Studies on Organic Reagents for the Colorimetric Analysis of Germanium. I. Reactions between Germanium and Some Organic Compounds

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Recently germanium, one of the less-common elements, found its special usefulness in electronics. This fact makes it very important for scientist to explore even the very poor resource of germanium in nature. The study on the distribution and migration of germanium in the earth's crust is also important from the standpoint of geochemistry.

For these reasons an excellent method for the quantitative analysis of germanium is urgently needed. Up to the present time a variety of analytical methods for germanium have been proposed, which covered gravimetric, volumetric, colorimetric, spectrographic and polarographic methods[1]. For a trace amount of germanium, however, the colorimetric method seems to be most excellent. In the colorimetric analysis choice of a reagent is always important. So far the use of many reagents such as ammonium molybdate[2], oxidized hematoxyline[3], phenylfluorone[4] quercetin[5], and quinalizarine acetate[6] has been proposed. But none of them was found to be entirely satisfactory. The difficulty lies in the complicated procedure required to remove interfering ions, as well as in the adjustment of hydrogen ion concentration within a narrow range. Moreover, for some reagents, the reagent itself or the compound between the reagent and germanium is not stable. Some other reagents form sparingly soluble precipitates with germanium. In such a case the colorimetric measurement has to be made on a colloidal solution.

In this report the authors tried to confirm the functional groups which combine with germanium. Special attention was paid to correlate the structure of the reagent to its reactivity with germanium. A search was made for a reagent which combines with germanium in a strongly acidic solution without forming any precipitates, its absorption spectrum being changed. In addition, the reaction should not be interfered with by foreign ions. A. Tchakirian and P. Bevillard studied the functional groups* which are supposed to combine with germanium. In their earlier studies[7a-e] they concluded as follows. (1) In order to react with germanium the organic molecule under consideration must have two hydroxyl groups on ortho positions and also a carbonyl- or quinoimine-group; the latter is able to bring about a tautomery between hydroxyl- and carbonyl-groups. (2) *Ortho* diamine groups, that are analogous to ortho dihydroxyl groups fail to react with germanium. (3) The larger the molecule, the more sensitive the reaction with germanium. A larger molecule reacts with germanium even at a low pH. Reaction at such a low pH excludes the interference by other elements. On the other hand, the molecule tends to be sparingly soluble in solvents. To increase the solubility of such a compound it is desirable to introduce an acidic group such as sulphonate into the compound. In their late studies[7f-g], they stated that the function of the carbonyl group was not clear and that a salt was formed by the combination of the quinoimine group with the dihydroxyl germanic acid which was preliminarily formed. They also stated that the ortho dihydroxyl groups react with germanium even in a compound without carbonyl- or quinoimine group. In order to confirm their results, the present authors examined the reaction between germanium and flurone-, naphthoquinone-, and cumarin derivatives. This study appears to give an orientaion to find a new reagent for the colorimetric analysis of germanium.

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1) H.H. Krause and O.H. Johnson, *Anal. Chem.*, **25**, 134 (1953).

2) N.A. Filippona and L.I. Kusentzowa, *Zavodskaya Lab.*, **16**, 536 (1950) (C.Z., **2**, 2503 (1951)). E.B. Sandell, "Colorimetric Determination of Trace of Metals", New York (1953), pp. 134, 333. L. Erday and E. Boder, *Z. Anal. Chem.*, **134**, 81 (1951).

3) H. Newcombe, W.A.E. Mcbryde, J. Bortlett and F.W. Beamish, *Anal. Chem.*, **23**, 1023 (1951).

4) H.J. Cluley, *Analyst*, **76**, 523 (1951). Y, Oka, T. Kanno and K. Shiba, *Japan Analyst*, **3**, 389 (1954).

5) Y. Oka and S. Matsuo, *J. Chem. Soc. Japan*, **76**, 610 (1955).

6) C.K.N. Nair and J. Gupta, *J. Sci. Ind. Research*, **10 B**, 300 (1951); ibid., **11 B**, 274 (1952).

* On the nomenclature of functional group, A. Tchakirian et al. had used "phenol-" and "quinon-". In the present paper, they are called "hydroxyl-" and "carbonyl-", respectively.

