Rapid Determination of Germanium in Coal, Soil and Rock

15756

Rapid Determination of Germanium in Coal, Soil and Rock

By HY ALMOND, HARRY E. CROWE, *and* CHARLES E. THOMPSON

A CONTRIBUTION TO GEOCHEMISTRY

GEOLOGICAL SURVEY BULLETIN 1036-B

UNITED STATES DEPARTMENT OF THE INTERIOR

Douglas McKay, *Secretary*

GEOLOGICAL SURVEY

W. E. Wrather, *Director*

CONTENTS

ILLUSTRATIONS

III

A CONTRIBUTION TO GEOCHEMISTRY

RAPID DETERMINATION OF GERMANIUM IN COAL, SOIL, AND ROCK

By Hy Almond, Harry E. Crowe, and Charles E. Thompson

ABSTRACT

Cluley's colorimetric method for the determination of germanium in coal with phenylfluorone is modified to speed up the rate at which coal samples can be analyzed. The method is also adapted to the determination of germanium in soils and rocks. To avoid the time-consuming step of neutralizing after the alkaline fusion, as described by Cluley, coal samples are ashed at 550° C. Soils and rocks are decomposed with hydrofluoric acid and the residue is fused with a mixed flux of potassium bisulfate and persulfate. The germanium in the coal ash or in the fusion product is then dissolved in $1+1$ hydrochloric acid and distilled on a specially designed distillation rack, on which six samples can be distilled at once.

Although the maximum absorbance of the germanium phenylfluorone complex was found to be between 500 and 505 mμ (millimicrons), the absorption is measured at 510 mμ to minimize interference by reagent. However, visual comparison with standards is preferred to the instrumental method of estimation. A sensitivity of 2 ppm (parts per million) germanium in the coal and 1 ppm in soils or rocks is obtained. About 50 coal samples can be analyzed per man-day.

INTRODUCTION
GENERAL DISCUSSION

The growing importance of germanium in the electrical industry has led to the search for germanium in coal as well as in other material. As part of a geochemical study of the occurrence of minor elements, including germanium, in American coals, Stadnichenko, Murata, Zubovic, and Hufschmidt (1953) reported values obtained spectrographically. Fleischer (written communication, 1954) collected data on the germanium content of igneous and sedimentary rocks. To supplement these studies a colorimetric method for the determination of germanium in coal, soils, and rocks was begun largely through the inspiration and suggestions of Stadnichenko and Zubovic.

The simplest method of decomposing coal is by ashing the coal sample, but Goldschmidt (1937) and Morgan and Davies (1937) report losses of germanium during the ashing process. Cluley (1951) decomposed coal by fusing the sample with a sodium carbonate-nitrate flux More recently Aubrey and Payne (1954) and Waring and Tucker (1954), using more reliable methods of analyses than that

used by the earlier workers, found little or no losses of germanium during the ashing process.

Aitkenhead and Middleton (1938) decomposed minerals with hydrofluoric, nitric, and sulfuric acid, and Hyblinette and Sandell (1942) used these acids to decompose silicate rocks.

Phenylfluorone, first described by Cluley for the determination of germanium, reacts with many elements, but by distilling from 1+1 hydrochloric acid Cluley was able to separate germanium from the interfering elements.

In the procedure described here for germanium in coals, soils, and rocks, Cluley's method is greatly simplified to provide the rapid and cheap results needed for a geochemical program.

FEATURES OF THE METHOD

Coal samples are decomposed by ashing in a muffle furnace starting at a temperature below 300° C, raising the temperature to 550° C, and maintaining at the latter temperature for about 1 hour. The ash samples are ready for distillation of germanium tetrachloride without neutralization of the solution as required in the technique described by Cluley.

