GERMANIUM IN KANSAS COALS

By

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1959 REPORTS OF STUDIES, PART 4, PAGES 161-179, FIGURES 1-2
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CONTENTS

ILLUSTRATIONS

TABLES

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ABSTRACT

A detailed spectrographic method for determining the germanium content of coal is described and the results of analyses of twenty Kansas coals from 117 different locations are reported. No definite conclusions are made as to geographic or stratigraphic variation in germanium content. The concentration of germanium in the coal ash ranges from .0018 percent to .0575 percent, and in the total coal from .0006 per cent to .0116 per cent.

INTRODUCTION

SCOPE OF STUDY

The demand for germanium in many phases of the electronic industry and its relatively short supply have prompted extensive research into possible sources of this element. Small amounts of germanium are found throughout the earth's crust, but it has not been found in sufficient concentration to permit its direct recovery. The chief source of germanium in the past has been certain residues derived from the smelting of zinc ores, from which it is obtained by distillation. The uncertain economics of zinc mining and smelting, however, have led to the investigation of other source materials, especially coal. Several plants now in operation in Germany, Japan, and England recover germanium from the fly-ash and residual ash of coal that is being used in industrial quantities. The possibility that Kansas coals might be a source of germanium prompted the State Geological Survey to begin a study, by spectrochemical analyses, of the germanium content of coals found in the state. A preliminary spectrographic investigation of germanium in Kansas coals was published by Schleicher and Hambleton (1954). The chief purpose of the preliminary investigation was to develop an accurate and rapid spectrographic method for determining germanium content of coals; analyses of six coals from 24 locations were included in the report. The present publication reports analyses of twenty coals from 117 locations; the spectrographic method is again described.

Since the publication of the preliminary report, Fredrick and others (1954) and Machin and Witters (1956) have completed similar studies. Results of these studies show good agreement with the results obtained in the Kansas Geological Survey laboratory. The ash of Kansas coals shows, in general, a higher germanium content than the coals from some other localities. Most of the Kansas coal seams are thin, and, seemingly, germanium is more abundant in thin coal beds than in the thicker coal beds.

The element silicon, being atomically, chemically, and physically very similar to germanium, also can be used in semiconducting devices. Silicon transistors have the advantage that, in general, they can operate at higher ambient temperatures than other semiconductors, but the disadvantage that their capacity is somewhat less than those made of germanium. Silicon probably will never completely replace germanium; however, the manufacture of silicon transistors has effectively reduced the shortage of germanium in the electronics industry as shown by price declines.

In April 1954, the price of germanium was $295 per pound (Eng. Mining Jour., 1954). In July 1955, the price had fallen to $250 per pound (Machin and Witters, 1956) and in June 1957 had been reduced to a low of $197 (Eng. Mining Jour., 1957). The price subsequently rose to $206 per pound in June 1958 (Eng. Mining Jour., 1958).

Hughes Product Group of Hughes Aircraft Corporation states (Chem. Eng. News, 1956) that improved chemical and metallurgical methods of producing and refining will lower the price still further to meet the estimated five-fold increase in market by 1960.

COALS ANALYZED

The study includes 93 (117 including Preliminary Study) analyses. The Pennsylvanian coals analyzed include the Weir-Pittsburg, Pilot, Tebo (from western Missouri), Mineral, Fleming, Croweburg, Bevier, and Mulky coals of the Cherokee Group, Desmoinesian Series (Howe, 1956); the Summit and Mulberry (partly from western Missouri) coals of the Marmaton Group, Desmoinesian Series (Schoewe, 1955); the Thayer coal of the Kansas City Group, Missourian Series (Schoewe, 1944); the Blue Mound, Ottawa, Sibley, and Williamsburg coals, two unnamed coals in the Tonganoxie Sandstone, and an unnamed coal in the

