Studies on Organic Reagents for the Colorimetric Analysis of Germanium. III.[1,2] *Colorimetric Determination of Germanium with a New Reagent*

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In the previous report[2], it was demonstrated that a new compound, 2,6,7-trihydroxy-9 [4′-dimethylaminophenyl]-fluorone (hereafter called "dimethylaminophenylfluorone"), is a suitable reagent for the colorimetric determination of germanium. In this paper, the authors describe a detailed procedure for the determination of germanium using this compound.

Experimental

As mentioned in the previous paper[2] dimethylaminophenylfluorone forms a soluble complex with germanium in ethanolic solution containing hydrochloric acid. In order to use this compound as a colorimetric reagent, it was necessary to explore favourable experimental conditions under which a stable germanium complex is formed with adequate absorption for colorimetry.

Reagents.—Standard germanium solutions: A series of solutions were prepared by the same procedure as described in the preceding paper[2].

One tenth per cent dimethylaminophenylfluorone solution (hereafter called "reagent solution"): One tenth gram of dimethylaminophenylfluorone was dissolved in a mixture of 80 ml. of ethanol and 5 ml. of 6 N hydrochloric acid. The resulting solution was diluted to 100 ml. with ethanol.

Effect of Acid Concentration on the Complex Formation.—Five milliliter portions of germanium standard solution were taken in 50-ml. measuring flasks. Then each solution was diluted to approximately 30-ml. with hydrochloric acid and water. The reagent was added to these solutions at room temperature. The final concentrations of hydrochloric acid and the reagent in these solutions ranged from 0.3 to 1.5 N and 0.006 to 0.020% by weight respectively. When the volume of the reagent solution to added was less than 10 ml., it was diluted to 10 ml. with ethanol before being mixed with germanium solution. After mixing, the solution was diluted to 50 ml. with water. The final solution contained 34.7 μg. of germanium. A reference solution was prepared by similar procedure without germanium. The results are shown in Fig. 1. It is clear from Fig. 1 that at acid concentrations over 0.6 N, the absorption of the complex decreases very slightly with the increase in acid concentration. At acid concentrations between 0.3 and 0.6 N, the absorption is almost constant.

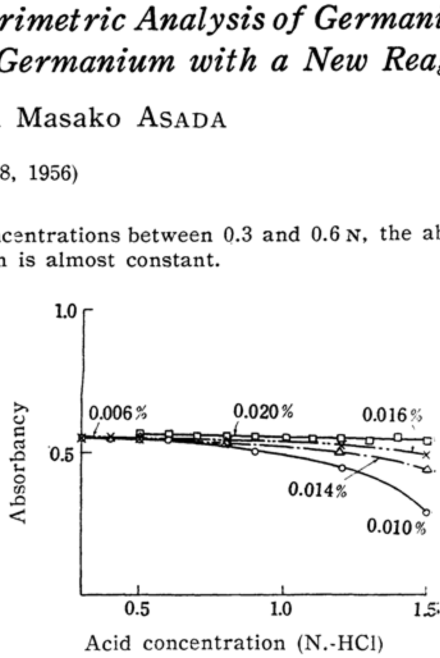

Fig. 1. Effect of Acid Concentration

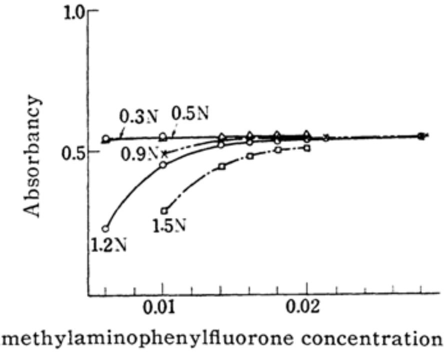

Fig. 2. Effect of Dimethylaminophenylfluorone Concentration

Effect of Reagent Concentration on the Complex Formation.—Test solutions were prepared by the same procedure as before and the effects of reagent concentrations were examined at hydrochloric acid concentrations between 0.3 N to 1.5 N. When the solutions contain more than 0.020% of dimethylaminophenylfluorone by weight, 0.15% reagent was used. The results of the measurements of the absorption are shown in Fig. 2. From Fig. 2 it is seen that the absorption remain almost unchanged in a 0.5 N acid solution, without regard to the change in the concentration of the reagent.

Effect of Time after the Addition of Reagent.—Five milliliters of a standard germanium solution was taken in a 50-ml. measuring flask. After the addition of 5 ml. of 6 N hydrochloric acid, it was diluted to approximately 30 ml. with water. The solution was cooled down to room tempera-

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[1] K. Kimura, K. Saito, M. Asada, This Bulletin, 29, 635 (1956).

[2] K. Kimura, H. Sano, M. Asada, ibid., 29, 640 (1956).

ture, mixed with 10 ml. of 0.05% reagent solution and then diluted to a difinite volume with water. The reference solution was prepared by a similar procedure without germanium. After the solution was kept in running water for thirty minutes at 6°C, the absorbancy was measured at 510 and 520 mμ. The results are shown in Fig. 3. It seems that the development of color of the complex is complete in less than fifteen minutes after the addition of the reagent.