Soil or rock samples are decomposed by eliminating a large amount of the silica with hydrofluoric acid, followed by fusing the residue with a mixture of potassium bisulfate and persulfate. This flux, when heated with the residue from the hydrofluoric acid treatment, drives off fluorides and oxidizes sulfides; the latter, if present, might prevent the quantitative distillation of germanium tetrachloride. This treatment is more rapid than the acid digestions used by Schneider and Sandell (1954). Alkaline fluxes are not used because large quantities of dissolved silica are introduced into the solution which prevent the quantitative distillation of germanium tetrachloride, as previously reported by Aitkenhead and Middleton (1938).

Separation of germanium from interferences by distillation with hydrochloric acid has been described by Cluley and many other workers. The unique feature presented here is an engineering one. A rack supporting six stills is designed to carry out six distillations at the same time (pl. 1). The volume of acid in each still has been decreased so that distillation time required is only 15 minutes for each group of six distillations.

Cluley's procedure for estimation of germanium with phenylfluorone also has been modified. The acidity of the solution has been changed from 1.15 N, used by Cluley, to 0.6 N to increase the sensititivy. The effect of acidity in absorption of the germanium phenylfluorone complex is tabulated below. The results, verifying a similar study made by Cluley, show that the 0.6 N solution is more sensitive than the more acid solution.

Effect of acidity on absorption of germanium phenylfluorone complex in 10 ml of solution, containing 1 microgram Ge.

Normality of solution	Absorption after 90 minutes
0. 2	0. 145
. 38	. 140
. 62	. 116
. 8	. 117
1. 0	. 112
1. 1	. 105

Absorptiometric studies, carried out with a Beckman D. U. spectrophotometer, showed that the germanium phenylfluorone complex adsorbed maximally between 500 and 505 mμ, whereas the reagent adsorbed maximally between 450 and 460 mμ (fig. 2). In the proposed method, readings are taken at 510 mμ, where there is little absorption by reagent to interfere with the determination. Adherence to Beer's law is good between 0.1 and 1 microgram of germanium per ml of solution.

As the absorption of reagent varied somewhat with acid concentration (see Cluley, 1951, table 3), the acid concentration of the sample solution was kept essentially the same as the solution from which the original standard curve was prepared. In the instrumental method described here, with each set of unknown solutions analyzed, a new curve is established with 3 standard germanium solutions, that is, 0, 1.0, and 5 micrograms of germanium per 10 ml of final solution.
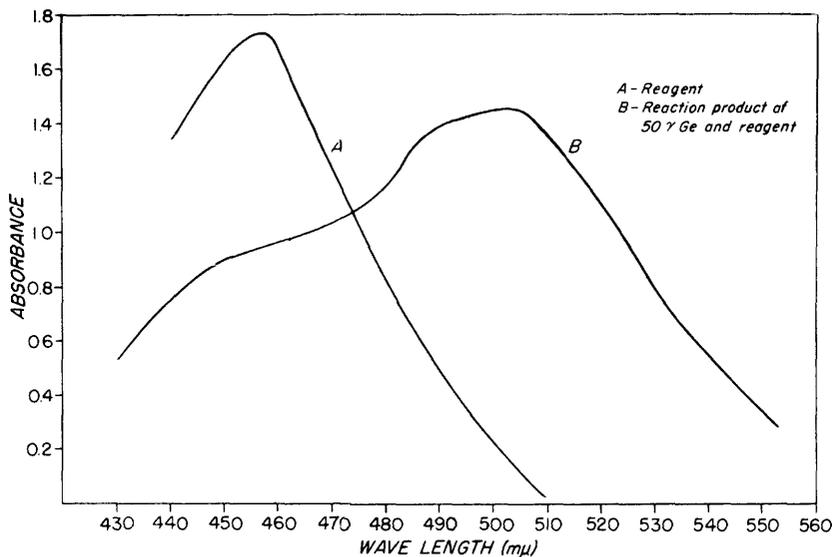

FIGURE 2.—Curves showing absorption by reagent (A) and of a reaction product (B).

