Analytical Methods in Geochemical Investigations of the Pierre Shale

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By L. F. RADER *and* F. S. GRIMALDI

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ABSTRACT

A study of the analytical precision of chemical methods for determination of selected minor elements in the Pierre shale is reported. The detailed procedures for the determination of titanium, vanadium, chromium, manganese, cobalt, nickel, copper, zinc, lead, arsenic, selenium, molybdenum, tungsten, uranium, carbonate carbon, total carbon, and organic matter are described. Alternative methods are also given for the determination of titanium, vanadium, nickel, copper, arsenic, molybdenum, and tungsten.

The precision of the analytical methods is established from replicate determinations made on different days by one chemist, replicate determinations by one chemist on paired hidden splits, and cross-check determinations on 10 selected samples by different chemists, laboratories, and methods. Graphic comparisons are made of determinations by different chemists to indicate either the agreement or the bias of results.

INTRODUCTION

GENERAL REMARKS

Geochemical investigations of the Pierre shale of Late Cretaceous age in the western interior part of the United States were begun in 1956. The purpose of the investigations was to correlate chemical data from a large body of typical marine shale and associated sedimentary rocks with their mineralogical compositions, physical characteristics, and geographic and stratigraphic variations. These data are important to the understanding of the composition of shale, the most abundant sedimentary rock, and to the interpretation of the geochemical and physical processes by which shale is formed. The data will also provide a basis for answers to such questions as the possibility that ore deposits are formed during the metamorphism of such rocks.

Utilization of laboratories of the U.S. Geological Survey was desirable because of the specialized services that they offer. The large volume and wide range of analytical work anticipated for the study of the Pierre shale, however, dictated distribution of analytical work to all the laboratories according to their specialties as well as to their limitations with regard to prior requests for analyses from other projects. As the shale study was planned to continue for several years, it was imperative that the analytical work be uniform and comparable in reliability and precision over the full period of the study not only with reference to the analyses made by each laboratory but also with reference to the analyses made by different laboratories. Because data on the performance of specific analytical methods were not available, particularly with regard to interlaboratory determinations, the analytical work was planned to obtain the required information on the precision of the methods under actual operating conditions in the laboratories. This plan included selection of methods mutually satisfactory to all participating laboratories. Accordingly the analytical methods agreed upon were prepared in mimeographed form, distributed to the analysts, and tested before the shale study started.

A total of 70 field samples of Pierre shale and related sedimentary rocks used in this study were collected by Harry A. Tourtelot, J. R. Gill, and L. G. Schultz. After these samples were partially dried and crushed, seven of the field samples were each divided into two portions and one sample was divided into four separate portions by Tourtelot and Gill without the chemists being informed of the operation. Each of the 10 new samples thus obtained were assigned new and different field numbers, ficticious field locations, and different serial numbers. This addition to the original 70 samples made a total of 80 samples. The disguised samples are referred to hereafter as the hidden splits.

The objectives of the analytical studies were to obtain information on the precision of the determinations for each element in three ways: (a) analysis of the 80 samples by the chemist for each specified element, with replicate determinations on eight or more samples to be made on each sample separately and at a different time; (b) the same determinations made by the same chemist on the disguised hidden splits included in the set of 80 samples; (c) the analyses made by the first laboratory checked by a different chemist in a different laboratory by analyzing 10 of the 80 samples selected by Tourtelot as representative of the shale with regard to metal concentration and type of material. The same 10 samples were used throughout the study as check samples for each of 15 different elements namely, carbon, titanium, vanadium, chromium, manganese, cobalt, nickel, copper, zinc, lead, arsenic, selenium, molybdenum, tungsten, and uranium, and are hereafter referred to as the check samples.

In addition, information also was sought on the reliability of the determinations in three ways: (a) analysis of the 10 check samples by another laboratory using a different method where feasible; (b) inclusion of quantitative spectrographic analyses for titanium, manganese, cobalt, and nickel on the 10 check samples; (c) analysis of standard analyzed samples or "certified" standard samples.

However, it was impossible and impractical to do all that had been planned in conference. Alternative methods were supplied for the determination of titanium, vanadium, nickel, copper, arsenic, molybdenum, and tungsten but not for the other elements. Thus the same methods for some elements were used both for the original and check analyses. Regardless of how the analyses were made each analyst always included reagent blanks and standard solutions with each set of determinations. Suitable standard analyzed samples were largely unavailable, except for determinations of titanium, chromium, tungsten, and uranium.

Detailed descriptions of all analytical methods prepared not only for this study but also for future analyses planned for the shale program over the next 5 years are included in this report. The data on the precision and reliability of the methods based on the analyses reported in this study are believed to be of general interest not only to the chemists involved directly, but also to many geologists and others engaged in similar work.

LABORATORIES

The laboratories of the U.S. Geological Survey that participated in this study are identified for convenience in the tables and discussions by the letters A to G, as shown below. Corresponding analyses of the laboratories are also identified by the letters A to G; additional analyses by a given laboratory are designated by inferior numbers after the appropriate letter, such as A_1, A_2, B_1, and B_2.

Laboratory A, Analytical services and research, Denver, Colo.
B, Analytical services and research, Washington, D.C.
C, General rock analysis, Denver, Colo.
D, Rapid rock analysis, Washington, D.C.
Laboratory E, Rock and mineral analysis, Washington, D.C.
F, Spectrographic services and research, Denver, Colo.
G, Spectrographic services and research, Washington, D.C.

ACKNOWLEDGMENTS

The authors gratefully acknowledge the aid of many coworkers. The study was arranged by Harry A. Tourtelot and J. J. Tregoning. The collection of samples, selection of the hidden splits, and selection of the cross-check samples were made by Tourtelot, James R. Gill, and Leonard G. Schultz. Earl Dingle, Algot Erickson, and William Weston aided in the preparation and distribution of the samples.

DIVISION OF WORK

The minor elements in the 80 shale samples were determined in laboratories A and B. The distribution of the analytical work, by mutual agreement, was for A to determine mineral, total, and organic carbon, vanadium, manganese, nickel, arsenic, selenium, molybdenum, and tungsten. Laboratory B determined titanium, chromium, cobalt, copper, zinc, lead, and uranium. The 10 check samples were analyzed in laboratory A for those elements originally determined in laboratory B and vice versa, except that total and organic carbon were determined only in laboratory A and tungsten finally was not determined on all the shale because analysis of the first 48 samples by laboratory A showed the concentration to be less than 2 ppm (parts per million).

A standard rock analysis was made in laboratory C on only 25 of the 80 samples of shale, with the additional 55 samples being anaylzed in laboratory D by rapid methods of analysis (Shapiro and Brannock, 1956). The work of laboratories C and D made possible the cross checking of all 80 determinations made in laboratory A for mineral carbon and manganese and the determinations made in laboratory B for titanium, because these three elements are included in both a standard and rapid analysis of rocks.

Quantitative spectrographic analyses of the 80 samples, chiefly for elements not determined by chemical methods, were made in laboratory F. Only the spectrographic data obtained for titanium, cobalt, and manganese on the 10 check samples analyzed by laboratory F and for titanium and cobalt determined by laboratory G are given in this report as the full data are reported elsewhere.

Organic matter was determined in laboratory E and the check work was done in laboratory A.

METHODS SELECTED AND TREATMENT OF DATA

The analytical methods described in this report and used for determination of selected minor elements in the shale are, to a large extent, adaptations of well-known procedures taken from the literature, with acknowledgment of the source in the literature citations. In general, specific instructions for applying a method to the determination of an element, if different from those reported in the literature, are the result of critical study and testing by either laboratory A or B while adapting the method to routine use. The methods described are suitable for the analysis of shale or silicate rock but are not intended for general application to other types of material without further investigation. The lower threshold limit of the methods was arbitrarily set at 1 ppm. In general, this limit meets the needs of most geologic or geochemical studies.

Methods are described for the determinations of titanium, vanadium, chromium, manganese, cobalt, nickel, copper, zinc, lead, arsenic, selenium, molybdenum, tungsten, uranium, carbonate carbon, total carbon, and organic matter. Alternative methods are given also for the determinations of titanium, vanadium, copper, nickel, arsenic, molybdenum, and tungsten. The arrangement of the methods is generally based on the atomic number of the element. Methods for copper, zinc, and lead are grouped together because of the common separation and determination with dithizone. Methods for carbon and organic matter are placed last.

Analytical data obtained in this study and upon which the precision and reliability of the methods are estimated are tabulated with the individual methods for each element. In general, the complete data for each element on all 80 of the samples are not included in this report, because they will be reported and discussed in another part of the study of the Pierre shale by H. A. Tourtelot and others. However, complete data are presented for mineral carbon, titanium, manganese, and uranium, because these four elements were determined on all 80 samples by two or more analysts or laboratories. The data for the other elements on only part of the samples are arranged to compare the replicate determinations by one analyst, the results of one analyst on the paired hidden splits, and the results of all analysts and laboratories on the check samples. Replicate determinations by one chemist are ranked according to concentration of the element in the samples, without regard to serial number, in order to facilitate study of the data. This arrangement was not used, however, for either the hidden splits or check samples because identification by sample number, in a systematic arrangement, is advantageous for cross comparisons between tables and elements on these selected special samples.

The data on the 10 cross-check samples are plotted to show the bias or the agreement between analysts and (or) methods. The data on the check samples obtained by the chemist in laboratory A or B when the analyses of the 80 samples were made are arbitrarily plotted as the ordinate. Data from other chemists or methods are plotted as the abscissa. The points representing each determination on the graph show the deviation of the results from the theoretical line connoting perfect agreement. It is neither assumed nor implied that the results of the chemist analyzing the 80 samples for a particular element are either more precise or more accurate than those of another analyst. Also, the consistent use of such data as the ordinate makes possible a systematic plot of original data to cross-check data.

Many of the analytical results reported in the tables are in good agreement and require but little study to determine the deviations between methods and analysts. Nevertheless the standard deviations of the determinations have been calculated in order to obtain a comparative evaluation for the work by different chemists, methods, and laboratories. The data for some elements are insufficient to give good estimates of the standard deviations and, therefore, such values must be used with caution. The calculation of the standard deviation for several definite concentration ranges was attempted but was only partly successful because of too few samples in each range for certain elements. The ranges of concentration arbitrarily selected are from 0.00005 to 0.0005 percent, 0.0005 to 0.005 percent, 0.005 to 0.05 percent, 0.05 to 0.5 percent, 0.5 to 5 percent, and 5 to 50 percent. The selection of 5, or the midpoint of a decimal unit, as the range limits, enables one to compare chemical with semiquantitative spectrographic data that are reported in a similar manner.

The calculation of the standard deviation was made using pairs of analytical determinations as described by Youden (1951, p. 16). The data for the 10 check samples are arranged to show the mean value for determinations on each sample as well as the maximum difference between determinations. These differences make possible the rapid calculation of an approximate standard deviation from limited data ranging from 2 to 10 determinations, as described by Dixon and Massey (1951, p. 239). Other statistical treatment of the data was not undertaken.

SAMPLE PREPARATION

The field samples, collected in 1957 by Harry A. Tourtelot, James R. Gill, and Leonard G. Schultz, were prepared for analysis by laboratory A, because control of the variables of grinding, mixing, and splitting to one controlled operation was desirable. The preliminary work of preparing the analytical splits, however, was done by Tourtelot and Gill. They removed the fine extraneous material from each field sample by emptying the sample sacks, one at a time, on a plastic-coated grating (about two holes per inch) and lifting the larger discrete pieces of shale away from the fine material by raising the grating. The large chunks of shale from the grating were resacked, assigned a serial number, and the sacks of shale placed in an electrically heated drying oven maintained at 93°C. The samples were dried under these conditions for about 48 hours to a moisture level ranging from about 2 to 10 percent in order to enable use of motor-driven crushing and grinding equipment. The partially dried samples were crushed to about 8-mesh size or finer by passing them, one at a time, through a motor-driven jaw crusher, and each crushed sample was resacked. The hidden splits were then prepared by Tourtelot and Gill as previously mentioned, and the 80 samples, including 65 samples of shale, 10 of bentonite, and 5 of marl were then ground to a finer size as described below.

The standard procedure and equipment used for sample preparation are those described by Huleatt (1950), except that the samples of shale were ground with alumina-ceramic plates mounted on a motor-driven sample pulverizer in order to avoid contamination from the alloying elements of steel plates (Barnett and others, 1955). As other details of sample preparation also differ somewhat from normal practice because of sample size (2 to 100 lb) and number of splits required, the procedure used is described briefly.

The crushed partially dried material was mixed for 4 hours, one sample at a time, in a power-driven rotating drum containing mixing baffles. Each sample was then split into four equal portions by use of a Jones splitter. One of these portions was further split until 1 pound of each sample was isolated as the portion for analytical work. These 1-pound samples were ground to approximately 80- to 100-mesh size, usually by one pass through the motor driven alumina-ceramic plates, except for nine samples that were ground on a special hammer mill (Ross and Hardesty, 1942). These nine samples could not be ground to the desired fineness on the alumina-ceramic plates, mostly because of differences in moisture content or in physical characteristics. Each sample was remixed for about 4 hours and split once more into four portions of about 4 ounces each, which were then bottled, labeled, and distributed to laboratories A, B, and C.

Laboratory C further processed its splits for use in standard and rapid rock analysis. The samples were spread out on clean paper for about 20 hours to reach equilibrium under moisture conditions existing in the laboratory. Each sample was then screened through 80-mesh bolting cloth. The part, if any, not passing through the 80-mesh cloth was reground in an agate mortar and mixed back into the sample by rolling it on a mixing cloth. Only about six samples failed to pass through the 80-mesh cloth completely when sieved and the part of these coarser than 80 mesh amounted to not more than 2 grams. One 35-gram portion of each sieved sample was split for distribution either to laboratory C or D. Of the 80 samples, 25 were for standard analysis and the remaining 55 for rapid analysis for the major oxides. In addition one 7-gram portion of each sieved sample was reserved for spectrographic analysis by laboratory F These small splits were further ground by an additional pass through the alumina-ceramic plates at the request of the spectrographers who desired a more finely ground material. Laboratory G was not supplied with sample splits at this time but later analyzed the 10 check samples, by obtaining 4 of them from laboratory F and the other 6 samples from laboratory D.

METHODS FOR THE DETERMINATION OF INDIVIDUAL CONSTITUENTS

TITANIUM

PEROXIDE METHOD

[Range in shale: 0.05 to 0.5 percent titanium]

PRINCIPLES

Titanium in acid solution reacts with hydrogen peroxide to give a yellow color whose intensity is proportional to the amount of titanium present (Weller, 1882). Several other elements, particularly vanadium, react in the same manner. The ratio of titanium to vanadium in shale is sufficiently high so that no provision is made to separate titanium from vanadium. The error introduced is small because the absorbance of the vanadium peroxide complex for a given weight of vanadium is only about one-third that given by an equal weight of titanium when measurements are made at 400 mμ (millimicron).

Titanium can be separated from vanadium, when desirable, by precipitation of the titanium from the solution of the sample with sodium hydroxide. A small amount of ferric iron is added as a carrier when the sample contains negligible amounts of iron.

In the spectrophotometric determination, phosphoric acid is added to bleach the color of ferric iron. It is important that the same amount of phosphoric acid and alkali sulfate be added to both samples and standards, as these reagents tend to bleach the peroxytitanium slightly. Fluoride must be completely absent.

The results obtained are corrected for the absorbance of a small amount of platinum dissolved during the pyrosulfate fusion. Ordinarily the correction corresponds to no more than 0.02 percent titanium for the size of sample recommended.

APPARATUS AND REAGENTS

Beckman DU spectrophotometer.

Hydrogen peroxide, 3 percent: Dilute 10 ml of 30 percent hydrogen peroxide to 100 ml with pure water. This solution tends to deteriorate on standing and should be made fresh when needed.

Standard titanium solution, 1 ml=0.4 mg Ti: Dry a portion of National Bureau of Standards standard sample 154 (98.7 percent TiO_2) at 105°C. Transfer 0.1690 g to a Vicor or silica crucible, blend thoroughly with 3 g potassium pyrosulfate, cover the crucible, and heat until the sample is completely fused. Cool the crucible, place crucible and contents in a beaker containing 50 ml 1+1 sulfuric acid, and digest the solution on a steam bath until the melt is completely dissolved. Cool the solution and dilute to 250 ml in a volumetric flask. An alternative procedure recommended on the certificate of standard sample 154 is given under the reagent section of the alternative tiron method for determination of titanium.

Standard titanium, dilute solution, 1 ml=20 micrograms Ti: Dilute 10 ml of the standard stock solution, prepared as directed, to 200 ml with water. Prepare this diluted solution fresh as needed.

Potassium pyrosulfate: Dissolve 28 g in 10 percent v/v sulfuric acid and dilute to 200 ml with 10 percent v/v sulfuric acid.

PROCEDURE

1. Weigh a 0.5-g sample into a 50–75-ml platinum dish. Remove organic matter by igniting gently at first and raising the temperature finally to about 700°C. Cool.
2. Moisten the sample with water. Add to the dish 10 ml hydrofluoric acid, 5 ml nitric acid, 2 ml 1+1 sulfuric acid. Cover the dish with a platinum cover and digest on the steam bath for 30 minutes. Remove the cover and evaporate the solution on the steam bath to remove water. Heat the solution to fumes of sulfuric acid. Cool. Carefully add 15 ml water to the dish and again evaporate to fumes of sulfuric acid. Cool.
3. Add 2.25 g of potassium sulfate to the dish and let stand a few minutes to allow the sulfate to be converted to potassium acid sulfate (the amount of K_2SO_4 specified will react with about 1.35 ml of 1+1 H_2SO_4). Heat the solution very gently on a hot plate at 200°C. to remove water and any free sulfuric acid not fixed as potassium pyrosulfate. Continue heating until a clear pyrosulfate melt is obtained and then for a few minutes longer to ensure that all fluoride is removed (fluoride seriously interferes by bleaching the peroxytitanium). Cool the melt. Add 20 ml of 10 percent v/v sulfuric acid to the dish and warm the solution to dissolve the salts.
4. Transfer the solution to a 25-ml volumetric flask using 10 percent sulfuric acid for the transfer and to adjust the volume to 25 ml.
5. Transfer 10 ml to a 50-ml volumetric flask. Add 2 ml 1+1 phosphoric acid, 3 ml of 3 percent hydrogen peroxide, and dilute to mark with 10 percent v/v sulfuric acid. Determine the absorbance of the solution against water at 400 mμ. A reagent-blank correction must be determined. This is conveniently done by analyzing several weighed portions of Portland cement, National Bureau of Standards standard sample 177. The difference between the certificate value for titanium and the average of the results obtained is taken as the blank correction for the unknown samples.
6. Calculate the percentage of titanium in the sample.

STANDARD CURVE

Transfer aliquots of standard titanium solution containing 0, 0.5, 1, and 2 mg of titanium to 50-ml volumetric flasks. Add 10 ml of potassium pyrosulfate solution to each flask. Although 10 ml of potassium pyrosulfate is specified, the amount required depends on the size of aliquot taken at step 5 for the sample. For every 1 ml of sample, 1 ml of pyrosulfate solution is used for the standards. Dilute the solution with 10 percent v/v sulfuric acid to 25-ml volume. Add 2 ml of 1+1 phosphoric acid and 3 ml of 3 percent hydrogen peroxide. Dilute to volume with 10 percent v/v sulfuric acid. Determine absorbance at 400 mμ against water as a reference.

ALTERNATIVE TIRON METHOD

[Range in shale: 0.05 to 0.5 percent titanium]

PRINCIPLES

Tiron (disodium-1,2-dihydroxybenzene-3, 5-disulfonate) forms yellow complexes with titanium, molybdenum, uranium, and osmium and purple complexes with vanadium and iron over the pH range 4.3 to 9.6. Yoe and Armstrong (1947) used tiron for the determination of titanium in siliceous materials. This method is an extension of the procedures of Yoe and Armstrong and of Shapiro and Brannock (1956, p. 36–37) to the determination of titanium in shale and related rocks. Iron interference is overcome by reducing iron to the ferrous state with sodium dithionite in a buffered solution at pH 4.7. The concentrations of vanadium, molybdenum, osmium, and uranium in the shale are too small to interfere significantly when the absorbance of the titanium complex is determined at 430 mμ. The titanium-tiron color complex follows Beer's law to as much as 150 micrograms titanium in a 50-ml volume when the absorbance of the solution is determined immediately after the iron is reduced.

REAGENTS

Tiron solution: 1.0 g tiron dissolved in 50 ml of water. This solution should be made up immediately before use.

Buffer solution: 40 g of ammonium acetate and 15 ml glacial acetic acid diluted to 1 liter with distilled water.

Sodium dithionite (sodium hydrosulphite): Dry powder.

Titanium standard solution, 1 ml=0.5 mg Ti. Method of Plechner and Jarmus (1934) is given on the certificate received with National Bureau of Standards standard sample 154: Weigh and transfer to a 250-ml beaker 0.4225 g standard sample 154 (98.7 percent titanium dioxide) that has been dried at 105°C. Add 10 g of ammonium sulfate and 25 ml of sulfuric acid to the beaker and heat the solution cautiously over flame to incipient boiling. Continue to heat the solution until all the titanium is dissolved. Cool the solution and rapidly pour it into 450 ml of cool water while stirring the water. Rinse the beaker with 5 percent v/v sulfuric acid, mix, and set aside overnight. Filter the solution through a glass-fritted crucible and dilute to 500 ml in a volumetric flask. Standard sample 154 contains 0.7 percent SiO_2 and 0.6 percent of other metals that are largely filtered from the solution of titanium by following this method of solution. Other samples of reagent grade TiO_2 probably are contaminated with certain impurities also, and if used for preparing a standard may require standardization of the solution as described, for example, by Hillebrand and others (1953, p. 582-583).

PROCEDURE

1. Weigh and transfer 0.5 g of sample to a 75-ml platinum crucible.
2. Remove organic matter by igniting gently at first and gradually raising the temperature to 700°C in a muffle furnace. Cool.
3. Moisten the sample with water. Add 3 ml of nitric acid, 5 ml sulfuric acid, and 10 ml of hydrofluoric acid.
4. Cover the crucible and digest the solution overnight on a steam bath.
5. Remove the cover. Evaporate the water and heat the solution on a hot plate until copious fumes of sulfuric acid form. Stop fuming the solution when about 4 ml of sulfuric acid remains.
6. Add 50 ml distilled water to the crucible, cover, and digest on steam bath to dissolve the salts.
7. Transfer the solution to a 250-ml volumetric flask, cool, and dilute to volume.
8. Transfer a 5-ml aliquot to a 100-ml beaker. A blank and standard also are started in two additional beakers. Add 5 ml of water to the first beaker for the blank and 5 ml of standard dilute titanium solution to the second beaker for the standard.
9. Add 10 ml of tiron solution to each beaker and adjust the pH to about 4.7 with dilute ammonium hydroxide. Then buffer the solutions by adding 50 ml buffer solution to each beaker and mix.
10. Add 10 to 20 mg sodium dithionite powder to the blank. Mix gently by rotating the beaker two or three times. After 1 minute, pour the blank solution into a 2-cm absorption cell and adjust the spectrophotometer to read zero absorbance at 430 mμ.
11. Repeat step 10 with each solution in turn, adding dithionite, waiting about 1 minute, and reading absorbance against the blank solution as a reference.
12. Calculate the percentage of titanium in the sample.

STANDARD CURVE

A standard curve generally is not constructed because the absorbance of the blank, standard, and unknown are determined separately for each sample solution. However, such a plot of previous data can be useful as a reference when the method is used at infrequent intervals.

PRECISION OF TITANIUM DETERMINATIONS

Titanium was determined on the 80 samples in laboratory B with the peroxide method as described. The range 0.05 to 0.5 percent titanium applied to all 80 samples. No duplicate determinations were reported by B and so the precision of determinations by one chemist cannot be calculated. A standard sample, National Bureau of Standards standard sample 177 (Portland cement), with a certificate value of 0.16 percent titanium, was analyzed three times for titanium in laboratory B while the titanium in the shale samples was being determined. Results of 0.15, 0.15, and 0.15 percent titanium were obtained.

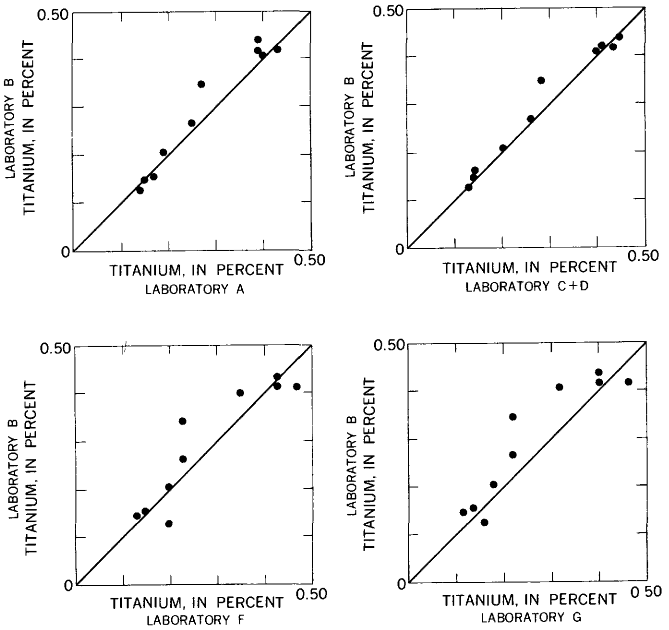

FIGURE 1.—Comparison of titanium determinations of B with those of A, C+D, F, and G.

Laboratories C and D jointly reported TiO_2 on all 80 samples of shale. These determinations, calculated to titanium, are compared with those of B in tables 1, 2, and 3. Table 1 gives the results, and standard deviations calculated from paired data for all samples except the hidden splits and the check samples. Table 2 gives similar data by laboratories B, C, and D on the hidden splits. The results on the check samples by laboratories A, B, C, D, F, and G are reported in table 3 together with the standard deviations calculated from paired data and from the maximum to minimum difference.

Figure 1 graphically compares the data of A, C+D, F, and G on the check samples with those of B.

TABLE 1.—*Determinations*[1] *of titanium, in percent, by different laboratories*

[Add 259500 to each sample number to form serial number]

Sample	B	C	Sample	B	D	Sample	B	D
42	0.15	0.13	88	0.14	0.10	89	0.37	0.36
57	.23	.25	60	.21	.22	35	.38	.36
41	.25	.04	36	.23	.23	61	.38	.41
56	.31	.30	44	.23	.21	95	.38	.37
58	.35	.33	29	.25	.25	73	.39	.40
77	.36	.34	67	.25	.25	34	.40	.38
78	.36	.33	38	.26	.25	66	.40	.40
75	.37	.35	83	.26	.27	76	.40	.40
59	.38	.37	51	.28	.29	30	.42	.39
47	.39	.37	40	.30	.29	70	.42	.42
43	.41	.37	50	.31	.31	84	.42	.42
26	.46	.44	62	.32	.32	27	.43	.44
79	.48	.46	55	.33	.35	32	.43	.41
81	.48	.47	72	.34	.35	87	.43	.44
			93	.34	.34	69	.44	.46
			91	.35	.33	71	.44	.43
			45	.36	.35	31	.45	.42
			54	.36	.38	85	.47	.47
			52	.37	.36	74	.49	.44
			64	.37	.36	90	.58	.44

[1] Precision and reliability of determinations in the range 0.05 to 0.5:

	Standard deviation	*Number of comparisons*
B, C	[1]0.015	14
B, D	.020	40

[1]One low result (sample 41) rejected.

B. Peroxide method of this report; Charles Kinser, analyst.
C. Standard rock analysis, peroxide method; Marguerite Seerveld and Vertie Smith, analysts.
D. Tiron method (Shapiro and Brannock, 1956); Leonard Shapiro, Paul Elmore, Samuel Botts and Marvin Mack, analysts.

TABLE 2.—*Determinations*[1] *of titanium, in percent, in hidden splits by three laboratories*

[Add 259500 to all sample numbers, except 03 and 04 to which add 259600, to form serial numbers. Groups indicate the samples that were duplicates]

Sample	B	C	D	Sample	B	C	D
33	0.21	0.20	------	68	0.42	0.41	------
97	.21	------	0.20	01	.44	------	0.43
49	.35	.28	------	80	.42	.40	------
96	.37	.38	------	00	.43	------	.41
99	.36	------	.30				
03	.36	------	.30	82	.33	.34	------
				02	.38	------	.37
53	.22	.22	------				
04	.23	------	.23	86	.44	.43	------
				05	.46	------	.43
65	.41	.40	------				
98	.42	------	.41				

[1] Precision and reliability of determinations in the range 0.05 to 0.5:

	Standard deviation	*Number of comparisons*
B	0.013	13
B, C+D	0.030	18

B. Peroxide method of this report; Charles Kinser, analyst.
C. Standard rock analysis, peroxide method; Marguerite Seerveld and Vertie Smith, analysts.
D. Tiron method (Shapiro and Brannock, 1956); Leonard Shapiro, Paul Elmore, Samuel Botts, and Marvin Mack, analysts.

TABLE 3.—*Determinations*[1] *of titanium, in percent, in check samples*

[Add 259500 to each sample number to form serial number]

Sample	B	A	D	C	G	F	Mean	Difference (max−min)	Standard deviation
28	0.13	0.14	0.13	------	0.16	0.20	0.15	0.07	0.030
33	.21	.19	------	0.20	.18	.20	.20	.03	.013
37	.16	.17	.14	------	.14	.15	.15	.03	.013
39	.27	.25	.26	------	.22	.23	.25	.05	.022
46	.41	.40	.40	------	.32	.35	.38	.09	.039
48	.15	.15	------	.14	.12	.13	.14	.03	.013
49	.35	.27	------	.28	.22	.23	.27	.13	.056
63	.42	.43	------	.43	.46	.47	.44	.05	.022
92	.42	.39	.41	------	.40	.43	.41	.04	.017
94	.44	.39	.44	------	.40	.43	.42	.05	.022

[1] Precision and reliability of determinations in the range 0.05 to 0.5:

	Standard deviation	*Number of comparisons*
B, A	0.024	10
B, C	.025	4
B, D	.008	6
B, F	.051	10
B, G	.058	10
Avg spectrographic, avg chemical	.029	10
All data	.026	100

B. Peroxide method of this report; Charles Kinser, analyst.
A. Alternative tiron method of this report; Claude Huffman, analyst.
D. Tiron method (Shapiro and Brannock, 1956); Leonard Shapiro, Paul Elmore, Samuel Botts, and Marvin Mack, analysts.
C. Standard rock analysis, peroxide method; Marguerite Seerveld and Vertie Smith, analysts.
G. Spectrographic analysis; Harry Rose, analyst.
F. Spectrographic analysis; Paul Barnett, analyst.

VANADIUM

FUSION-LEACH SEPARATION METHOD

[Range in shale: 0.001 to 0.5 percent vanadium]

PRINCIPLES

The sample is fused with a mixture of sodium carbonate and magnesium oxide. The alkaline melt is leached with water. Most of the silica is retained in the insoluble residue. Vanadium in the filtrate is determined spectrophotometrically as the phosphotungstovanadic acid (Sandell, 1950, p. 607–609). An aliquot of the original sample solution is used in the reference cell to compensate for small amounts of chromate, if some should remain.

Tests show that 10 parts of chromate are equivalent to 1 part vanadium under the conditions of the method. If a reagent blank is used as the reference solution, the results will be high to the extent of one-tenth of the chromate in the solution; however, the chromium content of the Pierre shale is ordinarily too small to interfere significantly.

APPARATUS AND REAGENTS

Beckman DU spectrophotometer with 1- and 5-cm cells.

Fusion mixture: Prepare an intimate mixture of four parts sodium carbonate to one part magnesium oxide by weight.

Sodium tungstate: Dissolve 20.6 g sodium tungstate dihydrate in water and dilute to 100 ml.

Standard vanadium stock solution, 1 ml=1 mg V: Dissolve 0.4592 g of ammonium metavanadate (NH_4VO_3) in water and dilute to 200 ml in volumetric flask.

Standard vanadium, dilute solution, 1 ml=10 micrograms V: Take 5 ml of stock solution and dilute to 500 ml in a volumetric flask.

PROCEDURE

1. Mix intimately 1 g sample with 6 g fusion mixture in a platinum crucible. Cover with 1 g more of mixture. Include a blank with each set of samples.
2. Heat the crucible at 650°C for 30 minutes, gradually raise temperature to 900°C and heat for 30 minutes longer or until organic matter is destroyed.
3. Leach the melt by gently boiling in a 150-ml beaker with 50 ml water containing a few drops of alcohol to destroy manganate. Break up all lumps. Let the insoluble material settle and filter the solution into a 250-ml beaker, washing with hot 0.1 percent sodium carbonate solution. Cool.
4. Carefully (otherwise CO_2 evolution may cause spillage of sample) add 1+1 nitric acid by graduated pipet until phenolphthalein is colorless, then add an equal volume of acid to convert sodium bicarbonate to carbon dioxide and sodium nitrate. Add 6 ml 1+1 nitric acid in excess. Place the beaker on a steam bath and evaporate the solution to about 50 ml. Transfer the solution to a 100-ml volumetric flask, cool, and dilute to volume with water.
5. Transfer a 20-ml aliquot to each of two 25-ml volumetric flasks. Add 2.5 ml of 1+2 phosphoric acid to each flask. Add 1 ml sodium tungstate solution to one flask but not to the other flask. Warm the flasks on a steam bath for 15 minutes, cool, and make to volume.
6. Determine the absorbance of the solutions in 5-cm cells at 400 mμ using the solution containing no tungstate as the reference.
7. Calculate the percentage of vanadium in the samples.

STANDARD CURVE

Take two sets of 0, 10, 30, 50, and 100 micrograms of standard vanadium solution in 25-ml volumetric flasks. Add 1.2 ml 1+1 nitric acid to each and enough water to make 18 ml. Add 2.5 ml of 1+2 phosphoric acid and 1.0 ml sodium tungstate solution to one set but only add 2.5 ml of 1+2 phosphoric acid to the second set of flasks. Warm the solutions on a steam bath for 15 minutes, cool, and dilute to volume. Determine the absorbance of the first set of solutions (containing added tungstate) against corresponding members of the second set (without added tungstate) at 400 mμ. Plot the absorbance differences against the vanadium concentrations.

Alternatively weigh five portions of flux, transfer to 150-ml beakers (omit fusion), and carry through the procedure beginning at step 3. Add standard vanadium solution to four of the five blank solutions at steps 3 or 5, as preferred, and complete the determinations as described.

ALTERNATIVE CUPFERRON SEPARATION METHOD

[Range in shale: 0.0001 to 0.025 percent vanadium]

PRINCIPLES

Although the first procedure for the determination of vanadium can be extended somewhat to determine smaller amounts of vanadium than indicated, the following procedure is more suitable for the determination of vanadium in concentrations below 0.01 percent in shale. A larger sample is used and vanadium is separated by precipitation with cupferron, iron from the sample acting as a carrier. The precipitate is ignited, transferred to a silver crucible, fused with sodium hydroxide, leached with water, and filtered to separate iron. Vanadium in the filtrate is again determined as the phosphotungstovanadic acid.

Attempts to use sodium carbonate in place of sodium hydroxide in the fusion of the ignited cupferron precipitate resulted generally in incomplete recovery of vanadium. The magnitude of the error from this source is largely determined by the amount of iron present and can be as much as 40 percent for samples containing 15 percent iron oxide. On the other hand, fusion with sodium hydroxide gives better than 96 percent recovery of the vanadium.

APPARATUS AND REAGENTS

Beckman DU spectrophotometer with 5-cm cells.

Sodium tungstate and standard vanadium solutions: Same as in first method.

Cupferron solution, 6 percent w/v aqueous: Prepare only when needed and keep it cold.

Ferric nitrate solution, 1 ml contains approximately 5 mg of ferric oxide: Dissolve 5.06 g of ferric nitrate 9-hydrate with 10 ml of 1+1 nitric acid and water and dilute to 200 ml. Five milliliters of this solution is used for the blank so that a precipitate will be obtained in the cupferron precipitation

PROCEDURE

1. Transfer a 2-g sample to a platinum dish and destroy organic matter by heating at 500° to 700°C.
2. A blank containing 5 ml of ferric nitrate solution is carried along with the samples. Reference is made only to the sample. Moisten the sample with water, add 20 ml hydrofluoric acid, 5 ml nitric acid, and 10 ml perchloric acid to the dish. Cover the dish and digest the solution 30 minutes on a steam bath. Evaporate solution to fumes of perchloric acid. Add 10 ml water and evaporate the solution to fumes again. Repeat the addition of water and evaporate the solution to fumes again.
3. Add 20 ml hydrochloric acid and 30 ml water to the dish and digest the solution to dissolve soluble salts. A clear solution should be obtained. Transfer the solution to a 500-ml Erlenmeyer flask, with enough water to make the volume 230 ml.