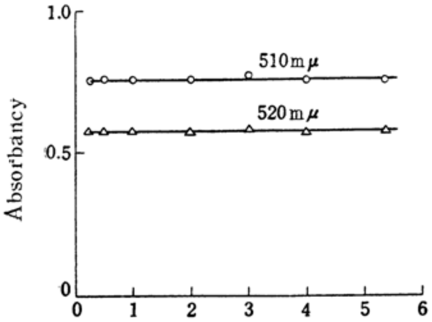


Fig. 3. Effect of Time

Effect of Temperature.—Test solutions were prepared by a similar method as described before. These solutions were allowed to stand for thirty minutes at various temperatures: 0°C, 6.0°C, 7.0°C, 17.3°C and 30.2°C. The absorption of these solutions was measured at 510 and 520 mμ. The results are shown in Fig. 4. It is clear that temperature has no effect on the absorption of the complex in a range 0° to 30.2°C. At 0°C, however, a slight precipitation of the reagent was observed after two hours since the solution was prepared. Hence, it is desirable to measure absorption within two hours after the reagent is added.

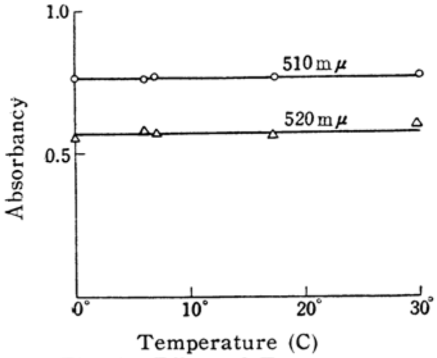
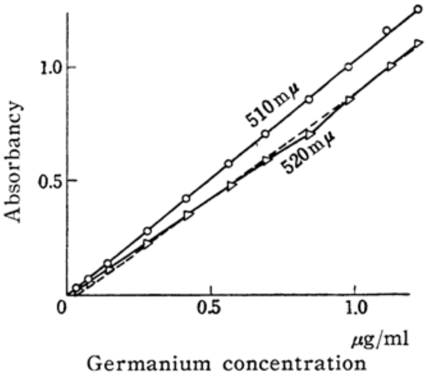


Fig. 4. Effect of Temperature

Effect of Germanium Concentration.—The experiment was carried out by a procedure simiar to that used for the experiment on the effect of temperature. In this case, germanium concentrations of the solutions ranged from 0.0278 to 1.25 μg. per ml. Each solution was introduced into a 50-ml. measuring flask and the volume was adjusted to 50 ml. Then the absorption of the solution was measured at 510 and 520 mμ, respectively, after the solution was kept standing for thirty minutes at temperature of about 17°C. The results were tabulated in Table I, and were also shown graphically in Fig. 5. The calculated values in Table I were obtained by using an empirical formula which was derived by the application of the method of least squares.



--- Calculated value

Fig. 5. Calibration Curves

TABLE I

EFFECT OF GERMANIUM CONCENTRATION UPON EXTINCTION

Germanium Concentration in Solution (μg/ml.)	510 mμ			520 mμ		
	Drum Readings	Calculated Values ($\varepsilon^* = 1.024\ C^{**}$)	Difference	Drum Readings	Calculated Values ($\varepsilon^* = 0.911\ C^{**} - 0.003$)	Difference
0.0278	0.020	0.028	−0.008	0.008	−0.004	0.012
0.0694	0.070	0.071	−0.001	0.048	0.030	0.018
0.139	0.142	0.142	0	0.112	0.094	0.018
0.278	0.284	0.284	0	0.226	0.220	0.006
0.416	0.429	0.426	0.003	0.348	0.346	0.002
0.555	0.575	0.568	0.007	0.474	0.472	0.002
0.694	0.707	0.711	−0.005	0.585	0.599	−0.014
0.833	0.845	0.853	−0.008	0.695	0.726	−0.031
0.970	0.980	0.993	−0.003	0.860	0.851	0.009
1.11	1.163	1.137	0.026	0.992	0.978	0.014
1.25	1.28	1.280	0	1.178	1.106	0.072

* ε: extinction of the complex between germanium and the reagent

** C: concentration of germanium

From the results it is concluded that the values of extinction at 510 and 520 mμ can be used for the analysis in a range of germanium concentration from 0.05 to 1.2 p.p.m.

Reproducibility of the Extinction.—In order to check the reproducibility of the extinction of a solution containing germanium complex at a given concentration, experiments were repeated at certain intervals over a period of about one week. The experimental conditions were the same as before. The results were shown in Table II.