7) A. Tchakirian and P. Bevillard, a) *Compt. rend.*, **233**, 256 (1951); b) ibid., 1003; c) ibid., 1112; d) P. Bevillard, ibid., **234**, 216 (1952); e) *Mikrochem.*, **39**, 209 (1952). f) *Compt. rend.*, **235**, 880 (1952). g) *Bull., Soc. Chim. France*, **1954**, 304.

Experiment

The following experiments were carried out to examine whether or not the presence of hydroxyl groups on ortho positions be essential for the compound to react with germanium.

The Reaction between Fluorone Derivatives and Germanium

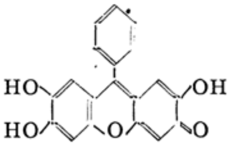
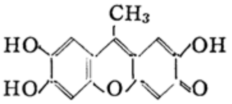
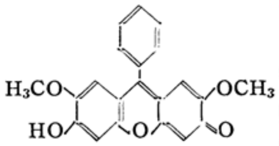
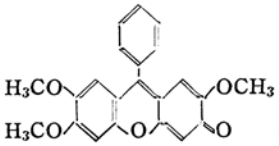
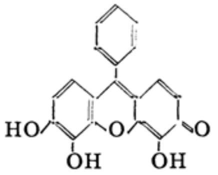
The following compounds were used in this experiment.

2, 6, 7-Trihydroxy-9-methylfluorone[8]
6-Hydroxy-2, 7-dimethoxy-9-phenylfluorone[9]
2, 6, 7-Trimethoxy-9-phenylfluorone[10]
4, 5, 6-Trihydroxy-9-phenylfluorone[11]

In the first place, the authors synthesized these compounds by conventional method. After the syntheses, the absorption spectra, the reactivity with germanium and the shift of the maximum of the absorption band, resulting from the addition of germanium, were examined for each compound. For the measurement of absorption spectrum the solution was prepared in the following way. A 10^{-4} mol. of each compound was dissolved in a mixture of about 80 ml. of ethanol (94%) and 5 ml. of 6 N sulphuric acid. The resulting solution was transferred into a measuring flask and its volume adjusted to 100 ml. A 2 ml. portion was diluted to 50 ml. with either pure water or water containing 13 ml. of ethanol and 10 ml. of 6 N hydrochloric acid. The concentration of each compound in the solution was 4×10^{-8} mol. per ml. The reactivity of these compounds with germanium was studied over a wide range of pH. The results are summarized in Table I; the absorption curves are shown in Fig. 1.

TABLE I

PROPERTIES OF FLUORONE DERIVATIVES

Name	Structure	M. p.	Colour of crystals	Colour of aq. and/or ethanolic soln.	Change in colour of an acidic soln. on the addition of germanium solution
(1) 2,6,7-Trihydroxy-9-phenylfluorone		350°C	Reddish orange	Dark red (b.) Orange (n.) Yellow (a.)	Change to reddish (similar to that in a neutral solution) Precipitate formed
(2) 2,6,7-Trihydroxy-9-methylfluorone		Decomp. at 279°C	Yellowish orange	Dark red (b.) Orange (n.) Yellow (a.)	Change to reddish (similar to that in a neutral solution) Precipitate formed
(3) 6-Hydroxy-2,7-dimethoxy-9-phenylfluorone		282°C	Dark red	Light orange (n.) Yellow (a.)	None
(4) 2,6,7-Trimethoxy-9-phenylfluorone		174°C	Orangish yellow	Insoluble (b.) Light orange (n.) Yellow (a.)	None
(5) 4,5,6-Trihydroxy-9-phenylfluorone		Decomp. at ca. 200°C	Dark purple	Violet blue (b.) Dark purple (n.) From red to yellow (a.)	Change to more reddish (similar to that in a neutral solution) Precipitate appeared after one day

b.: basic solution n.: neutral solution a.: acidic solution

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8) C. Lieberman and S. Lindenbaum, *Ber.*, 37, 1171 (1904); ibid., 2728.

9) F. Kehrmann and M. Gunther, *Ber.*, 45, 2884 (1923).

10) F. Kehrmann and M. Gunther, *Ber.*, 45, 2884 (1923).

11) W. R. Orndorff and C. Wang, *J. Amer. Chem. Soc.*, 47, 290 (1925); ibid., 49, 1284 (1927); R. N. Sen and N. N. Sarkar, ibid., 47, 1079 (1925).

