

An Application of Spectrographic Microphotometric Scanning

GEOLOGICAL SURVEY BULLETIN 1036-E

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By C. L. WARING, MONA FRANCK, and A. M. SHERWOOD

A CONTRIBUTION TO GEOCHEMISTRY

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UNITED STATES DEPARTMENT OF THE INTERIOR

Douglas McKay, *Secretary*

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AN APPLICATION OF SPECTROGRAPHIC MICROPHOTOMETRIC SCANNING

By C. L. WARING, MONA FRANCK, and A. M. SHERWOOD

ABSTRACT

A previously published semiquantitative spectrographic method was modified by applying microphotometric scanning of the spectrograms in such a way that the operator was free to do other work during a large part of the scanning time. The spectrograms of 5 ash samples from Dakota lignite and one synthetic mixture were scanned for 68 elements; 32 elements were found and those below 10 percent were reported quantitatively.

The tests included a spectrum-line study to provide lines least enhanced or depressed by matrix differences, information on accuracy, on human error, and eye fatigue.

In 93 percent of the cases the agreement with the chemical analysis was within a factor-of-10 bracket, 85 percent were within a factor-of-5 bracket, and 79 percent were within a factor-of-2 bracket.

INTRODUCTION AND ACKNOWLEDGMENTS

In a semiquantitative spectrographic method for the analysis of minerals, rocks, and ores, described by Waring and Annell (1953), the procedure included the analysis of an unknown for 68 elements in one exposure of a 10-mg sample. The final results were obtained by visually comparing spectral lines of the unknown with the same lines on standard plates.

The present study is a modification of the semiquantitative method to include the application of microphotometry to the spectrograms. An increase in the accuracy and precision of the results would make the data obtained more applicable to the geochemical problems being studied. The experiments were conducted with the expectation of applying the procedure to numerous types of samples and reporting the results quantitatively or in narrow concentration ranges.

The spectrograms were scanned and recorded automatically on a commercial microphotometer. The procedure permitted the operator to do other work during a large part of the scanning time, after adjusting the sensitivity of the instrument. Working with an enlarged chart (10X) was less fatiguing for the operator than using the mag-

nifying glass for plate interpretation. However, because 68 elements (table 3) are being determined spectrographically at the present time, photographic plates are still being used in most of our analytical work. Determining this large number of elements in rock samples that exhibit nonuniform burning characteristics is still difficult with available commercial direct-reading instruments. A permanent record of the spectrograms has definite reference value in the laboratory. We plan to determine the adaptability of the method with the instruments in the laboratory before attempting the direct reading approach.

The method was applied to the ash of five Dakota lignite auger-hole samples and one synthetic mixture. Because many semi-quantitative analyses of the ashes of low-rank coals are performed in our laboratory in connection with the geochemical studies of lignites, any improvement in the method could readily be applied to the lignite problem. The major components of the lignite ashes (usually consisting of iron, silicon, aluminum, sodium, and calcium) may vary considerably from sample to sample. Selection of these samples would fit into our plan of studying numerous lines and selecting those least enhanced or depressed by matrix differences.

The percentage composition of the synthetic sample was as follows: aluminum, 13; silicon, 11; iron, 8.75; sodium, 2.5; calcium, 8.08; magnesium, 1.5; potassium, 2; uranium, 1; titanium, arsenic, boron, barium, phosphorus, thorium, each 0.5; strontium, cobalt, manganese, nickel, lead, chromium, zirconium, zinc, cerium, copper, each 0.05; yttrium, molybdenum, germanium, gallium, tin, vanadium, scandium, lanthanum, each 0.005; and silver and ytterbium, each 0.0005.

A survey of the literature reveals that several similar methods (Eeckhout, 1945, and Meggers, 1950) are being applied in other laboratories on different materials with different standardization procedures and visual estimation of results.

Thanks are expressed to members of the Geological Survey who have aided in this investigation—especially to Helen Worthing and C. S. Annell who made many of the determinations and to F. S. Grimaldi who supervised the chemical analyses. This work is part of a program being conducted by the Geological Survey on behalf of the Division of Raw Materials of the U. S. Atomic Energy Commission.

EXPERIMENTAL DATA

PREPARATION OF STANDARDS

As in the procedure described previously (Waring and Annell, 1953), the standard solutions were made to contain 10 mg of the element per milliliter of solution. These solutions were diluted until 0.1 ml of each equals 10, 1, 0.1, 0.01, 0.001, and 0.0001 percent based on a 10-mg sample of the unknowns. A 0.1-ml aliquot of the solution was then

added from a micropipette to the sealed electrode cup. This was dried on an asbestos-covered hot plate at a temperature of approximately 100° C. A few milligrams of pure graphite were added to the remaining salts in the electrodes. Duplicate sets of electrodes were prepared, one set was arced (250 v, 12 amp, d-c) for 60 seconds and one for 120 seconds.