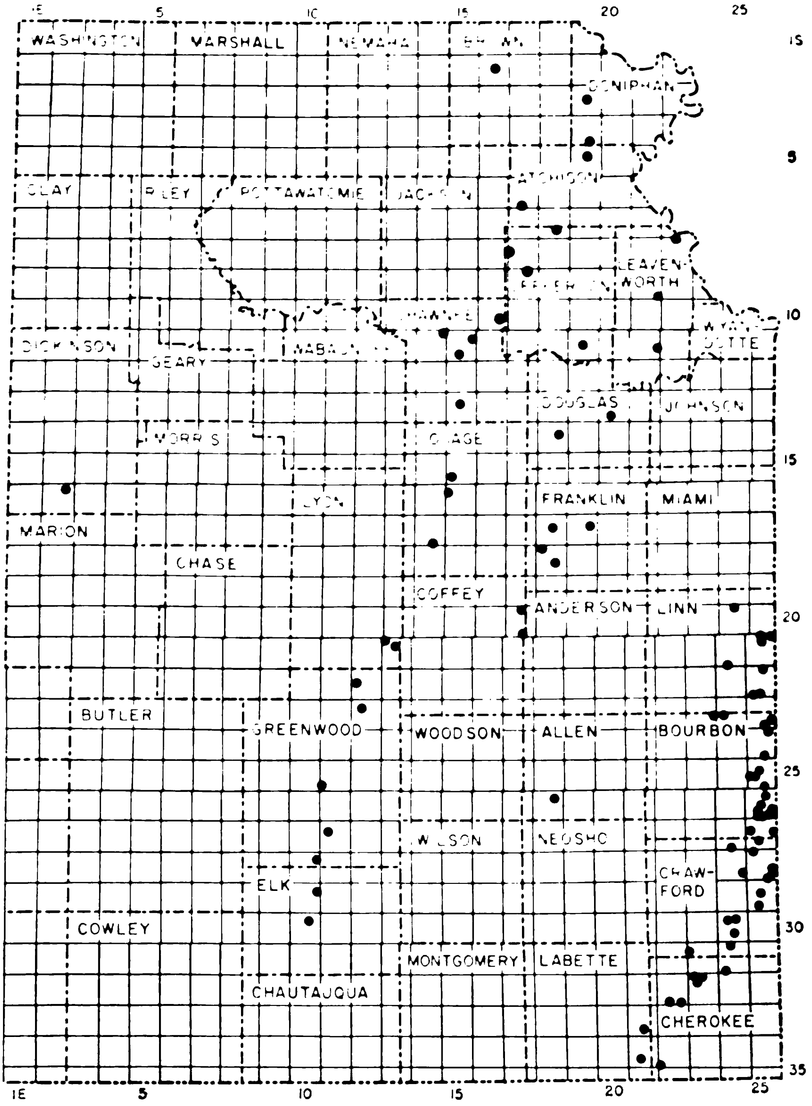

Fig. 1.—Map showing localities where coal samples were collected.

Lawrence Shale of the Douglas Group, Virgilian Series (Bowsher and Jewett, 1943), and the Nodaway, Elmo, and Lorton coals of the Waubaunsee Group, Virgilian Series (Schoewe, 1946). Analyses also were made of one sample of Permian coal in the Wellington Formation (Schoewe, 1951), two samples each of underclay and rash (impure coal), and eight samples of refuse piles of fines. Data pertaining to the location of the coal samples, name of coal seam, average thickness of the coal, and laboratory number of samples are presented in Table 1. Figure 1 shows the locations sampled.

ACKNOWLEDGMENT

The author thanks the Pittsburg-Midway Coal Company for cooperation in providing samples for analysis in this study.

SAMPLE PREPARATION

PRELIMINARY CHEMICAL TREATMENT

A sample of each coal sufficient in size to produce at least 150 mgm of ash, as calculated from the proximate analysis, was weighed and placed in a platinum dish of about 100 ml capacity. The dish was then covered with a tight pyrex watch glass and 25 to 35 ml of concentrated nitric acid was added through the pourout lip. The dish was heated on an electric hotplate in a fume hood at about 250°F until all the nitric acid either had reacted with the coal or had been distilled out through the pourout lip. The tight watch glass was used to prevent undesirable rapid evolution of the acid, because refluxing seemed to promote more efficient use of the acid's oxidizing properties. When the sample was completely dried by this method it looked like coke. To this hot substance, 15 ml of concentrated nitric acid was added and again permitted to fume off with refluxing as before. After complete dryness was again attained, the dish was placed in a cold muffle furnace and the temperature raised slowly (approximately 75 to 100°C per hour) to 450°C. When the sample was completely ashed, the furnace was immediately shut off. The immediate turning off of the furnace at 450°C is deemed desirable, as prolonged heating, even at the low temperature of 450°C, might result in the loss of volatile oxides, including germanium oxide. According to Tucker and Waring (1954), neither temperature (100 to 200°C) nor time of ignition (1 to 4 hours) affected the con-

TABLE 1.—*Coals studied for germanium content, location of samples, and thickness available*