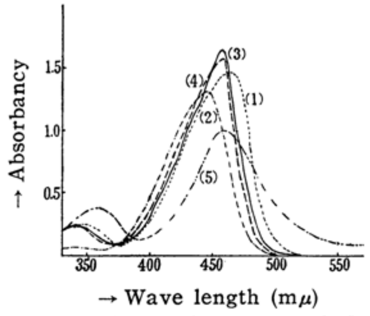


Fig. 1-(1). Absorption curve of fluorone derivatives.

(1) 2, 6, 7-trihydroxy-9-phenylfluorone
(2) 2, 6, 7-trihydroxy-9-methylfluorone
(3) 6-hydroxy-2, 7-methoxy-9-phenylfluorone
(4) 2, 6, 7-trimethoxy-9-phenylfluorone
(5) 4, 5, 6-trihydroxy-9-phenylfluorone

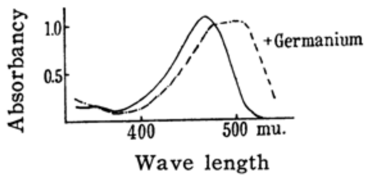


Fig. 1-(2). The absorption curve of 2,6,7-trihydroxy-9-phenylfluorone, (3×10^{-8} mol. per ml.) in acetone and that of the solution containing both germanium (6.94 μg. per ml.) and the reagent. (These are true solutions almost without water.)

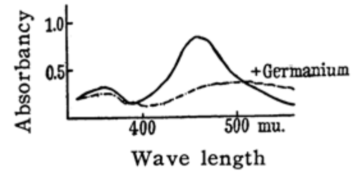


Fig. 1-(3). The absorption curve of 4,5,6-trihydroxy-9-phenylflourone (4×10^{-8} mol. per ml.) in ethanol and that of the soln. containing both germanium (13.9 μg. per ml.) and the reagent.

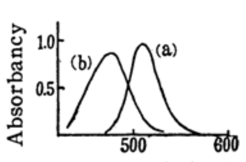


Fig. 1-(4). Absorption curves of complexes between germanium and 2, 6, 7-trihydroxy-9-phenylfluorone[a)] and 2, 6, 7-trihydroxy-9-methylflurone[b)]. These solutions contain germanium (8.33 μg. per ml.) and a large amount of reagent. Here reference soln. is an ethanolic solution of the reagent.

The synthesis of a new compound, 2-hydroxy-6, 7-dimethoxy-9-phenylflurone, was tried in vain by methylation of 2, 6, 7 trihydroxy-9-phenylfluorone with diazomethane. If this compound could have been synthesized, it would have been possible to decide whether the functional group which directly combines with germanium is only hydroxyl group. Since it is possible that not only hydroxyl but also carbonyl-group can combine with germanium such an experiment would be very important.

The Reaction between Naphthoquinone Derivatives and Germanium

In order to examine the relation between two hydroxyl groups and a carbonyl group with respect to the reaction with germanium, naphthoquinone derivatives were chosen. For these derivatives the reactivity and the change in the absorption band resulting from the complex formation were studied. The compounds used in the experiment are summarized in Table II.

About 5 mg. of each compound were dissolved in 10 ml. of ethanol (94%). To 1 ml. of this solution was added 1 ml. of ethanol and the volume adjusted to 10 ml. with water. One ml. of first solution was added to the mixture of 1 ml. of ethanol and 4 ml. of germanium standard solution (6.9 μg. per ml.). This solution was made up to 10 ml. with water and its absorption measured. The results are shown in Fig. 2. As was expected, neither the compounds without two hydroxyl groups (e. g. the compound No. 1.) nor those in which two hydroxyl groups are not located on ortho positions (e. g. the compounds No. 2 and 3) showed any significant reaction with germanium.