Visual comparison with standards is preferred because of greater sensitivity and because a new curve must be run each time the instrument is used due to variable absorption of the reagent itself. As little as 0.2 microgram of germanium can be detected in an aliquot of the distillate. A standard series ranging from 0.2 to 3 micrograms of germanium is prepared at the same time that aliquots of the distillates are prepared for final color development. After proper adjustment of the acidity of each solution and addition of necessary reagents, the color develops on standing. Visual comparison of unknown solutions with the standard series is made any time after 1 hour, but should be done within 3 hours, because precipitation of the germanium phenylfluorone complex takes place on prolonged standing.

REAGENTS AND APPARATUS

Phenylfluorone.—Dissolve 0.03 g in 85 ml ethyl alcohol and 5 ml $(1+6)$ sulfuric acid by warming on a steam bath, then dilute to 100 ml with ethyl alcohol.

Gum arabic.—Add 0.05 g to 100 ml water and warm until in solution.

Potassium bisulfate, potassium persulfate fusion mixture.—Mix equal weights of these two reagents.

Hydrochloric acid, conc. reagent grade.

Hydrochloric acid $(1+1)$.—To 2 liters of metal-free water add 2 liters of concentrated hydrochloric acid.

Hydrochloric acid, approximately 0.05 N.—Dilute 8.3 ml of $1+1$ hydrochloric acid to 1 liter.

Hydrofluoric acid, 48 percent.

Litmus paper.

Standard germanium solution, 0.01 percent.—Dissolve 0.144 g of germanium dioxide in 20 to 25 ml of 0.1 N sodium hydroxide and dilute to 1 liter. This solution has 100 micrograms of germanium per ml.

Culture tubes, 16×150 mm.—Marked at 10 ml.

Cylinders, graduate, 25 ml, borosilicate.

Stirring rod, borosilicate glass.

Pipets, 1, 5, 10 ml graduated.

Sieve, 80 mesh.

Mortar and pestle, mullite.

Platinum crucible, 45-ml capacity.

*Furnace, muffle;* thermostatically controlled.

Aluminum dishes. Made from aluminum foil (may be used for containers to hold coal during ashing).

GERMANIUM DISTILLATION APPARATUS

A 2-shelf rack supporting 6 distillation units, germanium still, as shown in plate 1. Each distillation unit consists of the following:

Erlenmeyer wash bottle, figure $3A$.—Modified as in figure $3B$. The tubing at position A is bent into a U-shape. At position B and C the glass tubings are cut off and sealed.

Tygon tubing.—Six-inch piece of tygon tubing is connected at position D (fig. 3b).
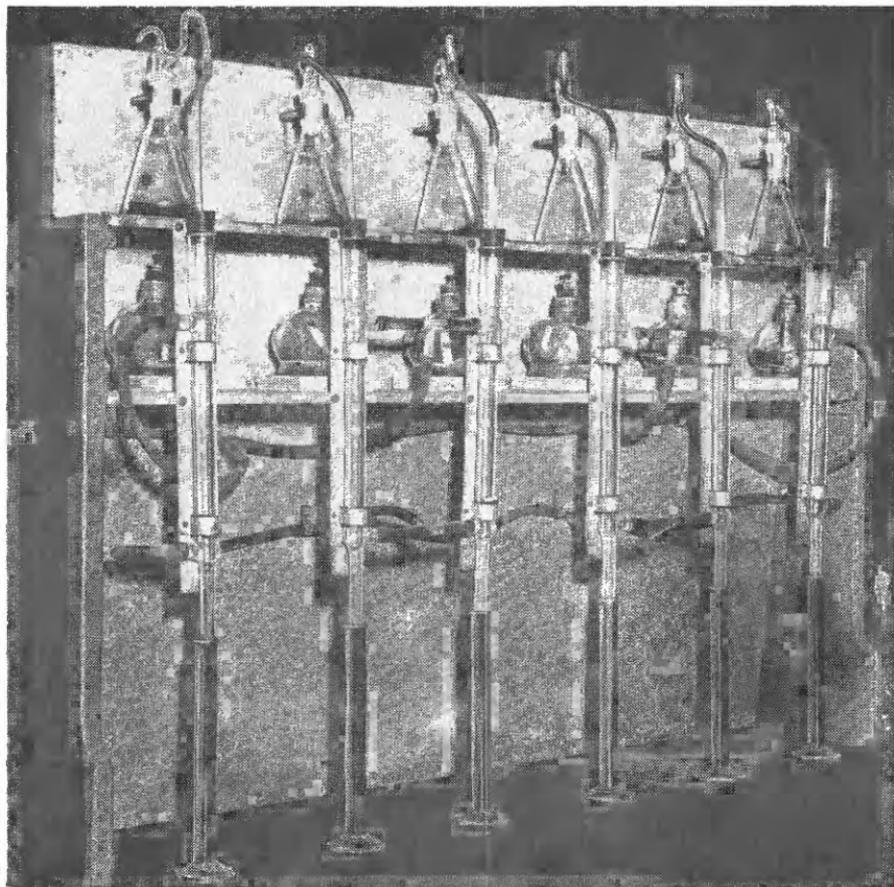
GERMANIUM DISTILLATION APPARATUS