4. Chill the solution in an ice bath. Add 70 ml of cold 6-percent cupferron solution (more if required to precipitate all the iron). Stir in paper pulp, and shake the stoppered flask vigorously to coagulate the precipitate. Filter the solution by suction, using a platinum filter cone and a close-textured paper.
5. Wash the precipitate with a cold solution containing 40 ml hydrochloric acid and 15 ml of cupferron to 500 ml of solution. Reject the filtrate and washings.
6. Transfer the filter and precipitate to a platinum crucible and dry carefully on a hot plate until charred or overnight in an oven at 50°C.
7. Ignite the precipitate at a low heat; very gradually raise the temperature to 625°C, then maintain this temperature until the carbon is removed.
8. Transfer the residue to a silver crucible and fuse with 3 g sodium hydroxide. Alternatively fuse the residue in a nickel crucible with 3 g sodium hydroxide containing 1 g sodium carbonate. Leach the melt with 20 ml of water by boiling in a small beaker on a hot plate.
9. Chill the solution in an ice bath and filter it into a 50-ml volumetric flask using a hardened paper. Wash the filter with 10 ml of 0.1 percent sodium hydroxide solution. Reject residue.
10. Titrate a solution from a blank fusion with concentrated nitric acid to the methyl orange end point to determine the amount of nitric acid required to neutralize the alkali. Add this amount of nitric acid to all samples plus 1.2 ml in excess.
11. Add 5.0 ml of 1+2 phosphoric acid and 2.0 ml sodium tungstate solution to each flask. Warm on steam bath 15 minutes, cool, and dilute to volume of 50 ml.
12. Determine the absorbance of the sample solution against a blank solution carried through the method. Use 5-cm cells and a wave length of 400 mμ.
13. Calculate the percentage of vanadium in the sample.

STANDARD CURVE

Establish a standard curve with aliquots of vanadium solution containing 0, 20, 40, 80, 100, and 200 micrograms vanadium in 50-ml flasks. Add 2.4 ml 1+1 nitric acid to each flask and follow the procedure from step 11, using the blank solution as reference.

PRECISION OF VANADIUM DETERMINATIONS

Vanadium was determined on the 80 samples of shale in laboratory A with the fusion-leach phosphotungstate method described. The ranges of concentration for vanadium were from 0.0005 to 0.005 percent (10 samples), 0.005 to 0.05 percent (61 samples), and 0.05 to 0.5 percent (9 samples). The results and the precision are given in tables 4, 5, and 6.

The alternative method (cupferron separation) includes a fusion of the ignited cupferrates to redissolve the vanadium completely. Sodium hydroxide or sodium hydroxide-sodium carbonate flux is specified for this fusion because small amounts of vanadium in the presence of large amounts of iron generally are not made completely soluble by the usual fusion with sodium carbonate alone. However, when the Fe_2O_3 content of the sample is less than 5 percent, simple carbonate fusion of the cupferrates is effective as shown in table 7. Here the results obtained are compared with those obtained by the fusion-leach method. The standard deviation of results by the two methods for 33 samples (table 7) is 0.0018 percent vanadium. When the iron content was greater than 5 percent, data not reported here on 47 samples showed a standard deviation from the first method of 0.0060 percent vanadium, all with a low bias.

Figure 2 is a plot of vanadium determinations of A compared with those of A_1, A_2, and B. The scatter on the vanadium results was greater than that usually obtained on the results of the four hidden splits (table 5) of one sample containing about 17 percent pyrite, as calculated from the sulfur content of the sample.

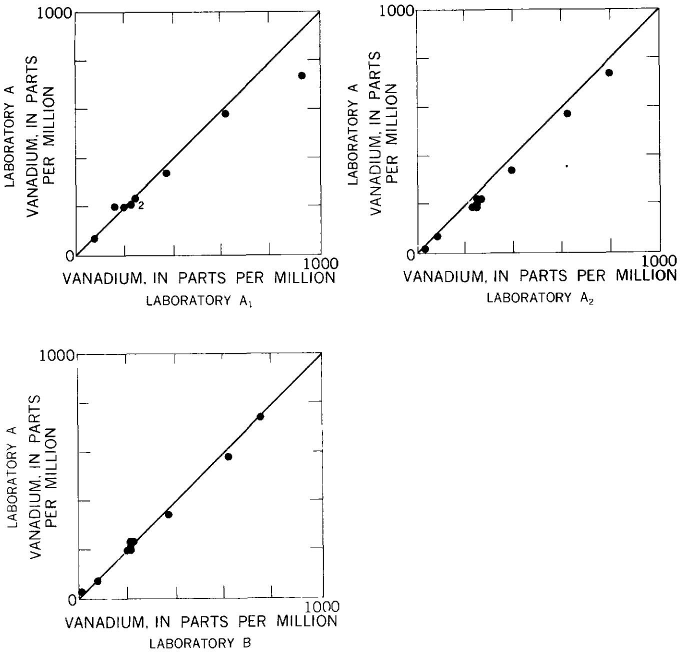

FIGURE 2.—Comparison of vanadium determinations of A with those of A_1, A_2, and B.

TABLE 4.—*Replicate determinations*[1] *of vanadium, in percent, by laboratory A*

[Analysis by fusion-leach phosphotungstate method, Wayne Mountjoy and William Goss, analysts. Add 259500 to all sample numbers, except 05 to which add 259600, to form serial numbers]

67	0.004	0.004	35	0.018	0.022
88	.004	.003	33	.020	.019
54	.006	.005	45	.024	.025
72	.006	.005	52	.026	.021
42	.006	.006	92	.020	.023
28	.007	.007	43	.029	.030
05	.017	.018			

[1] Precision and reliability of determinations in the range 0.005 to 0.5: standard deviation, 0.0015; number of comparisons. 11.

TABLE 5.—*Determinations*[1] *of vanadium, in percent, in hidden splits by laboratory A*

[Analyses by fusion-leach phosphotungstate method; Wayne Mountjoy and William Goss, analysts. Add 259500 to all sample numbers, except 00 to 05 to which add 259600, to form serial numbers. Groups indicate the samples that were duplicates]

33	0.020	53	0.021	80	0.013
97	.018	04	.019	00	.011
49	.074	65	.012	82	.038
96	.059	98	.013	02	.043
99	.075				
03	.081	68	.021	86	.021
		01	.022	05	.018

[1] Precision and reliability of determinations:

Range	*Standard deviations*	*Number of comparisons*
0.005–0.05	0.0019	7
.05– .5	.0098	6

TABLE 6.—*Determinations*[1] *of vanadium, in percent, in check samples*

[Add 259500 to each sample number to form serial number]

Sample	A	A_1	A_2	B	Mean	Difference (max−min)	Standard deviation
28	0.007	0.007	0.008	0.007	0.007	0.001	0.0005
33	.020	.016	.024	.020	.020	.008	.0039
37	.002	<.001	.003	.001	.002	.003	.0015
39	.020	.020	.023	.021	.021	.003	.0015
46	.023	.024	.025	.021	.023	.004	.0019
48	.058	.062	.062	.062	.061	.004	.0019
49	.074	.093	.079	.075	.080	.019	.0092
63	.034	.038	.039	.037	.037	.005	.0024
92	.023	.024	.024	.022	.023	.002	.0010
94	.021	,023	.024	,021	.022	.003	.0015

[1] Precision and reliability of determinations:

	Range			
	0.005 to 0.05		0.05 to 0.5	
	Standard deviation	Number of comparisons	Standard deviation	Number of comparisons
A, A_1	0.0016	8	0.0097	2
A, A_2	.0019	8	.0032	2
A, B	.0009	8	.0025	2
All data	.0018	48	.0064	12

A. Fusion-leach separation of vanadium; Wayne Mountjoy and William Goss, analysts.

A_1. Cupferron method, Na_2CO_3-NaOH fusion; Wayne Mountjoy and William Goss, analysts.

A_2. Fusion-leach separation of vanadium; Clande Huffman, analyst.

B. Fusion-leach separation of vanadium; Frank Grimaldi, analyst.

TABLE 7.—*Comparison of vanadium recovery by two methods, in percent, when iron content* (Fe_2O_3) *of shale is less than 5 percent*

[A, analysis by fusion-leach, first méthod; Wayne Mountjov and William Goss, analysts; A_3, by simple carbonate fusion of cupferrates, Wayne Mountjoy and William Goss, analysts. Add 259500 to all sample numbers, except 04 to which add 259600, to form serial numbers]

Sample	A	A_3	Difference	Sample	A	A_3	Difference
37	0.002	<0.001	0.002	51	0.018	0.017	0.001
93	.003	.003	None	36	.017	.019	.002
72	.005	.003	.002	38	.017	.019	.002
83	.005	.005	None	39	.020	.018	.002
28	.007	.007	None	94	.021	.019	.002
57	.008	.007	.001	81	.020	.020	None
60	.010	.009	.001	29	.022	.021	.001
75	.010	.010	None	85	.020	.022	.002
77	.012	.010	.002	47	.025	.022	.003
89	.010	.012	.002	55	.031	.024	.007
50	.015	.013	.002	74	.030	.030	None
04	.019	.013	.006	63	.034	.034	None
30	.016	.014	.002	27	.056	.055	.001
90	.016	.014	.002	61	.055	.055	None
53	.021	.015	.006	48	.058	.056	.002
97	.018	.015	.003	26	.064	.067	.003
33	.020	.016	.004				

Standard deviation, all samples 0.0018

CHROMIUM, FUSION-LEACH CHROMATE METHOD

[Range in shale: 0.001 to 0.05 percent chromium]

PRINCIPLES

The sample is fused with a mixture of potassium carbonate and potassium chlorate to convert chromium to chromate whose absorbance is determined at 370 mμ. Potassium nitrate cannot be used as the oxidant because any nitrite present or formed during the fusion absorbs strongly at 370 mμ and interferes. Chlorate and such products as perchlorate or chloride, however, do not absorb at this wavelength. The dissolution of platinum is kept to a minimum by carefully controlling the temperature and limiting the time of fusion. Small amounts of dissolved platinum are precipitated either as metal or oxide on digestion of the melt with water containing some alcohol. On filtering the solution, some iron may pass the filter in a colloidal state and subsequently interfere. A second digestion and filtration of the solution may be required to overcome this interference. Colored extractable compounds in filter paper are removed by washing the paper with potassium carbonate solution. Glassware should be cleaned with nitric acid; the use of dichromate-sulfuric acid cleaning solution should be avoided. A blank is carried through all steps of the procedure.

In general, the method is suitable for determining chromium in concentrations greater than 10 ppm. When less chromium is to be determined, some difficulty may result from stray yellow colors of unknown source that tend to give erratic results. Possibly substitution of silver crucibles for platinum in the fusion may overcome this. If silver is substituted, a lower temperature melting flux made by mixing sodium carbonate, potassium carbonate, and potassium chlorate in the proportions 25:25:1 by weight must be used, and the temperature of the fusion should not exceed 750°C.

APPARATUS AND REAGENTS

Beckman DU spectrophotometer supplied with 5-cm cells.

Fusion mixture: Mix intimately 25 parts potassium carbonate and 1 part ground potassium chlorate by weight.

Potassium carbonate, 10 percent w/v: Prepare the solution fresh as needed.

Standard chromate stock solution, 1 ml=1 mg Cr: Add 0.5656 g potassium dichromate and 1.0 g potassium carbonate to water in a volumetric flask. Dissolve the salts and dilute the solution to 200 ml.

Standard chromate, dilute solution, 1 ml=10 micrograms Cr: Take 5 ml of stock solution add 1 g of potassium carbonate, and dilute to 500 ml with water in a volumetric flask.

PROCEDURE

1. Transfer a 1-g sample to a platinum crucible and burn off the organic matter at 700° to 900°C. Carry a reagent blank through the entire method.

2. Add 5 g of fusion mixture to the crucible, mix intimately with the sample, and sprinkle a cover of 0.5 to 1 g more of fusion mixture over the charge. Cover the crucible with platinum lid.
3. Heat the charge gradually over a burner to the fusion point and keep molten at lowest possible temperature for at least 5 minutes. Too high a temperature in the fusion should be avoided to minimize attack of the platinum crucible.
4. Transfer the crucible and contents to a small beaker and add 35 to 50 ml of water and a few drops of alcohol (more if required to reduce manganate). Digest the solution on a steam bath, breaking up all lumps, until the precipitate is filterable. Cool the solution in an ice bath.
5. Filter the chilled solution into a beaker, using a dense filter paper previously washed with 10 percent potassium carbonate solution to remove the extractable colored compounds from the paper. Wash the residue with 0.1 percent potassium carbonate solution.
6. Place the filtrate on a team bath and evaporate the solution to about 70 ml. If the solution does not require evaporation, cover the beaker and heat for about 30 minutes. If no precipitate forms, cool the solution, transfer to a 100-ml volumetric flask, and dilute to volume. If a precipitate forms (generally owing to iron that has leaked through the filter paper in a colloidal state during filtration), chill the solution in an ice bath and filter it again through a prewashed paper and wash briefly. Dilute the solution to 100 ml in the volumetric flask.
7. Determine the absorbance of the solution at 370 mμ against water as reference.
8. Calculate the percentage of chromium in the sample.

STANDARD CURVE

Transfer aliquots of standard chromate solution containing 0, 20, 50, and 100 micrograms Cr to 100-ml volumetric flasks. Adjust to 100-ml volume with water and determine the absorbance of the solution at 370 mμ against water as a reference, using 1- or 5-cm cells.

PRECISION OF CHROMIUM DETERMINATIONS

Chromium was determined on the 80 samples of shale in laboratory B by the chromate method described. The ranges of concentration for chromium in the shale were from 0.00005 to 0.0005 percent (6 samples); 0.0005 to 0.005 percent (3 samples); 0.005 to 0.05 percent (71 samples). Standard deviations for the analytical work, tables 8, 9, and 10, apply only to the range 0.005 to 0.05 percent chromium.

A plastic clay (National Bureau of Standards, standard sample 98), with a certificate value 0.014 percent chromium, was analyzed for chromium with each set of analyses during the course of the work by laboratory B. Results of 0.0146, 0.0148, 0.0149, 0.0144, 0.0143, 0.0145, 0.0144, and 0.0144 percent chromium were obtained.

The differences in chromium concentration reported in table 10 are shown graphically in figure 3.

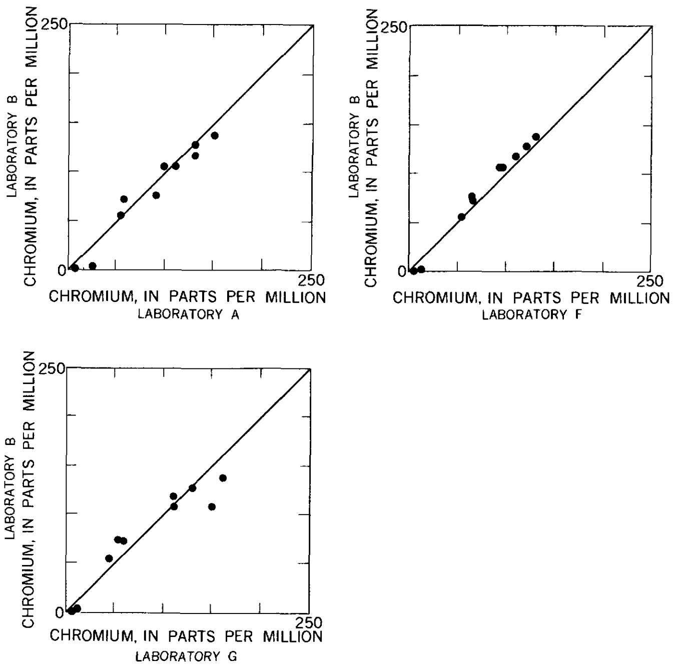

FIGURE 3.—Comparison of chromium determinations of B with those of A, F, and G

TABLE 8.—*Replicate determinations*[1] *of chromium, in percent, made in laboratory B by one chemist*

[Analysis by chromate method, Ivan Barlow, analyst. Add 259500 to all sample numbers, except 00 to 05 to which add 259600, to form serial numbers]

60	0.0056	0.0062	86	0.010	0.012
29	.0087	.0089	04	.010	.010
34	.0096	.0099	49	.013	.013
69	.010	.010	73	.013	.013

[1] Precision and reliability of determinations in the range 0.005 to 0.05: standard deviation, 0.0005; number of comparisons, 8.

TABLE 9.—*Determinations*[1] *of chromium, in percent, in hidden splits by laboratory B*

[Analysis by chromate method; Ivan Barlow, analyst. Add 259500 to all sample numbers, except 00 to 05 to which add 259600, to form serial numbers. Groups indicate the samples that were duplicates]

33	0.0056	53	0.010	80	0.010
97	.0053	04	.010	00	.010
49	.013	65	.0095	82	.0095
96	.013	98	.010	02	.0096
99	.014				
03	.013	68	.014	86	.011
		01	.013	05	.012

[1] Precision and reliability of determinations in the range 0.005 to 0.05: standard deviation, 0.00034; number of comparisons, 13.

TABLE 10.—*Determinations*[1] *of chromium, in percent, in check samples*

[Add 259500 to each sample number to form serial number]

Sample	B	A	F	G	Mean	Difference (max—min)	Standard deviation
28	0.0075	0.0056	0.0065	0.0058	0.0064	0.0019	0.00092
33	.0056	.0053	.0053	.0047	.0052	.0009	.00044
37	<.0003	.0006	.0003	.0003	<.0004	.0006	.00029
39	.0077	.0091	.0064	.0054	.0072	.0037	.0018
46	.011	.010	.0094	.011	.010	.0016	.00078
48	.0004	.0023	.0012	.0010	.0012	.0019	.00092
49	.013	.013	.012	.013	.013	.001	.00049
63	.014	.015	.013	.016	.015	.013	.0015
92	.012	.013	.011	.010	.012	.003	.0015
94	.011	.011	.0095	.015	.012	.006	.0029

[1] Precision and reliability of determinations in the range 0.005 to 0.05:

	Standard deviation	*Number of comparisons*
B, A	0.0008	10
B, F	.0007	10
B, G	.0013	10

B. Analysis by chromate method; Ivan Barlow, analyst.
A. Analysis by chromate method; Claude Huffman, analyst.
F. Spectrographic analysis; Paul Barnett, analyst.
G. Spectrographic analysis; Harry Rose and Sol Berman, analysts.

MANGANESE, PERSULFATE OXIDATION METHOD

[Range in shale: 0.001 to 5 percent manganese]

PRINCIPLES

Manganese is oxidized to permanganate by several oxidizing agents in acid solution. For oxidation of small amounts of manganese, persulfate in the presence of a small amount of silver nitrate is the preferred reagent (Nydahl, 1949) and (Sandell, 1950, p. 433). The oxidation is usually carried out in a medium of $0.3M$ nitric acid and at least $0.1M$ phosphoric acid. The addition of mercuric sulfate prevents the interference of small amounts of chloride by forming slightly dissociated mercuric chloride.

APPARATUS AND REAGENTS

Beckman DU or Model B spectrophotometer, adapted for both 1- and 5-cm cells.

Mercuric sulfate-silver nitrate solution: Dissolve 33 g of mercuric sulfate in 147 ml of 1+1 nitric acid and 200 ml of water. add 110 ml of 85 percent phosphoric acid and 17 mg silver nitrate and stir to dissolve. Cool and dilute to 500 ml with water.

Standard manganese stock solution, 1 ml=1 mg Mn: Heat manganese sulfate monohydrate at 500°C to convert to the anhydrous form. Dissolve 0.5498 g of anhydrous manganous sulfate in 50 ml of 1+99 nitric acid and dilute to 200 ml with 1+99 nitric acid in a volumetric flask.

Standard dilute manganese solution A, 1 ml=10 micrograms Mn: Take 5 ml of stock solution and dilute to 500 ml with 1+99 nitric acid.

Standard dilute manganese sulution B, 1 ml=50 micrograms Mn: Take 25 ml of stock solution and dilute to 500 ml with 1+99 nitric acid.

Nitric acid, 1+99: Dilute 10 ml nitric acid to 1 liter.

PROCEDURE

1. Transfer a 0.7- to 1.0-g sample to a 50- to 75-ml platinum dish. Remove organic matter by igniting gently at first and raising the temperature gradually to about 700°C.
2. Moisten the sample with water and add 5–10 ml nitric acid, 10 ml hydrofluoric acid, and 2–5 ml perchloric acid to the dish.
3. Cover the dish and digest the solution on a steam bath for 30 minutes.
4. Remove the cover from the dish and evaporate the solution to fumes of perchloric acid. Repeat steps 2 to 4 if the sample is not thoroughly decomposed.
5. Cool the dish, add 10 ml of water, rinsing down the sides of the dish, and evaporate the solution to fumes of perchloric acid. Repeat, but this time take to complete dryness, expelling all acid at 200°C to 220°C on a hot plate.
6. Wet the residue in the dish with 2 ml 1+1 nitric acid and evaporate to dryness on the steam bath.
7. Add exactly 2.0 ml 1+1 nitric acid to the dish and allow to stand a few minutes at room temperature. Add 18 ml water to the dish, cover, and digest to dissolve the residue. If a clear solution is obtained, transfer the solution to a a 100-ml volumetric flask and dilute to volume with water.
8. If a residue remains undissolved, filter the solution into a 100-ml volumetric flask, wash the residue with water and reserve the filtrate.
9. Ignite the residue and paper in a crucible and fuse the residue with 0.5 g of sodium carbonate. Cool the crucible, add 5 ml water, and carefully neutralize the carbonate by adding exactly 1.2 ml 1+1 nitric acid to convert the 0.5 g of sodium carbonate to carbonic acid and sodium nitrate. Warm the solution briefly to expel carbon dioxide, cool, and transfer this solution to the reserved portion in the 100-ml flask and dilute to volume with water. The solution is now 1 percent, by volume, nitric acid.
10. Transfer a 25-ml aliquot of the solution to a 125-ml Erlenmeyer flask. If smaller aliquots are required, dilute the aliquot to 25 ml with 1+99 nitric acid.
11. Add 0.5 ml 1+1 nitric acid, 19.5 ml of water, and 3 ml of the mercury-silver solution; stir the solution.
12. Add 1.0 g ammonium persulfate to the flask and heat over a flame just to boiling. Set the hot flask aside for 1 minute, then cool quickly in a cold-water bath until room temperature is reached.
13. Transfer the solution to a 50-ml volumetric flask and dilute to volume with water that has previously been boiled with ammonium persulfate and cooled.
14. Determine the absorbance of the solution at 525 mμ against a reagent blank carried through the method.
15. Calculate the percentage of manganese in the sample.

STANDARD CURVE

Pipet aliquots of standard manganese solution equivalent to 0, 10, 20, 40, 80, and 100 micrograms manganese and transfer to 125-ml flasks. These concentrations are suitable for establishing a standard curve for a 5-cm cell. If greater concentrations are to be determined using a 1-cm cell, aliquots containing 50, 100, 200, 400, 800 and 1,000 micrograms manganese are used. Develop the color of the solutions, with due regard for the proper acidity, by following the procedure steps 10 to 14. Draw standard curves for use with the method.

PRECISION OF MANGANESE DETERMINATIONS

Manganese was determined on the 80 samples in laboratory A by the method described. The ranges of concentration for manganese were from 0.005 to 0.05 percent (59 samples), 0.05 to 0.5 percent (17 samples), and 0.5 to 5.0 percent (4 samples). The results of replicate determinations are give in table 11, those on the hidden splits in table 12, and those on the check samples in table 13. Ordinarily laboratories C and D report manganese in the range below 0.1 percent MnO only to the nearest hundredth of a percent. However, the original notebook data of laboratories C and D were converted from MnO to Mn and reported to two significant figures for the comparative evaluation of the following tables. The results of A are compared with those of B, C+D, and F in figure 4.

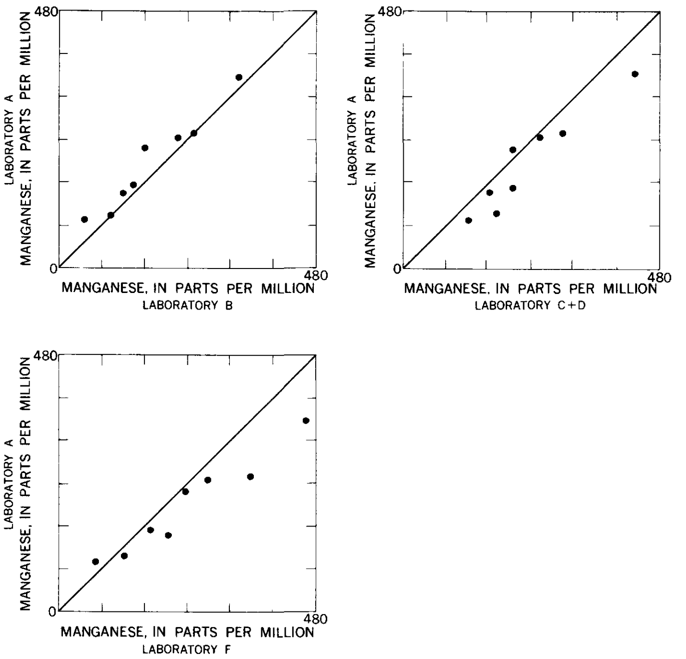

FIGURE 4.—Comparison of manganese determinations of A with those of B, C+D and F.

TABLE 11.—*Determinations* [1] *of manganese, in percent, by three laboratories*

[Add 259500 to all sample numbers, except 03 and 04 to which add 259600, to form serial numbers]

	A		C [2]		A		D [2]		A		D [2]
26	0.009	0.009	0.012	73	0.005	0.007	0.015	62	0.029	0.030	0.031
63	.008	.009	.012	61	.007	.008	.007	70	.029		.027
81	.008		.015	27	.008	.010	.014	71	.029	.030	.031
57	.015		.016	03	.010	.016	.020	66	.032		.036
65	.021	.026	.025	93	.012		.018	55	.033		.036
77	.021		.024	87	.012		.020	46	.034	.035	.042
78	.022		.026	99	.013	.013	.018	34	.040	.040	.042
59	.024	.024	.026	30	.013	.014	.017	67	.043		.053
75	.024		.028	84	.013	.016	.022	44	.047		.051
43	.033		.033	74	.015	.017	.022	45	.050		.050
56	.035		.035	90	.015		.018	85	.050		.057
47	.040		.039	91	.016		.018	54	.052		.054
68	.044	.044	.043	72	.019		.022	29	.056	.058	.058
42	.052		.053	50	.020		.031	51	.084		.090
58	.068		.069	89	.022	.022	.026	04	.085	.086	.089
79	.14	.14	.13	95	.022		.026	64	.089		.086
41	2.2	2.2	2.2	39	.024	.026	.029	35	.12	.12	.12
33	3.4	3.5	3.6	40	.025		.023	36	.15		.15
				32	.025	.026	.024	60	.19		.19
				69	.026		.025	31	.23	.24	.24
				76	.027		.036	28	.42	.42	.42
				52	.028		.033	38	.92	.96	.91

[1] Precison and reliability of determinations:

	Range					
	0.005 to 0.05		0.05 to 0.5		0.5 to 5	
	Standard deviation	Number of comparisons	Standard deviation	Number of comparisons	Standard deviation	Number of comparisons
A	0.0014	20	0.0032	6	0.043	3
A, C	.0021	18	.0050	4	.079	4
A, D	.0037	46	.0025	17	.025	2

[2] Reported MnO calculated to Mn: For reported values of 0.09 MnO (0.070 percent Mn) and less the last figure is the result of the calculation.

A. Persulfate method; Dwight Skinner, analyst.
C. Standard rock analysis, periodate method; Marguerite Seerveld and Vertie Smith, analysts.
D. Periodate method, Shapiro and Brannock, 1956; Leonard Shapiro, Paul Elmore, Samuel Botts, and Marvin Mack, analysts.

TABLE 12.—*Determinations* [1] *of manganese, in percent, in hidden splits*

[Add 259500 to all sample numbers, except 00 to 05 to which add 259600, to form serial numbers. Groups indicate the samples that were duplicates]

Sample	A	C	D	Sample	A	C	D
33	3.5	3.6		68	0.044	0.043	
97	3.4		3.4	01	.041		0.052
49	.014	.016		80	.047	.048	
96	.014	.016		00	.051		.049
99	.013		.018				
03	.013		.020	82	.028	.030	
				02	.028		.035
53	.084	.084					
04	.086		.089	86	.020	.022	
				05	.018		.023
65	.024	.025					
98	.025		.035				

[1] Precision and reliability of determinations:

	Range					
	0.005 to 0.05		0.05 to 0.5		0.5 to 5	
	Standard deviation	Number of comparisons	Standard deviation	Number of comparisons	Standard deviation	Number of comparisons
A	0.0013	11				
A, C + D	.0034	36	0.0021	4	0.086	4

A. Persulfate method; Dwight Skinner, analyst.
C. Standard rock analysis, periodate method; Marguerite Seerveld and Vertie Smith, analysts.
D. Periodate method (Shapiro and Brannock, 1956); Leonard Shapiro, Paul Elmore, Samuel Botts, and Marvin Mack, analysts.

TABLE 13.—*Determinations* [1] *of manganese, in percent, in check samples*

[Add 259500 to each sample number to form serial number]

Sample	A	B	C	D	F	Mean	Difference (max–min)	Standard deviation
28	0.42	0.44		0.42		0.43	0.02	0.012
33	3.5	3.5	3.6			3.5	.1	.059
37	.022	.016		.020	0.023	.020	.007	.0034
39	.025	.025		.029	.035	.029	.010	.0049
46	.035	.033		.042	.045	.039	.012	.0058
48	.024	.022	.025		.027	.025	.005	.0024
49	.014	.012	.016		.020	.016	.008	.0039
63	.009	.005	.012		.007	.008	.007	.0034
92	.010	.010		.017	.012	.012	.007	.0034
94	.015	.014		.020	.017	.017	.006	.0029

[1] Precision and reliability of determinations in the range 0.005 to 0.05:

	Standard deviation	*Number of comparisons*
A, B	0.0020	8
A, C + D	.0031	8
A, F	.0040	8

A. Persulfate method; Dwight Skinner, analyst.
B. Persulfate method; Charles Kinser, analyst.
C. Standard rock analysis, periodate method; Marguerite Seerveld and Vertie Smith, analysts.
D. Periodate method (Shapiro and Brannock, 1956); Paul Elmore, Samuel Botts, and Marvin Mack, analysts.
F. Spectrographic method; Paul Barnett, analyst.

COBALT, DITHIZONE-NITROSO-R-SALT METHOD

[Range in shale: 0.0005 to 0.005 percent cobalt]

PRINCIPLES

Cobalt is isolated by extraction of the dithizone complex in carbon tetrachloride from ammoniacal citrate solution according to Sandell and Perlich (1939). The cobalt is determined spectrophotometrically with nitroso-R-salt (1,nitroso, 2,hydroxynaphthalene, 3,6,disulfonate) in the presence of a citrate-phosphate-borate medium according to McNaught (1942). Copper, lead, zinc, and part of the nickel coextract with the cobalt in the dithizone separation. Interferences from these elements while determining cobalt in shale with the nitroso-R-salt method are a minimum because of the relatively small amount of copper, lead, zinc, and nickel found in shale. In addition, the nitroso-R-salt procedure will tolerate at least 10 mg iron, 5 to 10 mg copper, 0.2 mg nickel, and milligram amounts of manganese, zinc, cadmium, lead, and tin.

APPARATUS AND REAGENTS

Beckman DU spectrophotometer.

Citric acid, 50 percent w/v: British Drug House purified reagent or the equivalent.

Dithizone, 0.05 percent w/v in carbon tetrachloride.

Nitroso-R-salt, 0.05 percent aqueous solution.

Citric acid, 0.20*M*: Dissolve 4.2 g of citric acid monohydrate to give 100-ml aqueous solution.

Buffer solution, 6.2 g of boric acid, 35.6 g of disodium hydrogen phosphate heptahydrate, and 20 g of sodium hydroxide in a total volume of 1 liter aqueous solution.

Standard cobalt stock solution, 1 ml=1 mg Co: Dissolve 0.8074 g cobaltous chloride hexahydrate in 200 ml total volume aqueous solution containing 2-ml hydrochloric acid.

Standard cobalt solution, 1 ml=10 micrograms Co: Take 5 ml of cobalt stock solution and dilute to 500 ml with water in a volumetric flask.

Thymol blue indicator 0.1 percent: Take 0.1 g of thymol blue and dissolve it in 25-ml ethyl alcohol. Dilute to 100 ml with water.

PROCEDURE

1. Weigh a 1.0-g sample into a 50- to 75-ml platinum dish. Ignite organic matter at about 700°C. Carry a reagent blank through all steps of the procedure.
2. Moisten the sample with water. Add 10 ml hydrofluoric acid, 10 ml nitric acid, and 4 ml perchloric acid to the dish. Heat the solution 30 minutes on a steam bath with the dish covered with a platinum cover. Remove cover and evaporate the water. Heat the solution to fumes of perchloric acid. Cool. Add 5 ml water and fume again. Repeat. Fume the solution to moist dryness; avoid heating the solution to complete dryness.
3. Add 2 to 4 ml 1+1 hydrochloric acid and 10 ml water to the dish and digest to dissolve the salts. If undecomposed sample is present, it should be filtered off and the filtrate reserved. The residue is ignited and fused with about 0.5 g sodium carbonate and dissolved in 1+1 hydrochloric acid using 1.6 ml for every 0.5 g sodium carbonate used. The solution is combined with that reserved.
4. Evaporate the solution if necessary so that it can be transferred and made to 25 ml in a volumetric flask. Potassium perchlorate may precipitate on cooling. Disregard.
5. After any salts settle out transfer a 10-ml aliquot of solution to a small separatory funnel and add 5 ml of 50 percent w/v citric acid. Add 0.2 ml thymol blue indicator and neutralize the solution with ammonium hydroxide to a pH of 8.5 to 9.3 (intermediate color of thymol blue). Preferably a pH meter should be used and the pH of the solution adjusted to 9.0.
6. Add 5 ml dithizone, shake the solution vigorously for 1 minute, and draw off the carbon tetrachloride layer. Continue extracting the solution with 5 ml portions of dithizone solution until the last portion still shows a green color after shaking for 1 minute. Three to four extractions usually are required.
7. Wash the combined carbon tetrachloride extracts with 5 ml of 1+99 ammonium hydroxide. Transfer the carbon tetrachloride solution of cobalt to a 50-ml beaker and carefully evaporate the carbon tetrachloride by heating the beaker on a water bath.
8. Add 0.25 ml sulfuric acid and 0.25 to 0.5 ml perchloric acid to the beaker and heat at 200° to 250°C until the liquid is entirely colorless. Then fume off the sulfuric acid completely, including any drops that may have condensed on the upper portions of the beaker. The temperature should be less than 500°C.
9. Add 1 ml of 1+1 hydrochloric acid, swirl the beaker to wet the surface of the beaker with acid, wash down the sides with a minimum of water from a wash bottle and evaporate the solution to dryness. Finish the evaporation by heating the beaker in an oven at 140°C to drive off any acid that may have condensed on the sides of the beaker.
10. Add to the beaker 1.0 ml of 0.2*M* citric acid solution, and 1.2 ml of phosphate-borate buffer solution. Stir the solution while adding exactly 2 ml of nitroso-R salt solution. Boil the solution for 1 minute.
11. Add 1.0 ml nitric acid, and boil the solution again for 1 minute. Adjust the volume of the solution to 10 ml in a volumetric flask. Obtain the absorbance of the solution at 475 mμ against a blank solution as a reference. The blank solution is prepared by adding to a beaker 1.0 ml of citric acid, 1.2 ml of phosphate-borate buffer, 2 ml of nitroso-R-salt and boiling the solution for 1 minute; adding 1.0-ml nitric acid and again boiling for 1 minute; cooling the solution in the dark and adjusting the volume to 10 ml in a volumetric flask.
12. Calculate the percentage of cobalt in the sample.

STANDARD CURVE

Transfer aliquots of standard cobalt solution containing 0, 3, 5, 15, and 30 micrograms of cobalt to small beakers. Evaporate the solution to dryness to remove mineral acid and proceed with steps 10 and 11 of the procedure.

PRECISION OF COBALT DETERMINATIONS

Cobalt was determined on the 80 samples of shale in laboratory B with the nitroso-R-salt method described. The concentration of cobalt was in the range 0.0005 to 0.005 percent for all 80 samples. Only two replicate determinations were reported (table 14). The results of determinations on the hidden splits are given in table 15. Two separate analyses for cobalt in the check samples were made in laboratory A, with results also reported by B, F, and G except that G did not report cobalt in two samples. These data are given in table 16. Figure 5 compares the data of table 16 graphically.

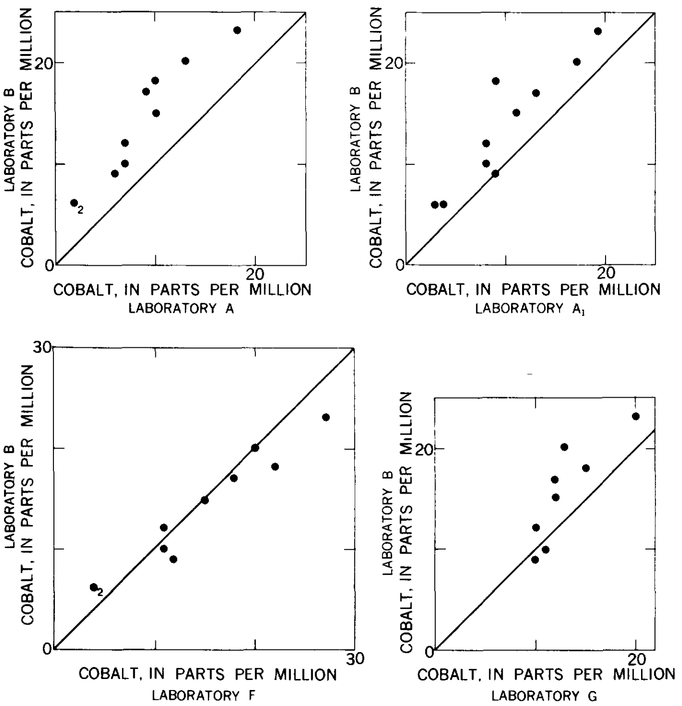

FIGURE 5.—Comparison of cobalt determinations of B with those of A A₁, F, and G. Plots that coincide are indicated with the number involved.