The spectrograms were scanned on a recording microphotometer. Data provided by the tracings, including wave length, percent transmittance, and width were recorded on cards as shown in table 1. Information on numerous lines was recorded and used in the search for lines least enhanced or depressed by the different elements present. Selected lines are listed in table 2.

PROCEDURE

A synthetic sample of known composition was analyzed with the unknowns. The synthetic sample was prepared by adding standard solutions of the minor elements to the oxides of the major components (table 3). After drying on a hot plate, the material was ignited at 500° C for four hours. The synthetic sample was ground in a boron carbide mortar to pass a 100-mesh stainless-steel screen and thoroughly mixed by passing repeatedly through an 80-mesh stainless-steel screen.

A 10-mg sample of lignite ash obtained according to the method of Fieldner and Selvig (1951) was weighed, mixed thoroughly with two parts by weight of pure graphite in the weighing pan, and placed in the electrode cup through a polished stainless-steel funnel. The unknowns were arced (250 v, 12 amp, d-c) for either 60 or 120 seconds, depending on the behavior of the sample in the arc or on past experience with the type of material. Experience has shown that the error is not great if the sample is arced for 60 seconds instead of 120 seconds.

After the plates were processed, the spectrograms were scanned with a recording microphotometer. The proper lines were located on the scannings and the height and, if necessary, the width determined.

The concentrations of the elements were interpolated by direct proportion from the data on transmission versus percent concentration. Information on the previously prepared cards (table 1) obtained from the standard plates was used in the interpolations. The precision and type of data sought did not warrant the use of the more precise logarithmic function-emulsion calibration method, especially in view of the other sources of error.

As previously described (Waring and Annell, 1953), on each plate, along with the spectra of the unknowns, were recorded spectra of

iron and of aluminum alloy (Aluminum Company of America standard SA 874). These latter spectra furnish reference points for locating lines and a general index of exposure, of plate sensitivity, and of development.

The measured transmission of the chromium line 2780.7 Å in the spectrum of the aluminum alloy (0.15 percent chromium) is used as a rough check on the plate sensitivity and other variables. The normal percent-transmittance value of the chromium line is 65 percent. When the percent transmittance of this line is below 60 percent or above 70 percent, the known variables such as temperature of development tank, age of developer, voltage and current of the source, electrode tips, and wall thickness of the lower electrodes are investigated. If these variables are found to be in order, the amount of light entering the spectrograph is readjusted with the aid of neutral filters to correct for the intensity drift.

DISCUSSION

The semiquantitative method has been applied to numerous types of materials, and the results were reported in factor-of-10 brackets. Experience with the method showed that the standardization, sample handling, method of arcing, and development of the plates were satisfactory. The weakest link was the visual plate reading. Microphotometric scanning showed that in 93 percent of the experiments the agreement with the chemical analysis was within a factor-of-10 bracket, 85 percent were within a factor-of-5 bracket, and 79 percent were within a factor-of-2 bracket. The precision gained by the introduction of microphotometry, as indicated by the tests, warrants reporting the values in brackets of smaller concentration ranges than for the previously reported semiquantitative method, with only a slight increase in total analysis time.

A detailed discussion on the observations of individual lines is given in table 2. Table 4 lists the authors' opinion of the value of the selected lines. The results obtained with the lines marked "good" generally fall within a factor-of-2 bracket of the chemical analysis, and the lines marked "fair" fall within a factor-of-5 bracket. The lines marked "poor" are considered undesirable for accurate testing by this method unless the results are to be reported in factor-of-10 brackets. The line magnesium 2781.4 Å, sample F84, table 2, illustrates this point; the chemical value was 0.126 and the spectrographic value was 0.58 percent, both results falling within a factor-of-10 bracket.

The time required for an analysis is greatly influenced by the skill of the analyst and especially the physical nature of the sample to be

analyzed. An approximate breakdown of the analysis time is as follows:

| | |
|--|-----------------|
| Number of samples (952 elements)..... | 14. |
| Quarter, weigh samples and proper reference samples..... | 4 hours. |
| Exposure..... | 1.5 hours. |
| Development..... | 0.75 hour. |
| Plate scanning and estimates..... | 15 to 20 hours. |

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- Fieldner, A. C., and Selvig, W. A., 1951, Methods of analyzing coal and coke: U. S. Bur. Mines Bull. 492.
- Meggers, W. F., 1950, Emission spectroscopy: Anal. Chemistry, v. 22, p. 18-23.
- Waring, C. L., and Annell, C. S., 1953, Semiquantitative spectrographic method for analysis of minerals, rocks, and ores: Anal. Chemistry, v. 25, p. 1174-1179.