Lab. no.	County	Location	Coal	Thickness (inches)
5693	Dickinson	21-16-2E	Unnamed (1)	5
5692	Brown	15-2-16E	Lorton	8
55228	Atchison	33-6-17E	Elmo	14
55229	Shawnee	1-11-14E	Elmo	20
54398	Elk	9-30-10E	Nodaway	5
54399	Elk	11-29-10E	Nodaway	6
54400	Greenwood	12-28-10E	Nodaway	4
54401	Greenwood	17-27-11E	Nodaway	4
54402	Greenwood	30-25-11E	Nodaway	2
54403	Greenwood	9-23-12E	Nodaway	6
54404	Greenwood	17-22-12E	Nodaway	2.5
54397	Lyon	9-21-13E	Nodaway	7
54396	Lyon	6-21-13E	Nodaway	6
54395	Osage	34-17-14E	Nodaway	10
54363	Osage	7-16-15E	Nodaway	16
54412	Osage	29-15-15E	Nodaway	14
54413	Shawnee	16-13-15E	Nodaway	9
54414	Shawnee	27-11-15E	Nodaway	14
54415	Shawnee	12-11-15E	Nodaway	12
54416	Shawnee	23-10-16E	Nodaway	15
54410	Jefferson	3-9-17E	Nodaway	11
54409	Jefferson	18-8-17E	Nodaway	10
54408	Jefferson	28-7-18E	Nodaway	9
54405	Atchison	21-5-19E	Nodaway	8
54406	Doniphan	34-4-19E	Nodaway	12
54407	Doniphan	15-3-19E	Nodaway	4
55227	Shawnee	27-11-15E	Nodaway	13
55220	Leavenworth	36-9-21E	Upper Sibley	6
55224	Leavenworth	4-8-22E	Upper Sibley	12
55225	Leavenworth	24-11-21E	Upper Sibley	26
55223	Leavenworth	24-11-21E	Lower Sibley	13
55221	Jefferson	22-11-19E	Unnamed (2)	6
5547	Douglas	28-13-20E	Unnamed (3)	6
5548	Douglas	28-13-20E	Unnamed (3)	2
5546	Douglas	28-13-20E	Unnamed (3)	2.4
55222	Coffey	34-20-17E	Upper Williamsburg	7
55194	Coffey	3-20-17E	Upper Williamsburg	7
55113	Franklin	22-18-18E	Upper Williamsburg	12
55114	Franklin	5-18-18E	Upper Williamsburg	16
55226	Franklin	15-17-18E	Upper Williamsburg	15
55115	Franklin	14-17-19E	Upper Williamsburg	9
54335	Douglas	14-14-18E	Lower Williamsburg	6
55117	Allen	11-26-18E	Thayer	7
53308*	Bourbon	20-23-24E	Mulberry	22
53309*	Bourbon	24-23-23E	Mulberry	13
53310*	Linn	33-22-25E	Mulberry	22
53311*	Linn	33-21-24E	Mulberry	23
53313*	Linn	3-20-24E	Mulberry	40
53314*	Linn	3-22-25E	Mulberry	24
53315*	Linn	32-22-25E	Mulberry	24
55184†	Linn	1-21-25E	Mulberry	28
55185†	Linn	10-21-25E	Mulberry	50
55186†	Bates (Mo.)	28-41N-33	Mulberry	12
55187†	Bates (Mo.)	21-40N-33	Mulberry	24

TABLE 1.—*Coals studied for germanium content, location of samples, and thickness available (continued)*

Lab. no.	County	Location	Coal	Thickness (inches)
55188†	Bates (Mo.)	27-40-33	Mulberry	26
55189†	Bates (Mo.)	6-39-33	Mulberry	24
55190†	Bates (Mo.)	16-40-33	Mulberry	36
55191†	Bates (Mo.)	32-41-33	Mulberry	38
55192†	Bates (Mo.)	33-40-33	Mulberry	20
55193†	Linn	3-21-25E	Mulberry	45
5685	Bourbon	16-25-25E	Summit	10
53305*	Bourbon	34-25-25E	Mulky	14
53306*	Bourbon	19-25-25E	Mulky	14
53307*	Bourbon	33-26-25E	Mulky	13
5691	Bourbon	25-23-25E	Mulky	17
5690	Bourbon	20-25-25E	Mulky	15
5689	Crawford	25-28-24E	Mulky	8
5686	Bourbon	11-26-25E	Mulky	6
5684	Crawford	34-27-24E	Mulky	8
5589	Crawford	5-28-25E	Mulky	9
5595	Bourbon	34-24-25E	Mulky	5
5598	Bourbon	22-26-25E	Mulky	18
5687	Bourbon	34-23-25E	Mulky	18
5682	Bourbon	2-24-25E	Mulky	14
53312*	Bourbon	34-26-25E	Bevier	15
BN-2-B*	Bourbon	25-26-25E	Bevier	17
BN-3-B*	Bourbon	35-26-25E	Bevier	17
CR-9-B*	Crawford	28-27-25E	Bevier	17
CR-6-B*	Crawford	16-29-25E	Bevier	10
CR-14-B*	Crawford	10-30-24E	Bevier	16
CR-13-B*	Crawford	7-31-23E	Bevier	17
CK-6-B*	Cherokee	31-34-22E	Bevier	24
54331	Crawford	9-30-24E	Bevier	24
5683	Bourbon	20-27-25E	Bevier	16
5688	Bourbon	28-26-25E	Bevier	13
5549+	Bourbon	34-26-25E	Bevier	
CR-1-C*	Crawford	28-29-25E	Croweburg	12
53143	Crawford	24-28-25E	Croweburg	12
5591	Cherokee	32-31-24E	Croweburg	11
5592	Labette	27-33-21E	Croweburg	8
5590	Cherokee	32-31-24E	Fleming	4-9
5593	Crawford	24-28-25E	Fleming	11
5594	Cherokee	4-31-24E	Fleming	9
5596	Labette	U.S. 69 (North of Chetopa)	Fleming	8
54330	Crawford	27-30-24E	Fleming	3
5597	Bourbon	13-27-25E	Fleming	5.5
5599	Cherokee	8-32-23E	Fleming	12
54333	Crawford	25-28-25E	Fleming	9
CK-4-M*	Cherokee	35-32-22E	Mineral	20
CR-8-M*	Crawford	28-29-25E	Mineral	18
CR-4-M*	Crawford	35-28-25E	Mineral	20
54332	Crawford	25-28-25E	Mineral	16
53142*	Crawford	24-28-25E	Pilot	9
54334	Crawford	24-28-25E	Weir-Pittsburg	(?)
54367†	St. Clair (Mo.)	9-39-28	Tebo	(?)
54368†	St. Clair (Mo.)	9-39-28	Tebo	(?)