TABLE 14.—*Replicate determinations of cobalt, in percent, made in laboratory B by one chemist*

[Analysis by nitroso-R-salt method; Joseph Dinnin, analyst. Add 259500 to each sample number to form serial number]

37	0.0005,	0.0006
40	.0013,	.0014

TABLE 15.—*Determinations[1] of cobalt, in percent, in hidden splits by laboratory B*

[Analyses by nitroso-R-salt method; Joseph Dinnin, analyst. Add 259500 to all sample numbers, except 00 to 05 to which add 259600, to form serial numbers. Groups indicate the samples that were duplicates]

33	0.0018	53	0.0015	80	0.0017
97	.0015	04	.0013	00	.0018
49	.0020	65	.0014	82	.0027
96	.0019	98	.0013	02	.0029
99	.0021				
03	.0020	68	.0018	86	.0016
		01	.0018	05	.0015

[1] Precision and reliability of determinations in the range 0.0005 to 0.005: standard deviation, 0.00010; number of comparisons, 13.

TABLE 16.—*Determinations[1] of cobalt, in percent, in check samples*

[Add 259500 to each sample number to form serial number]

Sample	B	A	A_1	F	G	Mean	Difference (max–min)	Standard deviation
28	0.0009	0.0006	0.0009	0.0012	0.0010	0.0009	0.0006	0.00026
33	.0018	.0010	.0009	.0022	.0015	.0015	.0013	.00056
37	.0006	.0002	.0003	.0004		.0004	.0004	.00019
39	.0012	.0007	.0008	.0011	.0010	.0010	.0005	.00022
46	.0023	.0018	.0019	.0027	.0020	.0021	.0009	.00039
48	.0017	.0009	.0013	.0018	.0012	.0014	.0009	.00039
49	.0020	.0013	.0017	.0020	.0013	.0017	.0007	.00030
63	.0006	.0002	.0004	.0004		.0004	.0004	.00019
92	.0015	.0010	.0011	.0015	.0012	.0013	.0005	.00022
94	.0010	.0007	.0008	.0011	.0011	.0009	.0004	.00017

[1] Precision and reliability of determinations in the range 0.0005 to 0.005:

	Standard deviation	*Number of comparisons*
B, A	0.00043	10
B, A_1	.00029	10
B, F	.00016	10
B, G	.00026	8
All data	.00031	92

B. Nitroso-R-salt method; Joseph Dinnin, analyst.
A. Nitroso-R-salt method; Howard Lipp, analyst.
A_1. Nitroso-R-salt method; Howard Lipp and Claude Huffman, analysts.
F. Spectrographic method; Paul Barnett, analyst.
G. Spectrographic method; Harry Rose, analyst.

NICKEL, DIMETHYLGLYOXIME METHOD

PERSULFATE OXIDATION

[Range in shale: 0.0005 to 0.05 percent nickel]

PRINCIPLES

Nickel is concentrated and separated from rock-forming elements by extraction of the nickelous dimethylglyoxime complex from an ammoniacal citrate solution with chloroform. The citrate solution prevents the precipitation of iron, aluminum, and other metals. Some copper accompanies nickel in the extraction, but it is removed by washing the extract with dilute ammonia. According to Sandell (1950, p. 469) much manganese interferes by preventing complete extraction of nickel. This interference can be prevented by adding hydroxylamine hydrochloride to keep manganese in the bivalent state. Nickel is returned to the aqueous phase by stripping with 0.5*N* hydrochloric acid. The solution containing nickel is made strongly basic, pH 12 to 13, in the presence of sodium citrate. The nickel is oxidized with potassium persulfate to form the colored nickelic dimethyglyoxime complex whose absorption is measured. The nickel complex formed under these conditions is complex B, of constant and reproducible composition (Furman and McDuffie, 1947). The effect of pH and concentration of persulfate on the color reaction was studied by White (1952) and by Bane and Grimes (1950, p. 435).

APPARATUS AND REAGENTS

Beckman DU spectrophotometer supplied with 1- and 5-cm cells.

Dimethylglyoxime solution: Dissolve 1 g of dimethylglyoxime in 100-ml ethyl alcohol in a volumetric flask. Stopper.

Sodium citrate, 10 percent in water, w/v.

Potassium persulfate, 10 ml=0.5 g: Dissolve 50 g of reagent grade potassium persulfate in water by heating and stirring. Cool, and dilute to 1 liter.

Chloroform, reagent grade.

Standard nickel stock solution, 1 ml=1 mg Ni: Dissolve 0.8100g nickel chloride hexahydrate with 5 ml hydrochloric acid and water. Dilute to 200 ml in a volumetric flask.

Standard nickel, dilute solution, 1 ml=10 micrograms Ni: Take 5 ml of stock solution and dilute to 500 ml with water in a volumetric flask.

Hydrochloric acid 0.5*N*: add 21 ml hydrochloric acid to water and dilute to 500 ml.

Ammonium hydroxide, 2 percent v/v.

Hydroxylamine hydrochloride, crystals.

Sodium hydroxide, 50 percent solution: Add 500 g sodium hydroxide to 500 ml water, shake to dissolve, cool, and allow carbonates to settle out.

PROCEDURE

1. Weigh 1 to 2 g of sample and transfer to a 100-ml platinum dish. Ignite organic matter at 500° to 600°C in a muffle.
2. Moisten the sample with water and add 5 ml nitric acid, 10 ml hydrofluoric acid, and 5 ml perchloric acid. Cover the dish and heat the solution 30 minutes on the steam

bath. Remove cover and evaporate the solution to remove water. Fume the solution to moist dryness on a hot plate. Add acids as mentioned above and repeat the operation.

3. Add 50 ml water and 10 ml hydrochloric acid to the dish, and digest to dissolve the salts. Transfer the solution to a 100-ml volumetric flask with water. Dilute to volume and mix. If undecomposed sample is present after digesting the solution, filter it off, ignite, and fuse with about 0.5 g of sodium carbonate. Dissolve the cake in 1+1 hydrochloric acid, using 1.6 ml for every 0.5 g sodium carbonate used. Combine solution with the reserved filtrate and dilute to 100 ml in a volumetric flask.
4. Take a 10- or 25-ml aliquot of solution and transfer it to a 60-ml separatory funnel. If less than a 25-ml aliquot is taken, make up the difference with water. Add 10 ml of sodium citrate solution (more if needed to keep Fe and Al in solution), and ammonium hydroxide until the solution is slightly ammoniacal. Adjust the pH to 9.0 or just pink to phenolphthalein with diluted ammonium hydroxide or hydrochloric acid.
5. Add a few crystals of hydroxylamine hydrochloride and 3 ml of dimethylglyoxime solution to the funnel. Shake the solution and allow to stand a few minutes.
6. Extract the solution twice with 10 ml chloroform each time, drawing the chloroform layer into a separatory funnel reserved for this purpose.
7. Shake the combined chloroform extracts with 10 ml of 1+49 ammonium hydroxide, and draw the chloroform into another separatory funnel. Shake the aqueous phase with 3 ml of chloroform for 30 seconds and combine the chloroform layer with the washed chloroform extract.
8. Extract the chloroform solution with two separate 10-ml portions of 0.5*N* hydrochloric acid and vigorously shake each portion for 1 minute. Transfer the hydrochloric acid solutions to a 50-ml volumetric flask by filtering through a 7-cm dense paper. Reject the chloroform. Wash the funnel by shaking with about 3 ml of water, filtering the water into the flask containing the acid solution of the nickel. Wash the filter paper once with water.
9. Add 2 ml sodium citrate solution to each flask and make the solutions strongly basic (pH 12 or more) by adding 12 to 15 drops of sodium hydroxide solution (50 percent w/v) to each.
10. Add 10 ml potassium persulfate solution and 3 ml dimethylglyoxime solution to each flask.
11. Dilute to 50-ml volume with water, mix, and then, after waiting 0.5 to 1 hour to develop full color, determine absorbance in 5-cm cells at 530 mμ. A blank carried through the method, beginning at step 4, is used as the reference solution.
12. Calculate the percentage of nickel in the sample.

STANDARD CURVE

Transfer aliquots of standard solution containing 0, 5, 10, 20, 40, and 60 micrograms of nickel to separatory funnels. Add a few drops 1+1 hydrochloric acid to each, dilute to 25 ml with water, and proceed with steps 4 through 11 of the procedure.

ALTERNATIVE BROMINE OXIDATION

[Range in shale: 0.0005 to 0.05 percent nickel]

PRINCIPLES

In the dimethylglyoxime method (Sandell and Perlich, 1939), the nickelic dimethylglyoxime is formed from slightly ammoniacal solution, using bromine as the oxidant (Rollet, 1926). The absorbance of the complex is determined within 5 minutes and at 450 mμ instead of at 530 mμ. The change in the color intensity with time, in this system, is due to complex A changing to complex B (Furman and McDuffie, 1947). In ammoniacal solutions of pH 9 to 10, complex A forms rapidly and then changes slowly to complex B, but at pH 10 to 11, the change to complex B is very rapid and results are not reproducible. Change in color intensity is partly overcome by making readings at 450 mμ, and the sensitivity also is increased at this wavelength (Mitchell and Mellon, 1945).

APPARATUS AND REAGENTS

The reagents and apparatus are given under the previous method for determination of nickel, except that a saturated solution of bromine in water is substituted for the potassium persulfate solution; the sodium hydroxide solution is not required.

PROCEDURE

1. Follow steps 1 through 8 of the previous procedure for the determination of nickel.
2. Add 2 ml of sodium citrate solution and 1 ml of saturated bromine water to each flask and allow the solution to stand for a few minutes. Then add ammonium hydroxide until the color of bromine is removed (the solution may not become entirely colorless, because enough dimethylglyoxime may be present to give a visible reaction with nickel). Add 1 ml ammonium hydroxide in excess.
3. Add 1 ml of dimethylglyoxime solution.
4. Dilute the solution to 50-ml volume with water and determine within 5 minutes the absorbance against water as a reference at 450 mμ. A reagent blank should be run with the samples.
5. Calculate the percentage of nickel in the sample.

PRECISION OF NICKEL DETERMINATIONS

Nickel was determined in the 80 samples in laboratory A with the dimethylglyoxime method, using persulfate as the oxidant. The ranges of concentration for nickel were from 0.0005 to 0.005 percent (46 samples) and from 0.005 to 0.05 percent (34 samples). The results on 38 replicate determinations are given in table 17, those on hidden splits in table 18, and those on the check samples in table 19. Figure 6 shows the data of B and F plotted against that of A. In general, the agreement between laboratories is good.

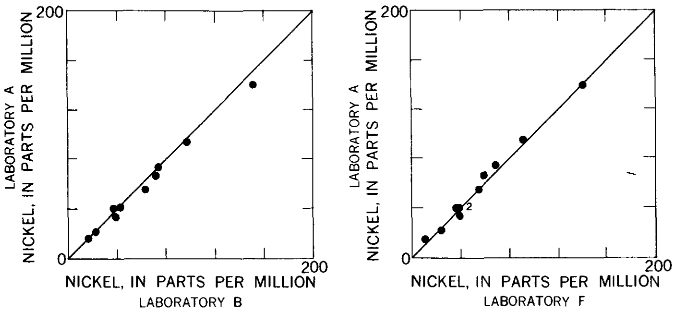

FIGURE 6.—Comparison of nickel determinations of A with those of B and F. Plots that coincide are indicated with the number involved.

TABLE 17.—*Replicate determinations* [1] *of nickel, in percent, made in laboratory A by one chemist*

[Analysis by persulfate oxidation method; Lewis Rader, analyst. Add 259500 to all sample numbers, except 00 to 05 to which add 259600, to form serial numbers]

88	0.0005	0.0006	78	0.0038	0.0039	56	0.0075	0.0076
41	.0009	.0010	00	.0040	.0044	38	.0081	.0083
83	.0010	.0011	05	.0040	.0043	58	.0084	.0084
26	.0013	.0014	28	.0041	.0041	33	.0092	.0094
61	.0016	.0016	01	.0044	.0046			.010
63	.0016	.0016	91	.0058	.0061	31	.0093	.0096
20	.0016	.0016	04	.0058	.0062	51	.0097	.010
73	.0019	.0019	03	.0059	.0066	97	.010	.011
93	.0024	.0024	53	.0060	.0060		.011	.011
27	.0026	.0028	99	.0064	.0067	54	.011	.011
81	.0028	.0032	49	.0066	.0068	55	.015	.015
76	.0032	.0033	43	.0068	.0068	82	.015	.016
98	.0036	.0037	48	.0074	.0076	02	.016	.016
68	.0038	.0040						

[1] Precision and reliability of determinations:

Range	*Standard deviations*	*Number of comparisons*
0.0005–0.005	0.00012	19
.005– .05	.00035	26

TABLE 18.—*Determinations* [1] *of nickel, in percent, in hidden splits*

[Analysis by persulfate oxidation method; Lewis Rader, analyst. Add 259500 to all sample numbers, except 00 to 05 to which add 259600, to form serial numbers. Groups indicate the samples that were duplicates]

33	0.0095	53	0.0060	80	0.0042
97	.011	04	.0060	00	.0042
49	.0067	65	.0037	82	.0016
96	.0061	98	.0037	02	.0016
99	.0066	68	.0039	86	.0041
03	.0063	01	.0045	05	.0042

[1] Precision and reliability of determinations:

Range	*Standard deviations*	*Number of comparisons*
0.0005–0.005	0.00019	5
.005– .05	.00044	8

TABLE 19.—*Determinations* [1] *of nickel, in percent, in check samples*

[Add 259500 to all sample numbers, except 00 to 05 to which add 259600, to form serial numbers]

Sample	A	B	F	Mean	Difference (max–min)	Standard deviation
28	0.0041	0.0042	0.0038	0.0040	0.0004	0.00024
33	.0095	.0096	.0090	.0094	.0006	.00035
37	.0035	.0039	.0039	.0038	.0004	.00024
39	.0055	.0063	.0056	.0058	.0008	.00047
46	.014	.015	.014	.014	.001	.00059
48	.0075	.0073	.0069	.0072	.0006	.00035
49	.0067	.0071	.0060	.0066	.0011	.00065
63	.0016	.0016	.0011	.0014	.0005	.00030
92	.0022	.0022	.0024	.0023	.0002	.00012
94	.0041	.0037	.0038	.0039	.0004	.00024

[1] Precision and reliability of determinations:

	Range			
	0.0005 to 0.005		0.005 to 0.05	
	Standard deviation	Number of comparisons	Standard deviation	Number of comparisons
A, B	0.00018	5	0.00043	5
A, F	.00025	5	.00046	5

A. Persulfate oxidation method; Lewis Rader, analyst.
B. Bromine oxidation, alternative method; Hyman Feinstein, analyst.
F. Spectrographic analysis; Paul Barnett, analyst.

COPPER, LEAD, AND ZINC

ISOLATION BY EXTRACTION

[Range in shale: Copper, 0.0003 to 0.010 percent; lead, 0.0003 to 0.0040 percent; zinc, 0.001 to 0.040 percent]

PRINCIPLES

Copper, lead, and zinc are concentrated together by extraction of their dithizonates from a slightly basic citrate solution, pH 9.0, with a solution of dithizone in carbon tetrachloride, as described by Sandell, (1937). Lead and zinc are stripped with dilute acid, leaving copper dithizonate in the carbon tetrachloride phase. The copper solution is evaporated, organic matter is destroyed, and the copper is determined either by dithizone or by the alternative 2,2′ biquinoline method (cuproine). The aqueous phase containing lead and zinc is made to volume and separate aliquots are taken for the determination of lead and zinc by the dithizone methods described in this report.

REAGENTS

Dithizone, 0.05 percent (w/v), in carbon tetrachloride: Purify the dithizone by dissolving 0.5 g in 50 ml chloroform. Filter the solution through a coarse dry fritted-glass crucible to remove any insoluble material. Shake the solution in a separatory funnel with four successive 50 to 75 ml portions of 1+100 ammonium hydroxide, prepared from tank ammonia. Separate the aqueous extracts from the chloroform and filter through a small plug of cotton to remove droplets of chloroform. Make the ammoniacal solution slightly acid with redistilled hydrochloric acid to precipitate dithizone. Add about 15 ml of choroform and extract the dithizone. Add one or two more portions of chloroform and shake. Combine the chloroform extracts and shake the solution twice with an equal volume of water (redistilled or demineralized). Transfer the chloroform solution to a beaker and evaporate the chloroform at 50°C. Dry the product in a desiccator. Use a portion to prepare the 0.05 percent dithizone solution in purified carbon tetrachloride. The solution is stable if kept cold in a dark place.

Carbon tetrachloride: Distill in the presence of a little calcium oxide and collect the distillate in a clean, dry Pyrex bottle.

Water redistilled from a Pyrex glass still.

Hydrofluoric acid: Likely to contain lead and should be purified by distillation in a platinum or plastic still.

Hydrochloric acid, 1+1: Use redistilled acid and Pyrex glass vessels for preparation of solution.

Hydrochloric acid, 0.02*N*: Add 3.33 ml 1+1 hydrochloric acid to redistilled water and dilute to 1 liter. Store in Pyrex bottle.

Ammonium hydroxide, sp gr 0.9: Distill concentrated ammonia or absorb the tank gas in water. Keep in a polyethylene bottle.

Citric acid, 50 percent w/v: Dissolve 250 g citric acid (British Drug House grade or equivalent) in approximately 300 ml water and dilute to 500 ml.

PROCEDURE

1. Add a 1-g sample to only one of two 100-ml platinum dishes. In the steps that follow, reference is made only to the sample, but it is understood that what is done to the sample must be done to the blank. Add 10 to 15 ml

hydrofluoric acid, 5 ml nitric acid, and 5 ml perchloric acid. Cover the dish with a platinum cover and digest on steam bath for 30 minutes. Remove cover and evaporate the solution on the steam bath to remove water.

2. Evaporate to fumes of perchloric acid, cover, and fume until organic matter is destroyed. Add 10 ml of water and evaporate to fumes of perchloric acid until about 1 ml remains. Cool. Add 2 ml 1+1 hydrochloric acid and 15 ml water and digest to dissolve the salts. If a clear solution is obtained, transfer the solution to a separatory funnel and dilute to 25 ml. If, however, undecomposed sample is present, filter it off and wash with water, reserving the filtrate. Ignite residue at about 500°C and fuse with 0.5 g sodium carbonate. Dissolve the melt with a slight excess of hydrochloric acid and combine the solution with the reserved solution. Evaporate the combined solution to about 18 ml and either transfer to a separatory funnel with enough water to make the total volume 25 ml, when the heavy-metal concentrations are known to be low, or transfer the solution to a volumetric flask and dilute to volume.
3. Take either the entire solution or an aliquot, depending on metal concentrations, add 10 ml citric acid solution; if necessary, add more to keep the iron and aluminum in solution. Neutralize the solution with ammonium hydroxide to a pH of 9.0, using a pH meter. Carry out steps 3 and 4 as rapidly as possible, otherwise samples containing significant amounts of calcium and phosphate may give some precipitation of calcium phosphate that may occlude lead and cause low recoveries of this element.
4. Add 5 ml of 0.05 percent dithizone and shake for 2 minutes. Draw off the carbon tetrachloride phase into another separatory funnel. Add 5 ml more of dithizone to the aqueous phase and shake for 2 minutes. Draw off the carbon tetrachloride phase and combine with that reserved. Repeat these steps until the final dithizone-carbon tetrachloride layer is green. Reject the water layer. If more than five extractions are required, use a smaller aliquot and start over.
5. Wash the combined carbon tetrachloride extracts twice with 5 ml of 1+99 ammonium hydroxide, reserving both the carbon tetrachloride and water layer. Add 2 ml dithizone to the water layer and shake. Draw off the dithizone layer and add it to the reserved carbon tetrachloride. It is important that the separated carbon tetrachloride be free of droplets of iron-containing solution.
6. Shake the combined carbon tetrachloride extracts for 2 minutes with 10ml of $0.02N$ hydrochloric acid. If the carbon tetrachloride remains red on shaking, add 1 to 2 ml of 0.05 percent dithizone before finishing the shaking. Draw off the carbon tetrachloride into another separatory funnel and shake vigorously for 2 minutes with a fresh 10-ml portion of $0.02N$ hydrochloric acid. Combine the two acid extracts; add a few drops of carbon tetrachloride and draw off to remove any colored droplets of carbon tetrachloride, which are added to the reserved carbon tetrachloride solution. Transfer the aqueous layer to a 25-ml volumetric flask, add 0.43 ml 1+1 hydrochloric acid, dilute to volume and mix. This solution is reserved for the determination of lead and zinc on separate aliquots of solution, as described on pages A–20 to A–22 The carbon tetrachloride layer contains the copper.
7. Evaporate the carbon tetrachloride containing the copper dithizonate to dryness in a 50- or 100-ml Pryex Erlenmeyer flask, add 0.5 ml nitric acid and 0.5 ml perchloric acid, and heat at 200° to 250°C until the solution is entirely colorless. Fume off all acid. Add 1 ml hydrochloric acid and 10 ml of water. Digest to dissolve the salts, cool and dilute to 50 ml with water in a volumetric flask. Reserve this solution for determination of copper by either the dithizone or cuproine methods described in the following section.

COPPER

DITHIZONE METHOD

[Range in shale: 0.0003 to 0.010 percent copper]

PRINCIPLES

The isolated copper in acid solution, obtained in step 7 of the previous procedure, is evaporated to dryness to remove excess acid. The residue is redissolved in $0.001N$ hydrochloric acid, the volume of the solution is adjusted to 10 ml at a pH of 3, and the copper dithizonate is extracted into carbon tetrachloride for spectrophotometric determination by the mixed-color method (Sandell, 1937).

APPARATUS AND REAGENTS

Beckman DU spectrophotometer.

Dithizone: 0.002 percent w/v purified dithizone in purified carbon tetrachloride. Prepare daily from the 0.05 percent dithizone solution that is stable if stored in a refrigerator.

Water: Redistill from an all-Pyrex apparatus.

Hydrochloric acid: Redistill.

Hydrochloric acid, $0.001N$.

Standard copper stock solution, 1 ml=0.5 mg copper: Dissolve 0.2500 g of pure copper by warming with 5 ml nitric acid. Add 10 ml of hydrochloric acid and evaporate the solution to dryness. Add 4 ml hydrochloric acid and dilute to 500 ml with water in a volumetric flask.

Standard copper dilute solution, 1 ml=2.5 micrograms copper: To a 5-ml aliquot of standard stock solution, add 20 ml hydrochloric acid and dilute to 1 liter in a volumetric flask.

PROCEDURE

1. Transfer a 5- or 10-ml aliquot of the solution containing the isolated copper (step 7, previous procedure) to a 50-ml beaker. Evaporate the aliquot, containing as much as 5 micrograms copper, to dryness on a steam bath. Dry the residue in an oven at 120°C to expel all acid; cool the beaker, pipet 5 ml of $0.001N$ hydrochloric acid, and warm briefly to dissolve the salts. Cool.
2. Transfer the solution to a dry separatory funnel. Rinse the beaker with 5 ml $0.001N$ hydrochloric acid from pipet and add the solution to the funnel that now contains a total volume of 10 ml.
3. Pipet 10 ml 0.002 percent dithizone and shake the solution for 2 minutes. The color of the solution should deviate from that of a pure copper dithizonate solution. (If the color of the carbon tetrachloride is red violet, too much copper is present, and a smaller aliquot of sample and blank solution should be taken in step 1.)

4. Draw off the carbon tetrachloride layer through a filter paper plug, rejecting the first 2 ml.
5. Determine the absorbance of the solution at 510 mμ, using 0.002 percent dithizone as a reference solution.
6. Calculate the percentage of copper in the sample.

STANDARD CURVE

Take aliquots of standard copper solutions containing 1, 2.5, and 5 micrograms of copper and follow steps 1 to 5 of the procedure. It is important that the volumes of the aliquoted solutions be made to 10 ml for extraction with 10 ml dithizone, as the unknown solutions are extracted under these conditions.

ALTERNATIVE 2, 2′ BIQUINOLINE METHOD

[Range in shale: 0.0003 to 0.010 percent copper]

PRINCIPLES

The method is substantially that of Hoste and others (1953) with modifications according to Cheng and Bray (1953). The intensity of the copper biquinoline color is independent of pH within the range 2 to 9. The following anions and cations, in the ratio of 1,000 to 1 of copper, do not interfere with the determination: aluminum, arsenic, barium, calcium, cadmium, cobalt, iron, lithium, magnesium, molybdenum(VI), manganese, ammonium, nickel, antimony(III), tin(II), strontium, titanium, vanadium(V), tungsten(VI), zinc, acetate, borate, bromide, chloride, chlorate, perchlorate, tartrate, nitrate, sulfate, and phosphate. There may be interference from oxalate, cyanide, citrate, and rhodamide.

REAGENTS

Isoamyl alcohol: Distill from a Pyrex still and store the reagent in a dry Pyrex bottle.

Cuproine (2,2′biquinoline), 0.02 percent w/v in isoamyl alcohol: The solution obtained should be colorless. If the solution is yellow, the reagent is impure and should not be used.

Tartaric acid, 10 percent w/v.

Acetate buffer. Dissolve 8.2 g of sodium acetate and 5.8 ml acetic acid in water, and make to 200 ml in a volumetric flask.

Sodium hydroxide solution, 20 percent w/v. Store in polyethylene bottle.

Hydroxylamine hydrochloride, 15 percent w/v.

Standard copper solution. See Copper, dithizone method (p. A–18).

PROCEDURE

1. Take a 10- or 20-ml aliquot from the reserved 50-ml solution containing the copper and transfer it to a separatory funnel. Adjust the volume to 20 ml with water, if a 10-ml aliquot is used. Alternatively, when only copper is to be determined and the dithizone separation has not been made, take a 20-ml aliquot of the acid sample solution at step 2 of the isolation procedure (p. A–18) and proceed with steps 2 to 6 below.
2. Add 1 ml tartaric acid, 1 ml of hydroxylamine hydrochloride, and then sodium hydroxide solution until a microdrop on a universal paper indicates a pH of 4 to 5.
3. Add 3 ml buffer solution; mix and let stand a few minutes.
4. Extract with a 20-ml portion of the cuproine solution for 2 minutes (a smaller portion of solution is not sufficient for a 5-cm cell). Let layers settle, insert a plug of filter paper in the stem of the funnel, and draw off the purplish isoamyl alcohol layer.
5. Measure the absorbance of the solution at 546 mμ against a blank prepared by taking 20 ml of water through steps 1 to 5.
6. Calculate the percentage of copper in the sample.

STANDARD CURVE

Aliquot standard copper solutions containing 0, 5, 20, and 50 micrograms of copper and dilute to 20 ml with water. Follow steps 1 through 5 of the procedure, using the blank solution for reference in the absorbance measurements.

PRECISION OF COPPER DETERMINATIONS

Copper was determined on the 80 samples in laboratory B with the dithizone method as described. The ranges of concentration for copper in the shale were from 0.0005 to 0.005 percent (57 samples) and from 0.005 to 0.05 percent (23 samples). The results of replicates are given in table 20, those on the hidden splits in table 21, and those on the check samples in table 22. On the check samples, the results of B, A, and A_1 were obtained with the dithizone method. The results of A_2 were determined with the dithizone separation method but were completed with the biquinoline method, and those of A_3 were determined with biquinoline without prior dithizone separation. The results of A_4 were obtained with the neocuproine (Smith and McCurdy, 1952) direct extraction of the copper without prior separation.

Graphical comparison of the data of B with those of A, A_1, A_2, A_3, and A_4 is given on figure 7.

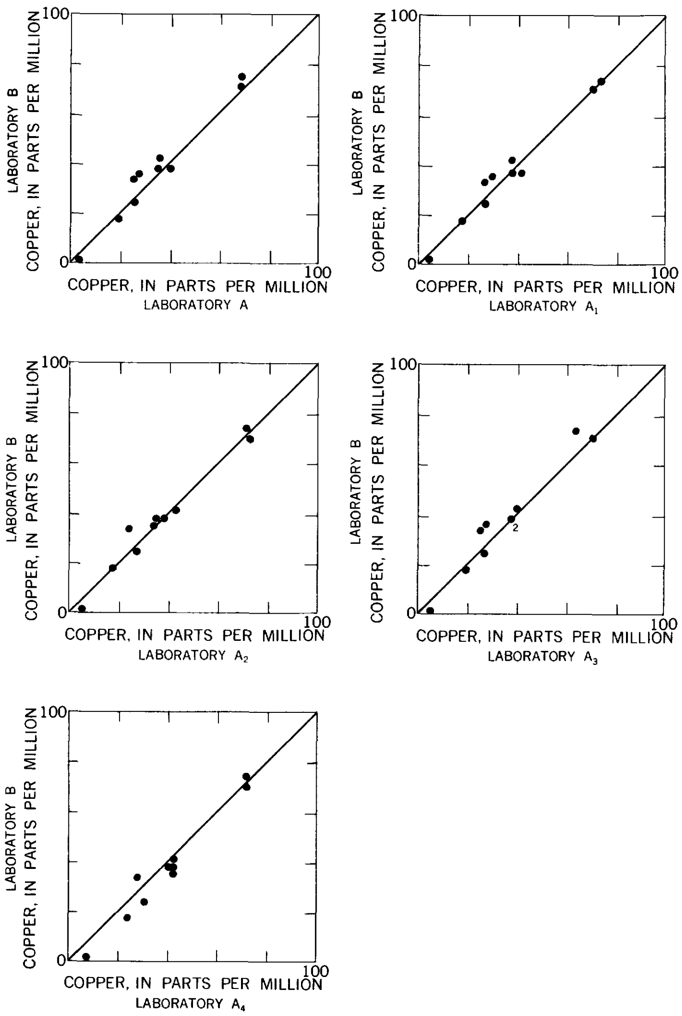

FIGURE 7.—Comparison of copper determinations of B with those of A, A_1, A_2, A_3 and A_4. Plots that coincide are indicated with the number involved.

TABLE 20.—*Replicate determinations*[1] *of copper, in percent, by laboratory B*

[Analysis by dithizone method; Joseph Dinnin, analyst. Add 259500 to all sample numbers, except 00 to 05 to which add 259600, to form serial numbers]

41	0.0003	0.0005	38	0.0030	0.0030
54	.0011	.0014	78	.0036	.0038
88	.0011	.0015	58	.0063	.0066
60	.0018	.0020	56	.0070	.0087
65	.0024	.0024	63	.0070	.0078
05	.0028	.0032	95	.0097	.010
52	.0029	.0034			

[1] Precision and reliability of determinations:

Range	*Standard deviations*	*Number of comparisons*
0.0005–0.005	0.00027	9
.005– .05	.00068	4

TABLE 21.—*Determinations*[1] *of copper, in percent, in hidden splits by laboratory B*

[Analysis by dithizone method; Joseph Dinnin, analyst. Add 259500 to all sample numbers, except 00 to 05 to which add 259600, to form serial numbers. Groups indicate the samples that were duplicates]

33	0.0036	53	0.0049	80	0.0032
97	.0030	04	.0059	00	.0035
49	.0071	65	.0024	82	.0084
96	.0072	98	.0024	02	.0080
99	.0077				
03	.0090	68	.0039	86	.0040
		01	.0040	05	.0030

[1] Precision and reliability of determinations:

Range	*Standard deviations*	*Number of comparisons*
0.0005–0.005	0.00038	5
.005– .05	.00080	8

TABLE 22.—*Determinations*[1] *of copper, in percent, in check samples*

[Add 259500 to each sample number to form serial number]

Sample	B	A	A_1	A_2	A_3	A_4	Mean	Difference (max—min)	Standard deviation
28	0.0018	0.0020	0.0018	0.0018	0.0019	0.0024	0.0020	0.0006	0.00024
33	.0036	.0028	.0030	.0035	.0027	.0043	.0033	.0016	.00063
37	.0001	.0004	.0004	.0005	.0005	.0008	.0005	.0007	.00028
39	.0025	.0026	.0027	.0028	.0026	.0031	.0027	.0006	.00024
46	.0038	.0036	.0039	.0038	.0037	.0042	.0038	.0006	.00024
48	.0038	.0041	.0042	.0036	.0037	.0043	.0040	.0007	.00028
49	.0071	.0070	.0071	.0072	.0071	.0072	.0071	.0002	.00008
63	.0074	.0070	.0074	.0071	.0064	.0072	.0071	.0010	.00040
92	.0042	.0037	.0038	.0043	.0040	.0043	.0041	.0006	.00024
94	.0034	.0026	.0027	.0024	.0025	.0028	.0027	.0010	.00040

[1] Precision and reliability of determinations:

	Range			
	0.0005 to 0.005		0.005 to 0.05	
	Standard deviation	Number of comparisons	Standard deviation	Number of comparisons
B, A	0.00034	8	0.00020	2
B, A_1	.00029	8	.00026	2
B, A_2	.00014	8	.00016	2
B, A_3	.00034	8	.00050	2
B, A_4	.00040	8	.00011	2

B . Dithizone method; Joseph Dinnin, analyst.
A . Dithizone method; William Goss, analyst.
A_1. Dithizone method; William Goss and Irving Frost, analysts.
A_2. Alternative method, dithizone separation-biquinoline determination; William Goss, analyst.
A_3. Biquinoline method, no prior dithizone separation; William Goss, analyst.
A_4. Direct neocuproine method (Smith and McCurdy, 1952); Dwight Skinner, analyst.

ZINC, DITHIZONE METHOD

[Range in shale: 0.001 to 0.040 percent zinc]

PRINCIPLES

Zinc dithizonate is extracted with carbon tetrachloride from an acid solution at a pH of about 4.8 in in the presence of thiosulfate to inhibit coextraction of lead, copper, silver, gold, mercury, bismuth, and cadmium (Fischer and Leopoldi, 1937). The reaction of zinc ions with dithizone at a pH of 4.8 is slow and incomplete; the volumes of solutions and time for extraction must be rigorously controlled for both the standard and unknown solutions.

REAGENTS

Dithizone, 0.0025 percent (w/v), in pure carbon tetrachloride.

Acetate buffer: Add 16.4 g sodium acetate and 11.6 ml glacial acetic acid to water and dilute to 200 ml. Remove heavy metals by shaking the solution with 0.01 percent dithizone in carbon tetrachloride. Filter the solution through a small quantitative paper to remove droplets of carbon tetrachloride.

Sodium thiosulfate, 25 g of sodium thiosulfate pentahydrate in 100 ml of water.

Standard stock solution of zinc, 1 ml=0.5 mg zinc: Dry reagent grade zinc sulfate at 450°C. Weigh 0.2469 g of the anhydrous salt, dissolve it in 1+99 hydrochloric acid, make the solution to 200 ml volume with 1+99 hydrochloric acid.

Standard dilute solution of zinc, 1 ml=2.5 micrograms zinc: Dilute 5 ml of the stock solution with 1+99 hydrochloric acid to 1 liter in a volumetric flask.

PROCEDURE

1. Dilute 5 ml of the reserved acid extract solution containing the lead and zinc with water to 25 ml in a volumetric flask.
2. Transfer 5 ml of the diluted solution to a small beaker and evaporate the solution to remove acid. Pipet 5 ml of 0.02*N* hydrochloric acid to the beaker and warm the solution briefly to dissolve the salts. Transfer the solution to a separatory funnel.
3. Rinse the beaker with 5 ml of water and transfer it to the separatory funnel.
4. Add 5 ml of buffer solution to the funnel and 1 ml of sodium thiosulfate solution.
5. Mix the solution and shake it vigorously for 3 minutes with 10 ml of 0.0025 percent dithizone in carbon tetrachloride.
6. Draw off the carbon tetrachloride layer through a filter-paper plug, rejecting the first 2 ml.
7. Determine the absorbance of the filtered carbon tetrachloride solution at 530 mμ against 0.0025 percent dithizone in carbon tetrachloride as a reference solution.
8. Calculate the percentage of zinc in the sample.

STANDARD CURVE

Transfer aliquots of standard solution containing 0, 2.5, 5, and 10 micrograms of zinc to small beakers and evaporate the solutions to dryness. Proceed with the method, steps 2 through 7, taking care to shake the standard solutions in the same manner (step 5) and for the same length of time as was done with the unknown solutions.