TABLE 1.—*Example of scanning information, for aluminum, recorded on card*

| Line (angstrom) | Percent transmission and width of line, at concentrations indicated in percent | | | | | | | | | | | |
|-----------------|--|------------------------------------|-------------------|-----------------------|-------------------|-----------------------|-------------------|-----------------------|-------------------|-----------------------|-------------------|-----------------------|
| | 10 | | 1.0 | | 0.1 | | 0.01 | | 0.001 | | 0.0001 | |
| | Trans- mission | Line width (mm) ¹ | Trans- mission | Line width (mm) | Trans- mission | Line width (mm) | Trans- mission | Line width (mm) | Trans- mission | Line width (mm) | Trans- mission | Line width (mm) |
| 2568.0 | 11.5 | 1 | 21 | N | V ² | N | ----- | ----- | ----- | ----- | ----- | ----- |
| 2575.1 | 8 | 2 | 12.5 | 1 | 79.5 | N | ----- | ----- | ----- | ----- | ----- | ----- |
| 2652.5 | 14.5 | 1 | 24 | N | ----- | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| 2660.4 | 10 | 1 | 16.5 | N | ----- | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| 3082.2 | 9.5 | 4 | 5.5 | 3 | 11.5 | 1 | 48.5 | N | 76 | N | 89 | N |
| 3092.7 | 10 | 5 | 6 | 3 | 4 | 1.5 | 26.5 | 1 | 55 | N | 74.5 | N |
| 3059.9 | 78 | N | 95 | ----- | ----- | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| 3064.3 | 47 | N | 87 | N | ----- | ----- | ----- | ----- | ----- | ----- | ----- | ----- |
| 3066.2 | 45.5 | N | 88.5 | N | ----- | ----- | ----- | ----- | ----- | ----- | ----- | ----- |

¹ Where the width of line was not normal (N), the width was measured at middle line (50) on chart.² Just visible.

TABLE 2.—*Spectrum lines used and comparison of spectrographic and chemical analyses of ashes*

| Element | Line (angstrom) | Sample | Spectrographic | | Chemical (percent) | True value (percent) | Remarks |
|---------|-----------------|--------------|---------------------------------------|------------------|--------------------|----------------------|--|
| | | | Micro-photo-metric scanning (percent) | Visual (percent) | | | |
| Ag... | 3280.7 | Synthetic... | 0.00068 | 0.0001-0.001 | ----- | 0.0005 | Line 3280 A satisfactory when background permits its use. |
| Al... | 2652.5 | Synthetic... | 10+ | 10+ | ----- | 13. | High iron content may interfere with 3059 A. |
| | 3059.9 | C18b..... | 7.1 | 1.0-10.0 | 6.75 | | |
| | 3059.9 | F84..... | 10+ | 1.0-10.0 | 10.1 | | |
| | 2575.1 | F95..... | 10+ | 1.0-10.0 | 11.6 | | |
| | 3059.9 | S29..... | 10+ | 1.0-10.0 | 9.3 | | |
| | 3059.9 | SC35..... | 10+ | 1.0-10.0 | 7.8 | | |
| As... | 2860.5 | Synthetic... | 0.94 | 0.1-1.0 | ----- | 0.5 | High result is probably due to interference by iron. |
| B.... | 2497.8 | Synthetic... | 0.4 | 0.1-1.0 | ----- | 0.5 | Line 2496.7 A may also be used when the boron is more than 0.1 percent. |