Glass tubing.—Six-inch piece of glass tubing is connected to the tygon tubing.

Rubber stopper, number 3.—Insert the glass tubing of item 3 into a 1-hole rubber stopper so that 2.5 inches of glass tube extends beyond the base of the rubber stopper.

Condenser, 20-mm length.—Place the rubber stopper of item 4 into the condenser. The 2.5 inches of glass tube beyond the base of the rubber stopper extends to the position where cooling takes place in the condenser.

Graduated cylinder, 25 ml.—Place at outlet of the condenser in position to collect distillate.

Burner, alcohol, glass, 4-oz capacity.

PROCEDURE

Decomposition of coal.—Transfer a 0.5-gram coal sample, previously ground to pass through an 80-mesh sieve, to a platinum crucible or aluminum dish. Place in a muffle furnace at temperature below 300° C. Raise the temperature in increments of 50° to a temperature of 550° C. Allow to remain at 550° for about 1 hour. Remove from the furnace and allow samples to cool. Transfer the ash to the Erlenmeyer distilling flask, then add about 15 ml hydrochloric acid (1+1).

A   *B*
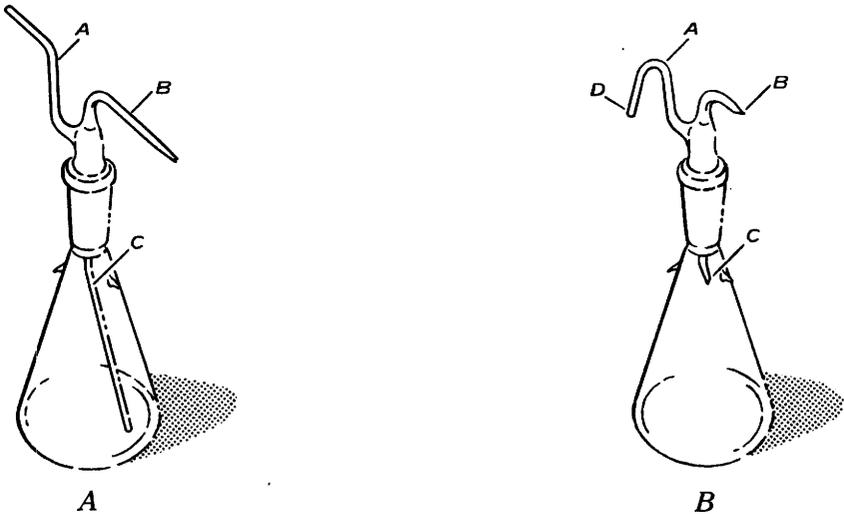
FIGURE 3.—Erlenmeyer wash bottle before modification (*A*) and after modification (*B*).