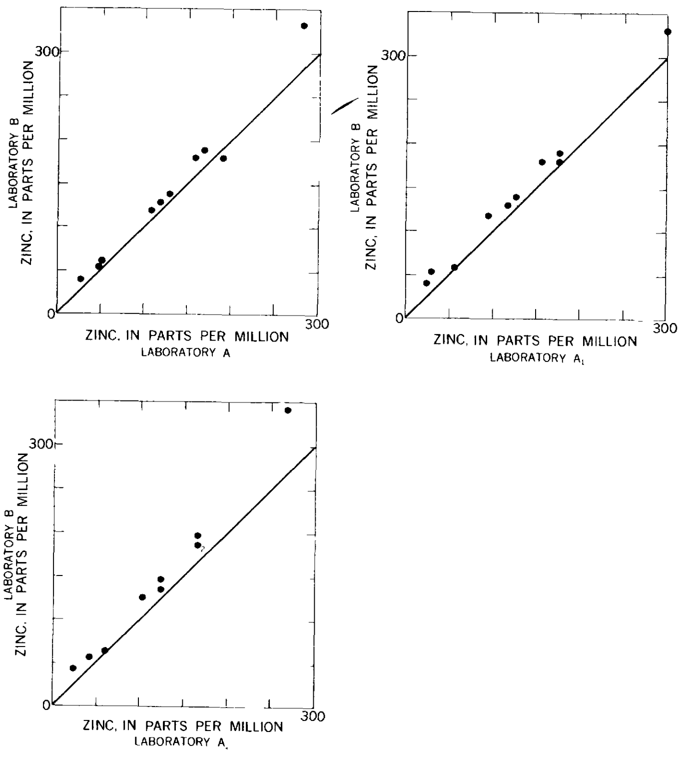

Figure 8.—Comparison of zinc determinations of B with those of A, A_1, and A_2. Plots that coincide are indicated with the number involved.

PRECISION OF ZINC DETERMINATIONS

Zinc was determined on the 80 samples of shale in laboratory B by the dithizone method described. The ranges of concentration for zinc were from 0.0005 to 0.005 percent (4 samples) and from 0.005 to 0.05 percent (76 samples). The results on replicate determinations of zinc by one chemist are given in table 23, those on hidden splits in table 24, and those on the check samples in table 25. On the check samples the results of B, A, and A_2 were obtained with the dithizone method, whereas those of A_1 were obtained with the zincon method of Rader and others (1960).

Figure 8 shows the results of A, A_1, and A_2 plotted against those of B.

Table 23.—*Replicate determinations*[1] *of zinc, in percent, by laboratory B*

[Analysis by dithizone method; Joseph Dinnin, analyst. Add 259500 to each sample number to form serial number]

41	0.0040	0.0043	52	0.011	0.014
54	.0083	.0090	65	.012	.012
60	.0085	.0087	78	.013	.013
38	.011	.013	58	.025	.027

[1] Precision and reliability of determinations in the range 0.005 to 0.05: standard deviation, 0.0010; number of comparisons, 8.

Table 24.—*Determinations*[1] *of zinc, in percent, in hidden splits by laboratory B*

[Analysis by dithizone method; Joseph Dinnin, analyst. Add 259500 to all sample numbers, except 00 to 05 to which add 259600, to form serial numbers. Groups indicate the samples that were duplicates]

33	0.018	53	0.015	80	0.011
97	.020	04	.014	00	.012
49	.012	65	.012	82	.038
96	.012	98	.012	02	.040
99	.012				
03	.012	68	.016	86	.013
		01	.017	05	.014

[1] Precision and reliability of determinations in the range 0.005 to 0.05: standard deviation, 0.00078; number of comparisons, 13.

Table 25.—*Determinations*[1] *of zinc, in percent, in check samples*

[Add 259500 to each sample number to form serial number]

Sample	B	A	A_1	A_2	Mean	Difference (max—min)	Standard deviation
28	0.0060	0.0054	0.0059	0.0057	0.0058	0.0006	0.00029
33	.018	.019	.018	.016	.018	.0003	.00015
37	.0040	.0029	.0029	.0022	.030	.0018	.00088
39	.014	.013	.013	.012	.013	.0020	.00097
46	.019	.017	.018	.016	.018	.0030	.0015
48	.033	.028	.030	.026	.029	.0070	.0034
49	.012	.011	.0097	.010	.011	.0093	.0045
63	.0053	.0050	.0034	.0042	.0045	.0019	.00092
92	.018	.016	.016	.016	.017	.0020	.00097
94	.013	.012	.012	.012	.012	.0010	.00049

[1] Precision and reliability of determinations in the range 0.005 to 0.05:

	Standard deviation	*Number of comparisons*
B, A	0.0014	10
B, A_1	.0011	10
B, A_2	.0020	10
All data	.0013	60

B. Dithizone method; Joseph Dinnin, analyst.
A. Dithizone method; Irving Frost, analyst.
A_1. Modified zincon method; Claude Huffman and Howard Lipp, analysts.
A_2. Dithizone method; William Goss, analyst.

LEAD, DITHIZONE METHOD

[Range in shale: 0.0003 to 0.004 percent lead]

PRINCIPLES

Lead is determined spectrophotometrically after extraction with dithizone in chloroform from an ammoniacal cyanide-citrate solution at a pH of slightly greater than 9. Cyanide prevents the reaction of zinc and small amounts of other metals.

REAGENTS

Sodium citrate, 10 percent w/v: Dissolve 10 g of trisodium citrate in 100 ml water and 0.5 ml ammonium hydroxide. Shake the solution with small portions of 0.01 percent dithizone in chloroform until the last portion is colored green. Reject the chloroform and store the solution in a polyethylene bottle.

Dithizone, 0.002 percent w/v, in chloroform: Prepared by dilution of a more concentrated dithizone solution in chloroform.

Potassium cyanide, 10 percent w/v: A milliliter of solution should impart no pink color to the chloroform phase when diluted with 2 ml of water and shaken with a milliliter or two of 0.002 percent dithizone. If necessary, potassium cyanide can be freed from lead as follows: Prepare an approximately saturated solution (50 g in 100 ml of solution) and shake with successive small portions of 0.01 percent dithizone in chloroform until a green color is obtained in the final extract. Extract the dithizone remaining in the aqueous layer with chloroform. Dilute the aqueous phase to 500 ml with water and store in polyethylene.

Hydrochloric acid, 1+99.

Ammonia-cyanide-citrate solution: Transfer 20 ml of 10 percent potassium cyanide solution and 5 ml of 10 percent sodium citrate solution to a 100-ml volumetric flask. Add a predetermined amount of pure concentrated ammonium hydroxide to the solution and dilute to 100 ml. The amount of ammonium hydroxide needed is such that when a 2-ml aliquot from the final volume of 100 ml is mixed with 10 ml of 1+99 hydrochloric acid a pH of 9.4 to 9.6 (measured with a meter) will be obtained. Tests show that about 20 ml of concentrated ammonium hydroxide generally are required for the 100 ml of mixed solution. Store the final solution in a polyethylene bottle.

Standard lead stock solution, 1 ml=0.5 mg lead: Dissolve 0.1599 g of dried lead nitrate to make exactly 200 ml of solution in 1+99 hydrochloric acid.

Standard lead dilute solution, 1 ml=2.5 micrograms lead: Take 5 ml of stock solution and dilute to 1 liter with 1+99 hydrochloric acid.

PROCEDURE

1. Transfer a 10-ml aliquot of the reserved acid extract solution containing the isolated lead and zinc to a 60-ml separatory funnel. If a smaller aliquot is used, add enough 1+99 hydrochloric acid to make the total volume 10 ml.
2. Add 2 ml of the ammonia-cyanide-citrate solution.
3. Shake the solution with 10 ml of 0.002 percent dithizone in chloroform for 5 minutes. It is important to have equal volumes of solution and dithizone for this extraction.
4. Draw off the chloroform layer through a filter-paper plug, rejecting the first 2 ml of solution
5. Determine the absorbance of the filtered chloroform solution at 520 mμ against 0.002 dithizone in chloroform as reference solution.
6. Calculate the percentage of lead in the sample.

STANDARD CURVE

Transfer aliquots of standard solution containing 0, 2.5, 5, and 12.5 micrograms of lead to separatory funnels. Pipet sufficient 1+99 hydrochloric acid to make the total volume exactly 10 ml. Proceed with steps 2 to 5 of the procedure.

PRECISION OF LEAD DETERMINATIONS

Lead was determined on the 80 samples in laboratory B with the dithizone method described. The range of concentration for lead in all the 80 samples of shale was from 0.0005 to 0.005 percent. The results on replicate determinations are given in table 26, those on the hidden splits in table 27, and those on the check samples in table 28. Two gross errors are apparent in the data, one in table 27 and one in table 28.

Figure 9 compares the results for lead of A and A_1 with those of B.

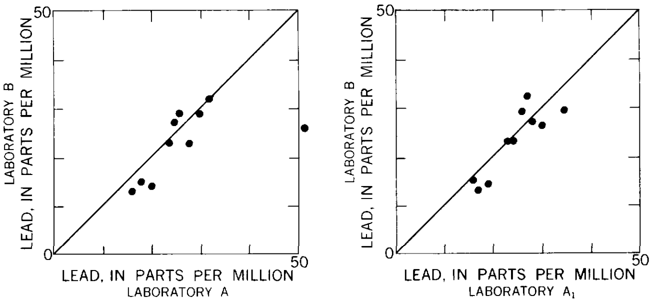

FIGURE 9.—Comparison of lead determinations of B with those of A and A_1.

TABLE 26.—*Replicate determinations*[1] *of lead, in percent, by laboratory B*

[Analysis by dithizone method; Joseph Dinnin, analyst. Add 259500 to each sample number to form serial number]

58	0.0012	0.0018	61	0.0018	0.0019
63	.0013	.0015	65	.0024	.0024
71	.0014	.0014	78	.0025	.0028
60	.0015	.0018	54	.0027	.0034
38	.0018	.0018	44	.0038	.0043
50	.0018	.0023	56	.0038	.0039
52	.0018	.0023			

[1] Precision and reliability of determinations in the range 0.00005 to 0.005: standard deviation, 0.00026; number of comparisons, 13.

TABLE 27.—*Determinations*[1] *of lead, in percent, in hidden splits by laboratory B*

[Analysis by the dithizone method; Joseph Dinnin, analyst. Add 259500 to all sample numbers, except 00 to 05 to which add 259600, to form the serial numbers. Groups indicate the samples that were duplicates]

33	0.0013	53	0.0013	80	0.0023
97	.0038	04	.0015	00	.0025
49	.0026	65	.0024	82	.0029
96	.0027	98	.0023	02	.0033
99	.0031				
03	.0030	68	.0024	86	.0018
		01	.0024	05	.0023

[1] Precision and reliability of determinations in the range 0.0005 to 0.005: standard deviation, 0.00053; number of comparisons, 13.

TABLE 28.—*Determinations*[1] *of lead, in percent, in check samples*

[Add 259500 to each sample number to form serial number]

Sample	B	A	A_1	Mean	Difference (max–min)	Standard deviation
28	0.0015	0.0018	0.0016	0.0016	0.0003	0.00018
33	.0013	.0016	.0017	.0015	.0004	.00024
37	.0032	.0032	.0027	.0030	.0005	.00030
39	.0027	.0025	.0028	.0027	.0003	.00018
46	.0029	.0026	.0026	.0027	.0003	.00018
48	.0029	.0030	.0034	.0031	.0005	.00030
49	.0026	.0051	.0030	.0036	.0025	.0015
63	.0014	.0020	.0019	.0018	.0006	.00035
92	.0023	.0028	.0024	.0025	.0005	.00030
94	.0023	.0024	.0023	.0023	.0001	.00006

[1] Precision and reliability of determinations in the range 0.0005 to 0.005:

	Standard deviation	*Number of comparisons*
B, A	0.00060	10
B, A_1	.00026	10
All data	.00047	30

B. Dithizone method; Joseph Dinnin, analyst.
A. Dithizone method; Irving Frost, analyst.
A_1. Dithizone method; William Goss, analyst.

ARSENIC

ACID DIGESTION, HETEROPOLY BLUE METHOD

[Range in shale: 0.0001 to 0.05 percent arsenic]

PRINCIPLES

Arsenic is distilled as arsenious chloride after reduction with bromide and hydrazine sulfate, and is determined spectrophotometrically with the heteropoly blue method (Maechling and Flinn, 1930; Morris and Calvery, 1937; and Sandell, 1950, p. 178–183). The blue color is stable for at least 24 hours. Germanium distills with the arsenic but does not interfere. Antimony, tin, and mercury may also distill with the arsenic, unless the temperature of distillation is below 108°C. The distillation of selenium is largely prevented if sufficient hydrazine sulfate is used. Small amounts of selenium in the distillate do not interfere. Sample decomposition and solution is made with nitric, perchloric, and sulfuric acids. Tests show that arsenic is completely recovered from the shale and associated sediments by using this method. Hydrofluoric acid is avoided for sample decomposition, because of possible loss of arsenic as volatile fluorides and because subsequent attack on the glassware can introduce extraneous arsenic and silica.

APPARATUS AND REAGENTS

Beckman DU spectrophotometer supplied with 1- and 5-cm cells.

Pyrex glass still, 125-ml capacity: Erlenmeyer flasks with standard 19/38 taper outer joints, supplied with condenser and spray trap. The same flask is used for both digestion and distillation of the sample.

Hot plate equipped with motor drive for variable speed oscillation.

Acids, low in As (that is, about 1 microgram per 100 ml or less): Hydrochloric, nitric, sulfuric, and perchloric acids are required and should be tested for arsenic.

Sodium hydroxide, solution about 1*N*.

Hydrazine sulfate.

Potassium bromide.

Glass beads.

Mixed reagent for color development:

Solution A. Dissolve 10 g ammonium molybdate, $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$, in 139 ml sulfuric acid and dilute to 1 liter.

Solution B. Dissolve 0.75 g hydrazine sulfate in 500 ml distilled water.

Solution C. Make this solution fresh as needed. Dilute 50 ml solution A to approximately 450 ml with water, add 15 ml solution B, and make to 500-ml volume.

Standard arsenic solution, 1 ml = 1 mg As: Dissolve 0.1320 g arsenous oxide (National Bureau of Standards standard sample 83a, As_2O_3) in 5 ml 1*N* sodium hydroxide and make the solution slightly acid with hydrochloric acid. Dilute to 1 liter.

Dilute standard arsenic solution, 1 ml = 10 micrograms As: Dilute 10 ml of standard stock solution to 100 ml.

PROCEDURE

1. Weigh 1.0 g of sample and transfer to a 125-ml Erlenmeyer flask with a 19/38 taper outer joint.
2. Add 10 ml nitric acid to the flask and place on steam bath for 15 minutes.
3. Remove flask from the steam bath, cool, add 5 ml sulfuric acid, 7 ml perchloric acid, and several glass beads.
4. Place flask on the shaking hot plate and fume just until the first sign of sulfuric acid fumes. Cool.
5. Repeat steps 3 and 4 if organic matter is detected after the first treatment. Cool.
6. Rinse down the sides and neck of the flask with at least 25 ml water; place on the shaking hot plate and bring to incipient fuming again to remove residual nitric acid. Cool.
7. Add 15 ml water to the flask and cool flask in pan of ice water; add 20 ml hydrochloric acid, 0.5 g potassium bromide, and 1 g hydrazine sulfate.
8. Connect flask to the all-glass distilling apparatus. Collect the distillate in a 100-ml Erlenmeyer flask immersed in ice water and containing 10 ml cold water. Keep the delivery tip under water during the entire distillation. Experiments show that the solution starts to boil at 100°C and the temperature rises to 108°C as the hydrochloric acid distills over. This temperature must not be exceeded.
9. Continue the distillation only until 25 ml distillate is caught in the receiving flask or a total volume of 35 ml including the water added (usually about 30 to 35 minutes are required).
10. Add 10 ml concentrated nitric acid to the distillate and evaporate to dryness on a hot plate.
11. Place the flask in a drying oven at 130°C for one-half hour to volatilize traces of nitric acid left in the flask.
12. Add exactly 25 ml color reagent (solution C) to the flask.
13. Heat the covered flask on the steam bath for 20 minutes to develop the color. Cool.
14. When the solution is light blue ($<$50 micrograms As), transfer a portion to a 1-cm cell and complete the determination (steps 16 and 17).
15. When color of the soultion is dark blue (high in As), transfer the solution to a 200-ml volumetric flask with 0.5*N* sulfuric acid solution and dilute to volume with the 0.5*N* acid. No additional color reagent need be added, unless the arsenic content exceeds 400 micrograms.
16. Determine the absorbance of the solution at 840 mμ, using 1-cm cells. A reagent blank carried through the method is used as a reference.
17. Calculate the percentage of arsenic in the sample.

STANDARD CURVE

A blank and standards containing 5, 10, 20, 30 and 40 micrograms of arsenic are carried through the procedure to establish a standard working curve for a 25-ml volume. A curve for 200 ml is similarly prepared from aliquots of standard solution containing 100, 200, 300 and 400 micrograms arsenic.

ALTERNATIVE FUSION-HETEROPOLY BLUE METHOD

[Range in shale: 0.0001 to 0.05 percent arsenic]

PRINCIPLES

The sample is decomposed by fusing with potassium carbonate-magnesium oxide mixture that destroys organic matter at the same time. Sodium carbonate cannot be substituted for potassium carbonate in the fusion mixture, because, in the distillation step, sodium chloride precipitates from the highly concentrated hydrochloric acid solution used. Although potassium chloride also tends to precipitate, this occurs only in the cold solution, because potassium chloride is soluble in the hot solution during the distillation. No provision is made to remove silica in this procedure; however silica remains in solution through most of the distillation, precipitating near the end.

APPARATUS AND REAGENTS

The appartus and reagents described in the previous method are required, except that a 200- or 250-ml distilling flask replaces the 125-ml flask used in the other method.

PROCEDURE

1. Take a 0.25- to 0.5-g sample into a 30-ml platinum crucible and add 2 to 3.5 g of fusion mixture (3 parts potassium carbonate to 1 part magnesium oxide, by weight, intimately mixed). Mix the charge. Sprinkle 0.5 g of fusion mixture over the top as a cover. Place the crucible in a furnace at 650°C and heat for 30 minutes. Gradually raise the temperature to 900°C and heat at 900°C for 30 minutes more or until organic matter is destroyed. Cool.
2. Place the crucible in a 200-ml tall-form beaker. Add 20 ml water, but do not add alcohol even if manganate is present. Place the beaker in a cold-water bath, cover, and add through the lip 60 ml concentrated hydrochloric acid, gently agitating the solution. Allow the melt to disintegrate in the cold. Remove the crucible and rinse it with 10 ml hydrochloric acid.
3. Transfer the solution to a 200-ml distillation flask and rinse the beaker with 10 ml hydrochloric acid (total volume solution, 100 ml). Add 2 ml hydrobromic acid and 0.5 g hydrazine sulfate crystals. Distill the solution into a tall-form beaker containing 50 ml of cold water. The condenser tip should dip just into the water, and the beaker is gradually lowered as distillate is collected. During the distillation, the beaker should be kept in an ice bath. Collect 50 ml of distillate.
4. Add 25 ml nitric acid to the distillate and evaporate the solution to dryness on a steam bath. Then heat the beaker in an oven at 130°C for 30 minutes to remove free nitric acid.
5. Add exactly 25 ml of mixed color reagent to the beaker. Cover and heat the solution for 20 minutes on the steam bath to develop color. Cool.
6. Determine the absorbance of the solution in a 1-cm cell at 840 mμ, using a reagent blank carried through the method as a reference.
7. Calculate the percentage of arsenic in the samples.

PRECISION OF ARSENIC DETERMINATIONS

Arsenic was determined on the 80 samples of shale in laboratory A by using the acid decomposition method described. The ranges of concentration for arsenic were from 0.0001 to 0.0005 percent (10 samples), 0.0005 to 0.005 percent (64 samples), and 0.005 to 0.05 percent (6 samples). The results on replicate determinations are given in table 29, those on the hidden splits in table 30, and those on the check samples in table 31. Figure 10 compares the determinations of A with B and of A with B_1. The data show that all the arsenic is obtained by simple acid digestion of the shale.

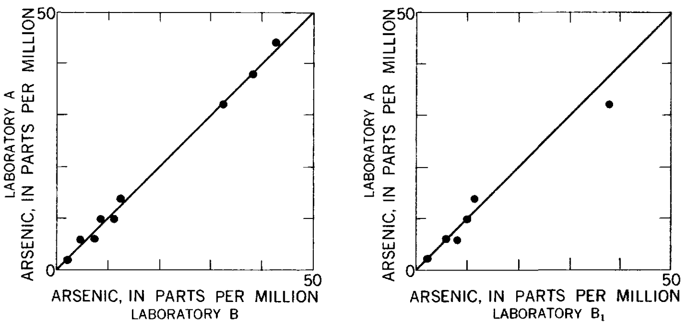

FIGURE 10.—Comparison of arsenic determinations of A with those of B and B_1.

TABLE 29.—*Replicate determinations*[1] *of arsenic, in percent, by laboratory A*

[Analysis by acid decomposition method; Claude Huffman, analyst. Add 259500 to all sample numbers, except 00 to 05 to which add 259600, to form serial numbers]

36	0.0003	0.0004	40	0.0010	0.0010	88	0.0019	0.0020
93	.0003	.0005	05	.0012	.0012	26	.0037	.0039
42	.0004	.0005	85	.0015	.0016	56	.0039	.0039
55	.0009	.0009	78	.0016	.0016	02	.0044	.0044
30	.0009	.0010	72	.0016	.0017	91	.0053	.0053
46	.0009	.0010	68	.0018	.0018	61	.0098	.010

[1] Precision and reliability of determinations:

Range	*Standard deviations*	*Number of comparisons*
0.0005–0.005	0.000056	16
.005 – .05	.00010	2

TABLE 30.—*Determinations*[1] *of arsenic, in percent, in hidden splits by laboratory A*

[Analysis by acid decomposition method; Claude Huffman, analyst. Add 259500 to all sample numbers, except 00 to 05 to which add 259600, to form serial numbers. Groups indicate the samples that were duplicates]

33	0.0014	53	0.0021	80	0.0013
97	.0014	04	.0022	00	.0013
49	.049	65	.0009	82	.0044
96	.049	98	.0009	02	.0044
99	.049				
03	.050	68	.0018	86	.0011
		01	.0018	05	.0012

[1] Precision and reliability of determinations:

Range	*Standard deviations*	*Number of comparisons*
0.0005–0.005	0.000037	7
.005 – .05	.00055	6

TABLE 31.—*Determinations*[1] *of arsenic, in percent, in check samples*

[Add 259500 to each sample number to form serial number]

Sample	A	B	B_1			Mean	Difference (max—min)	Standard deviation
28	0.0006	0.0005	0.0006	0.0003	0.0007	0.0005	0.0004	0.00017
33	.0014	.0013	.0012			.0013	.0002	.00012
37	.0002	.0002	.0003	.0002		.0002	.0001	.00005
39	.0006	.0007	.0007	.0006	.0007	.0007	.0001	.00005
46	.0010	.0009	.0010			.0010	.0001	.00005
48	.0032	.0032	.0038			.0034	.0006	.00035
49	.049	.048	.048			.048	.001	.0005
63	.0038	.0038	--------			.0038	0	0
92	.0044	.0043	--------			.0044	.0001	.00009
94	.0010	.0011	--------			.0011	.0001	.00009

[1] Precision and reliability of determinations:

	Range			
	0.0005 to 0.005		0.005 to 0.05	
	Standard deviation	Number of comparisons	Standard deviation	Number of comparisons
A, B	0.00057	9	0.00022	1
All data	.00013	37	.00057	3

A. Acid decomposition method; Claude Huffman, analyst.
B. Acid decomposition method; Irving May and Frank Grimaldi, analysts.
B_1. Alternative method, fusion decomposition; Irving May and Frank Grimaldi, analysts.

SELENIUM, DISTILLATION, VISUAL-ESTIMATION METHOD

[Range in shale: 0.0001 to 0.02 percent selenium]

PRINCIPLES

Selenium is distilled as the tetrabromide from a sulfuric acid solution of the sample that has been freed of organic matter by oxidation with nitric acid in the presence of mercury as a catalyst (Robinson and others, 1934; Mathews and others, 1937; Curl and Osborn, 1938; and Wernimont and Hopkinson, 1940). Only germanium and arsenic accompany the selenium under the conditions outlined for the distillation. These elements do not interfere when selenium in the distillate is precipitated in the elemental form, with sulfur dioxide, from strong acid solutions (3 to 6*N* acid). The reduced selenium from the distillate is redissolved and reprecipitated in order to purify and concentrate it in a total volume of 2 ml of solution. The intensity of the color imparted to the solution by the suspension of elemental selenium is compared visually against known standards treated in the same manner. Selenium in amounts greater than 15 micrograms, noted at time of the first reduction, is redissolved in 10- or 25-ml volumes and aliquots taken for reduction and estimation of selenium. Volumetric or gravimetric procedures for completion of the selenium determination were not used for the shale because of the relatively low concentration of selenium in the samples.

APPARATUS AND REAGENTS

Pyrex glass stills, standard taper joints, 125- to 250-ml capacities, supplied with condensers.

Color comparison light source: An oblong box, 9 cm wide by 19 cm long by 9 cm deep, with a slit for light passage, 0.1 by 10 cm, positioned in the top face of the box directly over a 25 watt tungsten filament tubular lamp, about 10 cm long, that is centered in the box by a socket mounted on one end of the box.

Vacuum pump and manifold, connected through a vapor trap to small bell-jar filter cells (Fisher Filtrators) equipped with filter sticks.

Fisher Filtrators, 7.5 by 12 cm, with an opening in the top for filter sticks and removable glass plate on the bottom.

Filter sticks, 3.5 by 1.2 cm with 9-cm stem length; medium to fine porosity.

Standard glass-fritted crucibles, about 20-ml size and medium porosity.

Tall-form flat-bottom glass vials with plastic screw crown: Capacities of 8 and 30 ml are preferable, but other tubes can be used.

A wire or metal rack designed to hold a series of vials partly immersed in a shallow pan containing water.

Sulfur dioxide: Compressed gas in cylinder with bleeder valve.

Sulfuric, nitric, red-fuming nitric, and 48 percent hydrobromic acids, all reagent grade.

Catalyst-acid: Five percent w/v mercuric oxide in concentrated nitric acid.

Bromine-hydrobromic acid mixture: Add 2 ml of bromine to 100 ml of 9*N* hydrobromic acid.

Hydroxylamine hydrochloride, small crystals.

Standard selenium stock solution, 1 ml = 1 mg Se: Dry selenious acid in an oven to remove water and form selenium dioxide. Precautions must be taken because the material is hygroscopic. Weigh 0.2811 g of selenium dioxide, transfer to a 200-ml volumetric flask with about 50 ml water, add 25 ml 2 percent bromine-hydrobromic acid solution, and dissolve the compound without heating. Dilute to volume with water. Alternatively, dissolve 0.2000 g selenium metal in 25 ml bromine-hydrobromic acid solution, dilute to 200 ml with water, and standardize the solution gravimetrically.

Standard dilute selenium solution, 1 ml = 10 micrograms Se: Dilute 5 ml of stock solution to 500 ml with (2+1) hydrobromic acid. Make other dilutions as required, so that aliquots of reasonable size can be taken with normal precision.

PROCEDURE

1. Weigh 2.0-g sample and transfer to either a 125-ml Erlenmeyer flask or 150-ml beaker.
2. Add 5 ml nitric acid containing 5 percent mercuric oxide; cover the flask and keep it cool until any vigorous reaction subsides.
3. Add 5 ml nitric acid and 10 ml sulfuric acid, cover, and carefully digest on the hot plate until there is no danger of frothing over. Frothing may occur for samples high in organic matter.
4. Add increments of red-fuming nitric acid, 1 ml at a time, until organic matter is destroyed. This must be done cautiously with the flask covered and the solutions raised to the incipient fuming point of sulfuric acid after each addition of fuming nitric acid. When all organic matter is oxidized, rinse and remove the cover glasses and evaporate the solutions to incipient fumes of sulfuric acid. Cool. Repeat the rinsing and fuming to remove all nitric acid.

5. Cool the solution, and transfer the solution and sludge to the distilling flask. Rinse the flask with exactly 5 ml of water, adding the rinses to the still. This addition of water is necessary to prevent decomposition of hydrobromic acid by the sulfuric acid. Rinse the flasks three times with 5 ml bromine-hydrobromic acid solution (total 15 ml) and pour the solution into the distilling flasks.
6. Connect the flask to the condenser at such an angle that insoluble sulfates go to one side on the bottom of the flask. Also place a receiver tube containing 2 to 3 ml water under the condenser with the tip of the condenser submerged and the tube supported in a beaker of ice water.
7. Start the distillation slowly with a small flame. Heat the the flask at a point above the sulfate sludge in order to minimize bumping. Controlled heating also can be done with an alcohol lamp. Glass beads or boiling tubes also will minimize bumping. The flame must be moved as the distillation proceeds, so that solution is over the flame at all times; otherwise, the flask may break. Distill over and collect about 18 to 20 ml of distillate. Stop the distillation when incipient fuming of sulfuric acid appears in the flask, indicating that all hydrobromic acid and water have distilled over.
8. Disconnect the distilling flask and rinse the condenser into the receiver tube with 2 to 3 ml of water. Arrange the tubes containing the distillates in a rack immersed in ice water. Pass a slow stream of sulfur dioxide to each solution, in turn, from a delivery tube placed just above the solution. Do not insert the delivery tube into the solution because of possible loss of selenium by sweeping out as the tetrabromide. Stir the distillates and continue gassing until the bromine is reduced to a colorless solution.
9. Add about 10 mg of hydroxylamine hydrochloride to each solution, stopper the tubes, and warm on the steam bath for 20 minutes at 80°C. An estimate of the selenium content can be made at this time as a guide for the selection of the concentration range for the standards (step 11). Allow the solutions to stand overnight at room temperature. This is especially necessary if little or no selenium can be seen in the solutions.
10. Filter the solution with suction through a glass filter stick with medium or fine glass frit on a Fisher Filtrator and wash with water. Reject the filtrate if clear, otherwise refilter through the same frit.
11. The precipitate, if small, is redissolved by passing 1 ml bromine-hydrobromic acid solution through the frit of the filter stick, collecting the solution in a flat-bottomed vial placed inside the filtrator jar under the filter stick. Wash the frit with 1 ml of water to make the total volume 2 ml of solution. At this time prepare a series of graded standards containing as much as 15 micrograms of selenium, each in a total volume of 2 ml of solution at the same acidity as the samples.
12. Gas the sample and standard solutions, as before, with sulfur dioxide and add 1 to 2 crystals of hydroxylamine hydrochloride to each. Stopper and warm the vials for 20 minutes at 80°C. Compare the color intensity of the sample against the standards by arranging the vials on the slit of light on top of the comparator box. The comparison can be made to advantage by estimating the intensity of color on the bottom of the meniscus of the solution or alternatively by looking down and across the vials at about a 60° angle to the vertical.
13. Calculate the percentage of selenium in the sample. Treat samples containing more than 15 micrograms of selenium as in steps 11 through 13, except that selenium on the frit is dissolved and made to 10- or 25-ml volume with bromine-hydrobromic acid solution, the final volume depending on the selenium content. Take a 1-ml aliquot of this solution for the selenium determination.

PRECISION OF SELENIUM DETERMINATIONS

Selenium was determined on the 80 samples of shale in laboratory A by the method described. The ranges of concentration for selenium were <0.0001 percent (12 samples), 0.0001 to 0.0005 percent (50 samples), 0.0005 to 0.005 percent (13 samples) and 0.005 to 0.05 percent (5 samples). The results on the replicate determinations are given in table 32, those on the hidden splits in table 33, and those on the check samples in table 34.

Figure 11 compares the determinations of A with those of B and B_1 graphically, but most of the check samples contained so little selenium that the comparison is of little value.

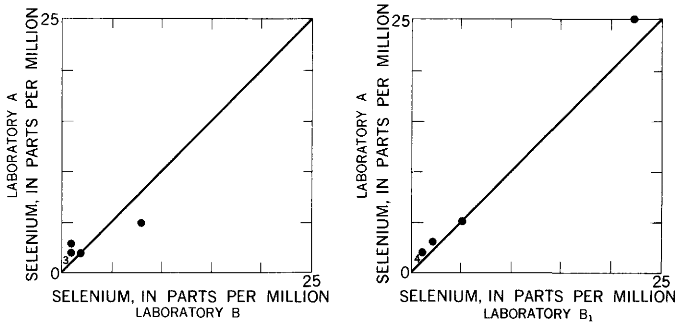

FIGURE 11.—Comparison of selenium determinations of A with those of B and B_1. Plots that coincide are indicated with the number involved.

TABLE 32.—*Replicate determinations*[1] *of selenium, in percent, by laboratory A*

[Analysis by method of this report; George Burrow, analyst. Add 259500 to all sample numbers, except 00 to 05 to which add 259600, to form serial numbers]

30	0.0001	0.0001	71	0.0008	0.0010	56	0.0030	0.0040	
35	.0001	.0001	91	.0010	.0010	62	.0030	.0030	
40	.0001	.0001	82	.0012	.0016	73	.0030	.0030	0.0040
45	.0001	.0001	95	.0014	.0015	04	.0030	.0040	
50	.0001	.0001	02	.0015	.0020	49	.012	.012	
55	.0002	.0002	63	.0024	.0025	96	.012	.013	
60	.0002	.0002	27	.0025	.0030	99	.012	.013	
65	.0002	.0002	26	.0030	.0030	03	.012	.013	
94	.0002	.0003	53	.0020	.0030	61	.015	.016	.016

[1] Precision and reliability of determinations:

Range	*Standard deviations*	*Number of comparisons*
0.00005–0.0005	0.000023	9
.0005 – .005	.00032	15
.005 – .05	.00059	7

TABLE 33.—*Determinations*[1] *of selenium, in percent, in hidden splits, by laboratory A*

[Analysis by method of this report; George Burrow, analyst. Add 259500 to all sample numbers, except 00 to 05 to which add 259600, to form serial numbers. Groups indicate the samples that were duplicates]

33	0.0002	53	0.0030	80	<0.0001
97	.0001	04	.0040	00	.0001
49	.012	65	.0002	82	.0014
96	.013	98	.0002	02	.0018
99	.013	68	.0001	86	.0001
03	.013	01	.0001	05	.0002

[1] Precision and reliability of determinations:

Range	*Standard deviations*	*Number of comparisons*
0.00005–0.0005	0.00012	5
.0005 – .005	.00022	2
.005 – .05	.00050	6

TABLE 34.—*Determinations*[1] *of selenium, in percent, in check samples*

[Add 259500 to each sample number to form serial number]

Sample	A	B	B_1	Mean	Difference (max −min)	Standard deviation
28	<0.0001	<0.0001	<0.0001	<0.0001	----------	----------
33	.0002	.0001	.0001	.0001	0.0001	0.00006
37	< .0001	< .0001	< .0001	< .0001	----------	----------
39	.0002	.0001	.0001	.0001	.0001	.00006
46	.0002	.0001	.0001	.0001	.0001	.00006
48	.0005	0008	.0005	.0006	.0003	.00018
49	.012	.010	.012	.011	.0020	.0012
63	.0025	----------	.0022	.0024	.0003	.00018
92	.0002	.0002	.0001	.0002	.0001	.00006
94	.0003	.0001	.0002	.0002	.0002	.00012

[1] Precision and reliability of determinations:

	Range					
	0.00005 to 0.0005		0.0005 to 0.005		0.005 to 0.05	
	Standard deviation	Number of comparisons	Standard deviation	Number of comparisons	Standard deviation	Number of comparisons
A, B	0.00026	7	0.00020	2	----------	----------
A, B_1	.00003	7	.00016	2	0.0021	1

A. Nitric and sulfuric acid digestion, method of this report; George Burrow, analyst.
B. Nitric and perchloric acid digestion; Mary Fletcher, analyst.
B_1. Digestion and distillation as in B, but distillate evaporated with nitric acid before reduction of selenium and development of selenium color; Mary Fletcher, analyst.

MOLYBDENUM AND TUNGSTEN

ISOLATION BY METHOD 1, ALPHA-BENZOINOXIME PRECIPITATION

[Range in shale: 0.0001 to 0.04 percent molybdenum. Tungsten method was designed for similar range, but tungsten was not found in the samples]

PRINCIPLES

Molybdenum and tungsten are isolated simultaneously from a solution of the sample in hydrochloric acid by precipitation with alpha-benzoinoxime, using vanadium as a collector. This separation (Knowles, 1932) is used because of its specificity, completeness, and rapidity. Only palladium, niobium, tantalum, chromium, and vandium also precipitate, and they do not interfere with the determination of molybdenum and tungsten under the conditions specified. Molybdenum is determined spectrophotometrically as the thyocyanate after reduction with stannous chloride (Hurd and Allen, 1935; Sandell, 1950, p. 455–459). Ethyl acetate is substituted for isoamyl alcohol as the solvent for the extraction, and tartaric acid is used to hold the tungsten in solution. At least 100 micrograms of tungsten can be tolerated during the extraction of the molybdenum under the conditions specified. Also at least 50 micrograms of molybdenum can be tolerated without effect on the tungsten determination under the conditions specified. Consequently, there is no interference either by tungsten in the molybdenum determination or by molybdenum in the tungsten determination in the analysis of shale, silicate rocks, and other materials containing trace amounts of these two elements.