| | | C18b..... | 0.022 | 0.01-0.1 | ----- | | |
| | | F84..... | 0.071 | 0.01-0.1 | ----- | | |
| | | F95..... | 0.066 | 0.01-0.1 | ----- | | |
| | | S29..... | 0.08 | 0.01-0.1 | ----- | | |
| | | SC35..... | 0.07 | 0.01-0.1 | ----- | | |
| Ba... | 2335.3 | Synthetic... | 0.6 | ----- | ----- | 0.5 | Line 2335 A was satisfactory in this range. |
| | | C18b..... | 0.32 | ----- | 0.27 | | |
| | | F84..... | 0.69 | 0.01-0.1 | ----- | | |
| | | F95..... | 0.65 | 0.01-0.1 | ----- | | |
| | | S29..... | 0.26 | 0.01-0.1 | ----- | | |
| | | SC35..... | 0.57 | 0.01-0.1 | ----- | | |
| Be... | 2348.6 | Synthetic... | ----- | ----- | ----- | ----- | Be Line 2348.6 A satisfactory for low Be content when iron content is not too high. |
| | | C18b..... | 0.0013 | 0.0001-0.001 | ----- | | |
| | | F84..... | 0.0037 | 0.001-0.01 | ----- | | |
| | | F95..... | ----- | ----- | ----- | | |
| | | S29..... | 0.00013 | 0.0001-0.001 | ----- | | |
| | | SC35..... | 0.004 | 0.001-0.01 | ----- | | |
| Ca... | 3000.9 | Synthetic... | 9.2 | 1.0-10.0 | ----- | 8.08 | High iron content interferes with Ca 3000 and 3009 A lines. The better line seems to be 2997 A. |
| | 3009.2 | ----- | 9.3 | ----- | ----- | | |
| | 3000.9 | C18b..... | 10+ | 1.0-10.0 | 11.1 | | |
| | 3009.2 | ----- | 10+ | ----- | ----- | | |
| | 2997.3 | F84..... | 4.75 | 1.0-10.0 | 2.9 | | |
| | 3000.9 | ----- | 7.78 | ----- | ----- | | |
| | 3009.2 | ----- | 7.66 | ----- | ----- | | |
| | 2997.3 | F95..... | 6.00 | 1.0-10.0 | 7.8 | | |
| | 2997.3 | S29..... | 8.07 | 1.0-10.0 | 8.6 | | |
| | 2997.3 | SC35..... | 9.4 | ----- | 14.4 | | |
| Co... | 3000.9 | ----- | 10+ | 1.0-10.0 | ----- | | |
| | 3009.2 | ----- | 10+ | ----- | ----- | | |
| | 3453.5 | Synthetic... | 0.054 | 0.01-0.1 | ----- | 0.05 | |
| Cr... | | F95..... | 0.05 | 0.1-1.0 | 0.04 | | Background interference apparently is not too serious. |
| | 2835.6 | Synthetic... | 0.043 | 0.01-0.1 | ----- | 0.05 | |
| | | C18b..... | 0.07 | 0.001-0.01 | ----- | | |
| Cu... | | F84..... | 0.01 | 0.001-0.01 | ----- | | Line 2835 A is satisfactory. |
| | | F95..... | ----- | ----- | ----- | | |
| | | S29..... | 0.01 | 0.001-0.01 | ----- | | |
| | | SC35..... | <0.01 | 0.001-0.01 | ----- | | |
| | 3247.6 | Synthetic... | 0.0088 | 0.001-0.01 | ----- | 0.005 | |
| | 3274.0 | ----- | 0.0089 | ----- | ----- | | |
| | 3247.6 | C18b..... | 0.1 | 0.001-0.01 | ----- | | |
| | | F84..... | ----- | ----- | ----- | | |
| | 3274.0 | F95..... | 0.0074 | 0.001-0.01 | ----- | | Lines 3247 and 3274 A are satisfactory when iron content is not too high. The line width factor is difficult to apply when copper content is high. |
| | 3247.6 | S29..... | 0.008 | 0.001-0.01 | ----- | | |
| | 3274.0 | SC35..... | 0.0093 | 0.001-0.01 | ----- | | |
| | | ----- | ----- | ----- | ----- | | |

