after a while from a solution containing no cyclohexanol and less than 5 ml. of ethanol. The colored solution becomes stable as an increasing amount of cyclohexanol is added, but cyclohexanol layer separates from ethanolic water layer when the amount of cyclohexanol becomes relatively great in comparison with that of ethanol. The solution shows no difference in the position of absorption maximum when the amount of cyclohexanol or ethanol added is changed, although there was a slight difference in the detailed shape of the absorption curve. From these results, 2.5 ml. of cyclohexanol, 5 ml. ethanol, and 5 ml. ethanolic solution of *m*-nitrophenylfluorone were taken as the optimum. In this condition, the solution gives no visible precipitate of *m*-nitrophenylfluoronate in zirconium concentration below 3 μg. per 25ml. by being allowed to stand for a day or more.

Effect of Acidity.—The effect of acid concentration upon the absorbance given by 20.7 μg. of zirconium and 3 mg. of *m*-nitrophenylfluorone is illustrated in Fig. 2, together with the case given by 20.7 μg. of zirconium and 3 mg. of phenylfluorone* for the purpose of comparison. The absorbances shown in Fig. 2, are the values observed thirty minutes after the preparation of the solution. In the acidity range higher than 1.5 N hydrochloric acid concentration, the absorbances increase slowly with increasing digestion time, so the plateau range of the curve extends a little. In the case of *m*-nitrophenylfluoronate the absorbance is almost independent of hydrochloric acid concentration in the region below 0.1 N, whereas no plateau range is found above 0.05 N acid concentration in the case of phenylfluoronate.

Effect of Digestion Time. — The effect of digestion time on the absorbance given by 5.0 μg. of zirconium and 3 mg. *m*-nitrophenylfluorone in 0.1 N hydrochloric acid solution is shown in Fig. 3. In a solution containing zirconium above 4 μg., a precipitate of zirconium *m*-nitrophenylfluoronate is obtained after the solution is allowed to stand for a day, but the stable suspension can regenerate with a short shaking by hand. The absorbance remains nearly constant for forty minutes after the preparation.



Hydrochloric acid concentration (log. scale)

Fig. 2. Effect of acidity.

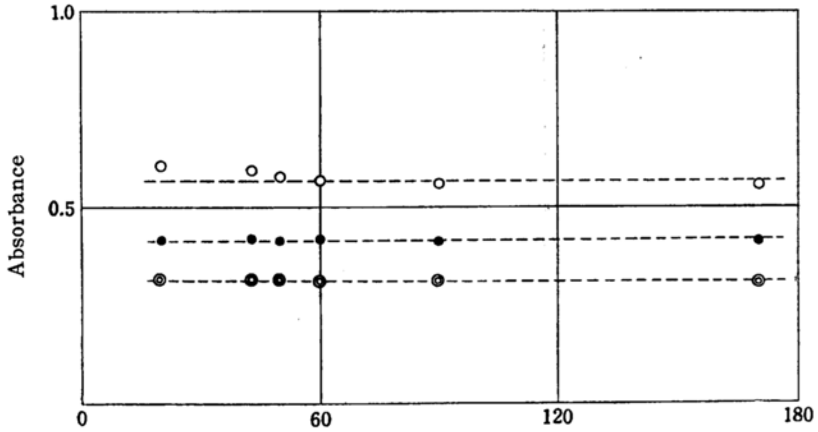
Curve A: Zirconium *m*-nitrophenylfluoronate (Reference solution: water)

Curve B: Zirconium phenylfluoronate (Reference solution: water)

Standard Procedure.—From the results above mentioned, the following was recommended as the optimum procedure.

Transfer the sample solution (less than 10 ml.) to a 25 ml. volumetric flask. When the sample contains more than 20 to 25 μg. zirconium, an aliquot portion of the sample solution containing the desired amount of zirconium in final volume is pipetted into a 25 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 *m*-nitrophenylfluorone. Adjust the volume to about 10 to 12 ml. with distilled water. Add 5 ml. of ethanol, 2.5 ml. of cyclohexanol, and 5 ml. of ethanolic solution containing 3 mg. of *m*-nitrophenylfluorone in this order. Make up the solution to the mark with distilled water, mix with shaking by hand, allow to stand for an hour, and obtain the absorbance of the solution in the spectrophotometer at 550 mμ using a 10 mm. glass cell and distilled water as a control solution. Determine the amount of zirconium by reference to the standard working curve prepared previously.

Working Curve.—Data for the working curve are given in Fig. 4. These data were obtained following the standard procedure. A straight-line relationship between the absorbance and the amount of zirconium is shown up to 0.6 p. p. m. Solutions containing from 0.6 to 1.0 p. p. m.



Time (min.)

Fig. 3. Effect of digestion time.

-○- 540 mμ (Reference solution: water)
-●- 550 mμ (〃)
-◎- 560 mμ (〃)

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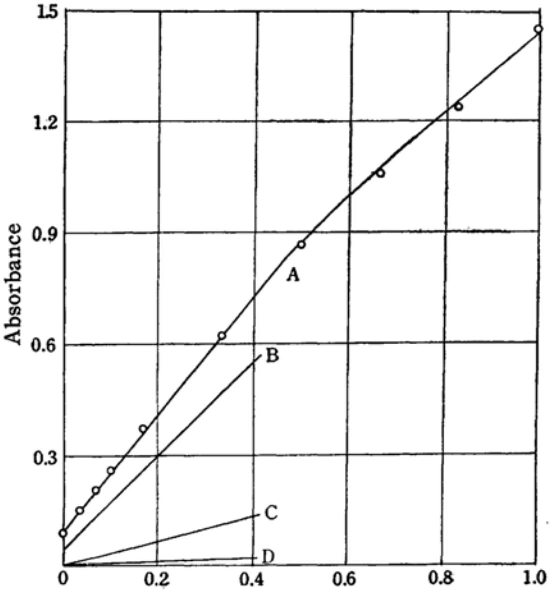
* The absorbance measurements were made by a procedure similar to that of *m*-nitrophenylfluoronate.

deviate slightly from Beer's law but their absorbances are reproducible. The region from 0 to 0.10 p. p. m. of zirconium was examined in detail for any deviation from the straight-line relationship, but none was found. In Fig. 4, the working curves used in the Alizarin Red S method4) and in the Phenylfluorone mothod1) are shown for the comparison of the sensitivities of the methods.