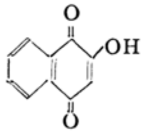
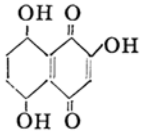
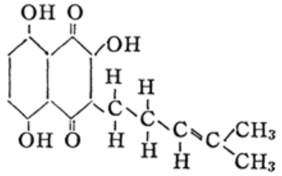
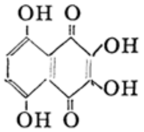
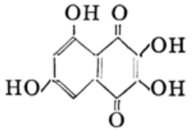
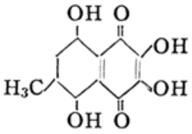
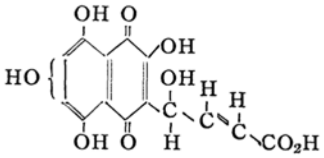
The reactions between germanium and those compounds which have a carbonyl group adjacent to a hydroxyl group were also negative. According to these results it was clear that one hydroxyl group is not one of the functional groups which directly combine with germanium.

The solutions of these compounds were true solutions and did not show any appreciable precipitate on the addition of germanium. The reaction of these compounds with germanium brings about a change in colour of the solution, from orange or red to purple or dark red. The extinction of the solution was slightly increased, whilst the absorption spectrum remained almost unchanged in each case. Since it is possible that they have a low tendency to react with germanium, further experiments were carried out by use of a larger quantity of germanium (70 μg. per ml.). As shown in Fig. 2-(4), however, the absorption spctra changed only very slightly.

The Reaction between Cumarin Derivatives and Germanium

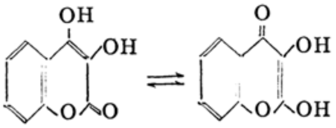
Compared with naphthoquinone derivatives, fluorone derivatives have many advantages in their reactivity with germanium. The syntheses of these compounds are easier; they react not only with a trace amount of germanium but also selectively in an acidic solution. Apart from the

TABLE II
NAPHTHOQUINONE DERIVATIVES

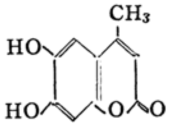
Conventional Name	Structure	Reaction with Germanium
(1) 2-Hydroxynaphthoquinone		Negative
(2) 2-Hydroxynaphthazarine		Nagative
(3) Shikonin		Negative
(4) Spinazarin		The colour of ethanolic solution changes from orange to reddish orange
(5) Spinochrome Bl		The colour of ethanolic solution changes from yellow to yellowish orange
(6) Spinochrome F	?	The colour of ethanolic solution changes from red to purple
(7) Spinochrome Aka		The colour of ethanolic solution changes from pale red to dark red
(8) Spinochrome Ml		The colour of ethanolic solution changes from pale red to dark red

number of benzene rings, the greatest difference in the structure of these two kinds of compound lies in the fact that the fluorone derivatives are heterocyclic and contain an oxygen atom in the ring, whilst the naphthoquinone derivatives are not. In order to find whether the difference in the structure of those compounds has any effect upon the reactivity with germanium, the reaction between germanium and the following two cumarin derivatives was similarly studied.

cumarin diol[12]



4-methyl-esculetin[13]



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[12] F. Arndt, L. Löwe, R. Un and E. Ayca, *Ber.*, 84, 319 (1951).

[13] "Organic Syntheses", Collective Volume I, New York (1932), p. 352.