TABLE 2.—*Spectrum lines used and comparison of spectrographic and chemical analyses of ashes—Continued*

| Element | Line (angstrom) | Sample | Spectrographic | | Chemical (percent) | True value (percent) | Remarks |
|---------|-----------------|-----------|---------------------------------------|------------------|--------------------|----------------------|---|
| | | | Micro-photo-metric scanning (percent) | Visual (percent) | | | |
| Fe | 2936.9 | Synthetic | 6.5 | 1.0-10.0 | | 8.75 | Lines 2936 and 2953 A seem best in this range. |
| | 2953.9 | | 7.0 | | | | |
| | 2936.9 | C18b | 10+ | 1.0-10.0 | 8.0 | | |
| | 2953.9 | | | | | | |
| | 2599.4 | F84 | 10+ | 10+ | 24 | | |
| | 2599.6 | | 10+ | 10+ | | | |
| | 2936.9 | F95 | 10+ | 10+ | 21.9 | | |
| | 3008.1 | S29 | 10+ | 10+ | 24.0 | | |
| | 2599.4 | | 10+ | 10+ | 24.0 | | |
| | 2953.9 | SC35 | 10+ | 10+ | 15.8 | | |
| | 2936.9 | | 10+ | 10+ | | | |
| Ga | 2943.7 | Synthetic | 0.03 | 0.001-0.01 | | 0.005 | As a result of previous work the visual Ga estimates were downgraded one bracket. This work is in agreement. The reason for this enhancement is unknown. |
| | | C18b | 0.04 | 0.001-0.01 | | | |
| | | F84 | 0.07 | 0.001-0.01 | | | |
| | | F95 | 0.30 | 0.01-0.1 | | | |
| | | S29 | 0.35 | 0.01-0.1 | | | |
| | | SC35 | 0.35 | 0.01-0.1 | | | |
| Ge | 3039.1 | Synthetic | 0.0075 | 0.001-0.01 | | | Line 3039 A satisfactory at this range. Ge not detected in other samples. |
| K | 3446.4 | Synthetic | 2.35 | 1.0-10.0 | | 2.0 | Background corrections apparently are necessary for certain samples. |
| | | C18b | 1 | 0.1-1.0 | 0.780 | | |
| | | F84 | 2.2 | 1.0-10.0 | 0.68 | | |
| | | F95 | 0.48 | 0.1-1.0 | 0.68 | | |
| | | S29 | 3.2 | 1.0-10.0 | 1.28 | | |
| | | SC35 | 3.2 | 1.0-10.0 | 0.92 | | |
| Mg | 2778.3 | Synthetic | 1 | 1.0-10.0 | | 1.5 | More work necessary to select the better lines for magnesium determinations. Line 2779 A is best in 0.1-1.0 percent range. Lines 2781 and 2778 A are best for the 1.0-10.0 percent range. |
| | | C18b | | 1.0-10.0 | 4.4 | | |
| | 2779.9 | | 0.9 | | | | |
| | 2778.3 | F84 | 0.764 | 0.1-1.0 | 0.126 | | |
| | 2779.9 | | 0.37 | | | | |
| | 2781.4 | | 0.58 | | | | |
| | 2778.3 | F95 | 0.923 | 0.1-1.0 | 0.13 | | |
| | 2779.9 | | 1.0 | | | | |
| | 2781.4 | | 2.6 | | | | |
| | 2779.9 | S29 | 0.78 | 0.1-1.0 | 0.138 | | |
| | 2798.0 | | 0.155 | | | | |
| | 2779.9 | SC35 | 0.78 | 0.1-1.0 | 0.072 | | |
| | | | 0.935 | | | | |
| | | | 0.5 | | | | |
| Mn | 2593.7 | Synthetic | 0.062 | | | 0.05 | Line 2801 A satisfactory only when Al content is very low. When Al content is high 2576 A is suggested. Lines 2593 and 2605 A are reliable. |
| | 2605.7 | | 0.056 | 0.01-0.1 | | | |
| | 2605.7 | C18b | 0.01 | | 0.04 | | |
| | 2576.1 | | 0.05 | 0.01-0.1 | | | |
| | 2593.7 | F84 | 0.092 | | 0.2 | | |
| | 2605.7 | | 0.088 | 0.01-0.1 | | | |
| | 2593.7 | F95 | 0.68 | | 0.78 | | |
| | 2605.7 | | 0.7 | 0.1-1.0 | | | |
| | 2801.1 | | 0.1 | | | | |
| | 2593.7 | S29 | 0.066 | | 0.11 | | |
| | 2605.7 | | 0.062 | 0.01-0.1 | | | |
| | 2593.7 | SC35 | 0.18 | | 0.2 | | |
| | 2605.7 | | 0.089 | | | | |
| | 2801.1 | | 0.325 | | | | |

TABLE 2.—*Spectrum lines used and comparison of spectrographic and chemical analyses of ashes—Continued*