Tungsten in the aqueous phase, after the separation of molybdenum, is reduced with titanous sulfate after making the solution strongly acid (about 44 percent v/v). The tungsten-dithiol complex is then formed and extracted into chloroform for spectrophotometric determination. This modification of the dithiol-tungsten method, using titanous sulfate as the reductant, is that of Claude Huffman (written communication, 1956) and differs in several respects from dithiol-tungsten methods (Miller, 1944; Short, 1951; Greenberg, 1957) and other methods dealing primarily with alloys.

APPARATUS AND REAGENTS

Beckman DU spectrophotometer supplied with both 1- and 2-cm cells.

Shaking hot plate.

Potassium thiocyanate, 10 percent w/v solution, in water.

Stannous chloride, 10 percent w/v solution, in about 1.5*N* hydrochloric acid: Dissolve 12.6 g tinfoil in 42 ml concentrated hydrochloric acid in a platinum dish. The platinum dish acts as a catalyst to dissolve the tin. Dilute the solution to 200 ml in a volumetric flask and add a small piece of metallic tin to minimize oxidation.

Ferrous ammonium sulfate, 1 percent w/v solution of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$, in 0.2*N* sulfuric acid.

Standard molybdenum solution, 1 ml=100 micrograms Mo: Dissolve 0.1840 g of ammonium molybdate, $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$, in water and dilute to 1 liter.

Ethyl acetate: Reagent grade, anhydrous.

Alpha-benzoinoxime solution: Dissolve 8 g alpha-benzoinoxime in 100 ml of concentrated acetic acid by warming the solution on the steam bath.

Chloroform: Reagent grade.

Dithiol (4 methyl, 1, 2 dimercaptobenzene), 0.2 percent w/v solution, in 1 percent w/v sodium hydroxide: The solution should be made fresh at least every 2 weeks because of air oxidation of the reagent.

Standard tungsten solution, 1 ml=100 micrograms W: Dissolve 0.1794 g sodium tungstate dihydrate in water and dilute to 1 liter.

Titanous sulfate solution: Mix 2 g of reagent-grade titanium dioxide with 4.5 g of ammonium sulfate. Add 12.5 ml of concentrated sulfuric acid. Heat cautiously over a burner, in a well-ventilated hood, until foaming stops. Increase the heat to boiling temperature and swirl the boiling liquid vigorously over the full flame until all the titanium dioxide dissolves. Cool. Add carefully, while swirling, enough cold distilled water to dilute the solution to about 50 ml. Decant or filter the solution immediately, to avoid hydrolysis, into a flask containing zinc amalgam, prepared by adding 0.8 g of granular zinc metal to 0.6 ml of mercury and 0.5 ml of 5 percent sulfuric acid. Stopper loosely and swirl the solution occasionally until the evolution of gas stops, and then stopper the flask tightly. This solution is kept at full reducing strength by storing with the zinc amalgam in the tightly stoppered flask.

Vanadium solution, 1 ml=500 micrograms V: Dissolve 0.2296 g ammonium metavanadate (NH_4VO_3) in water and dilute to 200 ml with water in a volumetric flask.

PROCEDURE

ISOLATION OF MOLYBDENUM AND TUNGSTEN

1. Weigh 1.0-g sample, and transfer to a platinum dish.
2. Add 10 ml concentrated nitric acid, 10 ml perchloric acid, and about 10 ml hydrofluoric acid to the dish. Place the solution on a steam bath and evaporate the water. Transfer the dish to a hot plate and fume the solution to near dryness. Add 10 ml water and repeat step 2, omitting the nitric acid. Cool.
3. Add 40 ml distilled water and 5 ml concentrated hydrochloric acid to the dish, cover, and heat on steam bath for 15 minutes. Transfer the solution to a 500-ml Erlenmeyer flask and dilute to 100 ml-volume with water.
4. Chill the solution by placing the flask in a pan of ice water. Add about eight drops bromine water to oxidize molybdenum and tungsten. Add 1 ml vanadium solution and 5 ml alpha-benzoinoxime solution and stir the solution thoroughly.
5. Allow the solution to stand 20 minutes for complete precipitation; filter off the precipitate, using a medium-porosity filter paper. Wash the flask and precipitate three times with a 1 percent hydrochloric acid solution containing 1 percent alpha-benzoinoxime (w/v).
6. Return the precipitate and filter paper to the same 500-ml Erlenmeyer flask.
7. Add 25 ml water, 10 ml nitric acid, 10 ml perchloric acid, and 5 ml sulfuric acid to the flask and place on shaking hot plate. Fume the solution to near dryness. Cool.
8. Cautiously add 5 ml ammonium hydroxide to the flask and agitate to redissolve any tungsten that may have precipitated at step 7.
9. Add 20 ml distilled water, 12.5 ml concentrated hydrochloric acid, and 1 g tartaric acid to the flask and heat on steam bath for 15 minutes. Cool.
10. Transfer the solution to a 50-ml volumetric flask and dilute to volume with water.

DETERMINATION OF MOLYBDENUM

1. Transfer a 15-ml aliquot of the solution to a 60-ml separatory funnel. Add a few crystals of tartaric acid to each solution and allow to dissolve. Add five drops ferrous ammonium sulfate solution, 1 ml 10 percent potassium thiocyanate solution, and 1 ml 10 percent stannous chloride solution; stopper the funnel and shake thoroughly.
2. Add exactly 10 ml ethyl acetate to the separatory funnel and shake vigorously for 30 seconds. Allow the two layers to separate, and draw off the water-acid layer into a clean 150-ml beaker.
3. Add 5 ml of 15 percent hydrocholoric acid to the separatory funnel to rinse the stem and draw off the acid solution into the same 150-ml beaker used in step 2. Reserve this solution for the tungsten determination.
4. Pour the ethyl acetate layer out the top of the separatory funnel into a 25-ml glass-stoppered Erlenmeyer flask. Transfer a portion of the solution to a 1-cm cell and determine its absorbance at 470 mμ against the reagent blank as reference.
5. Calculate the percentage of molybdenum in the sample.

STANDARD CURVE

Blanks and standards containing 5, 10, 20, and 40 micrograms of molybdenum are carried through steps 1 to 4 of the procedure to establish a standard working curve.

DETERMINATION OF TUNGSTEN

1. Add 12 ml concentrated hydrochloric acid to the solution reserved for the tungsten determination at step 3 of the molybdenum determination.
2. Add dropwise about 1 ml titanous sulfate solution, until a purple color persists and the tungsten is reduced.
3. Add 2 ml dithiol solution, stir, and heat the solution on a steam bath for 20 minutes. Cool.
4. Transfer the solution to a 125-ml separatory funnel.
5. Rinse the beaker with exactly 10 ml of chloroform and transfer it to the separatory funnel. Shake the separatory funnel for 1 minute to extract the tungsten-dithiol complex.
6. Draw off the chloroform layer into a 25-ml Erlenmeyer flask fitted with a glass stopper. Transfer portions of the solution to a 2-cm cell and determine the absorbance of the solution at 640 mμ, using a reagent blank as a reference.
7. Calculate percentage of tungsten in sample.

STANDARD CURVE

A blank and standards containing 5, 10, 15, and 20 micrograms of tungsten are carried through steps 1 to 6 of the procedure to establish a standard curve.

ISOLATION BY ALTERNATIVE METHOD 2, ALPHA-BENZOINOXIME EXTRACTION

[Range in shale: same as for method 1]

PRINCIPLES

Tungsten (and molybdenum) in 0.1 to 1.8*N* hydrochloric acid is concentrated by extraction of the alpha-benzoinoxime complexes with chloroform (Jeffery, 1956; Goldstein and others, 1958). Chromium(VI) and vanadium(V), which according to to Knowles (1932) also form insoluble precipitates with alpha-benzoinoxime, are not extracted under the conditions specified. Aluminum, iron, titanium, fluorine, and phosphate are not extracted nor do they interfere with the extraction of molybdenum and tungsten. The tungsten (or molybdenum) is then determined colorimetrically with thiocyanate in the presence of a reducing agent. Tungsten does not interfere in the thiocyanate method for the determination of molybdenum with potassium iodide and sodium sulfite as reducing agents (Hope, 1957). In 6 to 8*N* hydrochloric acid, molybdenum interference is negligible in the thiocyanate method for the determination of tungsten with stannous chloride as the reducing agent; the intensity of the color given by molybdenum is about one-fiftieth to one-hundredth as strong as that given by an equal weight of tungsten (Sandell, 1950, p. 584). Although some analysts carry out the tungsten-thiocyanate reaction in at least 8*N* hydrochloric acid, the method of Gran (1951) with 5*N* hydrochloric acid is used in the following procedure.

APPARATUS AND REAGENTS

Beckman DU spectrophotometer supplied with 5-cm cells.

Potassium thiocyanate solution, 25 percent w/v.

Stannous chloride solution, 10 percent w/v of the dihydrate in concentrated hydrochloric acid: The crystals are warmed with hydrochloric acid until a clear solution is obtained.

Sodium hydroxide, 1.5*N*: Dissolve 6.0 g of sodium hydroxide in water and dilute to 100 ml.

Alpha-benzoinoxime solution: Dissolve 2 g of reagent in 100 ml alcohol.

Standard tungsten stock solution, 1 ml = 1 mg W: Dissolve 0.3588 g sodium tungstate dihydrate in water and dilute to 200 ml with water.

Standard tungsten dilute solution, 1 ml = 10 micrograms W: Dilute 5 ml of stock solution with water to 500 ml.

Chloroform.

Fusion mixture: Mix intimately 10 parts potassium carbonate with 1 part ground potassium nitrate by weight.

PROCEDURE

1. Take a 2-g sample in a platinum crucible. Ignite to destroy organic matter ($<500°C$ if molybdenum is also to be determined; 700°C or less if only tungsten is to be determined).
2. Add 10 g of fusion mixture to the sample, mix, and cover with 0.5 to 1 g more of flux. Cover with platinum lid and heat for 15 minutes at 650°C.
3. Gradually increase the heat until a quiet, clear melt is obtained and continue heating at this temperature for at least 5 minutes more. Cool.
4. Transfer the crucible to a beaker. Add 100 ml of water and several drops of alcohol (more if required to reduce manganate), and heat to boiling, breaking all lumps. Remove crucible, rub with a policeman, and rinse, adding rinses to beaker. Digest the solution on steam bath until the precipitate is filterable. Filter, collecting filtrate in a beaker or casserole, and wash thoroughly with hot 0.1 percent potassium carbonate solution. Discard residue.
5. Carefully neutralize the filtrate with 1+1 hydrochloric acid until methyl orange is red and then add 20 ml more of the 1+1 acid.
6. Evaporate the solution to dryness to dehydrate the silica. Add 20 ml 1+1 hydrochloric acid, cover, and digest the solution on a steam bath. Add 20 ml of water and digest the solution to dissolve soluble salts.
7. Filter the solution on a fast paper and wash with water. Reserve filtrate.
8. Ignite residue in a platinum crucible. Cool and moisten with water. Add 10 to 15 ml hydrofluoric acid and five drops sulfuric acid and evaporate on a steam bath to volatilize silica and water. Bring to fumes of sulfuric acid and heat until all sulfuric acid is removed. Ignite at 400°C. Cool.
9. Add a very small amount of potassium carbonate to the crucible and fuse (even if no residue is present), allowing the melt to play over all surfaces of the crucible. Cool. Add 5 ml of water and a drop of methyl orange indicator. Cover and carefully add 1+1 hydrochloric acid through a small opening until methyl orange turns red and then add a drop or two of the 1+1 acid in excess. Combine with the reserved main solution.
10. Transfer the solution to a separatory funnel and dilute with water to about 95 ml. Add 3 ml alpha-benzoinoxime solution and shake well. Add 10 ml chloroform, and shake for 2 minutes to extract the molybdenum and tungsten into the organic phase.
11. Allow the two phases to separate, and carefully withdraw the lower organic layer into a 50-ml flask. Repeat the extraction three more times with 7-ml portions of chloroform, combining all chloroform extracts.
12. Evaporate the chloroform by gentle heating. Add 2 ml nitric acid and digest the solution. Add 0.5 ml perchloric acid to the flask and take to fumes to destroy organic matter completely. Heat at 200°C on sand bath to remove perchloric acid (including any condensate in the neck of the flask).
13. Add 5 ml 1+1 hydrochloric acid to the flask and evaporate the solution to dryness. Add 1 drop 1+1 hydrochloric acid and 5 ml water to the flask, cover, and digest. Pipet 2 ml 1.5*N* sodium hydroxide, cover, and digest. Cool the solution. If niobium has carried through the method, it will drop out of solution in dilute sodium hydroxide and can be filtered off on a very small filter and then washed with 2 ml of water.
14. If both molybdenum and tungsten are to be determined, transfer the solution to a 25-ml volumetric flask, adjust to volume, and mix the solution. Transfer an aliquot of solution to a 50-ml volumetric flask, and complete the determination of molybdenum according to the alternative method 3, starting at step 12 (p. A–30). A 10-ml aliquot can be used for the tungsten determination, steps 15 through 17, below. If only tungsten is to be determined, transfer the solution (step 13, alternative method 2) to the 25-ml volumetric flask and wash to give a total volume not exceeding 12 ml. Complete the determination of tungsten following steps 15 through 17 below.
15. Add 1 ml potassium thiocyanate solution to the flask containing the tungsten, and pipet 10 ml of stannous chloride in concentrated hydrochloric acid solution and mix. Exactly 60 minutes after the addition of the tin solution, dilute the solution to the mark with distilled water and mix.
16. Determine the absorbance of the solution at 395 mμ in 5-cm cells against a blank solution as reference. To prepare the blank solution, pipet 10 ml water, 1 drop 1+1 hydrochloric acid, and 2 ml sodium hydroxide into a flask and continue with step 15.
17. Calculate the percentage of tungsten in the samples. A blank should be carried throughout the procedure.

STANDARD CURVE

Standards and a blank solution should be prepared along with the samples at step 15 so that a standard curve can be made with each set of samples.

Pipet 0, 5, 10, 20, and 50 micrograms tungsten standard dilute solution into dry 25-ml volumetric flasks. Add by pipet sufficient water to make 10 ml of solution, 1 drop 1+1 hydrochloric acid, and 2 ml sodium hydroxide and proceed according to step 15 of the procedure.

ISOLATION OF MOLYBDENUM BY ALTERNATIVE METHOD 3, CUPFERRON SEPARATION

[Range in shale: 0.0001 to 0.04 percent molybdenum]

PRINCIPLES

Molybdenum is concentrated by cupferron precipitation in the presence of iron as a carrier. Iron is separated by sodium hydroxide fusion and leaching; molybdenum is determined in the filtrate spectrophotometrically.

This spectrophotometric method is a variation of the thiocyanate method, using potassium iodide and sodium sulfite as reducing agents in the presence of a trace of copper to increase rate of color development without altering the final intensity (Hope, 1957). At least 7 mg of tungsten and 10 mg of iron can be present in the final 50-ml volume without interference. The addition of 5 ml of 30 percent w/v ammonium citrate will allow as much as 50 mg of tungsten to be present without interference. Bismuth and vanadium complexes do not absorb at 460 mμ. Antimony does not interfere. Sulfuric acid concentrations greater than 0.3*N* in the final solution reduce the rate of color development. At least 1.5 g of sodium salts do not interfere.

APPARATUS AND REAGENTS

Beckman DU spectrophotometer supplied with 1- and 5-cm cells.

Ammonium molybdate standard stock solution, 1 ml = 1 mg Mo: Dissolve 0.3680 g ammonium molybdate, $(NH_4)_6 Mo_7O_{24} \cdot 4H_2O$, in water and dilute to 200 ml in a volumetric flask.

Standard molybdenum dilute solution, 1 ml = 10 micrograms Mo: Dilute 5 ml of standard stock solution to 500 ml in a volumetric flask.

Hydrochloric acid, 1+1.

Ammonium thiocyanate solution, 25 percent (w/v).

Potassium iodide, 50 percent (w/v).

Sodium sulfite, 1 percent (w/v).

Copper chloride solution, 0.1*M*: Dissolve 1.7 g cupric chloride dihydrate in water containing 1 ml hydrochloric acid and dilute to 100 ml.

Cupferron solution, 6 percent (w/v) aqueous: Prepare as needed and keep the solution cold.

PROCEDURE

1. Weigh a 2-g sample and transfer it to a platinum dish. Place the dish in a regulated muffle at 450°C to destroy as much organic matter as possible by ignition. At 500°C molybdenum trioxide begins to sublime.
2. Moisten the sample with water, add 20 ml hydrofluoric acid, 5 ml nitric acid, and 10 ml perchloric acid to the dish. Cover and digest 30 minutes on a steam bath. Take the solution to fumes of perchloric acid. Add 10 ml of water and evaporate to fumes again. Repeat.
3. Add 20 ml hydrochloric acid and 30 ml water to the dish. Digest to dissolve soluble salts. A clear solution should be obtained. Transfer the solution to a 400-ml beaker, and add water to a volume of about 230 ml.
4. Cool the solution in an ice bath. Add 70 ml of cold cupferron solution (more if required to precipitate all the iron); stir in paper pulp and filter the solution when the precipitate is fully clotted (in a few minutes).
5. Wash the precipitate with a cold solution containing 40 ml hydrochloric acid and 15 ml cupferron to 500 ml of solution. Reject filtrate.
6. Squeeze out as much water as possible by placing hand over funnel and pressing down until no more fluid is forced out.
7. Transfer the precipitate and paper to a silver crucible and dry overnight in an oven at 50°C.
8. Ignite the paper at low heat, very gradually raising the temperature to 500°C, but no higher, until all carbon is removed.
9. Add 2 g sodium hydroxide and fuse the residue. Leach the melt with boiling water.
10. Filter the solution into a platinum dish and wash the paper with 0.1 percent sodium hydroxide solution. Reject residue.
11. Concentrate the solution to less than 25 ml and transfer to a 25-ml volumetric flask. Dilute to volume and mix.
12. Transfer a 15-ml aliquot to a 50-ml volumetric flask. Add 20 ml 1+1 hydrochloric acid all at once. Swirl the flask for several minutes to remove the carbon dioxide from the solution.
13. Add the following solutions to the flask: 1 drop of copper chloride solution, 3 ml ammonium thiocyanate, 3 ml potassium iodide, and 2 ml sodium sulfite.
14. Dilute to volume, mix, and allow the solution to stand for 30 minutes.
15. Obtain the absorbance in 1- or 5-cm cells at 460 mμ (slit about 0.03 mm), using a blank as reference. Prepare the reference solution at the same time by following steps 12 to 15 and by using 15 ml of water containing 1.2 g of sodium hydroxide instead of sample solution at step 12.
16. Calculate the percentage of molybdenum in the sample. Carry a reagent blank through the complete procedure; use about 25 mg Fe_2O_3 (nitrate salt) so that a precipitate is obtained in the cupferron step.

STANDARD CURVE

Transfer 2, 5, 10, and 20 micrograms of molybdenum standard solution to 50-ml flasks and include a reagent blank; add 1.2 g of sodium hydroxide and water to 15 ml. After dissolution follow steps 12 to 15 of the procedure. Determine the absorbance with the blank solution as reference.

PRECISION OF TUNGSTEN DETERMINATIONS

Tungsten was assigned to laboratory A for the analysis of the 80 samples of shale. The concentration of tungsten was found to be less than 1 ppm, using method 1, for the first 48 samples of the set of 80. Because the samples analyzed represented all the different types of material and many of the different sample locations, the remaining 32 samples were not analyzed for tungsten. A further check for tungsten was made by method 1, using a 5-g portion of sample 259526. This test showed less than 0.00003 percent tungsten. Although no supporting data were obtained for the precision of either the method or alternative method for the determination of tungsten in shale, the methods are included for future use if needed.

PRECISION OF MOLYBDENUM DETERMINATIONS

Molybdenum was determined on the 80 samples of shale in laboratory A by method 1, described for the determination of molybdenum and tungsten. The ranges of concentration for molybdenum were less than 0.0001 percent (27 samples); 0.0001 to 0.0005 percent (33 samples); 0.0005 to 0.005 percent (14 samples), and 0.005 to 0.05 percent (6 samples).

The results on replicate determinations are given in table 35, those on the hidden splits in table 36, and those on the check samples in table 37. The results of A are compared graphically with those of B in figure 12.

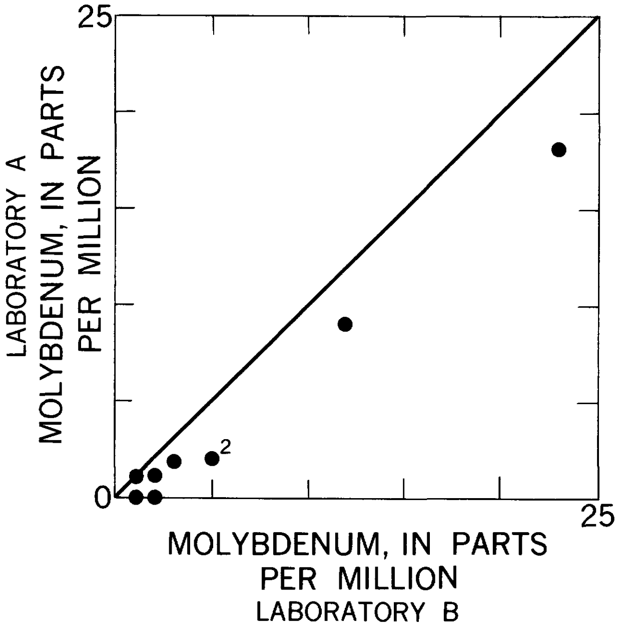

FIGURE 12.—Comparison of molybdenum determinations of A with those of B. Plots that coincide are indicated with the number involved.

TABLE 35.—*Replicate determinations*[1] *of molybdenum, in percent, by laboratory A*

[Analysis by alpha-benzoinoxime precipitation, method 1; Dorothy Ferguson and Claude Huffman, analysts. Add 259500 to all sample numbers, except 00 to 05 to which add 259600, to form serial numbers]

58	<0.0001	<0.0001	78	0.0001	0.0001	63	0.0016	0.0017	0.0020
81	< .0001	< .0001	33	.0001	.0002	61	.0022	.0022	
93	< .0001	< .0001	41	.0001	.0003	73	.0028	.0028	
98	< .0001	< .0001	45	.0001	.0002	27	.0039	.0046	
53	< .0001	.0001	83	.0005	.0005	91	.0048	.0048	
68	< .0001	.0001	88	.0007	.0009	82	.0058	.0058	
28	.0001	.0001	48	.0009	.0009	99	.032	.036	
38	.0001	.0001	56	.0010	.0011	03	.032	.033	.035
43	.0001	.0001	26	.0012	.0013	49	.035	.035	

[1] Precision and reliability of determinations:

Range	*Standard deviations*	*Number of comparisons*
0.0005–0.005	0.00018	12
.005–.05	.0016	6

TABLE 36.—*Determinations*[1] *of molybdenum, in percent, in hidden splits by laboratory A*

[Analysis by alpha-benzoinoxime precipitation, method 1; Dorothy Ferguson and Claude Huffman, analysts. Add 259500 to all sample numbers, except 00 to 05 to which add 259600, to form serial numbers. Groups indicate the samples that were duplicates]

33	0.0002	53	0.0001	80	<0.0001
97	<.0001	04	.0001	00	<.0001
49	.035	65	<.0001	82	.0058
96	.033	98	<.0001	02	.0063
99	.034				
03	.033	68	.0001	86	<.0001
		01	<.0001	05	.0002

[1] Precision and reliability of determinations in the range 0.005 to 0.05: standard deviation, 0.00095; number of comparisons, 7.

TABLE 37.—*Determinations*[1] *of molybdenum, in percent, in check samples*

[Add 259500 to each sample number to form serial number]

Sample	A	B	Mean	Difference (max −min)	Standard deviation
28	0.0001	0.0001	0.0001	0	0
33	.0002	.0003	.0003	.0001	.00009
37	<.0001	.0001	<.0001	.0001	.00009
39	.0002	.0005	.0004	.0003	.00027
46	.0001	.0002	.0002	.0001	.00009
48	.0009	.0012	.0011	.0003	.00027
49	.035	.032	.034	.003	.0027
63	.0018	.0023	.0021	.0005	.00044
92	.0002	.0005	.0004	.0003	.00027
94	<.0001	.0002	.0001	.0002	.00018

[1] Precision and reliability of determinations in the range 0.0005 to 0.005: standard deviation, 0.00029; number of comparisons, 2.

A. Alpha-benzoinoxime precipitation, method 1; Dorothy Ferguson and Claude Huffman, analysts.
B. Cupferron separation, method 3; Marian Schnepfe and Frank Grimaldi, analysts.

URANIUM, FLUOROMETRIC METHOD

[Range in shale: 0.00005 to 0.003 percent uranium]

PRINCIPLES

The extraction procedure for the fluorometric determination of uranium is based on the method of Grimaldi and others (1954). Uranyl nitrate is extracted from nitric acid solution with ethyl acetate, using aluminum nitrate as a salting agent. A portion of the extract is evaporated and the residue fused with a carbonate-fluoride flux to prepare a fluorescent melt. The extraction separates uranium from most elements that quench its fluorescence in the melt. The sample is usually completely decomposed by treatment with nitric and hydrofluoric acids; any undecomposed sample remaining is fused with sodium carbonate and dissolved in nitric acid. The relative fluorescence of the prepared phosphor is determined in a sensitive transmission-type fluorometer calibrated with phosphors containing known amounts of uranium.

APPARATUS AND REAGENTS

Fluorometer: Suitable fluorometers are described by Grimaldi and others (1954), Kinser (1954), Parshall and Rader (1957), and Galvanek and Morrison (1954).

Machine for preparing phosphors: The one described by Stevens and others (1959) is advantageous for routine work, but suitable phosphors also can be prepared manually over a burner.

Shallow platinum dishes, about 7-ml capacity: Described by Grimaldi and others (1954, p. 103).

Platinum dishes, about 60- to 100-ml capacity.

Platinum-tipped tongs: The curved-tipped (Blair) and straight-tipped tongs are both useful.

Centrifuge: A large centrifuge with adapters to hold test tubes about 145 mm long is advantageous but not necessary.

Motor-driven shaking machine: Equipped to extract a suite of solutions in test tubes at one time.

Test tubes, Pyrex, standard taper 19/17, 22 by 145 mm.

Aluminum nitrate, $Al(NO_3)_3 \cdot 9H_2O$: This reagent must be substantially free from uranium, as determined with blanks carried through the method. Two or three extractions of the acid solution of the salt with ether followed by recrystallization from 10 percent nitric acid v/v generally yield a satisfactory product.

Flux: 45.5 percent by weight sodium carbonate, 45.5 percent potassium carbonate, and 9.0 percent sodium fluoride (Grimaldi and others, 1954). It is essential that all ingredients in the flux be of very fine and equivalent mesh size and thoroughly mixed.

Ethyl acetate, anhydrous, reagent grade.

Standard uranium solution, 1.0 ml = 1 mg U: Weigh and transfer 1.1804 g black uranium oxide, at least 99.9 percent U_3O_8, to a 1-liter flask. Dissolve by warming the uranium in sufficient nitric acid to make the final solution 7 to 8 percent v/v nitric acid and dilute to 1 liter.

Diluted uranium standard: Various concentrations of dilute uranium solutions in 7.5 percent nitric acid v/v are required. Prepare the dilute solutions frequently as needed to avoid possible loss of uranium to the glass during storage.

PROCEDURE

1. Transfer 1.0-g sample to a 60-ml platinum dish.
2. Ignite the sample over a burner to destroy organic matter.
3. Cool the sample and moisten with a few drops of water. Add 5 ml of nitric acid, place the dish on a steam bath and evaporate to dryness.
4. Add 10 ml nitric acid and 10 ml hydrofluoric acid to the dish and evaporate to dryness again. Repeat step 4 if undecomposed sample remains.
5. Add 10 ml nitric acid to the residue and evaporate to dryness to break up insoluble fluorides. Repeat this step to remove as much fluoride as possible.
6. Digest the residue with 30 ml water and 7 ml 1+1 nitric acid and filter the solution through a small filter paper into a 100-ml volumetric flask.
7. Ignite the paper in a platinum crucible and fuse the residue with a minimum amount of sodium carbonate.
8. Dissolve the fusion cake in 10 ml of hot water by digestion in the covered crucible on the steam bath. Add a drop or two of methyl orange indicator and then add dilute nitric acid dropwise until the solution is just red, and combine with the original solution. Add sufficient 1+1 nitric acid to the flask to make the solution 7 percent v/v in nitric acid after dilution and dilute to 100 ml with water.
9. Transfer 5 ml of the sample solution to a test tube, made to hold a ground-glass stopper, which contains 9.5 g of aluminum nitrate.
10. Immerse the tubes containing the sample solutions in hot water to dissolve the aluminum nitrate. Cool the tubes to room temperature, add exactly 10 ml of ethyl acetate to each tube, stopper, and place the tubes in a shaking machine.
11. Shake the tubes for 2 minutes and remove from the shaker. Either allow the solutions to stand for a few minutes to separate into layers or place the tubes in a centrifuge to separate the solutions.
12. Filter a portion of the upper ethyl acetate layer in each tube through dry 7- or 9-cm dense filter paper into dry, clean tubes.
13. Arrange the platinum flux dishes in the same order in a shallow pan containing about an eighth of an inch of cold water or arrange them on several thicknesses of wet-paper toweling.
14. Pipet 2-ml aliquots of each of the filtered ethyl acetate extracts and transfer them to each dish in order, igniting the ethyl acetate after each transfer with a match or lighted taper.
15. When the ethyl acetate has finished burning, a small residue and perhaps a few drops of acetic acid will remain. Dry this on a steam bath or by careful heating on a hot plate, and burn off the organic residue, including any residual nitric acid, below 500° C over a burner.
16. Transfer 2.0 g of the premixed carbonate-fluoride flux to each dish. Weigh the flux with a sensitive torsion or trip balance.
17. Prepare the phosphors by fusing the flux at as low a temperature as possible (below 700° C), swirling the molten flux over the entire area inside the dish. This is done best by placing the dishes on the quartz rods of the rotating disk of the phosphor machine (Stevens and others, 1959). The fusion requires about 4 to 5 minutes with the machine in the tilted position. Level the machine and anneal the melts by allowing the machine to run for 10 minutes after the gas is turned off. If the phosphor melts are prepared manually, follow the instructions given by Grimaldi and others (1954). In any event, the melt must be cooled slowly to achieve the maximum and most reproducible fluorescence, and all standards must be prepared the same way.
18. Compare the fluorescence of phosphors containing unknown amounts of uranium with phosphors containing known amounts of uranium, using a sensitive, stable fluorometer.
19. Calculate the percentage of uranium in the samples.

STANDARD CURVE

Transfer aliquots of standard uranium solution containing 0, 0.01, 0.02, 0.03, and 0.04 micrograms of uranium to test tubes containing 9.5 g aluminum nitrate and continue the determinations, beginning at step 9 of the procedure.

The sensitivity of fluorometers can be adjusted within wide limits. Laboratory B reported that 50 scale divisions on the fluorometer corresponded to 0.09 micrograms of uranium. When so adjusted readings of three scale divisions were obtained for the reagent blank and eight scale divisions for a sample solution containing 1 ppm uranium. Laboratory A reported that 100 scale divisions on the fluorometer corresponded to 0.044 micrograms of uranium. When so adjusted readings of 13 scale divisions were obtained for the reagent blank and 33 scale divisions for a sample solution containing 1 ppm uranium.

PRECISION OF URANIUM DETERMINATIONS

Uranium was determined fluorometrically on the 80 samples of shale in laboratory B by two analysts. The ranges of concentration for uranium were from 0.00005 to 0.0005 percent (48 samples) and 0.0005 to 0.005 percent (32 samples). The results of the two analysts are compared in tables 38, 39, and 40. The results on the hidden splits are given in table 39 and those on the check samples in table 40. The results of B on the check samples are compared with those of B_1 and A graphically on figure 13.

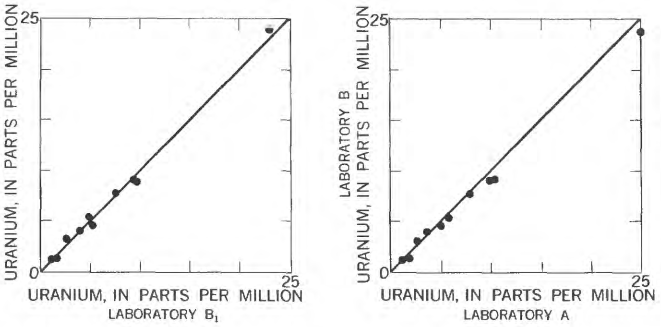

FIGURE 13.—Comparison of uranium determinations of B with those of B₁ and A.

TABLE 38.—*Determinations*[1] *of uranium, in percent, by different chemists, in laboratory B*

[Add 259500 to all sample numbers, except 00 to 05 to which add 259600, to form serial numbers]

Sample	B	B₁	Sample	B	B₁	Sample	B	B₁
57	0.00009	0.00008	59	0.00034	0.00032	40	0.00055	0.00056
88	.00010	.00012	60	.00034	.00031	67	.00050	.00054
36	.00016	.00013	64	.00033	.00034	87	.00053	.00052
29	.00017	.00014	66	.00030	.00033	83	.00057	.00059
35	.00023	.00016	77	.00031	.00034	55	.00058	.00056
38	.00024	.00020	85	.00033	.00034	71	.00063	.00064
30	.00028	.00025	90	.00032	.00038	62	.00063	.00070
45	.00026	.00024	89	.00034	.00037	72	.00070	.00068
50	.00028	.00028	84	.00034	.00036	42	.00087	.00083
70	.00026	.00028	81	.00037	.00039	44	.00087	.00076
79	.00026	.00024	75	.00037	.00035	47	.00085	.00094
69	.00028	.00031	76	.00039	.00039	91	.00085	.00090
32	.00031	.00026	74	.00043	.00043	54	.00089	.00079
34	.00031	.00027	52	.00045	.00045	56	.00094	.00090
41	.00033	.00032	27	.00045	.00047	95	.00096	.0010
51	.00032	.00030	43	.00049	.00050	73	.0012	.0012
58	.00033	.00029	78	.00050	.00050	26	.0018	.0017
31	.00035	.00028	93	.00052	.00052	61	.0029	.0026

[1] Precision and reliability of determinations:

Range	*Standard deviations*	*Number of comparisons*
0.00005–0.0005	0.000022	33
.0005 – .005	.000058	21

B. Fluorometric method; Ivan Barlow, analyst.
B₁. Fluorometric method; Joseph Budinsky, analyst.

TABLE 39.—*Determinations*[1] *of uranium, in percent, in hidden splits*

[Add 259500 to all sample numbers, except 00 to 05 to which add 259600, to form serial numbers. Groups indicate the samples that were duplicates]

Sample	B	B₁	Sample	B	B₁	Sample	B	B₁
33	0.00013	0.00012	53	0.00082	0.00080	80	0.00035	0.00034
97	.00016	.00016	04	.00077	.00078	00	.00031	.00030
49	.00079	.00076	65	.00036	.00038	82	.0021	.0021
96	.00073	.00077	98	.00039	.00039	02	.0019	.0021
99	.00076	.00080						
03	.00078	.00078	68	.00045	.00048	86	.00032	.00032
			01	.00042	.00043	05	.00032	.00033

[1] Precision and reliability of determinations:

	Range			
	0.00005 to 0.0005		0.0005 to 0.005	
	Standard deviation	Number of comparisons	Standard deviation	Number of comparisons
B	0.000040	5	0.000090	8
B₁	.000022	5	.000028	8
B, B₁	.000010	10	.000015	8

B. Fluorometric method; Ivan Barlow, analyst.
B₁. Fluorometric method; Joseph Budinsky, analyst.

TABLE 40.—*Determinations*[1] *of uranium, in percent, in the check samples*

[Add 259500 to each sample number to form serial number]

Sample	B	B₁	A		Mean	Difference (max–min)	Standard deviation
28	0.00015	0.00016	0.00020	0.00017	0.00017	0.00005	0.000024
33	.00013	.00012	.00014	.00013	.00013	.00002	.000010
37	.00092	.00097	.0011	.0011	.0010	.00018	.000088
39	.00055	.00050	.00057	.00062	.00056	.00012	.000058
46	.00047	.00052	.00052	.00052	.00051	.00003	.000015
48	.00031	.00027	.00029	.00025	.00028	.00006	.000029
49	.00079	.00076	.00091	.00085	.00083	.00015	.000073
63	.0024	.0023	.0026	.0025	.0025	.00030	.00015
92	.00094	.00095	.0011	.0010	.0010	.00016	.000078
94	.00040	.00039	.00037	.00038	.00039	.00003	.000015

[1] Precision and reliability of determinations:

	Range			
	0.00005 to 0.0005		0.0005 to 0.005	
	Standard deviation	Number of comparisons	Standard deviation	Number of comparisons
Average of A compared with average of B and B₁	0.000015	4	0.000012	6
All data	.000018	24	.000081	36

B. Fluorometric method; Ivan Barlow, analyst.
B₁. Fluorometric method; Joseph Budinsky, analyst.
A. Fluorometric method; Edward Fennelly, analyst.