Decomposition of soil or rock.—Grind the soil or rock to pass through an 80-mesh sieve. Thoroughly mix and transfer a 2.0-gram representative sample to a platinum crucible. Add about 20 ml of hydrofluoric acid to the crucible and mix with the sample. Evaporate to dryness on the steam or hot water bath. Add about 2.5 grams of potassium bisulfate, persulfate fusion mixture and fuse to a clear melt. Allow to cool. Add about 5 ml of 1+1 hydrochloric acid. Break up the flux in the cold, then transfer the contents of the crucible to the Erlen-

meyer distilling flask. Wash the crucible with 5-ml portions of $1+1$ hydrochloric acid three times, adding the washings to the distilling flask.

Distillation.—Connect the distilling flask in the distilling apparatus, light the alcohol burner, turn on the water condenser, and collect about 10 ml of distillate in the graduated cylinder. Record the volume of distillate. Avoid any possible contamination with iron. To do the maximum number of determinations in a work day, carry out distillations in groups of six. About 30 to 50 distillations can be made per man-day.

Color development.—About 2 hours before the end of the work day, begin the operations for color development of standards and unknowns for visual or for photometric estimation, whichever is preferred. Transfer exactly 1 ml of distillate to a culture tube. Add 1 ml of gum arabic, then dilute to 10 ml with water. Add exactly 0.5 ml of phenylfluorone reagent, stopper with a cork stopper and shake several times to insure good mixing. Allow to stand about 1 hour, but less than 3 hours, then compare unknowns with the standard series prepared at the same time or with a standard curve.

Standards for visual estimation.—To a series of culture tubes add 0, 0.2, 0.4, 0.6, 1.0, 1.2, 1.5, 2.0, and 3.0 micrograms of germanium, respectively, from standard solutions. Add about 1 ml of water and just neutralize with 0.05 N hydrochloric acid, testing with litmus paper. Add exactly 1 ml $1+1$ hydrochloric acid and proceed as described under "Color development," beginning with "addition of 1 ml of gum arabic."

Standards for photometric estimation.—To a series of culture tubes add 0, 0.5, 1.0, 2.0, 4.0, 8.0, and 15 micrograms of germanium, respectively, from standard solutions. Neutralize with 0.05 N hydrochloric acid, testing with litmus paper. Add exactly 1 ml of $1+1$ hydrochloric acid and proceed as described under "Color development" beginning with "addition of 1 ml of gum arabic." After 90 minutes determine the absorbance at 510 mμ of each solution. Plot the micrograms of germanium against the absorbance.

With each set of distillates carried through the color development operation, prepare a set of 0-, 1.0- and 5.0-microgram standards in culture tubes and carry these standards through the color development. Determine the absorbance of standards and unknown solutions. Check the three absorbances of the standard solutions with the standard curve and, if necessary, prepare a new absorption curve. This may be necessary because absorbance varies with concentration of reagent or acidity of solution or both.

Measurement.—Estimate the germanium content of the unknown solution visually by comparison with standards or with a spectro-

photometer by comparison with a standard absorbance curve prepared at 510 mμ wave length.

Calculation.—The calculation of parts per million (ppm) of germanium in the original sample may be done simply by application of the following formula:

$$\text{Ge (ppm)} = \frac{\text{ml of distillate} \times \text{micrograms found in the aliquot}}{\text{wt of sample}}$$

RESULTS

Results of colorimetric determinations on coal samples are compared with spectrographic results below.