TABLE 1.—*Coals studied for germanium content, location of samples, and thickness available (concluded)*

Lab. no.	County	Location	Coal	Thickness (inches)
5550‡	Underclay			
5551‡	Underclay			
5552‡	Rash			
54355†	Cherokee	4-32-23E	Composite samples of refuse piles, Fleming, Mineral, and Bevier coal.	
54356†	Cherokee	4-32-23E		
54357†	Cherokee	4-32-23E		
54358†	Cherokee	4-32-23E		
54359†	Cherokee	4-32-23E		
54360†	Cherokee	5-32-23E		
54361†	Cherokee	33-32-22E		
54362†	Cherokee	33-32-22E		

‡ Samples supplied by Mr. J. H. Vincent, 701½ West 9th, Pittsburg, Kansas.
* Samples analyzed for preliminary report.
† Samples obtained from drill holes, Pittsburg-Midway Coal Company.
(1)—Unnamed coal in shale below Wellington limestone.
(2)—Unnamed coal in Lawrence Shale.
(3)—Unnamed coal in Tonganoxie Sandstone.

centration of germanium in their coal samples, whereas Goldschmidt and Peters (1933, cited by Ahrens, 1950, p. 215) have reported otherwise. For the purposes of this investigation, the relatively "safe" temperature of 450°C was chosen. The electric muffle furnace used was a Hoskins, equipped with a manually operated panel rheostat and controlled by a Brown recording potentiometer, which automatically turned off the furnace when the desired 450°C temperature was reached. The last 25°C rise in temperature was accompanied by evolution of voluminous fumes both of organic material and inorganic acids, which were dispersed by the use of an efficient exhaust fan. Upon cooling, the ash was weighed and percent "wet" ash calculated. In every case, the percent "wet" ash calculated exceeded the actual ash content of the coal; the addition of the nitrate radical, the oxidation of sulfur to sulfate, and the lack of high-temperature ignition all tend to increase the weight of the ash fraction. The calculated percentage of "wet" ash was used later to calculate the concentration of germanium in the total coal.

PREPARATION OF SAMPLES FOR SPECTROGRAPHIC ANALYSIS

Bismuth was chosen as the internal standard element (Rusanov, 1940, as reported by Ahrens, 1950, p. 216). Comparison of the properties of germanium and bismuth indicated the following similarities:

	Ge	Bi
Ionization potential	8.09 V	Ca 8.0 V
Excitation potential (for the lines chosen).	4.94 V	5.5 V

The melting points and boiling points of both the elements and their oxides are relatively low, and as nearly as one could judge from theoretical evidence, they seem to be well suited as an element pair. From the weight of ash it was possible to calculate, weigh, and add the amount of bismuth trioxide necessary to produce a concentration of one percent bismuth in the ash. The density of bismuth trioxide would introduce difficulties in the addition and thorough mixing of an amount smaller than one percent. The bismuth trioxide used was germanium-free Johnson, Matthey, and Company, Ltd. "Specpure" grade, distributed by Jarrell-Ash Company. The first samples of ash were ground and mixed with the bismuth trioxide for about two hours each in a 5.5 cm mullite mortar. In the interest of time saving, seven subsequent samples were ground in a Fisher improved mortar grinder with a mullite mortar and pestle for only 30 minutes, inasmuch as after that time the particles had been reduced to a size where compaction in the mortar resulted. Scraping them off the mortar and further grinding resulted in immediate recompaction. It was found that although the mechanical grinder was very efficient in reducing the particle size, its mixing action (at least on samples of only 150 mgm size) was not satisfactory. By experimentation it was found that the hand-grinding time could be reduced to about 20 minutes, maintaining a satisfactorily thorough mixing, but that any attempt to reduce this time further led to a loss of precision in the spectrographic results.