| Element | Line (angstrom) | Sample | Spectrographic | | Chemical (percent) | True value (percent) | Remarks |
|---------|-----------------|--------------|-------------------------------------|------------------|--------------------|----------------------|--|
| | | | Microphotometric scanning (percent) | Visual (percent) | | | |
| Mo... | 3170.4 | Synthetic... | 0.004 | 0.001-0.01 | ----- | 0.005 | Use width of 3170 A line for high Mo. Line 3170 A satisfactory for 0.01-0.1 range. Indications are that 3122 A should be used above 0.1 percent. |
| | 3132.6 | C18b..... | 0.046 | 0.01-0.1 | ----- | | |
| | 3170.4 | F84..... | ----- | 0.1-1.0 | ----- | | |
| | 3122.0 | ----- | 0.24 | 0.1-1.0 | ----- | | |
| | 3170.4 | F95..... | 0.041 | 0.01-0.1 | ----- | | |
| | 3122.0 | S29..... | 0.1 | 0.1-1.0 | 0.15 | | |
| | 3170.4 | ----- | 0.1 | 0.1-1.0 | ----- | | |
| | 3122.0 | SC35..... | 0.2 | 0.1-1.0 | ----- | | |
| Na... | 3302.3 | Synthetic... | 3.7 | 1.0-10.0 | ----- | 2.5 | Both lines in doublet are satisfactory. |
| | 3302.3 | C18b..... | 10. + | 10. + | 17. | | |
| | 3302.3 | F84..... | 4.15 | 1.0-10.0 | 2.6 | | |
| | 3302.9 | F95..... | 0.98 | 1.0-10.0 | 1.41 | | |
| | 3302.9 | S29..... | 2.85 | 1.0-10.0 | 3.26 | | |
| | 3302.9 | SC35..... | 3.7 | 1.0-10.0 | 2.33 | | |
| | 3303.0 | Synthetic... | 0.3 | ----- | ----- | | |
| Ni... | 3423.7 | ----- | 0.1 | 0.01-0.1 | ----- | 0.5 | Slightly high results are probably due to background. |
| | 3414.8 | C18b..... | 0.026 | 0.01-0.1 | ----- | | |
| | 2535.6 | Synthetic... | 0.25 | 0.01-0.1 | ----- | | |
| P.... | 2535.6 | Synthetic... | 0.25 | 0.01-0.1 | ----- | 0.5 | Beware of iron interference. |
| Pb... | 2833.1 | Synthetic... | 0.68 | 0.01-0.1 | ----- | 0.5 | Previous work indicated that lead in the low percentages was enhanced by one bracket. Visual results were downgraded one bracket. Confirmation is indicated by these tests. No explanation is available. |
| | ----- | C18b..... | 0.04 | <0.01-0.1 | ----- | | |
| | ----- | F84..... | 0.043 | <0.01-0.1 | ----- | | |
| | ----- | F95..... | 0.059 | <0.01-0.1 | ----- | | |
| | ----- | S29..... | 0.057 | <0.01-0.1 | ----- | | |
| | ----- | SC35..... | 0.0575 | <0.01-0.1 | ----- | | |
| Sc.... | 3273.6 | Synthetic... | 0.005 | ----- | ----- | 0.005 | |
| | 3353.7 | ----- | 0.001 | ----- | ----- | | |
| | 3359.7 | ----- | 0.007 | ----- | ----- | | |
| Si.... | 2506.9 | Synthetic... | 10. + | 10+.. | ----- | 11. | If Si line 2881 is 3 to 4mm at 50 and line 2506 A is normal in width but reads off the scale, use line 2435 A because Si is under 10 percent in these cases. |
| | 2435.2 | C18b..... | 7.9 | 1.0-10.0 | 5.35 | | |
| | 2506.9 | F84..... | 10. + | 1.0-10.0 | 13.1 | | |
| | 2506.9 | F95..... | 10. + | 1.0-10.0 | 15.0 | | |
| | 2435.2 | S29..... | 7.9 | 1.0-10.0 | 7.1 | | |
| | 2435.2 | SC35..... | 6.88 | 1.0-10.0 | 4.45 | | |
| Sn... | 3175.0 | Synthetic... | 0.1 | ----- | ----- | 0.005 | Sn line 3262 A satisfactory. |
| | 3262.3 | ----- | 0.0035 | ----- | ----- | | |
| | 3646.6 | Synthetic... | 0.008 | 0.01-0.1 | ----- | | |
| Sr.... | 3380.7 | C18b..... | 1. | 0.1-1.0 | 0.45 | 0.05 | A survey for more satisfactory strontium lines is in progress. |
| | 3464.5 | ----- | 1. | ----- | ----- | | |
| | 3464.5 | F84..... | 0.05 | 0.01-0.1 | ----- | | |
| | 3464.5 | F95..... | 0.26 | 0.1-1.0 | ----- | | |
| | 3464.5 | S29..... | 0.07 | 0.1-1.0 | ----- | | |
| | 3464.5 | SC35..... | 0.67 | 0.1-1.0 | ----- | | |
| | 3236.6 | Synthetic... | 0.085 | 0.1-1.0 | ----- | | |
| | 3242.0 | ----- | 0.05 | ----- | ----- | | |
| Ti.... | 3242.0 | C18b..... | ----- | 0.01-0.1 | 0.06 | 0.5 | A survey for more satisfactory titanium lines is in progress. 3242 A is satisfactory in 0.01-1.0 percent range. |
| | 3242.0 | F84..... | ----- | 0.1-1.0 | 0.36 | | |
| | 3242.0 | F95..... | ----- | 0.1-1.0 | 0.36 | | |
| | 3242.0 | S29..... | 0.08 | 0.01-0.1 | 0.06 | | |
| | 3242.0 | SC35..... | 0.071 | 0.01-0.1 | 0.06 | | |
| | ----- | ----- | ----- | ----- | ----- | | |

TABLE 2.—*Spectrum lines used and comparison of spectrophotographic and chemical analyses of ashes—Continued*