TABLE II

TEST ON THE REPRODUCIBILITY

(1) Measured at 510 mμ

Germanium Concentration (μg/ml)	Run # 1	# 2	# 3	# 4	# 5	# 6	# 7	Number of Measurement	Average Value	Probable Error of Observed Value
0.276	0.267	0.256	0.272	0.265	0.274	0.284	0.271	7	0.270 $\pm 0.002_2$	0.006
0.690	0.687	0.699	0.690	0.674	0.690	0.707	0.700	7	0.692 $\pm 0.002_7$	0.007
0.966				0.980	0.982	0.980	1.000	4	0.985 $\pm 0.003_3$	

(2) Measured at 520 mμ

Germanium Concentration (μg/ml)	Run # 1	# 2	# 3	# 4	# 5	# 6	# 7	Number of Measurement	Average Value	Probable Error of Observed Value
0.276	0.208	0.200	0.224	0.218	0.218	0.226	0.225	7	0.217 $\pm 0.002_5$	0.007
0.690	0.571	0.579	0.576	0.590	0.589	0.585	0.590	7	0.583 $\pm 0.001_9$	0.006
0.966				0.860	0.862	0.860	0.860	4	0.861 $\pm 0.000_3$	

From these results, it is concluded that the reproducibility is satisfactory. But another series of experiments showed that the values slightly fluctuated when a different batch of reagent was used. In order to obtain a better reproducibility, the method for the purification of the reagent should be studied further.

Effect of Other Elements.—The following ions interfere with the colorimetric determination of germanium using this reagent, Sn^{4+}(1), Sb^{3+}(10), Zr^{4+}(100), Ce^{4+}(1), Fe^{3+}(10), MnO_4^{2-}(1). The numerical values in parentheses are maximum permissible ratios of interfering ions to germanium by weight. To eliminate the interference, the ratios of interfering ion to germanium in solution should be lower than these values. The wavelengths of absorption bands of these coloured compounds are similar to those of germanium complex.

In the presence of a small quantity of oxidizing agent, the reagent solution shows an absorption at a wavelength near 500 mμ; this colour and that of the complex disappear when the solution is boiled. A large quantity of oxidizing agent completely prevents the development of the colour of the germanium complex. It is likely that the reagent was decomposed by an oxidizing reagent.

When 50 mg. were present in 50 ml., the following ions failed to form any compound having absorption near 500 mμ. This amount is approximately one thausand times the weight of germanium in the solution.

Li^+, Na^+, K^+, Rb^+, Cs^+, NH_4^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Zn^{2+}, Cd^{2+}, Cu^{2+}, Hg^{2+}, As^{3+}, Bi^{3+}, Pb^{2+}, Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Al^{3+}, Ti^{4+}, Cl^-, I^-, SO_4^{2-}, NO_3^-, CH_3COO^-, PO_4^{3-}, $B_4O_7^{2-}$.

Interference may result from the presence of a very large quantity of these ions, because under a great ionic strength they are apt to cause precipitation of either the reagent or the germanium complex. The degree of precipitation depends on the temperature. In the presence of 4.4 g. of sodium chloride, no precipitate appeared at 30°C in 50 ml. of the solution containing germanium complex and the reagent, whereas some precipitates are formed on standing at 6°C for one hour, in the presence of only 1.8 g. of sodium chloride.

Recommended Procedure

A sample is exactly weighed, decomposed eigher with acid* or by fusion with alkali and extraction with hot water. After being cooled, it is transferred to a 300 ml. round bottomed flask. If there is any possibility of the presence of an oxidizing reagent in the solution, an adequate quantity of ferrous sulphate should be added. The resulting solution is diluted to 70 ml., to which 70 ml. of conc. hydrochloric acid is added and germanium is distilled. The distillate is collected in a receiver containing approximately 20 ml. of water. The distillation is continued until 50 ml. of the distillate are obtained. Then the distillate is transferred to a measuring flask and diluted to 100 ml. with water. The acid concentration of this solution is determined by titration with 3 N sodium hydroxide. An aliquot of the solution containing germanium in a range

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* At the decomposition of the sample, hydrochloric acid and halide must not be present because germanium halide is easily formed and tends to escape from the solution.

from 3 to 60 μg is taken in a 50 ml. measuring flask and the acid concentration is adjusted to 0.5 N by adding either sodium hydroxide or hydrochloric acid. It is diluted to approximately 30 ml. with water and cooled down to room temperature. Ten ml. of 0.05% ethanol solution of dimethylaminophenylfluorone is added to the solution. Then the resulting solution is diluted to 50 ml. with water. A reference solution is similarly prepared without germanium. The extinction of the solution is measured at 510 and 520 mμ and the quantity of germanium is determined with the aid of calibration curves.

Conclusion

Although a new compound, dimethylaminophenylfluorone, is not a specific reagent for germanium, the colorimetric method using this compound is recommended because of its simplicity. The advantage of this method is very similar to that of phenylfluorone method. Germanium is separated from interfering ions by distillation and the resulting solution is subjected to colorimetric analysis. The disadvantage of the phenylfluorone method consists in the fact that the germanium complex is insoluble or only slightly soluble in water and in organic solvents. In this new method such a disadvantage is eliminated. Dimethylaminophenylfluorone forms a soluble complex with germanium in ethanolic solution containing hydrochloric acid. The colour of the complex is stable. The extinction can be measured more easily than in the case of the phenylfluorone method. The only disadvantage of this method is that the molar extinction coefficient of germanium complex can not be obtained because the extinction of the complex slightly fluctuates, when a different batch of the reagent is used.

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