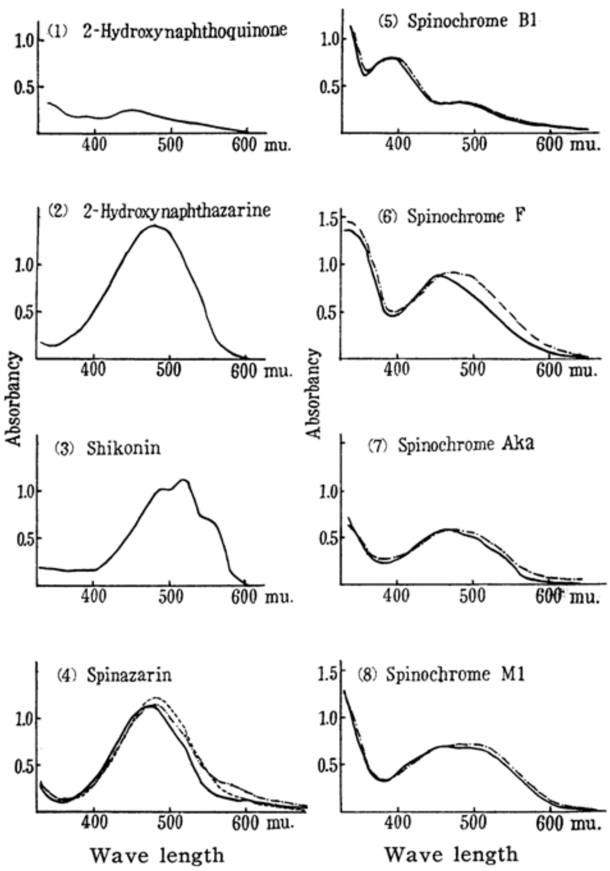

Fig. 2. Absorption curves of naphthoquinone derivatives contaning 5.5 μg. of germanium per ml.
(1) (2) and (3) do not change by the addition of germanium.

The compounds were synthesized by the conventional methods. Their colour ranges from colorless to yellow. The absorption spectrum of the solution of each compound as well as of a mixed solution with germanium was studied, both in neutral and 1 N-hydrochloric acid solutions. It was disclosed that cumarindiol fails to react with germanium, whereas 4-methyl esculetin shifts the absorption band from ultra violet to visible. This seems to arise from the formation of germano-complex in a neutral solution. The red shift was more remarkable than in the cases of naphthoquinone derivatives. The results are shown in Fig. 3.

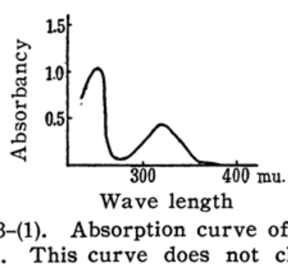

Fig. 3-(1). Absorption curve of cumarindiol. This curve does not change by the addition of germanium.

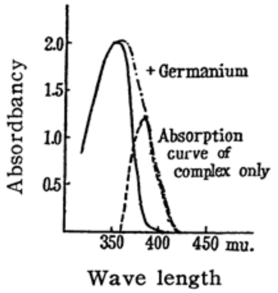

Fig. 3-(2). Absorption curve of 4-methyl-esculetin.

This compound appears, however, not very suitable for the colorimeteric analysis of germanium. In the presence of sodium- or ammonium chloride, the above-mentioned red shift does not take place. Moreover, these compounds are less sensitive for the detection than fluorone derivatives. The wave length of the absorption maximum lies in the boundary between ultraviolet and visible regions.

Conclusion

In order to find an organic compound which is suitable for the colorimetric analysis of germanium, several compounds including fluorone-, naphthoquinone- and cumarin derivatives were studied. The relation between the structure of these compounds and the reactivity with germanium, as well as the shift of the maximum of the absorption spectrum on reaction with germanium, were closely studied. The results confirmed one of the conclusions previously presented by A. Tchakirian and his co-loborators. That is, the presence of two hydroxyl groups on ortho positions is essential for the reaction with germanium. The larger the molecule, the more marked the reaction with germanium. The reactivity with germanium at a low pH is increased with increase in moleculer weight. A compound such as spinazarine, shikonin and 2-hydroxy-naphthoquinone in which one of the two hydroxyl groups on ortho positions is replaced by a carbonyl oxygen, fails to show any reaction with germanium. Cumarindiol has two hydroxyl groups on ortho positions, but in this compound there is a tautomery between the hydroxyl group and the carbonyl oxygen. This could be the reason why this compound does not show any appreciable reaction with germanium, although it has two hydroxyl groups on ortho positions. Accordingly, it is clear that the functional groups which combine directly with germanium are ortho hydroxyl groups. Carbonyl group provides negative results even when it is situated ortho to the hydroxyl group. Present results also indicate that heterocyclic compounds such as fluorone- and cumarin derivatives are more advantageous than homocyclic ones such as naphthoquinons as a reagent which selectively combines with germanium at a low pH. The former compounds are also superior in the fact that their absorption spectra are much more affected by the addition of germanium. Concerning the structures of the compound between germanium and these organic compounds, no diffinite conclusion can be drawn from this study. Further studies are in progress.

The authors wish to express their sincere thanks to Dr. Chika Kuroda for supplying precious samples of naphthoquinone derivatives, and to the late Dr. Fujiro Iimura of Tokyo University for helpful advice in this study. The expenses were defrayed from a grant given by the Ministry of Education to which the authors' thanks are due.

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