| Element | Line (angstrom) | Sample | Spectrographic | | Chemical (percent) | True value (percent) | Remarks |
|---------|-----------------|--------------|---------------------------------------|------------------|--------------------|----------------------|--|
| | | | Micro-photo-metric scanning (percent) | Visual (percent) | | | |
| Th... | 2837.3 | Synthetic... | 0.7 | 0.1-1.0 | ----- | 0.5 | These lines are satisfactory when uranium is less than 1 percent. 3267 and 3276 A are satisfactory for low vanadium. |
| | 2870.4 | ----- | 0.4 | 0.1-1.0 | ----- | | |
| V... | 3267.7 | Synthetic... | 0.009 | 0.001-0.01 | ----- | 0.005 | |
| | 3276.1 | C18b..... | 0.0036 | 0.01-0.1 | ----- | | |
| | 3276.1 | F84..... | 0.009 | 0.01-0.1 | ----- | | |
| | 3276.1 | F95..... | 0.0087 | 0.01-0.1 | ----- | | |
| | 3276.1 | S29..... | 0.044 | 0.001-0.01 | ----- | | |
| | 3276.1 | SC35..... | 0.03 | 0.01-0.1 | ----- | | |
| Y.... | 3327.9 | Synthetic... | 0.0062 | 0.001-0.01 | ----- | 0.005 | 3327 and 3242 A are satisfactory. |
| | 3242.3 | ----- | 0.0075 | 0.001-0.01 | ----- | | |
| | 3216.7 | ----- | 0.019 | ----- | ----- | | |
| | 3327.9 | C18b..... | 0.017 | 0.001-0.01 | ----- | | |
| | 3327.9 | F84..... | 0.01 | 0.01-0.1 | ----- | | |
| | 3327.9 | S29..... | ----- | 0.001-0.01 | ----- | | |
| | 3327.9 | SC35..... | ----- | 0.001-0.01 | ----- | | |
| Yb... | 3289.4 | Synthetic... | <0.001 | 0.001-0.01 | ----- | 0.005 | Search for better lines in progress. |
| | | C18b..... | ----- | 0.001-0.01 | ----- | | |
| | | F84..... | 0.002 | 0.001-0.01 | ----- | | |
| | | S29..... | ----- | ----- | ----- | | |
| | | SC35..... | ----- | ----- | ----- | | |
| Zn... | 3345.0 | Synthetic... | 0.006 | 0.001-0.01 | ----- | 0.05 | Search for better lines indicated. |
| | 3345.0 | ----- | 0.008 | 0.001-0.01 | ----- | | |
| Zr.... | 3391.9 | Synthetic... | 0.03 | 0.01-0.1 | ----- | 0.05 | Line 3392 A satisfactory when background is low. Line 3273 A satisfactory when copper is low. |
| | 3273.0 | F84..... | 0.008 | 0.1-1.0 | ----- | | |
| | 3273.0 | SC35..... | 0.036 | 0.1-1.0 | ----- | | |
| | 3273.0 | C18b..... | 0.17 | 0.01-0.1 | ----- | | |
| | 3273.0 | S29..... | 0.004 | 0.001-0.01 | ----- | | |

Elements looked for but not found: Au, Bi, Cd, Ce, Cs, Dy, Er, Eu, F, Gd, Hf, Hg, Ho, In, Ir, La, Li, Lu, Nb, Nd, Os, Pd, Pr, Pt, Rb, Re, Rh, Ru, Sb, Sm, Ta, Tb, Te, Tl, U, and W.

TABLE 3.—Standard sensitivities for the elements determined by the microphotometric scanning method

| Percent | | Percent | | Percent | |
|---------|-----------|---------|---------------|---------|-------|
| Ag | 0.00001 | Hf | 0.03 | Re | 0.04 |
| Al | .0001 | Hg | .08 | Rh | .004 |
| As | .01 | Ho | .001 | Ru | .008 |
| Au | .001 | In | .0004 | Sb | .01 |
| B | .005 | Ir | .03 | Se | .001 |
| Ba | .001 | *K | .005 (0.3) | Si | .005 |
| Be | .00005 | La | .003 | Sm | .008 |
| Bi | .005 | *Li | .00003 (0.04) | Sn | .004 |
| Ca | .01 | Lu | .005 | Sr | .001 |
| Cd | .005 | Mg | .00003 | Ta | .1 |
| Ce | .03 | Mo | .0005 | Tb | .01 |
| Co | .008 | Mn | .0007 | Te | .08 |
| Cr | .0006 | Nb | .001 | Th | .08 |
| *Cs | .01 (0.8) | *Na | .0003 (0.01) | Ti | .0005 |
| Cu | .00005 | Nd | .006 | Tl | .04 |
| Dy | .006 | Ni | .005 | Tm | .001 |
| Eu | .003 | Os | .1 | U | .08 |
| Er | .003 | P | .07 | V | .001 |
| **F | .08 | Pb | .001 | W | .07 |
| Fe | .0008 | Pd | .003 | Y | .003 |
| Ga | .004 | Pr | .01 | Yb | .0003 |
| Gd | .006 | Pt | .003 | Zn | .008 |
| Ge | .001 | *Rb | .007 (7) | Zr | .0008 |

*A second exposure is required for the high sensitivity listed.
**A third exposure is required for fluorine estimation.