Comparison of duplicate determinations of germanium in coal by the colorimetric method and by the spectrographic method

Sample no.	Germanium (ppm)		
	Colorimetric method (Visual comparison)		Spectrographic method [1]
1	40	[2] 40	42
2	0	[2] 0	0
3	5	[2] 3	6
4	13	[2] 17	8
5	0	[2] 1	3
6	12	[2] 11	12
7	25	[2] 23	30
8	22	[2] 28	21
9	0	[2] 0	0
10	14	[2] 25	10
11	7	[2] 14	8
12	165	[2] 135	134
13	29	26	34
14	27	30	44
15	12	7	12
16	33	34	50
17	9	10	12
18	2	1. 3	4. 5
19	12	11	21
20	3	2	3. 9
21	36	32	20
22	15	12	25
23	12	10	23
24	4	3. 2	7. 6

[1] Spectrographic analyses by K. J. Murata and Elizabeth Hufschmidt, U. S. Geological Survey.

[2] Only 0.2-gram samples used for analyses.

Of the 24 samples used, serious variations in results by the two methods of analysis were found in only 4 samples (19, 21, 22, and 23). As these samples were not finely ground, they may not have been of uniform composition.

In soils and rocks the method for the determination of germanium was tested in two ways. First, various known amounts of germanium were added to 0.1-gram fractions of a well mixed soil. Their recoveries were as follows:

Recovery of germanium added to soil

Ge added (micrograms)	Ge recovered (micrograms)
0	0. 9
2. 0	2. 8
4. 0	4. 7
8. 0	9. 2
15. 0	13. 0
30. 0	31. 1

Second, the method was tested by comparing results obtained by the colorimetric method with those obtained spectrographically. The results were as follows:

Comparison of colorimetric and spectrographic results on three soil or rock samples (Germanium content in ppm)

Spectrographic analyses by A. T. Myers, U. S. Geological Survey.]

Sample no.	Colorimetric by visual comparison	Spectrographic
25	1, 200	1, 700
26	180	190
27	24	30

Although sample 26 is high in sulfides, the results compare as favorably with the spectrographic method as those for samples 25 and 27. There is a tendency for the colorimetric to be a little lower than the spectrographic results, perhaps because not quite all of the germanium is distilled in the brief distillation period. By distillation of larger volumes of hydrochloric acid or by use of smaller samples, better recoveries can be made, but the method as described gives suitable recoveries for the geochemical study of trace amounts of germanium.

LITERATURE CITED

Aitkenhead, W. C., and Middleton, A. R., 1938, Determination of germanium in minerals and solutions: Indus. and Eng. Chemistry, Anal. ed., v. 10, p. 633–635.

Aubrey, K. V., and Payne, K. W., 1954, Volatilization of germanium during the ashing of coal; Fuel, v. 33, p. 20–25.

Cluley, H. J., 1951, Determination of germanium, Part II: Absorptiometric determination with phenylfluorone; Part III: Determination in flue dust, coal and coke: Analyst, v. 76, p. 523–536.

Goldschmidt, V. M., 1937, The laws of the geochemical distribution of the elements: Chem. Soc. London Jour., p. 655–675.

Hyblinette, A. G., and Sandell, E. B., 1942, Determination of germanium in silicate rocks: Indus. and Eng. Chemistry, Anal. ed., v. 14, p. 715–716.

Morgan, Gilbert, and Davies, G. R., 1937, Germanium and gallium in coal ash and flue dust: Chemistry and Industry, p. 717–721.

Schneider, William A., Jr., and Sandell, E. B., 1954, Photometric determination of traces of germanium after carbon tetrachloride extraction: Microchimica Acta, Heft 2, p. 263–268.

Stadnichenko, Taisia, Murata, K. G., Zubovic, Peter, and Hufschmidt, E. L., 1953, Concentration of germanium in the ash of American coals, a progress report: U. S. Geol. Survey Circ. 272.

Waring, Claude L., and Tucker, Wendell, P., 1954, Effect of ashing temperature on the volatility of germanium in low-rank coal samples: Anal. Chemistry, v. 26, p. 1188–1199.