CARBON

CARBONATE CARBON, GASOMETRIC DETERMINATION

[Range in shale: 0.02 to 8 percent carbonate carbon]

PRINCIPLES

Carbon dioxide is liberated by the action of 1+1 hydrochloric acid on the sample. The volume of the liberated carbon dioxide plus the air present in the reaction flask is measured at a definite temperature and atmospheric pressure. The combined gases are then scrubbed free of carbon dioxide by passage through an alkali solution. The volume of the residual gases is again measured at the same temperature and pressure. The difference in the observed volumes, due to the volume of carbon dioxide, is calculated to standard conditions of temperature and pressure, using the ideal gas relationships. The weight of carbon dioxide is then calculated from its volume at standard temperature and pressure. The method is an adaptation made by I. C. Frost from procedures in books (Treadwell and Hall, 1947, p. 328–339; Association of Official Agricultural Chemists, 1950, p. 118–119)

SPECIAL EQUIPMENT

The apparatus for the liberation, measurement, and absorption of carbon dioxide (fig. 14) consists of a reaction flask, *a*, of approximately 30-ml capacity, fitted with a two-hole stopper. A small separatory funnel, *b*, entering one hole of the stopper, is used to introduce the acid for liberation of carbon dioxide from the sample. A small water condenser, *c*, is placed in the second outlet that in turn leads through a two-way stopcock,

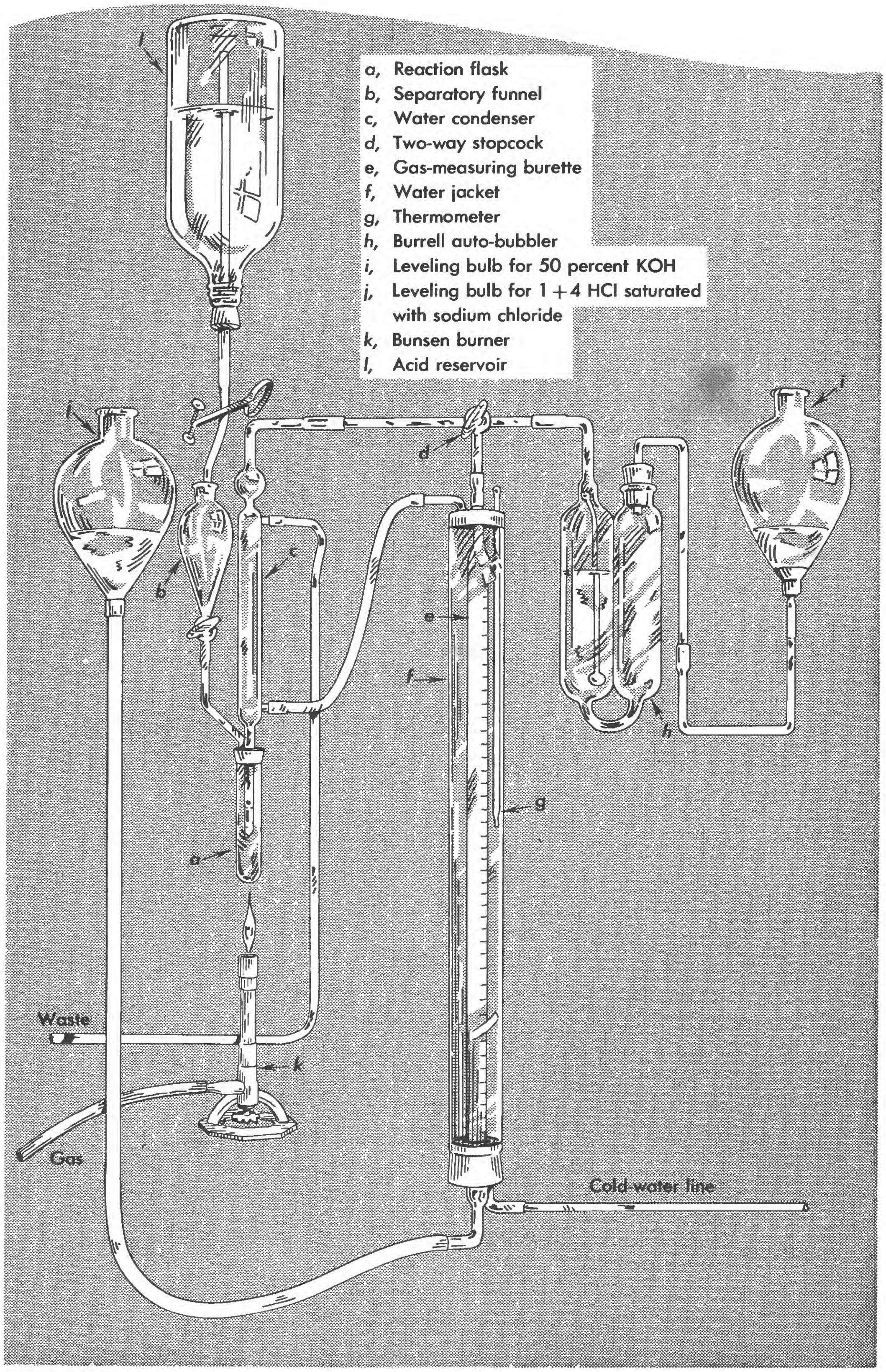

FIGURE 14.—Apparatus for gasometric determination of carbon dioxide.

d, at the top of a gas-measuring burette, *e*, of 100-ml capacity. The gas-measuring burette is enclosed in a glass tube of sufficient diameter (50 mm) to serve as a cooling water jacket, *f*, for the gas burette and to help maintain a relatively constant temperature. The water-jacket inlet at the bottom is attached to the water supply, and cooling water is circulated through the jacket during use. A thermometer, *g*, is suspended in the water jacket for reading the temperature of the water and indirectly that of the gas in the burette. The other side of the two-way stopcock, *d*, leads to a Burrell auto-bubbler, *h*, for absorption of carbon dioxide. The outlet from the Burrell auto-bubbler is attached to a leveling bulb, *i*, containing 50 percent w/v potassium hydroxide solution. Sufficient potassium hydroxide solution to completely fill the auto-bubbler plus 100 ml excess is required.

The outlet from the bottom of the gas burette is connected with a leveling bulb, *j*, containing 1+4 hydrochloric acid saturated with sodium chloride. Methyl red indicator also is added to color this solution and facilitate readings of gas volumes. The apparatus is supported on a frame. Open ring supports are used to adjust the leveling bulbs to the heights required for operation of the equipment. A Bunsen burner, *k*, and acid reservoir, *l*, complete the gasometric apparatus.

A barometer located near the apparatus is used to determine the atmospheric pressure.

PROCEDURE

1. Accurately weigh and quantitatively transfer to the reaction flask an appropriate weight of sample to yield from 5.0 to 50.0 ml of carbon dioxide, as shown in figure 15. Usually 0.2 to 5 g is required. Add 2 or 3 glass beads and approximately 10 ml of water to the sample. When the sample contains sulfides, add approximately 0.1 g of mercuric chloride to the reaction flask to prevent liberation of hydrogen sulfide.
2. Adjust the gas-burette leveling bulb to completely fill the gas burette with acidified sodium chloride solution.
3. Attach the reaction flask tightly to the stopper bearing the condenser and small separatory funnel. Close the stopcock on the separatory funnel and turn the stopcock at the top of the gas burette to connect the gas burette with the reaction flask. Clamp the leveling bulb in position well below the water level in the gas burette to give reduced pressure in the system.

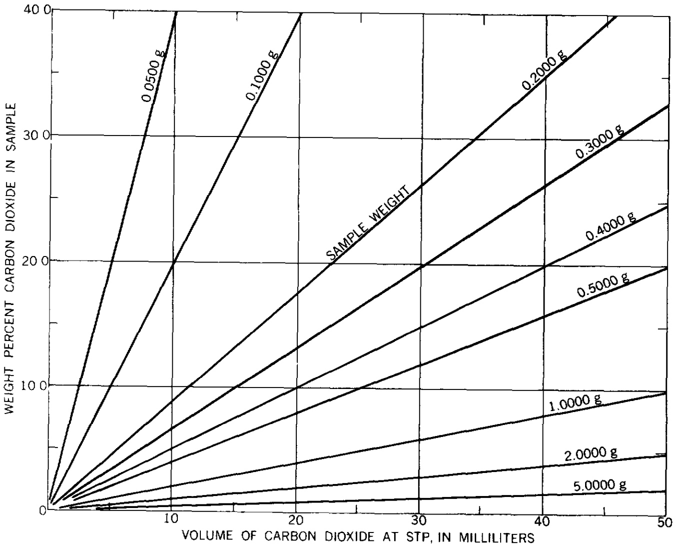

FIGURE 15.—The relation between the percentage of carbon dioxide in the sample and its volume at standard conditions.

4. Pour 20 ml of 1+1 hydrochloric acid into the separatory funnel and open the stopcock just enough to allow the acid to slowly enter the reaction flask and react with carbonate in the sample. During the liberation of carbon dioxide from the sample, keep the pressure in the gas burette below atmospheric pressure by adjusting the leveling bulb.
5. After the reaction has subsided, heat the reaction flask and boil the solution for 2 to 4 minutes.
6. Purge the reaction flask and condenser of all gas by passing water through the separatory funnel into the reaction flask, condenser, and just up to the stopcock above the gas burette This is accomplished by lowering the gas-burette leveling bulb and closing the stopcock when the water has reached it.
7. Wait 2 to 3 minutes for the gas to adjust to the temperature of the water jacket. Read and record the temperature in the water jacket.
8. Adjust the liquid level in the burette leveling bulb to that in the gas burette by holding the bulb against the burette and moving it up or down as required to match the levels. Read and record the volume (*A*) of gas in the burette.
9. Raise the leveling bulb and adjust the stopcock above the gas burette to allow the gas to pass slowly through the Burrell auto-bubbler. Lower the leveling bulb to return the gas to the burette. Repeat three times. Finally close the stopcock above the gas burette when the caustic absorbing solution has reached a fixed point in the capillary leading to the stopcock.
10. Wait 2 to 3 minutes for the gas to adjust to the temperature in the water jacket. Read and record the temperature in the water jacket.
11. Adjust the gas to atmospheric pressure with the leveling bulb, as in step 8, and read and record the volume (*B*) of gas in the burette.
12. Read and record the barometric pressure.
13. Calculate the CO_2 content of the sample as follows: Reduce the observed volume of gas to 0°C (273° K) and 760 mm pressure by substituting determined values in the following formula and solving for Vs, where Vs = volume of CO_2 calculated to standard conditions.

$$Vs=\frac{(A-B)\times P\times 273}{760\ (273+t)}\quad\text{or}\quad Vs=\frac{P(A-B)}{2.78t+760},$$

where A=total volume of gas measured in milliliters; B=residual volume of gas, in milliliters, after absorption of CO_2; P=observed barometric pressure, in millimeters of mercury, after instrumental correction for temperature; and t=observed temperature, in °C. Using the value of Vs obtained, the percentage CO_2 is calculated as follows:

$$\text{Percent } CO_2=\frac{Vs\times 44.011\times 100}{22{,}269\times W}$$

$$\text{or percent } CO_2=\frac{Vs\times 0.1976}{W},$$

where 44.011=weight of 1 mole of CO_2, in grams; 22,269= volume of 1 mole of CO_2, in milliliters, at 0°C and 1 atmosphere; and W=weight of sample, in grams. The calculated value of CO_2 is multiplied by 0.2727 to obtain the percentage of carbon when this conversion is desired. Table 41 gives factors for calculating CO_2 and C for various sample weights from the volume of carbon dioxide at

0°C and 1 atmosphere. Factors for various conditions of temperature and pressure for a sample weight of 1.7 g are tabulated by the Association of Official Agricultural Chemists (1950, p. 871). The analyst can calculate these factors advantageously for other sample weights.

TABLE 41.—*Factors for calculating percent of carbon dioxide and percent of carbon for various sample weights from the volume of carbon dioxide under standard conditions*

[Multiply volume of CO_2 at STP by factor corresponding to weight of sample]

Sample weight (grams)	*Factor for percent* CO_2	*Factor for percent* C
0. 0500	3. 9527	1. 0787
. 1000	1. 9763	. 5394
. 2000	. 9882	. 2697
. 2500	. 7905	. 2157
. 3000	. 6581	. 1798
. 4000	. 4941	. 1348
. 5000	. 3953	. 1079
1. 0000	. 1976	. 05394
2. 0000	. 09882	. 02697
5. 0000	. 03953	. 01079

PRECISION OF CARBONATE CARBON DETERMINATIONS

Carbonate carbon was determined on the 80 samples of shale in laboratory A by the gasometric method described. The ranges of concentration for carbon were <0.05 percent (31 samples), 0.05 to 0.5 percent (31 samples), 0.5 to 5 precent (15 samples), and >5 percent (3 samples). The lowest range is not included in calculations because of the 0.02 percent carbon cutoff level generally used with the method. The percentages of carbon dioxide reported on the shale by laboratories A, C, and D, calculated to carbonate carbon, are given in tables 42, 43, and 44. The results of replicate determinations are given in table 42, those on the hidden splits in tables 43, and those on the check sample in table 44. The results of A on the check samples are compared with those of A_1 and those of C+D in figure 16.

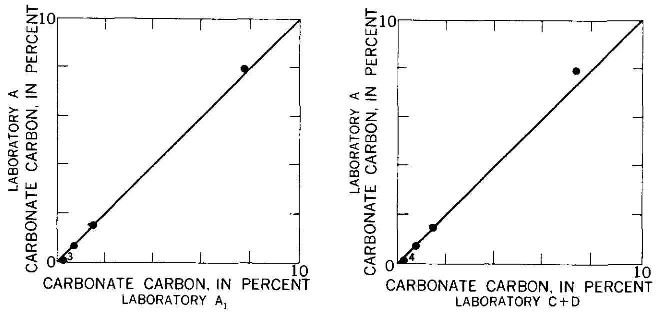

FIGURE 16.—Comparison of carbonate carbon determinations of A with those of A_1 and of C+D. Plots that coincide are indicated with the number involved.

TABLE 42.—*Determinations*[1] *of carbonate carbon, in percent, by different methods and laboratories*

[Add 259500 to each sample number to form serial number]

Sample	A	C	D	Sample	A	C	D
51	0. 06	--------	0. 13	45	0. 27 0. 28	--------	0. 20
83	. 08	--------	. 03	38	. 35	--------	. 35
79	. 09	0. 09	--------	85	. 36 . 37	--------	. 44
44	. 10	--------	. 11	70	. 47 . 48	--------	. 55
35	. 11 0. 11	--------	. 13	75	. 53 . 56	0. 56	--------
32	. 12	--------	. 15	77	. 58	. 56	--------
36	. 14	--------	. 14	64	. 59	--------	. 95
50	. 14 . 19	--------	. 17	76	. 61	--------	. 46
74	. 19	--------	. 23	34	. 61 . 62	--------	. 57
78	. 19	. 19	--------	47	. 76 . 76	. 77	--------
89	. 21	--------	. 20	62	2. 4	--------	2. 5
42	. 24	. 20	--------	56	2. 9 3. 0	2. 9	--------
67	. 23 . 24	--------	. 24	60	5. 9 6. 0	--------	5. 9
69	. 25 . 25	--------	. 19	41	6. 8 6. 9	6. 9	--------

[1] Precision and reliability of determinations:

	Range			
	0. 05 to 0. 5		0. 5 to 5	
	Standard Deviation	Number of comparisons	Standard deviation	Number of comparisons
A	0. 014	7	0. 011	4
A, C	. 016	3	. 036	7
A, D	. 034	22	. 14	5

A. Gasometric method described; Edward Fennelly, analyst.
C. Absorption tube-gravimetric method, (Hillebrand and others, 1953, p. 768-770); Marguerite Seerveld and Vertie Smith, analysts.
D. Gasometric method (Shapiro and Brannock, 1956); Leonard Shapiro, Paul Elmore, Samuel Botts, and Marvin Mack, analysts.

TABLE 43.—*Determinations*[1] *of carbonate carbon, in percent, in hidden splits*

[Add 259500 to all sample numbers, except 00 to 05 to which add 259600, to form serial numbers. Groups indicate the samples that were duplicates]

Sample	A	C	D	Sample	A	C	D
33	1. 5	1. 5	--------	68	0. 34	0. 35	--------
97	1. 5	--------	1. 5	01	. 33	--------	0. 30
49	<. 02	<. 01	--------	80	. 66	. 67	--------
96	<. 02	. 01	--------	00	. 65	--------	. 65
99	<. 02	--------	. 02				
03	<. 02	--------	. 02	82	. 21	. 23	--------
				02	. 21	--------	. 14
53	4. 8	4. 8	--------				
04	4. 8	--------	4. 8	86	. 02	<. 01	--------
				05	. 02	--------	. 02
65	. 08	. 09	--------				
98	. 10	--------	. 11				

[1] Precision and reliability of determinations:

	Range			
	0. 05 to 0. 5		0. 5 to 5	
	Standard Deviation	Number of comparisons	Standard deviation	Number of comparisons
A	0. 0024	3	0. 005	3
A, C	. 012	6	. 008	6
A, D	. 028	6	. 005	6

A. Gasometric method described; Edward Fennelly, analyst.
C. Absorption tube-gravimetric method (Hillebrand and others, 1953, p. 768-770); Marguerite Seerveld and Vertie Smith, analysts.
D. Gasometric method (Shapiro and Brannock, 1956); Leonard Shapiro, Paul Elmore, Samuel Botts, and Marvin Mack, analysts.

TABLE 44.—*Determinations*[1] *of carbonate carbon, in percent, in check samples*

[Add 259500 to each sample number to form serial number]

Sample	A	A_1	C	D	Mean	Difference (max–min)	Standard deviation
28	7.9	7.7	--------	7.4	7.7	0.5	0.24
33	1.5	1.5	1.5	--------	1.5	0	0
37	.04	.13	--------	.11	.09	.09	.043
39	.04	.07	--------	.11	.07	.07	.034
46	.02	.02	--------	.08	.04	.06	.029
48	<.02	<.02	<.01	--------	<.02	--------	--------
49	<.02	<.02	<.01	--------	<.02	--------	--------
63	<.02	<.02	<.01	--------	<.02	--------	--------
92	<.02	<.02	--------	.02	<.02	--------	--------
94	.67	.66	--------	.65	.66	.02	.010

[1] Precision and reliability of determinations:

	Range			
	0.05 to 0.5		0.5 to 5	
	Standard Deviation	Number of comparisons	Standard deviation	Number of comparisons
A, A_1	0.048	2	0.005	2
A, C+D	.048	2	.010	2

A. Gasometric method described; Edward Fennelly, analyst.
A_1. Gasometric method described; Irving Frost, analyst.
C. Absorption tube-gravimetric method (Hillebrand and others, 1953, p. 768–770); Marguerite Seerveld and Vertie Smith, analysts.
D. Gasometric method (Shapiro and Brannock, 1956); Leonard Shapiro, Paul Elmore Samuel Botts, and Marvin Mack, analysts.

TOTAL CARBON, GASOMETRIC DETERMINATION

[Range in shale: 0.2 to 9 percent total carbon]

PRINCIPLES

Organic matter is oxidized and converted to sodium carbonate by heating with sodium peroxide in a Parr microbomb in the presence of small amounts of potassium perchlorate and magnesium powder that act as combustion aids. The fused sample is leached from the bomb, and the peroxide is decomposed by removal of excess oxygen by gently heating the solution while covered to avoid absorption of carbon dioxide from the air. The carbon dioxide is liberated with hydrochloric acid and determined gasometrically, as described previously under the determination of carbonate carbon. A blank run is made to correct for the carbonate content of the sodium peroxide used. The method is that of I. C. Frost (written communication, 1955).

The method is applicable to carbonaceous materials that can be reduced to fine powder. Samples of coal, asphaltites, graphite, and unidentified carbonaceous materials have all been satisfactorily analyzed by using this method.

APPARATUS AND REAGENTS

Apparatus for the liberation, measurement, and absorption of carbon dioxide: Described under determination of carbonate carbon.

Complete Parr microbomb assembly with sodium peroxide measure.

Air-gas blast burner adjustable to a fine-pointed flame.

Additional fusion cups with a sufficient number of covers for several oxidations to be made in sequence.

Sodium peroxide: Fresh, dry sodium peroxide must be used. After use, the reagent should be stored in a tightly closed bottle in a desiccator.

Magnesium powder, reagent grade: The metal is washed with acetone to remove traces of organic matter and then dried before use.

PROCEDURE

1. Accurately weigh a sample of 0.050 to 0.50 g, depending on the apparent organic-matter content, and transfer to the fusion cup of a Parr microbomb. A 0.50-g sample is the maximum that can be oxidized in the parr microbomb, but a smaller sample size must be used when much organic matter is present because the oxidation is rapid and the reaction is difficult to control. A 0.050-g sample yields sufficient carbon dioxide for the determination and minimizes the hazard of the fusion.
2. Add 1 measure (about 1.25 g) of sodium peroxide, about 50 mg of potassium perchlorate, and 75 mg of magnesium powder to the fusion cup.
3. Place cover on the fusion cup and fasten in place. Shake the cup vigorously for several minutes to insure complete mixing of reagents. Open the cup and add sufficient additional sodium peroxide to just cover the fusion mixture. Clamp the lid on the fusion cup securely.
4. Heat the fusion cup and contents over an air-gas blast flame behind a safety shield, until oxidation occurs. Oxidation is generally shown by a dull redness or a noticeable blue coloring of the fusion cup.
5. Cool the fusion-cup assembly by immersion in cold water. Transfer the lid and cup to a reaction flask and slowly add sufficient water to cover the fusion cup. It is essential that the bomb be cooled immediately after the fusion, otherwise the lead gasket in the lid may be destroyed.
6. Place the reaction flask upright in a beaker containing water, cover the flask by inverting a small beaker over it, and heat the solution on a water bath for at least an hour to decompose the peroxide and remove excess oxygen from the solution.
7. Wash down the sides of the reaction flask with a small stream of water and attach it to the gas-liberation apparatus.
8. Liberate and measure carbon dioxide, as described in the method for determination of carbonate carbon.
9. Determine carbon dioxide in the reagents in a similar manner to obtain the reagent blank.
10. Calculate the total carbon content of the sample as follows: Convert the observed volume of gas to 0°C (273°K) and 760 mm pressure by substituting determined values in the formula given for this purpose in step 13 of the gasometric determination of carbonate carbon (p. A–35). Calculate the volume of carbon dioxide due to the reagent blank to standard conditions. The difference between the two volumes is the volume of carbon dioxide due to the sample.

$$\text{Percentage of total carbon} = \frac{Vs \times 12.01 \times 100}{22{,}269 \times W} = \frac{Vs}{18.542 \times W}$$

where Vs = volume of CO_2 corrected for reagent blank and corrected to standard conditions; 12.01 = atomic weight of carbon, in grams; 22,269 = volume of 1.0 mole of CO_2, in milliliters, at standard temperature and pressure; and W = weight of sample, in grams.

PRECISION OF TOTAL CARBON DETERMINATIONS

Total carbon was determined on the 80 samples of shale in laboratory A by use of the gasometric method described. The ranges of concentration for total carbon were <0.2 to 0. 5 percent (27 samples), 0. 5 to 5 percent (38 samples), and >5 percent (15 samples). Because 0.2 percent total carbon is the threshold limit of the determination, no deviations have been calculated for determinations below this level of concentration. The results on replicate determinations are given in table 45, those on the hidden splits in table 46, and those on the check samples in table 47.

The determinations of total carbon on the check samples by A, using the gasometric method, are plotted in figure 17 against those of A_2, using the same method.

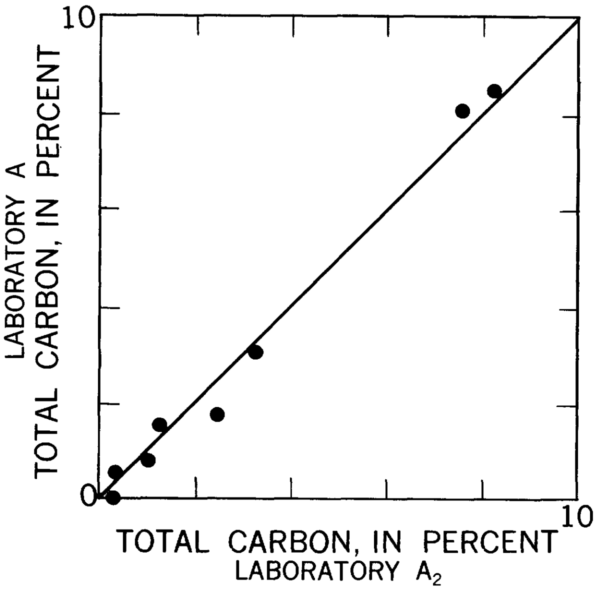

FIGURE 17.—Comparison of total carbon determinations of A with those of A_2.

TABLE 45.—*Replicate determinations*[1] *of total carbon, in percent, by laboratory A*

[Analysis by gasometric method described; Edward Fennelly, analyst. Add 259500 to all sample numbers, except 00 to 05 to which add 259600, to form serial numbers]

Sample			
40	0.21	0.27	
42	.26	.27	
65	.28	.29	
67	.28	.47	
50	.30	.37	
05	.40	.43	
30	.41	.48	
35	.41	.49	
29	.49	.51	
90	.67	.69	
34	.75	.81	0.84
80	.76	.79	
	.88	.91	
00	0.80	0.87	
	.89	.94	
85	.94	1.1	
45	.96	1.1	
43	1.0	1.1	
75	1.0	1.1	
55	1.1	1.1	
70	1.1	1.2	
47	1.8	2.0	
	2.1	2.2	
63	3.0	3.1	3.3
73	3.3	3.3	
26	4.4	4.7	
	4.8	5.2	
95	4.9	4.9	5.0
61	5.3	5.6	
91	5.7	5.7	
02	6.6	6.8	
	8.4	8.5	
60	6.6	6.6	
82	6.6	6.8	
04	7.2	7.3	
03	7.7	7.9	
	8.0	8.3	
28	8.1	8.1	
96	8.2	8.3	
49	8.4	8.5	

[1] Precision and reliability of determinations:

Range	Standard deviations	Number of comparisons
0.05 - 0.5	0.056	8
.5 - 5	.16	42
5 - 50	.57	20

TABLE 46.—*Determinations*[1] *of total carbon, in percent, in hidden splits by laboratory A*

[Analysis by gasometric method described; Edward Fennelly, analyst. Add 259500. to all sample numbers, except 00 to 05 to which add 259600, to form serial numbers Groups indicate the samples that were duplicates]

Sample	Percent
33	1.8
97	1.9
49	8.5
96	8.3
99	8.2
03	8.0
53	7.4
04	7.3
65	.29
98	.27
68	.94
01	.99
80	0.84
00	.88
82	6.7
02	7.4
86	.45
05	.42

[1] Precision and reliability of determinations:

Range	Standard deviations	Number of comparisons
0.50 - 0.5	0.018	2
.5 - 5	.048	3
5 - 50	.20	8

TABLE 47.—*Determinations*[1] *of total carbon, in percent, in check and other samples*

[Add 259500 to each sample number to form serial number]

Sample	A	A_1	A_2	A_3	Mean	Difference (max—min)	Standard deviation
26	4.8			4.9	4.9	0.1	0.06
28	8.1		7.6		7.9	.5	.30
31	.8	0.8		.9	.8	.1	.06
32	1.0	1.0		1.1	1.0	.1	.06
33	1.8		2.4		2.1	.6	.35
37	<.2		.2		.2	.2	.12
39	<.2		<.2		<.2		
46	.5		.4		.5	.1	.06
47	2.0	2.2		2.4	2.4	.4	.24
48	<.2		<.2		<.2		
49	8.5		8.3		8.4	.2	.12
60	6.6			6.6	6.6	0	0
63	3.1		3.2		3.2	.1	.06
87	.9	.8		.8	.8	.1	.06
91	5.7			5.8	5.8	.1	.06
92	.8		1.0		.9	.2	.12
94	1.5		1.3		1.4	.2	.12

[1] Precision and reliability of determinations in the range 0.5 to 5:

	Standard deviation	Number of comparisons
All data	0.17	17
All methods	.24	9

A. Gasometric method; Edward Fennelly, analyst.
A_1. Gasometric method; Wayne Mountjoy, analyst.
A_2. Gasometric method; Irving Frost, analyst.
A_3. Tube furnace-combustion train; Wayne Mountjoy, analyst.

DETERMINATIONS OF ORGANIC CARBON

[Range in shale: 0.2 to 9 percent organic carbon]

Organic carbon determinations are based on separate determinations of total carbon and carbonate carbon, the difference being taken as organic carbon.

Organic carbon was calculated for the 80 samples of shale by using the data obtained in laboratory A for total and carbonate carbon. The lower cutoff limit of 0.2 percent for the determination of total carbon applies also to organic carbon; 16 samples contained less than 0.2 percent organic carbon. The ranges of concentration for organic carbon in the other 64 samples were from 0.2 to 0.5 percent (21 samples), 0.5 to 5 percent (34 samples) and > 5 percent (9 samples). The results of replicate determinations are given in table 48, those on the hidden splits in table 49, and those on the check samples in table 50. The results of A and A_1 on the check samples, using the same method, are compared in figure 18.

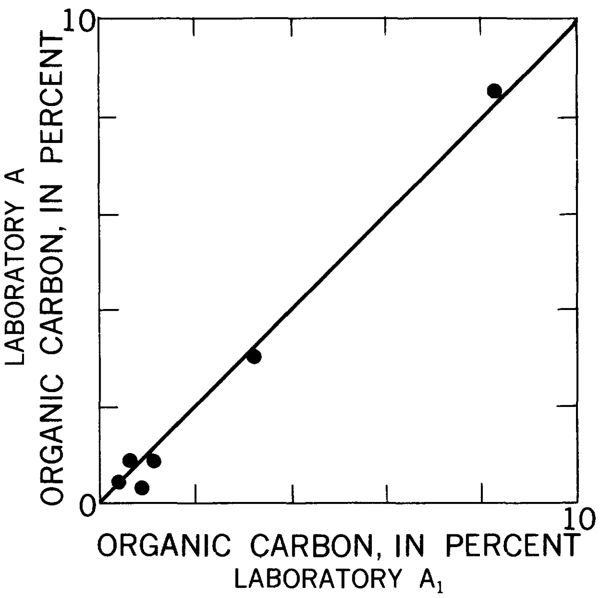

FIGURE 18.—Comparison of organic carbon determinations of A with those of A_1.

TABLE 48.—*Replicate determinations*[1] *of organic carbon, in percent, made in laboratory A by one chemist*

[Calculated from total carbon minus carbonate carbon, using data of Edward Fennelly, analyst. Add 259500 to all sample numbers, except 00 to which add 259600, to form the serial numbers]

40	0.2	0.3	47	1.0	1.4
00	.2	.3	55	1.1	1.1
30	.4	.5	56	2.8	2.9
75	.4	.6	63	3.0	3.3
29	.5	.6	73	3.3	3.3
60	.6	.7	26	4.4	5.2
85	.6	.7	95	4.9	5.0
45	.7	.8	61	5.3	5.6
90	.7	.7	91	5.7	5.7
43	1.0	1.1			

[1] Precision and reliability of determinations:

Range	*Standard deviations*	*Number of comparisons*
0.05– 0.5	0.093	3
.5 – 5	.12	13
5 –50	.34	3

TABLE 49.—*Determinations*[1] *of organic carbon, in percent, in hidden splits by laboratory A*

[Calculated from total carbon minus carbonate carbon, using data of Edward Fennelly, analyst. Add 259500 to all sample numbers except 00 to 05 to which add 259600, to form serial numbers. Groups indicate the samples that were duplicates]

33	0.3	53	2.6	80	<0.2
97	.5	04	2.4	00	.2
49	8.5	65	.2	82	6.5
96	8.2	98	<.2	02	7.2
99	8.2				
03	8.0	68	.6	86	.4
		01	.7	05	.4

[1] Precision and reliability of determinations:

Range	*Standard deviations*	*Number of comparisons*
0.05– 0.5	0.12	4
.5 – 5	.11	2
5 –50	.25	7

TABLE 50.—*Determinations*[1] *of organic carbon, in percent, in check samples*

[Add 259500 to each sample number to form serial number]

Sample	A	A_1	Mean	Difference (max—min)	Standard deviation
28	<0.2	<0.2	<0.2		
33	.3	.9	.6	0.6	0.53
37	≤.2	≤.2	≤.2		
39	<.2	<.2	<.2		
46	.4	.4	.4	0	0
48	<.2	<.2	<.2		
49	8.5	8.3	8.4	.2	.18
63	3.1	3.2	3.2	.1	.09
92	.8	1.0	.9	.2	.18
94	.8	.7	.8	.1	.09

[1] Precision and reliability of determinations in the range of 0.5 to 5: standard deviation, 0.10; number of comparisons, 3.

A. Calculated from total carbon minus carbonate carbon, using data of Edward Fennelly, analyst.

A_1. Calculated from total carbon minus carbonate carbon, using data of Irving Frost, analyst.

ORGANIC MATTER

[Range in shale: 0.2 to 15 percent organic matter]

PRINCIPLES

Organic matter in shale is generally believed to consist of a complex substance that is about 90 percent kerogen. This substance is slightly soluble in common organic solvents to the extent of about 5 percent and is intimately mixed throughout the shale making it difficult to separate from the inorganic constituents of shale.

In the chemical separation of organic matter, the shale is treated with hydrochloric and hydrofluoric acids, which do not appreciably alter or dissolve the organic matter. The acids decompose and dissolve most of the inorganic constituents of shale, with the exception of pyrite and related mineral compounds. The residue from the acid treatment is heated to constant weight at 80°C and then ignited at 1000°C; the loss on ignition is taken as a measure of the organic matter. Loss of water from hydrated materials in the residue during the ignition may cause errors in the results. Pyrite is substantially unattacked by the acid treatment and is corrected for by determining iron in the residue after ignition. The method is empirical and is not used to determine any specific type of organic matter. Similar separation procedures have been used by others (Guthrie, 1938) to separate organic matter from large samples for organic analysis and identification.

APPARATUS AND REAGENTS

Platinum crucibles, 30- and 50-ml capacities, with lids.
Platinum dishes, 100-ml capacity.
Hard rubber or plastic funnels and beakers.
Hydrochloric acid, analytical grade.
Hydrofluoric acid, analytical grade.

PROCEDURE

1. Regrind a portion of the prepared sample pulp to pass a 200-mesh sieve.
2. Weigh 1.0 g of the finely ground sample and transfer it to a 50-ml platinum crucible.
3. Moisten the sample with water and add 20 to 30 ml of hydrofluoric acid slowly and cautiously to prevent spattering. Cover the crucible tightly and digest on the steam bath over night.
4. Cool the hydrofluoric acid solution in the crucible and filter it through an 11-cm hardened paper, using a plastic funnel and beaker. Work under a fume hood and guard against exposure to hydrofluoric acid or its vapor.
5. Transfer the residue from the filter paper back to the original crucible with a stream of water. Add hydrochloric acid equal to about one-half the volume of the solution in the crucible, cover, and digest for about 4 hours on the steam bath.
6. Filter the solution on hardened paper and thoroughly wash the residue with hot water.
7. Transfer the residue from the paper with a stream of water to a tared 30-ml platinum crucible. Carefully dry the residue on the steam bath and finally in an oven to constant weight at 80°C. Cool and weigh.
8. Ignite the organic matter for 1 hour at 1000°C. Cool and reweigh.
9. Examine the residue for Fe_2O_3, shown by a brown color. Generally shale contains some pyrite, FeS_2, and correction must be made for its conversion to Fe_2O_3 on ignition.
10. If Fe_2O_3 is present, weigh a portion of the residue, transfer to a platinum dish, fume with a mixture of nitric, perchloric, and hydrofluoric acids, dissolve in hydrochloric acid, and determine Fe_2O_3 colorimetrically.
11. Calculate the percentage of organic matter in the sample as follows, correcting for pyrite if iron has been found in the residue:

$$\text{Percentage of organic matter} = 100 \times \frac{(R_1 - R_2 - (0.5 \times Fe_2O_3)}{Sw}$$

where R_1=weight of residue, in grams, after drying at 80°C; R_2=weight of residue, in grams, after ignition at 1000°C; 0.5=loss in weight of FeS_2, in grams, when converted to 1 g of Fe_2O_3; Fe_2O_3=weight of Fe_2O_3 in residue, in grams, calculated from the colorimetric determination; and Sw=sample weight, usually 1.0 g.

PRECISION OF ORGANIC MATTER DETERMINATIONS

Organic matter was determined in laboratory E on 40 samples selected by H. A. Tourtelot after organic carbon had been reported. The other 40 samples were not analyzed for organic matter, because the organic carbon determinations indicated that the organic matter would probably be <0.5 percent. The concentration ranges for organic matter were 0.5 percent, (45 samples); from 0.5 to 5 percent (25 samples); and from 5 to 13 percent (10 samples). The results on replicate determinations are given in table 51, those on the hidden splits in table 52, and those on the check samples in table 53.

Results of laboratory E on the check samples are compared with those of A in figure 19.