During the grinding of all the hand-ground samples, any compacted sample in the mortar was scraped loose frequently and broken up with a small platinum spatula.

PREPARATION OF SPECTROGRAPHIC STANDARDS

A matrix approximating closely the composition of an average coal ash was prepared by grinding and mixing together 9.14 gm silica, 2.76 gm calcium carbonate, 3.90 gm ferric oxide, and 3.54 gm alumina. As internal standard 9.2787 gm bismuth trioxide was added. Chemical analyses were used to determine the major constituents of the average coal "wet" ash, and the composition of the matrix was so arranged that 7.85 gm of the matrix was equivalent in composition to 10.00 gm of the average "wet" ash. The discrepancy in equivalence was due to the use of oxides and carbonates, which were available in pure form, in the preparation of the matrix; in the "wet" ash, the major metallic constituents were present as sulfates. The effect of sulfate ion on the ignition of ash was compensated for in the prepared matrix by the use of lithium sulfate as buffer; this is standard practice for the Kansas Geological Survey laboratory.

To 3.925 gm of the matrix plus bismuth was added 5 mgm of germanium as germanium dioxide. The resulting mixture contained the equivalent of 0.1 percent germanium. Successive dilutions were made with portions of the original matrix plus bismuth until standards containing 0.1 percent, 0.05 percent, 0.01 percent, 0.005 percent, and 0.001 percent germanium, in essentially identical matrices, were available. These standards and the unknown coal ashes were ignited under identical conditions. Seven spectra were run for each standard, a total of 210 mgm equivalent for each standard, then averaged to give the points from which the working curve for the germanium-bismuth ratio was constructed (Fig. 2).

SPECTROGRAPHIC TECHNIQUE

Equipment Used

The spectrograph used was an Applied Research Laboratories 1.5 meter grating spectrograph powered by a D.C. arc source unit. The electrodes were National Carbon Company standard electrode-grade graphite rods cut to 5 cm in length and formed as an undercut crater electrode similar to the standard Harvey electrode but with thinner wall. The crater is 3.0 mm deep and 5.25 mm inside diameter. The counterelectrode is the standard ARL platform electrode with center-post, selected because the concave platform seems to increase the arc sensitivity by reflective increase of the temperature of the sample. The arc was stabilized by a rotating magnet of the type suggested by Meyers and Brunstetter (1947). The rotating sector was set at 10 percent, the grating doors closed to a setting of 4.7 or about 67 percent of the maximum opening, and the electrodes at the beginning of ignition were 4 mm apart, the lower electrode containing the positive charge. No attempt was made to keep the electrode distance constant throughout the ignition. The arc strike was made each time with a rubber-handled sharpened graphite rod from the centerpost of the counterelectrode to the crater edge below; this procedure contributed to the stability of the arc by preventing it from striking from the rim of the platform and thus being able to wander around the outside of the counterelectrode. The film used was Eastman spectrum analysis No. 1.

TECHNIQUE EMPLOYED

Several moving film spectra were made to determine persistance of both the germanium and bismuth lines in the samples and their sensitivity at various current ratings and with varying amounts of buffer. Optimum results were obtained using an 8-amp arc for an exposure of 60 seconds. The buffer, lithium sulfate, was added experimentally in various amounts. The combination of 10 mgm of ash and 5 mgm of lithium sulfate gave the greatest buffering action, a reasonable cyanogen-band suppression, a higher sensitivity than lesser amounts of buffer, and a more rapid evolution of the element pair than was afforded by a larger proportion of buffer. The ash and buffer were mixed perfunctorily and introduced into the craters of the electrodes after which the