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 into a volumetric flask prior to the addition of the zirconium solution. The concentrations of zirconium and diverse ion are expressed on the basis of the final volume 25 ml. The change in absorbance was then measured at 550 mμ. Errors of less than 3% of the zirconium present were considered to be negligible. A negligible error was obtained with the following maximum about;

2000 p. p. m. of: sodium, potassium, ammonium and magnesium ions.
1000 p. p. m. of: calcium, barium, strontium and mercuric ions.
500 p. p. m. of: lanthanum, neodymium, cerrous, cadmium and zinc ions.
100 p. p. m. of: aluminum and thorium ions.

Chloride, bromide, nitrate (2000 p. p. m.) and sulfate (1000 p. p. m.) ion do not interfere with the reaction. Some elements give interference by increasing the color intensity. Some elements quench the color due to zirconium *m*-nitrophenylfluoronate. Table I lists the interfering ions and their effect. Serious interference is given by the following ions: titanium, germanium, tin, iron (III), antimony, oxalate, phosphate and fluoride.



Zirconium (p. p. m.)

Fig. 4. Working curve.
Curve A: This method.
Curve B: Phenylfluorone method.
Curve C: Quercetin method.
Curve D: Alizarin S method.

TABLE I
INTERFERING DIVERSE IONS

Ion	Amount added p. p. m.	Error %	Permissible amount p. p. m.
Fe(II)	2.0	2	3
Fe(III)	2.0	10	0.6
Ti(IV)	0.2	40	0.01
Ge(IV)	0.4	20	0.06
Sn(IV)	0.4	10	0.1
As(III)	10	2	15
As(V)	10	10	3
Sb(III)	2	10	0.6
Sb(V)	2	10	0.6
F^-	2	25	0.2
$C_2O_4^{2-}$	5	20	0.7
HPO_4^{2-}	5	20	0.7

Discussion

The color change arising from the reaction of *m*-nitrophenylfluorone with zirconium closely resembles the case of phenylfluorone, namely the shift of the absorption maximum caused by chelate formation is 75 mμ in *m*-nitrophenylfluorone, and 72 mμ in phenylfluorone2), whereas the differences of the absorption maximum between the phenylfluorone or its zirconium chelate and *m*-nitrophenylfluorone or its zirconium chelate are 7 and 10 mμ, respetively. The trend in the effect of the acidity of the solution on the absorbance is, however, considerably different. In the *m*-nitrophenylfluorone method recommended here the constancy of the absorbance is obtained at the region of the acidity below 0.10 N hydrochloric acid concentration, whereas there is no such constancy in the phenylfluorone method. This will be caused by the effect of the *m*-nitro group attracting the electron of the —OH group at 3 position and increasing the electronegativity of the oxygen atom. Furthermore, it was fortunately found that the absorbance of *m*-nitrophenylfluoronate was greater than that of the corresponding phenylfluoronate. The comparison of the sensitivities by several methods is shown in Fig. 4. The sensitivity of this method, given by the inclination of the working curve, is nearly fifty times as great as that the alizarin red S method4), about five times that of the quercetin method7), and about 1.2 times for the phenylfluorone method1). In

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7) F. S. Grimaldi and C. E. White, *Anal. Chem.*, **25**, 1886 (1953).

the region from zero to 0.15 p. p. m. of zirconium, the solution remains without any visible precipitation for three days or more, so the stability of the absorbance seems to be greater than that in the phenylfluorone method. These facts show the method is excellent for the determination of a micro amount of zirconium.

Summary

The spectrophotometric determination of a micro amount zirconium, using *m*-nitrophenylfluorone, has been described. The method recommended here, which is carried out in 0.1 N hydrochloric acid solution, shows nearly fifty times the sensitivity of the alizarin red S method, about five times that of the quercetin method, and about 1.2 times that of the phenylfluorone method reported previously as the most sensitive reagent by the author and K. Kimura. The solution becomes stable enough to carry on the spectrophotometric determination by adding some cyclohexanol and ethanol, and no precipitation is found for the small amount of zirconium. Furthermore, the stability for increasing acidity in the solution is greater than that of the phenylfluorone method. The method is found to be suitable for the determination of 0 to 0.5 p. p. m. of zirconium. Transfer the sample solution (less than 10 ml.) to a 25 ml. volumetric flask. Then add additional acid to bring the acidity up to 1.0 N hydrochloric acid and 7.5 ml. cyclohexanol-ethanol (1 : 2) mixed solution, and 5 ml. ethanolic solution containing 3 mg. *m*-nitrophenylfluorone in that order. Adjust the volume to 25 ml., shake the solution, allow to stand for one hour, and read the absorbance of the solution with a spectrophotometer at 550 mμ with 1-cm. glass cells and distilled water as a control solution. Oxalate, fluoride, phosphate, titanium, germanium, iron(III) and antimony cause serious interference.

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