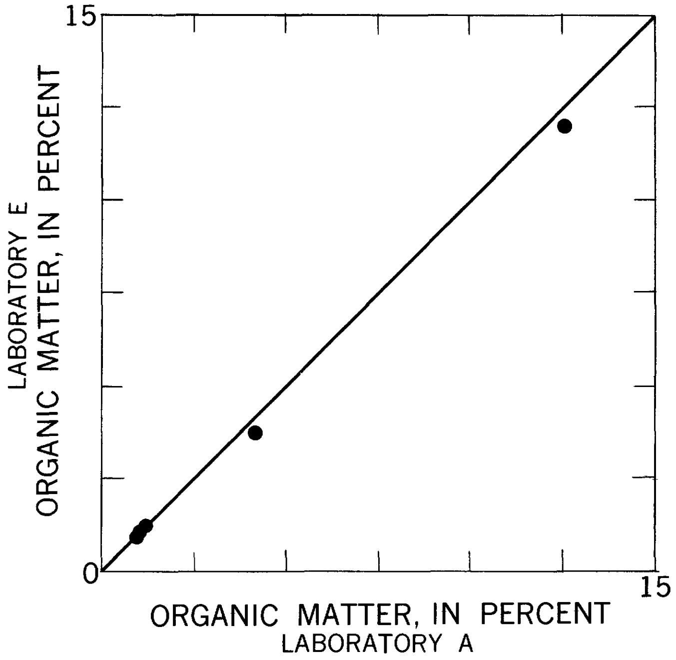

FIGURE 19.—Comparison of organic-matter determinations of E with those of A.

TABLE 51.—*Replicate determinations*[1] *of organic matter, in percent, made in laboratory E*

[Analysis by method described; Sarah Berthold, analyst. Add 259500 to all sample numbers except 00 to which add 259600, to form serial numbers]

36	0.2	0.2	43	1.5	1.5
00	.2	.2	74	2.5	2.4
31	.4	.4	56	3.1	3.2
52	.5	.6	63	3.7	3.8
85	.7	.8	26	5.0	4.9
77	.9	.8	82	8.4	8.4
60	.9	.9	99	12.2	12.1
97	.9	.9	03	12.2	12.1
55	1.1	1.1			

[1] Precision and reliability of determination:

Range	Standard deviations	Number of comparisons
0.5–5	0.056	11
5 –50	.57	3

TABLE 52.—*Determinations*[1] *of organic matter, in percent, in hidden splits by laboratory E*

[Analysis by method described; Sarah Berthold, analyst. Add 259500 to all sample numbers, except 00 to 05 to which add 259500, to form serial numbers. Groups indicate the samples that were duplicates]

33	0.9	53	3.5	80	0.2
97	.9	04	3.3	00	.2
49	12.2	65	.2	82	8.4
96	12.2	98	.2	02	8.4
99	12.1	68	1.0	86	.3
03	12.2	01	1.0	05	.2

[1] Precision and reliability of determinations:

Range	Standard deviations	Number of comparisons
0.5–5	0.081	3
5 –50	.046	7

TABLE 53.—*Determinations*[1] *of organic matter, in percent, in check samples*

[Add 259500 to each sample number to form serial number]

Sample	E	A	Mean	Difference (max–min)	Standard deviation
28	-------	<0.2	-------	-------	-------
33	0.9	.9	0.9	0	0
37	-------	<.2	-------	-------	-------
39	-------	<.2	-------	-------	-------
46	-------	.4	0.4	-------	-------
48	-------	1.2	1.2	-------	-------
49	12.2	12.6	12.4	0.4	0.18
63	3.8	4.2	4.0	.4	.18
92	1.3	1.3	1.3	0	0
94	1.2	1.1	1.2	.1	.09

[1] Precision and reliability of determinations in the range 0.5 to 5: standard deviation, 0.15; number of comparisons, 4.

E. Method described; Sarah Berthold, analyst.
A. Method described; Edward Fennelly, analyst.

SUMMARY

Methods for the chemical determination of minor elements in Pierre shale, comprising 26 different procedures are given in detail. Standard deviations of the various determinations covering the predominant concentration ranges of each element are reported with the methods. The very narrow, low range of 1.0 to 5.0 ppm included selenium, 50 samples; molybdenum, 33 samples; and uranium, 48 samples. The concentration range 5 to 50 ppm included cobalt, 80 samples; lead, 80 samples; copper, 57 samples; nickel, 46 samples; and arsenic, 64 samples. Elements predominantly in the range 50 to 500 ppm were vanadium, 61 samples; zinc, 76 samples; chromium, 71 samples; and manganese, 59 samples. All 80 samples of shale contained from 0.05 to 0.5 percent titanium, whereas less than 2 ppm of tungsten were found in 48 of the samples analyzed for this element.

Determinations and methods, for carbon and organic matter, are included in this report not only because of their importance to the study of shale but because of the general paucity of data for these substances in the literature. The ratio of organic matter to organic carbon in the shale is 1.36. The correlation of certain minor elements with organic matter warrants further study.

A summary of the average minor-element content of the check samples and the standard deviations calculated from data reported by all analysts and laboratories are given in table 54. The standard deviations were calculated, using the maximum difference in the determinations as a measure of the dispersion for a very small number of observations (Dixon and Massey, 1951, p. 239). The large range of concentration covered by the 10 selected samples point out some of the problems in calculating the precision.

A final summary of the precision and reliability of all the results for the various elements according to concentration range is given in table 55. These data are to be used with discretion when camparing the precisions of the determination of one element with those of another.

In general, duplicate determinations made by one analyst, or made in one laboratory, have smaller standard deviations than determinations made in different laboratories or with different methods. Very frequently, differences have no statistical significance. Where limited data were available, standard deviations were calculated largely to be consistent and with the attitude that some data are possibly better than no data at all.

TABLE 54.—*Mean element content and standard deviation of 10 check samples*

[Standard deviation calculated according to Dixon and Massey, 1951. Mean determinations of the upper group are given in percent, those of the lower group are given in parts per million]

	28		33		37		39		46		48		49		63		92		94	
	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation	Mean	Standard deviation
Carbonate carbon	7.7	0.24	1.5	0	0.09	0.043	0.07	0.034	0.04	0.029	<0.02	-------	<0.02	-------	<0.02	-------	<0.02	-------	0.66	0.01
Total carbon	7.9	.30	2.1	0.35	.2	.12	<.2	-------	.5	.06	<.2	-------	8.4	0.12	3.2	0.06	.9	0.12	1.4	.12
Organic carbon	<.2	-------	.6	.53	<.2	-------	<.2	-------	.4	0	<.2	-------	8.4	.18	3.2	.09	.9	.18	.8	.09
Organic matter	<.2	-------	.9	0	<.2	-------	<.2	-------	.4	-------	1.2	-------	12.4	.18	4.0	.18	1.3	0	1.2	.09
Titanium	.15	.030	.20	.013	.15	.013	.25	.022	.38	.039	.14	.013	.27	.056	.44	.022	.41,	.017	.42	.022
Manganese	.43	.012	3.5	.059	.020	.0034	.029	.0049	.039	.0058	.025	.0024	.016	.0039	.008	.0034	.012	.0034	.017	.0029
Vanadium	70	5.0	200	39	20	15	210	15	230	19	610	19	800	92	370	24	230	10	220	15
Chromium	64	9.2	52	4.4	<4	2.9	72	18	100	7.8	12	9.2	130	4.9	150	15	120	15	120	29
Cobalt	9	2.6	15	5.6	4	1.9	10	2.2	.21	3.9	14	3.9	17	3.0	4	1.9	13	2.2	9	1.7
Nickel	40	2.4	94	3.5	38	2.4	58	4.7	140	5.9	72	3.5	66	6.5	14	3.0	23	1.2	39	2.4
Copper	20	2.4	33	6.3	5	2.8	27	2.4	38	2.4	40	2.8	71	.8	71	4.0	41	2.4	27	4.0
Zinc	58	2.9	180	1.5	300	8.8	130	9.7	180	15	290	34	110	45	45	9.2	170	9.7	120	4.9
Lead	16	1.8	15	2.4	30	3.0	27	1.8	27	1.8	31	3.0	36	15	18	3.5	25	3.0	23	.6
Arsenic	5	1.7	13	1.2	2	.5	7	.5	10	.5	34	3.5	48	5	38	0	44	.9	11	.9
Selenium	<1	-------	1	.6	<1	-------	1	.6	1	.6	6	1.8	110	12	24	1.8	2	.6	2	1.2
Molybdenum	1	0	3	.9	<1	.9	4	2.7	2	.9	11	2.7	340	27	21	4.4	4	2.7	1	1.8
Uranium	1.7	.2	1.3	.1	10	.9	5.6	.6	5.1	.2	2.8	.3	8.3	.7	25	1.5	10	.8	3.9	.2

TABLE 55.—*Summary of the precision and reliability of the determinations for various elements*

	0.00005 to 0.0005		0.0005 to 0.005		0.005 to 0.05		0.05 to 0.5		0.5 to 5		5 to 50	
	Standard deviation	Number of comparisons	Standard deviation	Number of comparisons	Standard deviation	Number of comparisons	Standard deviation	Number of comparisons	Standard deviation	Number of comparisons	Standard deviation	Number of comparisons
Titanium												
Replicates:												
B, C	----	----	----	----	----	----	0.015	14	----	----	----	----
B, D	----	----	----	----	----	----	.020	40	----	----	----	----
Hidden splits:												
B	----	----	----	----	----	----	.013	13	----	----	----	----
B, C+D	----	----	----	----	----	----	.030	18	----	----	----	----
Check samples:												
B, A	----	----	----	----	----	----	.024	10	----	----	----	----
B, C	----	----	----	----	----	----	.025	4	----	----	----	----
B, D	----	----	----	----	----	----	.008	6	----	----	----	----
B, F	----	----	----	----	----	----	.051	10	----	----	----	----
B, G	----	----	----	----	----	----	.058	10	----	----	----	----
Average spectrographic, to chemical	----	----	----	----	----	----	.029	10	----	----	----	----
All data	----	----	----	----	----	----	.026	100	----	----	----	----
Vanadium												
Replicates:												
A	----	----	----	----	0.0015	11	----	----	----	----	----	----
Hidden splits:												
A	----	----	----	----	.0019	7	0.0098	6	----	----	----	----
Check samples:												
A, A_1	----	----	----	----	.0016	8	.0097	2	----	----	----	----
A, A_2	----	----	----	----	.0019	8	.0032	2	----	----	----	----
A, B	----	----	----	----	.0009	8	.0025	2	----	----	----	----
All data	----	----	----	----	.0018	48	.0064	12	----	----	----	----
Chromium												
Replicates:												
B	----	----	----	----	0.0005	8	----	----	----	----	----	----
Hidden splits:												
B	----	----	----	----	.00034	13	----	----	----	----	----	----
Check samples:												
B, A	----	----	----	----	.0008	10	----	----	----	----	----	----
B, F	----	----	----	----	.0007	10	----	----	----	----	----	----
B, G	----	----	----	----	.0013	10	----	----	----	----	----	----
Manganese												
Replicates:												
A	----	----	----	----	0.0014	20	0.0032	6	0.043	3	----	----
A, C	----	----	----	----	.0021	18	.0050	4	.079	4	----	----
A, D	----	----	----	----	.0037	46	.0025	17	.025	2	----	----
Hidden splits:												
A	----	----	----	----	.0013	11	----	----	----	----	----	----
A, C+D	----	----	----	----	.0034	36	.0021	4	.086	4	----	----
Check samples:												
A, B	----	----	----	----	.0020	8	----	----	----	----	----	----
A, C+D	----	----	----	----	.0031	8	----	----	----	----	----	----
A, F	----	----	----	----	.0040	8	----	----	----	----	----	----
Cobalt												
Hidden splits:												
B	----	----	0.00010	13	----	----	----	----	----	----	----	----
Check samples:												
B, A	----	----	.00043	10	----	----	----	----	----	----	----	----
B, A_1	----	----	.00029	10	----	----	----	----	----	----	----	----
B, F	----	----	.00016	10	----	----	----	----	----	----	----	----
B, G	----	----	.00026	8	----	----	----	----	----	----	----	----
All data	----	----	.00031	92	----	----	----	----	----	----	----	----
Nickel												
Replicates:												
A	----	----	0.00012	19	0.00035	26	----	----	----	----	----	----
Hidden splits:												
A	----	----	.00019	5	.00044	8	----	----	----	----	----	----
Check samples:												
A, B	----	----	.00018	5	.00043	5	----	----	----	----	----	----
A, F	----	----	.00025	5	.00046	5	----	----	----	----	----	----

TABLE 55.—*Summary of the precision and reliability of the determinations for various elements*—Continued

	0.00005 to 0.0005		0.0005 to 0.005		0.005 to 0.05		0.05 to 0.5		0.5 to 5		5 to 50	
	Standard deviation	Number of comparisons	Standard deviation	Number of comparisons	Standard deviation	Number of comparisons	Standard deviation	Number of comparisons	Standard deviation	Number of comparisons	Standard deviation	Number of comparisons
Copper												
Replicates:												
B	--------	--------	0.00027	9	0.00068	4	--------	--------	--------	--------	--------	--------
Hidden splits:												
B	--------	--------	.00038	5	.00080	8	--------	--------	--------	--------	--------	--------
Check samples:												
B, A	--------	--------	.00034	8	.00020	2	--------	--------	--------	--------	--------	--------
B, A_1	--------	--------	.00029	8	.00026	2	--------	--------	--------	--------	--------	--------
B, A_2	--------	--------	.00014	8	.00016	2	--------	--------	--------	--------	--------	--------
B, A_3	--------	--------	.00034	8	.00050	2	--------	--------	--------	--------	--------	--------
B, A_4	--------	--------	.00040	8	.00011	2	--------	--------	--------	--------	--------	--------
Zinc												
Replicates:												
B	--------	--------	--------	--------	0.0010	8	--------	--------	--------	--------	--------	--------
Hidden splits:												
B	--------	--------	--------	--------	.00078	13	--------	--------	--------	--------	--------	--------
Check samples:												
B, A	--------	--------	--------	--------	.0014	10	--------	--------	--------	--------	--------	--------
B, A_1	--------	--------	--------	--------	.0011	10	--------	--------	--------	--------	--------	--------
B, A_2	--------	--------	--------	--------	.0020	10	--------	--------	--------	--------	--------	--------
All data	--------	--------	--------	--------	.0013	60	--------	--------	--------	--------	--------	--------
Lead												
Replicates:												
B	--------	--------	0.00026	13	--------	--------	--------	--------	--------	--------	--------	--------
Hidden splits:												
B	--------	--------	.00053	13	--------	--------	--------	--------	--------	--------	--------	--------
Check samples:												
B, A	--------	--------	.00060	10	--------	--------	--------	--------	--------	--------	--------	--------
B, A_1	--------	--------	.00026	10	--------	--------	--------	--------	--------	--------	--------	--------
All data	--------	--------	.00047	30	--------	--------	--------	--------	--------	--------	--------	--------
Arsenic												
Replicates:												
A	--------	--------	0.000056	16	0.00010	2	--------	--------	--------	--------	--------	--------
Hidden splits:												
A	--------	--------	.000037	7	.00055	6	--------	--------	--------	--------	--------	--------
Check samples:												
A, B	--------	--------	.00057	9	.00022	1	--------	--------	--------	--------	--------	--------
All data	--------	--------	.00013	37	.00057	3	--------	--------	--------	--------	--------	--------
Selenium												
Replicates:												
A	0.000023	9	0.00032	15	0.00059	7	--------	--------	--------	--------	--------	--------
Hidden splits:												
A	.00012	5	.00022	2	.00050	6	--------	--------	--------	--------	--------	--------
Check samples:												
A, B	.00026	7	.00020	2	--------	1	--------	--------	--------	--------	--------	--------
A, B_1	.00003	7	.00016	2	.0021	1	--------	--------	--------	--------	--------	--------
Molybdenum												
Replicates:												
A	--------	--------	0.00018	12	0.0016	6	--------	--------	--------	--------	--------	--------
Hidden splits												
A	--------	--------	--------	--------	.00095	7	--------	--------	--------	--------	--------	--------
Check samples:												
A, B	--------	--------	.00029	2	--------	--------	--------	--------	--------	--------	--------	--------
Uranium												
Replicates:												
B, B_1	0.000022	33	0.000058	21	--------	--------	--------	--------	--------	--------	--------	--------
Hidden splits:												
B	.000040	5	.000090	8	--------	--------	--------	--------	--------	--------	--------	--------
B_1	.000022	5	.000028	8	--------	--------	--------	--------	--------	--------	--------	--------
B, B_1	.000010	10	.000015	8	--------	--------	--------	--------	--------	--------	--------	--------
Check samples:												
Avg of A, avg $B+B_1$	.000015	4	.000012	6	--------	--------	--------	--------	--------	--------	--------	--------
All data	.000018	24	.000081	36	--------	--------	--------	--------	--------	--------	--------	--------

TABLE 55.—*Summary of the precision and reliability of the determinations for various elements*—Continued

	0.00005 to 0.0005		0.0005 to 0.005		0.005 to 0.05		0.05 to 0.5		0.5 to 5		5 to 50	
	Standard deviation	Number of comparisons	Standard deviation	Number of comparisons	Standard deviation	Number of comparisons	Standard deviation	Number of comparisons	Standard deviation	Number of comparisons	Standard deviation	Number of comparisons
Carbonate carbon												
Replicates:												
A	--------	--------	--------	--------	--------	--------	0.014	7	0.011	4	--------	--------
A, C	--------	--------	--------	--------	--------	--------	.016	3	.036	7	--------	--------
A, D	--------	--------	--------	--------	--------	--------	.034	22	.14	5	--------	--------
Hidden splits:												
A	--------	--------	--------	--------	--------	--------	.0024	3	.005	3	--------	--------
A, C	--------	--------	--------	--------	--------	--------	.012	6	.008	6	--------	--------
A, D	--------	--------	--------	--------	--------	--------	.028	6	.005	6	--------	--------
Check samples:												
A, A_1	--------	--------	--------	--------	--------	--------	.048	2	.005	2	--------	--------
A, C+D	--------	--------	--------	--------	--------	--------	.048	2	.010	2	--------	--------
Total carbon												
Replicates:												
A	--------	--------	--------	--------	--------	--------	0.056	8	0.16	42	0.57	20
Hidden splits:												
A	--------	--------	--------	--------	--------	--------	.018	2	.048	3	.20	8
Ckeck samples:												
All data	--------	--------	--------	--------	--------	--------	--------	--------	.17	17	--------	--------
Methods	--------	--------	--------	--------	--------	--------	--------	--------	.24	9	--------	--------
Organic carbon												
Replicates:												
A	--------	--------	--------	--------	--------	--------	0.093	3	0.12	13	0.34	3
Hidden splits:												
A	--------	--------	--------	--------	--------	--------	.12	4	.11	2	.25	7
Check samples:												
A, A_1	--------	--------	--------	--------	--------	--------	--------	--------	.10	3	--------	--------
Organic matter												
Replicates:												
E	--------	--------	--------	--------	--------	--------	--------	--------	0.056	11	0.057	3
Hidden splits:												
E	--------	--------	--------	--------	--------	--------	--------	--------	.081	3	.046	7
Check samples:												
E, A	--------	--------	--------	--------	--------	--------	--------	--------	.15	4	--------	--------

NOTE.—See table giving determinations of respective element for explanation of letter symbols.

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Spectrographic Analysis For Selected Minor Elements in Pierre Shale

By PAUL R. BARNETT

ANALYTICAL METHODS IN GEOCHEMICAL INVESTIGATIONS OF THE PIERRE SHALE

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SPECTROGRAPHIC ANALYSIS FOR SELECTED MINOR ELEMENTS IN PIERRE SHALE

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ABSTRACT

Spectrographic determinations were made by one spectrographic laboratory on 80 samples of Pierre shale (Late Cretaceous) for 10 elements. The precision of single measurements of these elements, in terms of the coefficient of variation, is: boron, 10 percent; barium, 11; cobalt, 7; chromium, 9; gallium, 20; nickel, 7; scandium, 10; strontium, 13; titanium, 6; and zirconium, 10 percent. Eight of these elements in 10 check samples were determined by a second spectrographic laboratory. The precision, in percent, between laboratories for each indicated element is: boron, 10; barium, 12; cobalt, 16; chromium, 11; gallium, 16; scandium, 12; strontium, 10; and titanium, 10. As computed from data on all 80 samples, the coefficients of variation between determinations by chemical and by spectrographic methods are: barium, 34 percent; cobalt, 12; chromium, 10; nickel, 7; and titanium, 10 percent. The precision of the first spectrographic laboratory on disguised replicate samples is: boron, 6 percent; barium, 8; cobalt, 10; chromium, 5; gallium, 12; nickel, 5; scandium, 12; strontium, 20; titanium, 4; and zirconium, 14 percent.

INTRODUCTION

GENERAL REMARKS

Geochemical investigations of the Pierre shale of Late Cretaceous age in the western interior of the United States were begun in 1956. The investigations seek to relate the chemical and mineralogical composition of a large body of typical marine shale with the lithological characteristics and geographic and stratigraphic distribution of rock units within the shale. The nature of the problem and the results of preliminary investigations are described by Tourtelot (written communication).

The data on chemical composition are provided by standard and rapid rock analyses, by chemical analyses for selected elements occurring in trace amounts, and by spectrographic analyses for boron, barium, cobalt, chromium, gallium, nickel, scandium, strontium, titanium, and zirconium. In order that the significance of differences in content of the elements in various samples could be judged, the precision of the different analytical methods was determined. The methods of chemical analyses for selected minor elements and their precision have been described by Rader and Grimaldi (1961). The purpose of this report is to examine the precision of spectrographic determinations for minor elements in samples of Pierre shale and to compare the spectrographic determinations with chemical determinations.

MATERIAL ANALYZED

Seventy samples of shale and claystone, bentonite, and marlstone from the Pierre shale were collected by Harry A. Tourtelot, James R. Gill, and Leonard G. Schultz. After drying and preliminary crushing (Rader and Grimaldi, 1961), seven of the samples were divided by Tourtelot and Gill into two portions, yielding seven additional samples; and one sample was divided into four separate portions, yielding three additional samples. Each of the 10 new samples thus obtained was assigned a new and different field number, a fictitious field location, and a different serial number. The disguised samples are referred to as hidden splits and bring the total number of samples analyzed to 80. After the 80 samples were analyzed, Tourtelot selected 10 samples believed to be representative of the shale samples with regard to element concentration and type of material. These 10 check samples were then analyzed spectrographically by a different spectrographer in a different laboratory for most of the elements that had been determined in the 80 samples. The hidden splits and 10 check samples were also used to obtain data on precision of chemical analyses as described by Rader and Grimaldi. The spectrographic analyses of the hidden splits are shown in table 1 and the spectrographic analyses by two different laboratories of the 10 check samples are shown in table 2.

METHODS OF ANALYSIS

The methods used by the U.S. Geological Survey for spectrographic analysis are described in detail by Bastron, Barnett, and Murata (1960). These methods as applied to the analysis of samples of Pierre shale are briefly reviewed below.

A 7-gram split, reduced to approximately —200 mesh, of each of the 80 samples was received for analysis (Rader and Grimaldi, 1961). Each sample was prepared for arcing by mixing a 100-mg portion of the sample with 95 mg of pure quartz, 5 mg of pure sodium carbonate, and 50 mg of pure graphite powder. The quartz was added to raise the silica content of the material to be analyzed to the approximate level of that in the synthetic standards used. The sodium carbonate stabilizes the arc and the graphite powder tends to reduce selective volatilization during arcing. After thorough grinding and mixing in an agate mortar, 25-mg quantities of the mixture were weighed into cupped graphite electrodes for arcing.

Apparatus and operating conditions

Spectrograph	Wadsworth mounted grating, dispersion 5.2 A/mm in first order.
Wavelength region	2250–4750 A, first order.
Power source	Varisource, approx 16 amp d-c arc.
Slit	25 microns.
Optics	Center part of arc focused on collimating mirror.
Emulsion	Eastman type III–O.
Development	4 min at 20°C in D–19.
Arc gap	4 to 5 mm maintained throughout arcing.
Transmission	12, 16, or 20 percent, depending upon the sensitivity of the particular set of plates being used. Adjusted with neutral quartz filters.
Arcing time	Sample burned to completion.
Anode	Sample electrode; United Carbon type 1590.
Cathode	High-purity graphite rod, one-eighth inch diameter.
Emulsion calibration	Selected iron lines after method of Dieke and Crosswhite (1943) and Crosswhite (1950).
Microphotometer	Nonrecording projection comparator microphotometer.

STANDARDS

When the quantitative spectrographic analysis of the Pierre shale was started in 1957 it was not the practice in laboratory F to photograph the spectra of standards on each plate along with the samples being determined. Although the advantages of including the spectra of standards were recognized, no single set of standards was available that contained more than a minority of the elements usually determined in the unknowns. If sets of standards containing all the elements to be determined in the unknowns were recorded on each plate, little or no space was left for the unknowns. Alternatively, when each new set of plates (all with the same emulsion number) was received from the manufacturer, spectra of standards for all elements ordinarily determined were recorded in duplicate or triplicate on separate plates. Working curves for each element were prepared by drawing on log-log paper the regression line for the intensity of the given element line versus the concentration. Spectra of unknowns were then recorded on separate plates from the same set as that from which the standard plates were taken. Even though plate calibrations tend to minimize plate differences, all conditions leading up to the finished plate were carefully controlled and made as nearly the same as possible for all plates. Unknowns were duplicated on separate plates so that if something should go awry with one plate the deviation would be detected by comparison with the duplicate plate. The 10 elements in all 80 samples of Pierre shale were initially determined in this way.

The standards used were prepared by thoroughly mixing the carefully weighed pure oxides of the elements with a matrix consisting of 60 parts pure quartz, 40 parts microcline or perthite, and 1 part ferric oxide. In this study such a matrix is called pegmatite base. Each constituent of the matrix was carefully chosen to insure the absence of the element whose standard was being prepared. This requirement made necessary the several sets of standards referred to previously.

In 1958 Sol Berman (written communication) of the U.S. Geological Survey prepared a single set of standards containing all the elements determined in the Pierre shale, except barium and strontium. The analysis of the 80 samples was repeated for cobalt, chromium, nickel, and titanium, but this time the spectra of this new set of standards were recorded on each plate along with those of the samples. About half the samples were duplicated on separate plates and half on the same plate. This procedure affords an opportunity to study the precision within plates and between plates and the comparison of the average of two spectrographic results by each method of duplication to results by chemical methods.

By the use of a little logic, the outcome of this study might be predicted. Duplicates on the same plate should have greater precision because both determinations are made from one working curve, which is constructed from the standard on the plate. This precision does not depend upon correctness of the working curve. However, the accuracy of the average of the two determinations does depend upon the correctness of the working curve and could be inaccurate even with good precision. Duplicates on separate plates should have the poorer precision, since each is determined from the working curve constructed from its own plate. However, the accuracy of the average of the two determinations should be improved, because one of two working curves has a greater probability of being constructed correctly than one alone. This difference in accuracy should be reflected in the comparison to the chemical determinations if the latter are sufficiently close to the unknown true value.

Of course, determinations made with standards on each plate should be more accurate than those made with standards on separate plates, if the standards themselves are equally accurate.

MEASUREMENT OF PRECISION

Precision is measured by comparison of duplicate determinations of a single sample, comparison of the analyses of the hidden splits, and comparison with results reported by a second spectrographic laboratory on the 10 check samples. In addition, some comparisons are made with chemical analyses for some elements. The precision and comparisons are expressed, in percent, in terms of the coefficient of variation, ν, which is computed by the formula:

$$\nu = \frac{SD}{\bar{x}} \times 100$$

where SD is the standard deviation and $\bar{x}$ is the arithmetic average of the numbers from which the standard deviation was computed. The standard deviation is a convenient way of expressing the precision of measurements of a single quantity, or of two or more quantities that are relatively close together. However, the precision of replicate measurements of two or more quantities differing in value by even a factor of two, can be better expressed by the coefficient of variations, sometimes aptly termed the "relative standard deviation."

The laboratories of the U.S. Geological Survey that provided data for the study of precision of both chemical and spectrographic methods of analysis were identified by Rader and Grimaldi (1961) by the letter, A to G.

ANALYTICAL RESULTS

The analytical results obtained by the several laboratories are discussed element by element in the following sections. The data are presented in the tables and figures.

BORON

For the determination of boron a special series of standards was prepared by successive dilutions of the National Bureau of Standards standard sample No. 92 with boron-free pegmatite base. This procedure was believed necessary, because standards prepared from boric acid have sometimes been found to be unreliable. Standard sample No. 92 is a glass containing 0.70 percent boric acid. The standards were arced on each plate of samples. All samples were arced in duplicate, on one plate or on separate plates with approximately equal frequency. Those samples whose duplicates did not check closely enough were arced again; and if a sample had to be repeated for analyzing some other element, the boron was redetermined. The reported values for boron, and for the other elements, are the arithmetic averages of 2 to 6 determinations.

The coefficient of variation for a single determination as computed from the first two boron determinations on each sample is 7.5 percent for duplicates on the same plate (49 pairs), 12.5 percent for duplicates on separate plates (32 pairs), and 10.2 percent for both methods taken together. The coefficient of variation for an average of two determinations can be determined by dividing the coefficient of variation for a single determination by $\sqrt{2}$, and it is 7.2 percent for the 10.2 percent given above. The coefficient of variation as computed from the results reported on the 10 samples and their hidden splits (table 1) is 6.1 percent. This greater precision reflects the greater number of determinations used in reporting the average.

TABLE 1.—*Spectrographic determination, in percent, by laboratory F of selected minor elements in hidden splits*

Sample	B	Co	Cr	Ga	Ni	Sc	Sr	Ti	Zr
259533....	0.014	0.0020	0.0050	0.0007	0.0094	0.0012	0.011	0.20	0.009
259597....	.012	.0020	.0058	.0008	.0100	.0015	.013	.20	.011
259549....	.013	.0017	.013	.0009	.0065	.0011	.013	.23	.014
259596....	.012	.0018	.012	.0012	.0068	.0018	.017	.23	.021
259599....	.013	.0019	.013	.0012	.0070	.0015	.017	.24	.015
259603....	.012	.0016	.013	.0011	.0063	.0015	.018	.22	.015
259553....	.006	.0016	.0098	.0012	.0057	.0022	.12	.23	.015
259604....	.007	.0012	.0100	.0011	.0063	.0028	.10	.22	.015
259565....	.008	.0014	.0090	.0019	.0036	.0023	.012	.33	.020
259598....	.009	.0012	.0090	.0016	.0039	.0022	.018	.36	.019
259568....	.012	.0020	.013	.0019	.0042	.0022	.015	.36	.023
259601....	.013	.0018	.012	.0015	.0049	.0019	.020	.36	.019
259580....	.011	.0017	.011	.0016	.0038	.0024	.019	.34	.018
259600....	.010	.0014	.011	.0016	.0041	.0024	.018	.35	.019
259582....	.012	.0034	.0091	.0014	.017	.0025	.0082	.34	.015
259602....	.012	.0028	.0100	.0017	.016	.0023	.0087	.31	.016
259586....	.012	.0015	.0096	.0017	.0044	.0025	.014	.38	.019
259605....	.012	.0014	.011	.0014	.0042	.0023	.013	.38	.017
Coefficient of variation.....	6.1	10.3	5.2	12.0	5.4	12.3	20.3	4.2	14.4

Laboratory G determined boron spectrographically in the 10 check samples. The coefficient of variation between the values reported by the two laboratories is 9.6 percent as computed from the paired results given in table 2. These reported results are also compared graphically in figure 1.

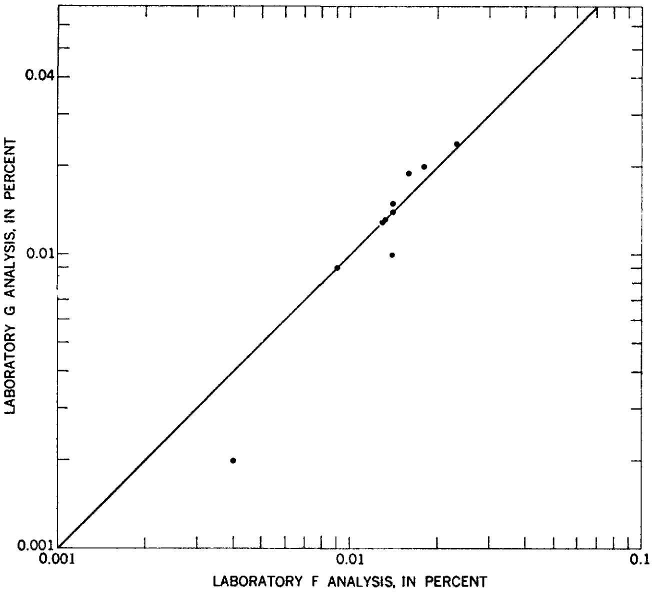

Figure 1.—Comparison of determinations of boron in 10 check samples by two spectrographic laboratories.

The various comparisons are summarized in the following table. Boron was not determined chemically.

Summary of precision of spectrographic determination of boron

	Number of comparisons	Range of concentration (percent)	Average concentration (percent)	Standard deviation	Coefficient of variation
Duplicates on same plate.....	49	0.0050 – 0.021	0.0114	0.00085	7.5
Duplicates on different plates.	32	.0030 – .024	.0136	.0017	12.5
Hidden splits, laboratory F...	13	.0060 – .014	.0111	.00069	6.1
Check samples, laboratories F and G.......	10	.0020 – .024	.0138	.0013	9.6

BARIUM

Barium was analyzed spectrographically by the use of the line at 4554 A. At the concentrations in the Pierre shale, even with the 1:1 dilution, this line is too heavy to measure with a densitometer. Analytical curves were prepared by plotting on a linear scale the measured width of the lines against the concentration of the prepared standard on a logarithmic scale. These curves are straight lines, except near their ends. It is imperative that the standards be arced on each plate of samples, because the plate is not calibrated for this type of measurement.

The precision of a single spectrographic determination was 11.2 percent for samples diluted 1:1 and arced on separate plates and was 14.5 percent for samples with higher barium content diluted 1:4 with barium-free pegmatite base and arced on one plate. The poorer precision of determinations for the samples of greater dilution, even with the greater dilution on the same plate and the lesser dilution on separate plates, may indicate the greater hazards of weighing and thorough mixing for the greater dilutions.

The coefficient of variation between the results of laboratories F and G in the 10 check samples is 11.7 percent. (See following table.) These analyses are compared graphically in figure 2. The coefficient of variation between the spectrochemical analyses

Table 2.—*Spectrographic determinations, in percent, by laboratories F and G of selected minor elements in check samples*

Sample	B		Co		Cr		Ga		Sc		Sr		Ti	
	F	G	F	G	F	G	F	G	F	G	F	G	F	G
259528...........	0.004	0.002	0.0011	0.0010	0.0060	0.0058	0.0006	0.0006	0.0016	0.0012	0.23	0.20	0.14	0.16
259533...........	.014	.010	.0020	.0015	.0050	.0047	.0007	.0	.0012	.0010	.011	.0080	.20	.18
259537...........	.009	.009	.0004	.0	.0005	.0003	.0020	.0024	.0008	.0009	.022	.028	.15	.14
259539...........	.014	.014	.0012	.0010	.0060	.0047	.0016	.0014	.0012	.0013	.017	.0092	.24	.22
259546...........	.018	.020	.0024	.0020	.0095	.011	.0018	.0024	.0018	.0018	.011	.011	.35	.32
259548...........	.023	.024	.0016	.0012	.0014	.0010	.0018	.0012	.0005	.0007	.011	.010	.13	.12
259549...........	.013	.013	.0017	.0013	.013	.013	.0009	.0010	.0011	.0010	.013	.010	.23	.22
259563...........	.014	.015	.0004	.0	.013	.016	.0019	.0015	.0016	.0018	.0073	.0090	.38	.46
259592...........	.013	.013	.0014	.0012	.011	.010	.0020	.0023	.0025	.0020	.010	.010	.35	.40
259594...........	.016	.019	.0012	.0011	.0095	.0095	.0018	.0020	.0020	.0022	.017	.016	.40	.40
Coefficient of variation.......	9.6		15.9		10.6		16.1		12.3		[1] 9.7		9.9	

[1] 19.6 percent for the determinations that range in concentration from 0.0073 to 0.028 percent.

of laboratory F and the chemical analyses of laboratories C and D in these samples is 33.9 percent.

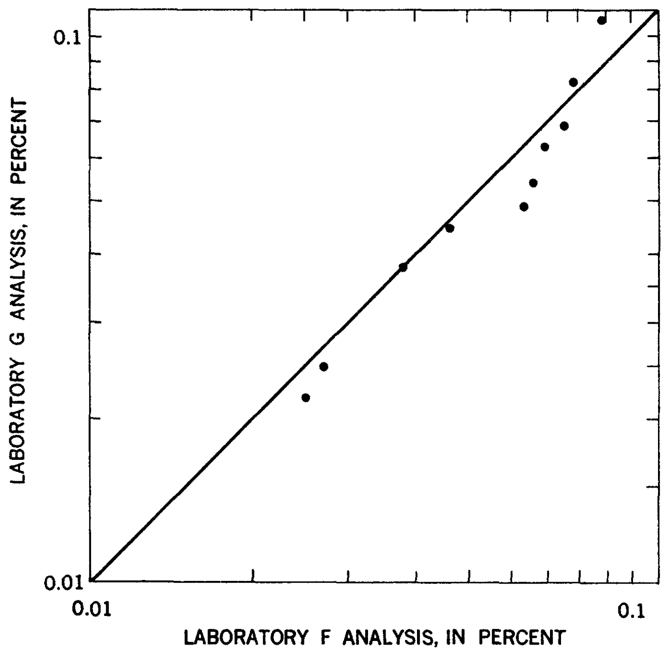

Figure 2.—Comparison of determinations of barium oxide (converted from barium) in 10 check samples by two spectographic laboratories.