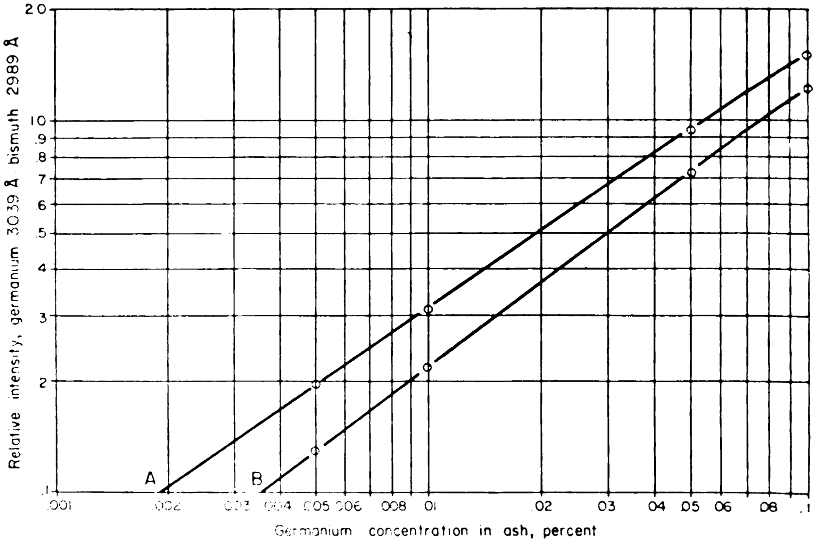

FIG. 2.—Graph showing relation of germanium content in coal ash to intensity ratio of spectrum lines used, (A) preliminary study, (B) total study. Displacement is due to changed variables.

mixture was firmly compacted with a flat-faced glass rod of the same diameter as the electrode crater.

After exposure, the film was developed for 3 minutes in D-19, short-stopped for 10 seconds in 3 percent acetic acid, and fixed for 1 minute in Kodak rapid liquid fixer with hardener. After a 1-minute tap-water rinse and a 30-second distilled-water rinse, the film was sponged and dried on an infra-red forced-air film dryer. Density measurements were then read on an ARL densitometer-comparitor.

The lines chosen for density measurements were the germanium line at 3039.0 A and the bismuth line at 2989 A (Harrison, 1946). This particular bismuth line was chosen because of its nearness to the germanium line. The relatively high (1 percent) bismuth concentration caused more sensitive and more commonly used lines in this region to be too intense. The results of the spectral intensity ratios as plotted on the working curve, their averages, the mean deviation, the standard deviation, and the percent mean deviation are shown in Table 2.

To further eliminate the effect of arc instability, three samples of each ash were ignited consecutively and superimposed as one spectrum, producing a type of "internal average" of the three samples. Three or four spectra of each sample were obtained in this way, and the results averaged; if the first three spectra (nine samples) did not agree, however, a fourth spectrum of three samples was obtained, and the four averaged.

If one of the four spectra differed widely from the other three, statistical methods were employed to determine the validity of discarding the divergent results. If the deviation of one of the results from the mean of the other three was found to be greater than four times the mean deviation of the other three, and greater than three standard deviations from the mean of the other three, the one result was judged to be trivial, on a weighted basis, and was discarded. By commonly accepted statistical principles, 68 percent of all results should be one standard deviation or less from the mean, 28 percent should be one to two standard deviations from the mean, and the remaining 4 percent should fall not farther than three standard deviations from the mean.

SUMMARY AND DISCUSSION OF RESULTS

The range of concentration of germanium found in the samples analyzed was .0018 to .099 percent in the ash, and .0005 to .0116

TABLE 2.—*Results of analyses*

Lab. no.	Thickness, inches	Percent wet ash in coal	Percent Ge in ash	Percent Ge in coal	Ge in coal, ounces/ton	Number of determinations	Mean deviation	Percent mean deviation
Unnamed coal in Wellington								
5693	5	90.85	.001	.0011	.35	1	....	....
Lorton coal								
5692	8	48.37	.0021	.0010	.32	3	.03	5.0
Elmo coal								
55228	14	39.46	.0099	.0039	1.25	3	.0005	5.05
55229	20	26.84	.0056	.0015	.48	4	.00035	6.2
Nodaway coal								
54398	5	17.06	.0199	.0034	1.09	3	.0015	7.54
54399	6	12.11	.049	.0059	1.89	7	.005	10.2
54400	4	20.32	.0167	.0034	1.09	3	.0010	6.0
54401	4	35.12	.0084	.0030	.96	3	.0002	2.4
54402	2	10.92	.099	.0108	3.46	3	.003	3.0
54403	6	16.54	.0186	.0031	.99	4	.0010	5.4
54404	2.5	21.35	.053	.0113	3.62	3	.003	5.7
54397	7	17.96	.0343	.0062	1.98	3	.0022	6.4
54396	6	22.76	.0153	.0035	1.12	3	.0006	3.9
54395	10	35.40	.0184	.0065	2.08	4	.0012	6.5
54363	16	15.75	.021	.0033	1.06	3	.0007	3.3
54412	14	20.20	.0148	.0031	.99	7	.0019	12.8
54413	9	57.02	.002	.0011	.35	1	....	......
54414	14	6.48	.107	.0069	2.21	5	.008	7.5
54415	12	10.81	.0475	.0051	1.63	3	.0022	4.2
54416	15	64.44	N.D.	N.D.	......	..	....	......
54410	11	10.11	.061	.0062	1.98	3	.003	4.9
54409	10	40.48	.0188	.0076	2.43	4	.0022	11.7
54408	9	9.19	.075	.0069	2.21	3	.006	8.0
54405	8	45.30	.0089	.0040	1.28	3	.0004	4.5
54406	12	14.87	.0216	.0032	1.02	3	.0016	7.4
54407	4	49.15	.0125	.0061	1.95	3	.0004	3.2
55227	13	20.83	.0142	.0030	.96	3	.0004	2.82
Upper Sibley coal								
55220	6	49.15	.0033	.0016	.51	3	.0001	3.3
55224	12	36.20	.0062	.0022	.70	3	.0003	4.84
55225	26	50.15	.0027	.00135	.44	3	.0001	3.7