TABLE 4.—Summary of lines used, percentage range, and rating of line in spectrographic analysis of ashes.

| Element | Line (Å) | Range (percent) | Rating |
|---------|----------|-----------------|--------|
| Ag | 3280. 7 | 0. 0001–0. 001 | Good. |
| Al | 2575. 1 | 10. + | Good. |
| | 2652. 5 | 10. + | Good. |
| | 3059. 9 | 1. 0–10. + | Fair. |
| | 2680. 5 | 0. 1–1. 0 | Fair. |
| B | 2497. 8 | 0. 01–1. 0 | Good. |
| Ba | 2335. 3 | 0. 1–1. 0 | Good. |
| Be | 2348. 6 | 0. 0001–0. 001 | Fair. |
| Ca | 2997. 3 | 1. 0–10. | Good. |
| | 3000. 9 | 1. 0–10. | Good. |
| | 3009. 2 | 1. 0–10. | Fair. |
| | 3453. 5 | 0. 01–0. 1 | Good. |
| Co | 2835. 6 | 0. 01–0. 1 | Good. |
| Cr | 3247. 6 | 0. 001–0. 1 | Fair. |
| | 3274. 0 | 0. 001–0. 01 | Fair. |
| | 2936. 9 | 1. 0–10. | Fair. |
| | 2953. 9 | 1. 0–10. | Fair. |
| Fe | 2599. 4 | 10. + | Fair. |
| | 3008. 1 | 10. + | Fair. |

TABLE 4.—*Summary of lines used, percentage range, and rating of line in spectrographic analysis of ashes—Continued*

| Element | Line (A) | Range (percent) | Rating |
|---------|----------|-----------------|--------------------|
| Ga..... | 2943. 7 | 0. 001-0. 01 | Poor. ¹ |
| Ge..... | 3039. 1 | 0. 001-0. 01 | Fair. |
| K..... | 3446. 6 | 0. 1-10. | Fair. |
| Mg..... | 2778. 3 | 1. 0-10. | Fair. |
| | 2779. 9 | 0. 1-1. 0 | Fair. |
| | 2781. 4 | 0. 1-1. 0 | Poor. |
| | 2798. 0 | 0. 1-1. 0 | Fair. |
| Mn..... | 2593. 7 | 0. 01-1. | Good. |
| | 2576. 1 | 0. 01-0. 1 | Good. |
| | 2605. 7 | 0. 01-0. 1 | Fair. |
| | 2801. 1 | 0. 1-1. 0 | Fair. |
| Mo..... | 3170. 4 | 0. 001-0. 01 | Good. |
| | 3132. 6 | 0. 001-0. 01 | Good. |
| | 3122. 0 | 0. 01-0. 1 | Good. |
| | 3122. 0 | 0. 1-1. 0 | Good. |
| Na..... | 3302. 3 | 1. 0-10. + | Fair. |
| | 3302. 9 | 1. 0-10. | Fair. |
| Ni..... | 3393. 0 | 0. 01-0. 1 | Poor. |
| | 3423. 7 | 0. 01-0. 1 | Fair. |
| | 3414. 8 | 0. 01-0. 1 | Fair. |
| P..... | 2535. 6 | 0. 1-1. 0 | Fair. |
| Pb..... | 2833. 1 | 0. 01-1. 0 | Poor. ¹ |
| Sc..... | 3273. 6 | 0. 001-0. 01 | Good. |
| | 3353. 7 | 0. 001-0. 01 | Poor. |
| | 3359. 7 | 0. 001-0. 01 | Good. |
| Si..... | 2506. 9 | 10. + | Good. |
| | 2435. 2 | 1. 0-10. | Good. |
| Sn..... | 3175. 0 | 0. 001-0. 01 | Poor. |
| | 3262. 3 | 0. 001-0. 01 | Fair. |
| Sr..... | 3464. 5 | 0. 001-0. 01 | Poor. |
| | 3380. 7 | 0. 01-0. 1 | Fair. |
| Ti..... | 3236. 6 | 0. 01-1. | Poor. |
| | 3242. 0 | 0. 01-1. | Good. |
| Th..... | 2837. 3 | 0. 1-1. | Poor. |
| | 2870. 4 | 0. 1-1. | Poor. |
| V..... | 3267. 7 | 0. 001-0. 01 | Fair. |
| | 3276. 1 | 0. 001-0. 01 | Good. |
| Y..... | 3327. 9 | 0. 001-0. 01 | Good. |
| | 3242. 3 | 0. 001-0. 01 | Good. |
| | 3216. 7 | 0. 001-0. 01 | Fair. |
| Yb..... | 3289. 4 | 0. 001-0. 01 | Fair. |
| Zn..... | 3345. 0 | 0. 001-0. 01 | Poor. |
| Zr..... | 3391. 9 | 0. 01-0. 1 | Good. |
| | 3273. 0 | 0. 01-0. 1 | Good. |

¹ Downgrading the spectrographic results by a factor of 10 will bring chemical and spectrographic analyses in agreement. No explanation is available at present.