Lower Sibley coal								
55223	13	32.65	.0037	.0012	.38	3	.0002	5.41
Upper Williamsburg coal								
55222	6	40.87	.0120	.0049	1.57	3	.0004	3.3
55194	7	21.91	.0066	.0014	.44	3	.0003	4.5
55113	12	20.20	.0575	.0116	3.71	4	.0040	7.0
55114	16	14.69	.0543	.0080	2.56	5	.0010	1.8
55226	15	52.17	.0029	.0015	.48	3	.0001	3.45
55115	9	35.79	.0103	.0037	1.18	3	.0001	1.0
Lower Williamsburg coal								
54336	6	20.24	.047	.0095	3.04	3	.001	2.1
Unnamed coal in Lawrence Shale								
55221	6	43.44	.0211	.0092	2.94	6	.0022	10.43
Unnamed coals in Tonganoxie Sandstone								
5547	6	20.44	.0272	.0056	1.79	3	.0019	6.9
5548	2.4	58.10	.0038	.0022	.70	3	.0003	7.9
5546	2.4	11.25	.037	.0042	1.34	3	.0033	8.9
Thayer coal								
55117	7	15.15	.0203	.0031	.99	4	.0012	5.9
Mulberry coal								
53308	22	15.03	.0125	.00188	.60	4	.0002	1.6
53309	13	15.54	.0148	.00230	.74	3	.0004	2.7
53310	22	19.78	.0065	.00129	.41	3	.0003	4.6
53311	23	7.06	.0680	.00480	1.54	3	.0013	1.9
53313	40	20.80	.0075	.00156	.50	3	.0003	4.0
53314	24	13.23	.0184	.00243	.78	4	.0013	7.1
53315	24	18.26	.0105	.00175	.56	4	.0016	16.7
55184	28	20.41	.0090	.0018	.58	4	.0006	6.7
55185	50	17.41	.0035	.0006	.19	4	.0001	2.9
55186	12	19.31	.0116	.0022	.70	3	.0006	5.2
55187	24	19.06	.0100	.0019	.61	3	.0003	3.0
55188	26	18.06	.0130	.0023	.74	3	.0008	6.2
55189	24	23.41	.0089	.0021	.67	3	.0005	5.6
55190	36	18.96	.0090	.0017	.54	6	.0008	8.9
55191	38	28.28	.0045	.0013	.42	3	.0003	6.7
55192	20	22.66	.0044	.0010	.32	3	.0002	4.5
55193	45	16.65	.0055	.0009	.29	3	.0001	1.8

TABLE 2.—*Results of analyses (continued)*

Lab. no.	Thickness, inches	Percent wet ash in coal	Percent Ge in ash	Percent Ge in coal	Ge in coal ounces/ton	Number of determinations	Mean deviation	Percent mean deviation
Summit coal								
5685	10	48.69	N.D.	....	......	..	....	......
Mulky coal								
53305	14	11.44	.0178	.00204	.65	3	.0004	2.2
53306	14	28.96	.0086	.00249	.80	3	.0007	8.1
53307	13	14.30	.0290	.00414	1.32	4	.0025	8.6
5691	17	19.14	.0044	.0008	.26	3	.00057	13.0
5690	15	10.65	.0180	.0019	.61	3	.00013	4.2
5689	8	19.06	.0239	.0045	1.44	3	.0009	6.7
5686	6	36.02	.0018	.0006	.19	3	.0003	12.9
5684	9	14.98	.0236	.0035	1.12	3	.0009	3.8
5589	9	9.30	.0525	.0049	1.57	4	.0015	2.9
5595	5	49.90	.0025	.0012	.38	1	....	......
5598	18	30.00	.0047	.0014	.45	5	.0003	6.3
5687	21	20.65	.0091	.0019	.61	3	.00003	0.3
5682	15	19.63	.0048	.0009	.29	4	.0006	12.5
Bevier coal								
53312	15	16.66	.0134	.00223	.71	3	.0006	4.5
BN-2-B	17	18.32	.0101	.00185	.59	3	.0011	10.9
BN-3-B	17	20.47	.0044	.00098	.31	4	.0006	12.5
CR-9-B	17	11.52	.0274	.00242	.77	4	.0032	15.2
CR-6-B	10	15.54	.0153	.00238	.76	3	.0003	2.0
CR-14-B	16	18.81	.0078	.00147	.47	3	.0004	5.1
CR-13-B	17	17.40	.0135	.00235	.75	3	.0006	4.4
54331	17	10.06	.0198	.0020	.64	3	.0006	3.03
5683	16	19.14	.0236	.0045	1.44	2	.0004	1.7
5688	13	31.18	.0092	.0030	.96	3	.0005	5.4
CK-6-B	24	20.31	.0086	.00175	.56	3	.0006	7.0
Croweburg coal								
CR-1-C	12	19.60	.0107	.00174	.56	4	.0014	15.7
53143	12	7.50	.0209	.00157	.50	3	.0009	4.3
5591	11	7.23	.0120	.0009	.29	5	.0022	18.3
5592	8	11.41	.0223	.0025	.80	4	.0017	7.6

Fleming coal								
54333	9	18.53	.0054	.0010	.32	3	.0001	1.85
5590	57	17.13	.0083	.0014	.45	3	.0005	6.0
5593	11	9.55	.0051	.0005	.16	5	.0006	11.8
5594	9	10.21	.012	.0012	.38	3	.0003	2.5
5596	8	2.95	.100	.0030	.96	3	.0023	2.3
5599	12	23.45	.0071	.0017	.54	3	.0004	5.6
5597	5.5	12.34	.0218	.0027	.86	3	.0008	3.7
Mineral coal								
CK-4-M	20	13.24	.0052	.00069	.22	4	.0010	19.2
CR-8-M	18	15.16	.0052	.00079	.25	4	.00045	8.7
CR-4-M	20	19.52	.0036	.0007	.22	4	.0005	13.9
54332	16	9.75	.0064	.0006	.19	3	.0003	4.7
Pilot coal								
53142	9	14.98	.0118	.00177	.57	3	.0010	8.5
Weir-Pittsburg coal								
54334	....	13.26	.0054	.0007	.22	4	.0004	7.4
Tebo coal								
54367	....	29.12	.0083	.0024	.77	3	.0001	1.2
54368	....	35.18	.0061	.0021	.67	4	.0006	9.8
Underclays								
5550	....	65.07	N.D.	....	......	..	....	......
5551	....	96.79	N.D.	....	......	..	....	......
Rash								
5552	....	26.85	.0058	.0016	.51	3	.0007	12.1
5549	....	21.15	.0098	.0020	.64	3	.0004	4.3
Refuse piles—Composite of Fleming, Mineral, and Bevier coals								
54355	....	56.28	N.D.	....	......	..	....	......
54356	....	42.89	.001	.0004	.12	1	....	......
54357	....	48.86	N.D.	....	......	..	....	......
54358	....	70.10	N.D.	....	......	..	....	......
54359	....	60.21	N.D.	....	......	..	....	......
54360	....	82.26	N.D.	....	......	..	....	......
54361	....	20.00	.0059	.0012	.38	5	.0002	3.4
54362	....	33.33	.0041	.0013	.42	4	.0003	7.3

(N.D.=not detected.)

percent in the air-dry coal (Table 2). Calculated in the more practical unit of ounces per ton of coal, the range of values is 0.16 in Sample No. 5593, Fleming coal of the Cherokee Group, to 3.71 in Sample No. 55113, Williamsburg coal from the Lawrence Shale. On the basis of the current retail price of germanium ($12.90 per ounce), the coals range in value from $2.06 to $47.86 per ton. Evaluation of the coals with respect to their ash content indicates that the ash of Sample No. 54402, containing 31.69 ounces per ton of ash, would have a value of $408.70 per ton, if no germanium were lost in the ignition. Coal seems to compare favorably with other sources of the metal, both foreign and domestic. Although germanium is a very common constituent of the earth's crust, no deposits of ore-grade germanium minerals have yet been found.

Some investigators have adopted a pessimistic attitude toward the recovery of germanium from coal (Thompson and Musgrave, 1952) because of low concentrations of germanium found in the thicker eastern coals. The analyses shown in this study, however, represent the entire coal at the location sampled, and although the total eastern coals are said rarely to contain as much as 0.003 percent germanium, 55 samples of the coal analyzed in this study showed 0.002 percent or more germanium, and 22 samples contained more than .004 percent germanium.

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