Determination of barium oxide, in percent, in check samples

Sample	Spectrographic		Chemical	
	Laboratory F	Laboratory G	Laboratory E	Laboratory C
259528	0.027	0.025	0.03	
259533	.038	.038		0.00
259537	.078	.083	.08	
259539	.069	.063	.07	
259546	.075	.069	.05	
259548	.025	.022		.00
259549	.063	.049		.08
259563	.046	.045		.03
259592	.067	.054	.02	
259594	.089	.109	.07	

Chemical barium oxide was reported on 25 samples by laboratory C and on 55 samples by laboratory E. These 80 analyses are compared graphically in figure 3 with the results reported by laboratory F. The coefficient of variation between the results of laboratory C and those of laboratory F is 32.7 percent, and between the results of laboratory E and those of laboratory F is 23.0 percent; spectrographic values were converted from barium.

The precision of laboratory F on the hidden splits (see the following table) is 8.1 percent. The precision of chemical determination of barium oxide on these samples is 33.0 percent.

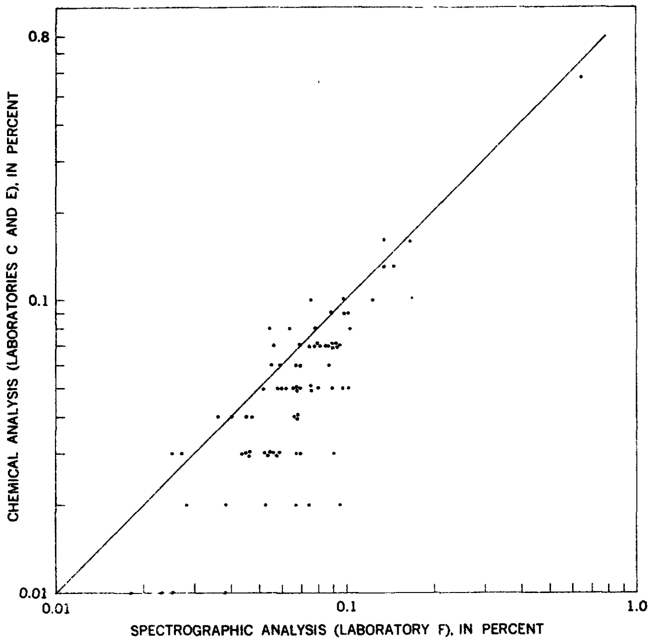

Figure 3.—Comparison of spectrographic with chemical determinations of barium in 80 samples.

Determination of barium oxide, in percent, in hidden splits by laboratories F, C, and E

Sample	Spectrographic	Chemical	
	F	C	E
259533	0.038	0.00	
259597	.038		0.02
259549	.062	.08	
259596	.054	.03	
259599	.058		.05
259603	.069		.05
259553	.045	.04	
259604	.047		.04
259565	.090	.03	
259598	.087		.06
259568	.10	.08	
259601	.099		.09
259580	.068	.05	
259600	.078		.07
259582	.054	.08	
259602	.060		.05
259586	.056	.07	
259605	.055		0.06

COBALT

The precision of the spectrographic determinations for cobalt and a comparison of the spectrographic results of laboratory F to the chemical results of laboratory B are given in the following table.

Examination of the data shows that precision was improved from 9.9 percent to 8.3 percent when the standard was on the plate with the samples. However, there was not a corresponding improvement in the comparison of spectrographic to chemi-

Coefficient of variation of cobalt determinations

[Letters in parentheses indicate laboratory furnishing data]

	Standard not on plate	Standard on plate
Duplicates on same plate:		
Precision of a single spectrographic determination (F)		5.2
Spectrographic (F) versus chemical (B) determinations		11.9
Duplicates on separate plates:		
Precision of a single spectrographic determination (F)	9.9	8.3
Spectrographic (F) versus chemical (B) determinations	11.4	11.2

cal determinations. Perhaps this is in part due to the relatively poor precision of the chemical determinations as shown by Rader and Grimaldi (1961). Spectrographic precision is better when the duplicates are on the same plate but the comparison of the average of two spectrographic determinations to the chemical determination is better when the duplicates are on separate plates.

The spectrographic values reported are the averages of two or more determinations. Approximately 40 samples were duplicated on the same plate and 40 samples on separate plates with the standard on each plate. The coefficient of variation between these values and the reported chemical results is 11.7 percent. This comparison is made graphically in figure 4.

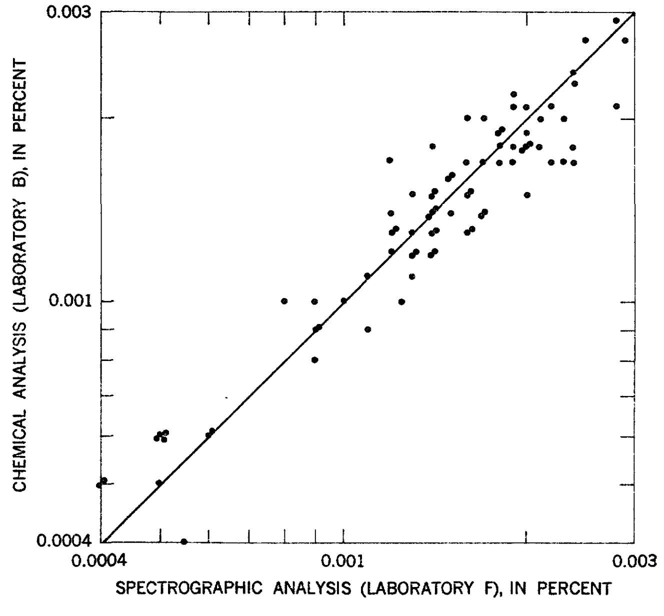

FIGURE 4.—Comparison of spectrographic with chemical determinations of cobalt in 80 samples.

On the eight check samples in which the concentration of cobalt was above the limit of sensitivity for laboratory G (table 2), the coefficient of variation between the results of laboratories G and F is 15.9 percent. Figure 5 compares these paired values graphically.

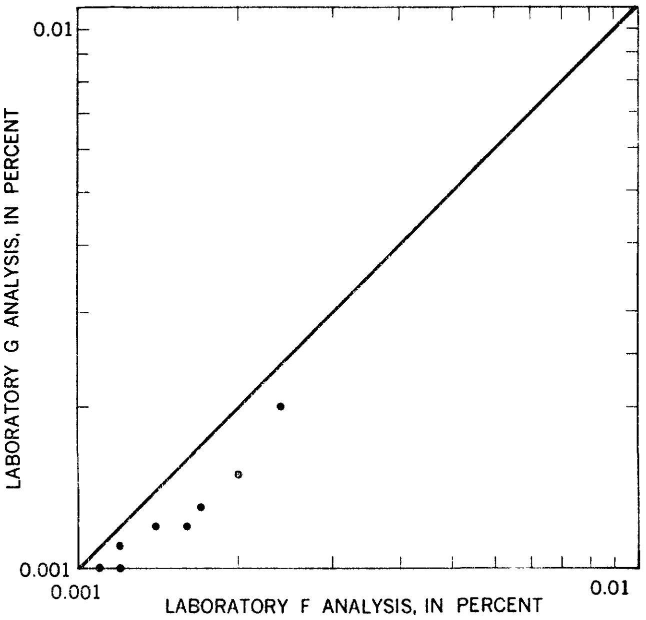

FIGURE 5.—Comparison of determinations of cobalt in 10 check samples by two spectrographic laboratories.

The results by laboratory F on the hidden splits are given in table 1. The coefficient of variation for these numbers is 10.3 percent.

CHROMIUM

The precision of a single spectrographic determination of chromium computed from duplicates on the same plate is 5.9 percent and from duplicates on separate plates, 11.6 percent. The precision as computed from the reported results given in table 1 for the hidden splits is 5.2 percent. Each reported value is an average of two or more individual determinations. The coefficient of variation between the values given for spectrographic laboratories F and G in table 2 is 10.6 percent. These results are graphed in figure 6. The comparisons between the results reported by laboratories F and B are given in the following table and in figure 7.

Comparison of chromium values determined spectrographically by laboratory F and chemically by laboratory B

Number of comparisons	Range of concentration (percent)	Average concentration (percent)	Coefficient of variation
36	0.010 - 0.020	0.012	9.0
33	.001 - .010	.0073	12.1
5	.0004 - .001	.00076	45.9
74	.0004 - .020	.0096	10.3

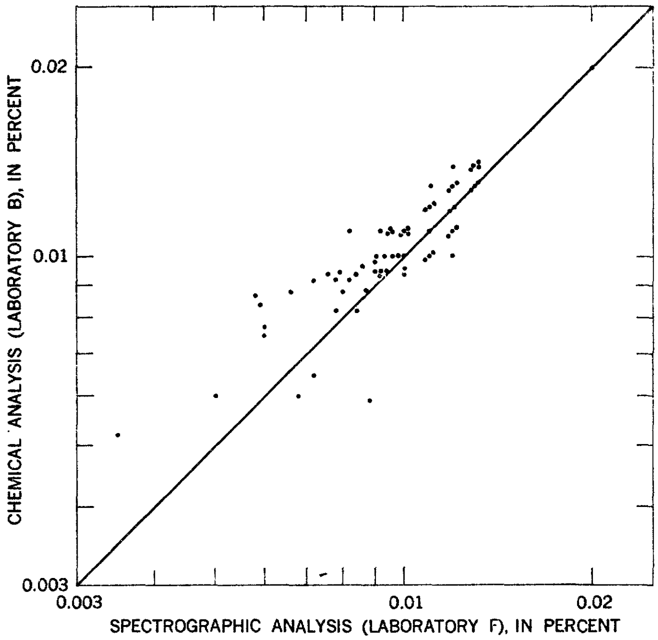

FIGURE 6.—Comparison of spectrographic and chemical determinations of chromium in 80 samples.

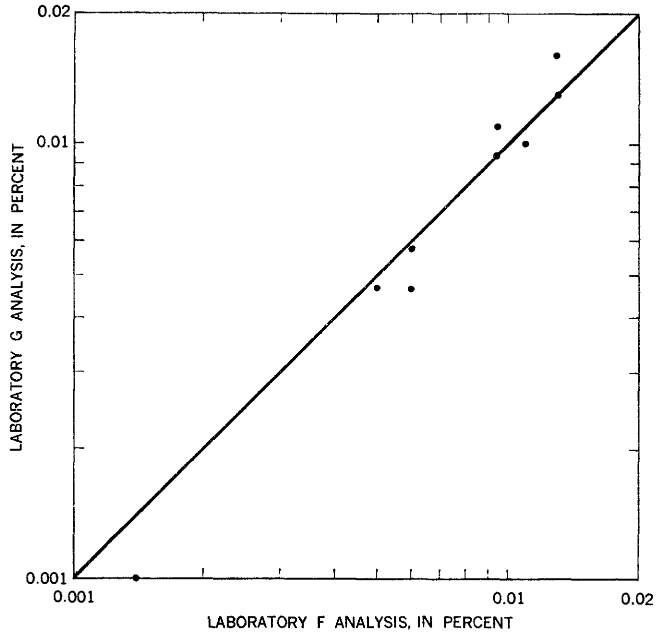

FIGURE 7.—Comparison of chromium determinations in 10 check samples by two spectrographic laboratories.

National Bureau of Standards standard sample No. 98, a plastic clay with a chemical composition similar to the Pierre shale, was prepared for arcing in the same way as were the shales, and its spectrum was recorded in duplicate on each plate of samples. The chromium determinations for this sample are 146, 150, 146, 124, 153, 168, 157, 152, 162, 142, 157, 176, 135 ppm. These determinations indicate a precision of 6.0 percent and, when compared to the certified chromium determination of 144 ppm, a deviation of 7.4 percent for a single determination or 5.2 percent for an average of two determinations.

GALLIUM

The precision of a single measurement, computed from duplicates on separate plates and with standards not on these plates, is 19.6 percent. The results of the gallium determinations on the hidden splits are given in table 1. The coefficient of variation for these values is 12.0 percent. The results reported by laboratories F and G on the check samples are given in table 2 and compared in figure 8. The coefficient of variation for these determinations is 16.1 percent. Gallium was not determined chemically.

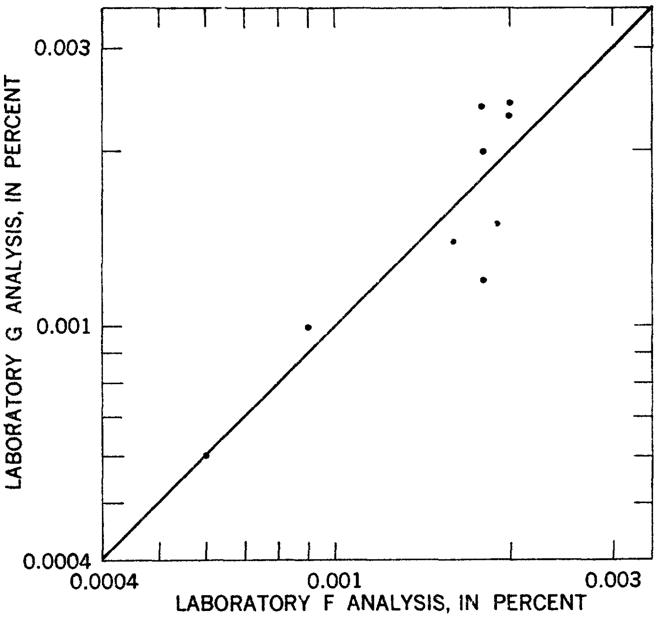

FIGURE 8.—Comparison of gallium determinations in 10 check samples by two spectrographic laboratories.

NICKEL

The precision of the spectrographic determinations for nickel and a comparison of the spectrographic results of laboratory F with the chemical results of laboratory A are given in the following table. Although precision is poorer when duplicates are arced on separate plates, the comparison with chemical results is better than when duplicates are on the same plate. Also having the standard on the plate improves the precision of determinations and improves the comparison with chemical results even more.

Coefficient of variation of nickel determinations

[Letters in parentheses indicate laboratory furnishing data]

	Standard not on plate	Standard on plate
Duplicates on same plate:		
Precision of a single spectrographic determination		4.0
Spectrographic (F) versus chemical (A) determinations		8.4
Duplicates on different plates:		
Precision of a single spectrographic determination	11.5	9.3
Spectrographic (F) versus chemical (A) determinations	10.5	6.6

The coefficient of variation between the reported spectrographic and chemical results for all 80 samples (fig. 9) is 6.7 percent. The average concentration of nickel is 0.0053 percent and ranges from 0.0010 to 0.016 percent.

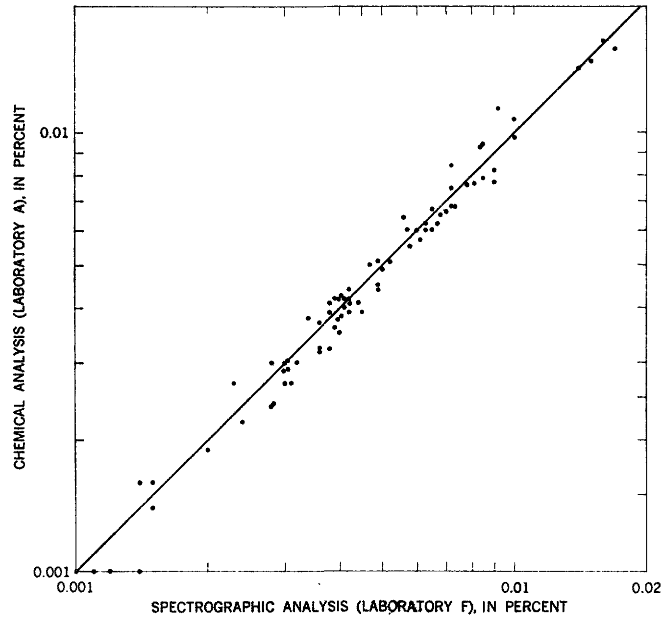

FIGURE 9.—Comparison of spectrographic and chemical determinations of nickel in 80 samples.

The spectrographic results on the hidden splits are given in table 1. The coefficient of variation for these determinations is 5.4 percent. Nickel was not determined by laboratory G.

SCANDIUM

The precision of a single scandium measurement, computed from duplicates on separate plates and with standards not on these plates, is 10.0 percent. The reported values for the hidden splits are given in table 1. The coefficient of variation between the results of the two spectrographic laboratories, computed from the data in table 2, is 12.3 percent. These paired values are graphed in figure 10. Scandium was not determined chemically.

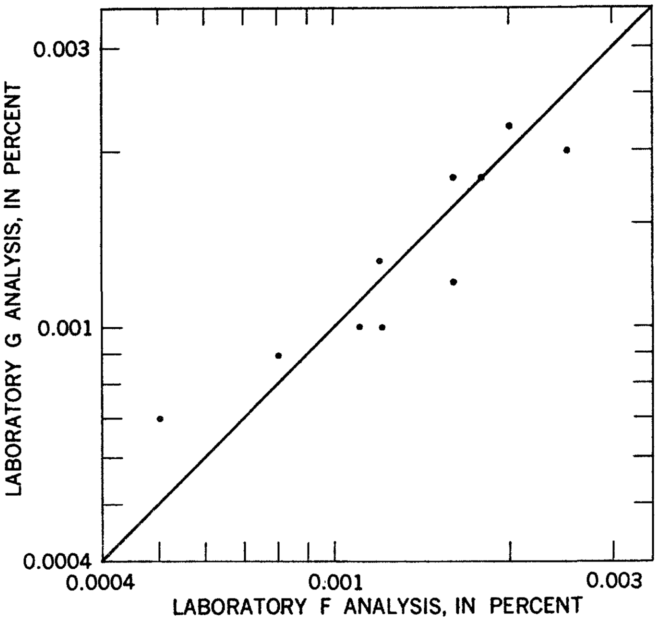

FIGURE 10.—Comparison of determinations of scandium in 10 check samples by two spectrographic laboratories.

STRONTIUM

The precision of a single measurement of strontium as determined from duplicate arcings on separate plates is 13.1 percent for 68 samples with an average concentration of 0.0137 percent and a range of 0.003 to 0.02 percent. The coefficient of variation is 24.8 percent for 11 samples with an average concentration of 0.048 percent and a range of 0.02 to 0.13 percent.

The precision of the determinations on the hidden splits (table 1) is 20.3 percent.

The reported results of the two spectrographic laboratories on the check samples are given in table 2. The coefficient of variation for all the paired determinations, graphed in figure 11, is 9.7 percent; but it is 19.6 percent for the determinations that range in concentration from 0.0073 to 0.028 percent. Strontium was not determined chemically.

TITANIUM

The following table gives the precision of the spectrographic determinations for titanium. It is significant that precision is better when the standard is on each plate. The poorer precision for duplicates on the same plate is not explained.

The coefficient of variation for laboratory F compared to laboratory C on 25 samples is 10.6 percent;

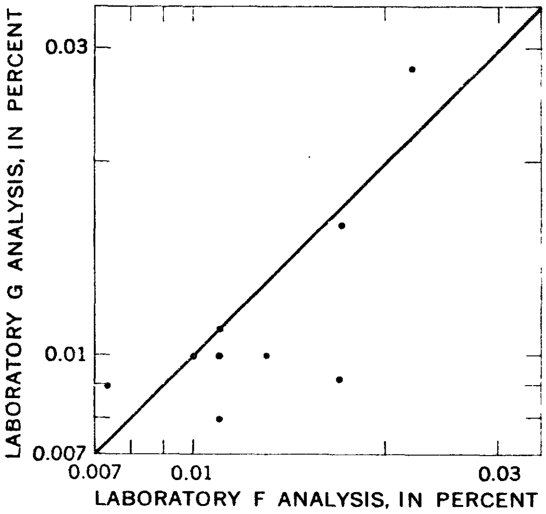

FIGURE 11.—Comparison of strontium determinations in 10 check samples by two spectrographic laboratories.

Coefficient of variation of spectrographic determinations for titanium

	Standard not on plate	Standard on plate
Duplicates on same plate	....	5.9
Duplicates on different plates	9.9	5.0

for laboratory F compared to laboratory D on 55 samples, 10.1 percent; for laboratory F compared to laboratories C and D combined (the peroxide method), 10.2 percent; and for laboratory F compared to laboratory B (the tiron method), 13.9 percent. Comparisons of determinations of laboratory F to those of C and D combined are shown graphically in figure 12.

The results of laboratories F and G on the check samples are given in table 2 and compared in figure 13. The coefficient of variation for these results is 9.9 percent.

The precision of titanium determinations on the hidden splits (table 1) is 4.2 percent.

ZIRCONIUM

The precision of a single zirconium determination, computed from duplicates on the same plate and with the zirconium standard not on the plate, is 10.0 percent. Zirconium was not replicated in any other way. The coefficient of variation on the hidden splits (table 1) is 14.4 percent. Zirconium was not determined chemically or by laboratory G.

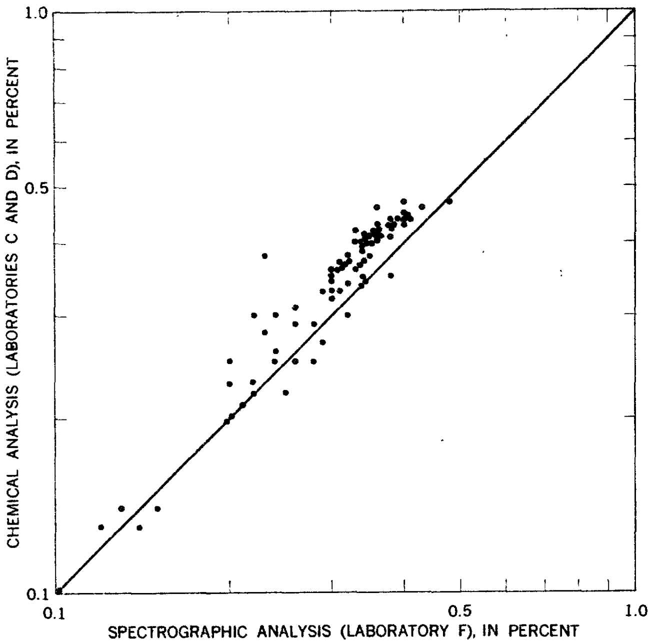

FIGURE 12.—Comparison of spectrographic and chemical (hydrogen peroxide) method of determination of titanium in 80 samples.

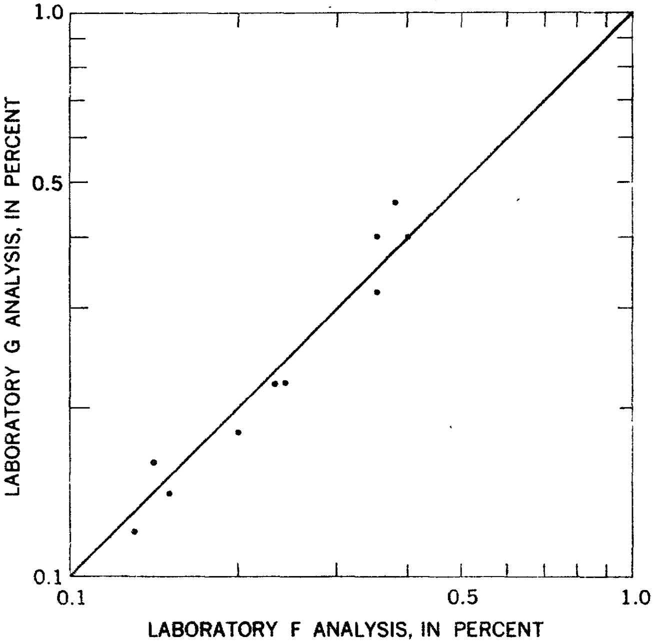

FIGURE 13.—Comparison of determinations of titanium in 10 check samples by two spectrographic laboratories.

SUMMARY AND CONCLUSIONS

PRECISION

The precision of a single measurement of each of the elements by the various methods of duplication are summarized in the following table. In general, the best precision results when the duplicates and standards are on the same plate. The poorest preci-

Precision, in terms of the coefficient of variation, of a single spectrographic measurement in the Pierre shale and in miscellaneous igneous rocks

	B	Ba	Co	Cr	Ga	Ni	Sc	Sr	Ti	Zr
Duplicates on separate plates, standards not on plate	.....	.....	9.9	.....	19.6	11.5	10.0	13.1	9.9	10.0
Duplicates on same plate, standards on plate	7.5	.....	5.2	5.2	.....	4.0	.....	.....	5.9	.....
Duplicates on separate plates, standards on plate	12.5	11.2	8.3	11.6	.....	9.3	.....	.....	5.0	.....
In igneous rocks, from Bastron and others (1960)	.....	15.6	9.5	16.8	12.4	10.6	14.4	17.4	6.9	10.2

sion results when duplicates are on separate plates and standards are on a third plate.

This table also gives the precision of single measurements of elements in igneous rocks computed from the precision of the average of two determinations (Bastron, Barnett, and Murata, 1960). These data were obtained in large part from duplicates on separate plates and standards on a third plate. The precision of the measurement of the elements in the Pierre shale, when computed from duplicates on separate plates and with standards not on these plates, is comparable to that for igneous rocks. The poorer precision for gallium is probably due to the lower range of concentration of gallium in the Pierre shale (near limit of sensitivity in the diluted sample) than in the igneous rocks analyzed.

The precision, in percent, as determined from the results reported on the hidden splits is: boron, 6.1; barium, 8.1; cobalt, 10.3; chromium, 5.2; gallium, 12.0; nickel, 5.4; scandium, 12.3; strontium, 20.3; titanium, 4.2; and zirconium, 14.4.

COMPARISON WITH CHEMICAL ANALYSIS

Computed from the data on all 80 samples and given in percent, the coefficients of variation between determinations by chemical and by spectrographic methods are: barium, 34; cobalt, 12; chromium, 10; nickel, 7; and titanium, 10. Only the data for cobalt and nickel are complete enough to make comparisons with the chemical results with respect to the three variables in the spectrographic method. These data are given in the following table. The improvement in the comparison of nickel with each successive change in the spectrographic method might also be expected to hold true for cobalt, because these two elements can be analyzed spectrographically with equal facility. The fact that there is no improvement in the comparison of cobalt may be a reflection of the relatively poorer precision of the chemical determination of cobalt as contrasted to that of nickel (Rader and Grimaldi, 1961).

Comparison of spectrographic results with chemical results, in terms of the coefficient of variation

	Cobalt	Nickel
Duplicates on separate plates, standards not on plate	9.9	10.5
Duplicates on same plate, standards not on plate	11.9	8.4
Duplicates on separate plates, standards on plate	11.2	6.6

ACCURACY

Because no shale has been certified as a standard, it is not possible to draw conclusions about the accuracy of the spectrographic determination of minor elements in the Pierre. However, the comparison of the nickel determinations with the chemical determinations as set forth above probably is not an unreasonable estimate of the accuracy expected for most of the elements.

One certified standard, National Bureau of Standards sample No. 98, with a chemical composition comparable to that of shale, was repeatedly analyzed for chromium. The deviation from the certified value of an average of two determinations is 5.2 percent.

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Quantitative Interpretation of Mineralogical Composition from X-ray and Chemical Data for the Pierre Shale

By LEONARD G. SCHULTZ

ANALYTICAL METHODS IN GEOCHEMICAL INVESTIGATIONS OF THE PIERRE SHALE

GEOLOGICAL SURVEY PROFESSIONAL PAPER 391-C

Derivation, reproducibility, and accuracy of modal analyses and calculation of composition of montmorillonitic components

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QUANTITATIVE INTERPRETATION OF MINERALOGICAL COMPOSITION FROM X-RAY AND CHEMICAL DATA FOR THE PIERRE SHALE

By Leonard G. Schultz

ABSTRACT

Quantitative X-ray determinations for total amounts of clay, quartz, feldspar, carbonate, and other minerals common in the Pierre Shale are based on heights of peaks on diffractometer traces of unoriented powder samples. Conversion factors are derived from X-ray analyses of prepared mixtures, from weight loss due to solution by dilute acid of carbonate minerals in Pierre samples, and from comparison of X-ray and chemical data for Pierre samples. Proportions of kaolinite, chlorite, illite, montmorillonite, and mixed-layer clay are interpreted from the relative sizes of basal reflections from oriented clay aggregates.

Repeated analyses indicate that variations in (1) sampling, (2) sample preparation, (3) machine response, and (4) interpretation by the operator all affect the precision of the X-ray determinations. Inconsistency of interpretation has the greatest effect on the determination of the clay minerals. If a mineral is present in an amount greater than 15 percent of the sample, the precision of its determination generally is ±10 percent. Minerals present in amounts of a few percent or less are not consistently detected. Comparison of chemical analyses for carbon dioxide and alumina and quantitative interpretations for carbonate minerals and total clay, respectively, indicates accuracy of the X-ray interpretations to be generally about the same as the precision.

Calculations of mineral compositions from chemical analyses are based, in part, on the X-ray data. The amounts of apatite, barite, pyrite, and of sulfate and carbonate minerals are calculated from their essential constituents; X-ray data for these minerals serve only to indicate the variety of sulfate or carbonate minerals to be calculated. X-ray quantitative data and mineral compositions for quartz, cristobalite, feldspars, zeolite, kaolinite, chlorite, and illite determine the amounts of chemical constituents assigned to each of these minerals; X-ray and chemical data, and, to some extent, necessary assumptions determine the composition for minerals that are extremely variable, such as chlorite, illite, and feldspar. The remaining chemical constitutents, amounting to about half of most samples, are assigned to montmorillonite and mixed-layer clay. The composition assigned to these two minerals is expressed as a combined structural formula. The structural formula partly determines which montmorillonitic clays contain interlayer gibbsite- or brucitelike structures. The rationality of the structural formula and the extent of agreement between the X-ray-mineralogical and chemical-mineralogical calculations check the gross accuracy of the calculations for individual samples of Pierre Shale.

INTRODUCTION

The geochemical investigation of the Pierre Shale is a continuing study (Tourtelot, Schultz, and Gill, 1960; Rader and Grimaldi, 1961; Tourtelot, 1962) which will attempt to relate data on mineralogical and chemical composition of a large body of fine-grained sedimentary rocks to their physical and lithologic characteristics and to their stratigraphic and geographic positions. Because much of the Pierre Shale is fairly homogeneous, such an investigation requires reasonably precise quantitative data and knowledge of the accuracy and reproducibility of the data.

Quantitative analyses based on X-ray diffraction data have been described for clay minerals by numerous investigators (Talvenheimo and White, 1952; Johns, Grim, and Bradley, 1954; Degens, Williams, and Keith, 1957; Weaver, 1958; Jarvis, 1958; Sudo, Oinuma, and Kobayashi, 1961; and others). The author (1960) described general methods used by him for analyses of some aluminous clay minerals. X-ray methods also have been used for quantitative analyses of other minerals in samples, as for example, the quartz determinations reported by Rex and Goldberg (1958), the determinations of minerals in bauxite by Black (1953), and the determinations of feldspar, quartz, and calcite in prepared mixtures by Mitchell (1960). Schmalz and Zen (1959) used X-ray diffraction techniques for quantitative evaluation of both clay and other minerals in modern sediments from the Peru-Chile Trench. Descriptions of methods for complete X-ray quantitative mineralogical analyses of sedimentary rocks that have a clay mineral suite as complex as that of the Pierre Shale, however, have not previously been published.

This report describes techniques of X-ray analyses used in the investigations of the Pierre shale, presents data on the reproducibility and accuracy of the results, and describes the calculations used to assign chemical constituents to the minerals identified in each sample.

The chemical analyses used in parts of this report will be presented in a subsequent report.

X-RAY ANALYSIS

SAMPLE PREPARATION AND TREATMENT

Two types of mounts were made from each sample for X-ray analysis. An unoriented mount was prepared by packing a finely ground powder into a holder, and a oriented aggregate was prepared by using the porous tile technique of Kinter and Diamond (1956). An X-ray diffraction trace was run of the powder, and four traces were run of the oriented aggregate in the following order: (1) dried at room temperature, (2) glycol treated, (3) heated at 300°C for half an hour, and (4) heated at 550°C for half an hour. Traces were run by using nickel-filtered copper radiation generated at 40 kilovolts and 20 milliamperes, 1° beam slit and a 0.006-inch detector slit, and scanning at 2° per minute. Uniform response of the X-ray machine was maintained by periodic alinement checks and calibration with a standard sample. Before preparation of the oriented aggregate, the calcareous samples were first treated with cold 1*N* (normal) hydrochloric acid and washed with distilled water; they were then treated like the noncalcareous samples. Samples containing abundant organic material were treated either with warm 10 percent hydrogen peroxide or 5 percent chlorox and then washed in distilled water.

INTERPRETATION

WHOLE ROCK DATA

The abundance of nonclay minerals is interpreted from the size of the strongest diffraction peak for each mineral on the X-ray trace of the unoriented powder. Diffraction peaks and intensity factors used in interpreting mineral percent from peak size are shown in table 1. Most of the intensity factors shown in table 1 are derived from several diffractometer traces of prepared mixtures in which the concentration range of each mineral is similar to its concentration range in the Pierre Shale. Minerals in prepared mixtures used to develop the intensity factors came from Pierre material, insofar as possible. For example, the diluting agent in the mixtures was a Pierre bentonite composed entirely of montmorillonite which had a chemical composition reasonably close to that of the clays in the Pierre Shale; it therefore had an absorption factor similar to the clays in the Pierre Shale. If sufficiently pure Pierre materials were not available, as for quartz and feldspar, the materials used in the prepared mixtures were as similar as possible to the Pierre minerals in composition and particle size. Because an internal standard was not used, some control was lost over absorption effects. However, as will be discussed later, absorption apparently does not cause much variation in diffracted X-ray intensities within the concentration range of minerals common in the Pierre Shale; by not using an internal standard, a diluting effect on diffracted intensities is avoided as is interference between reflections from the internal standard and the dozen or so minerals in the Pierre Shale.

Clinoptilolite is used as defined by Mumpton (1960) because in the Pierre Shale this mineral is stable when heated at 550°C for half an hour.

Peak intensities for the different varieties of feldspar vary with the chemical composition of the feldspar. The intensity factors in table 1 correspond to oligoclase, because this variety apparently is the most common in the Pierre Shale. Further refinement of the factor for feldspar seemed unwarranted, because in the small amounts commonly present in the Pierre Shale, the variety of feldspar could not be determined consistently.

Although the intensity factors recorded in table 1 would probably be different if other X-ray equipment were used, they are included here for comparative purposes.

TABLE 1.—*Factors for X-ray quantitative interpretation of minerals in the Pierre Shale*

Minerals	Peak position in degrees 2*θ* (CuK*α* radiation)	Intensity factor in counts per second per 100 percent
Quartz (SiO_2)	26.6	2,000
Disordered cristobalite (SiO_2)	21.8	570
Plagioclase (oligoclase)	28.0	1,000
K-feldspar ($KAlSi_3O_8$)	27.5	1,000
Calcite, pure ($CaCO_3$)	29.4	1,000
Calcite, mixed [1] ($CaCO_3$)	29.6–30.0	500
Dolomite, pure ($CaMg(CO_3)_2$)	31.0	1,000
Siderite, mixed [2] ($FeCO_3$)	31.7–31.9	[3] 600
Rhodochrosite, mixed [4] ($MnCO_3$)	[5] 30.8–31.5	300
Gypsum ($CaSO_4 \cdot 2H_2O$)	11.6	1,500
Jarosite [6] ($KFe_3(OH)_6(SO_4)_2$)	29.1	[3] 550
Alunite ($KAl_3(OH)_6(SO_4)_2$)	30.0	750
Pyrite (FeS_2)	33.1	[3] 250
Clinoptilolite [7] ($Na_2Al_2Si_{10}O_{24} \cdot 7H_2O$)	10.0	800
Clay minerals [8]	19.9	100(150)
	34.6	60(60)
	61.9	30(40)

[1] Mg^{+2}, Fe^{+2}, or Mn^{+2} substitution.
[2] Ca^{+2}, Mg^{+2}, or Mn^{+2} substitution.
[3] In amounts less than 10 percent.
[4] Ca^{+2}, Mg^{+2}, or Fe^{+2} substitution.
[5] Commonly a very broad peak.
[6] Probably extensive substitution of H^{+1} for K^{+1}.
[7] Some K^{+1} and Ca^{+2} substitution.
[8] Values in parentheses are for bentonite. See text for explanation of these three values.

CARBONATE MINERALS

Intensity factors for calcite and dolomite (table 1) are based on determinations of acid-soluble carbonate and X-ray measurements for 58 samples of calcareous shale and marlstone, and 5 carbonate nodules from the Pierre Shale (fig. 1). The amount of acid-soluble carbonate was determined by weight loss resulting from repeated treatment with 1N hydrochloric acid until effervescence stopped. X-ray patterns that were run before and after the acid treatment indicated that all the carbonate minerals had been removed and that no minerals other than carbonates were discernibly affected by the

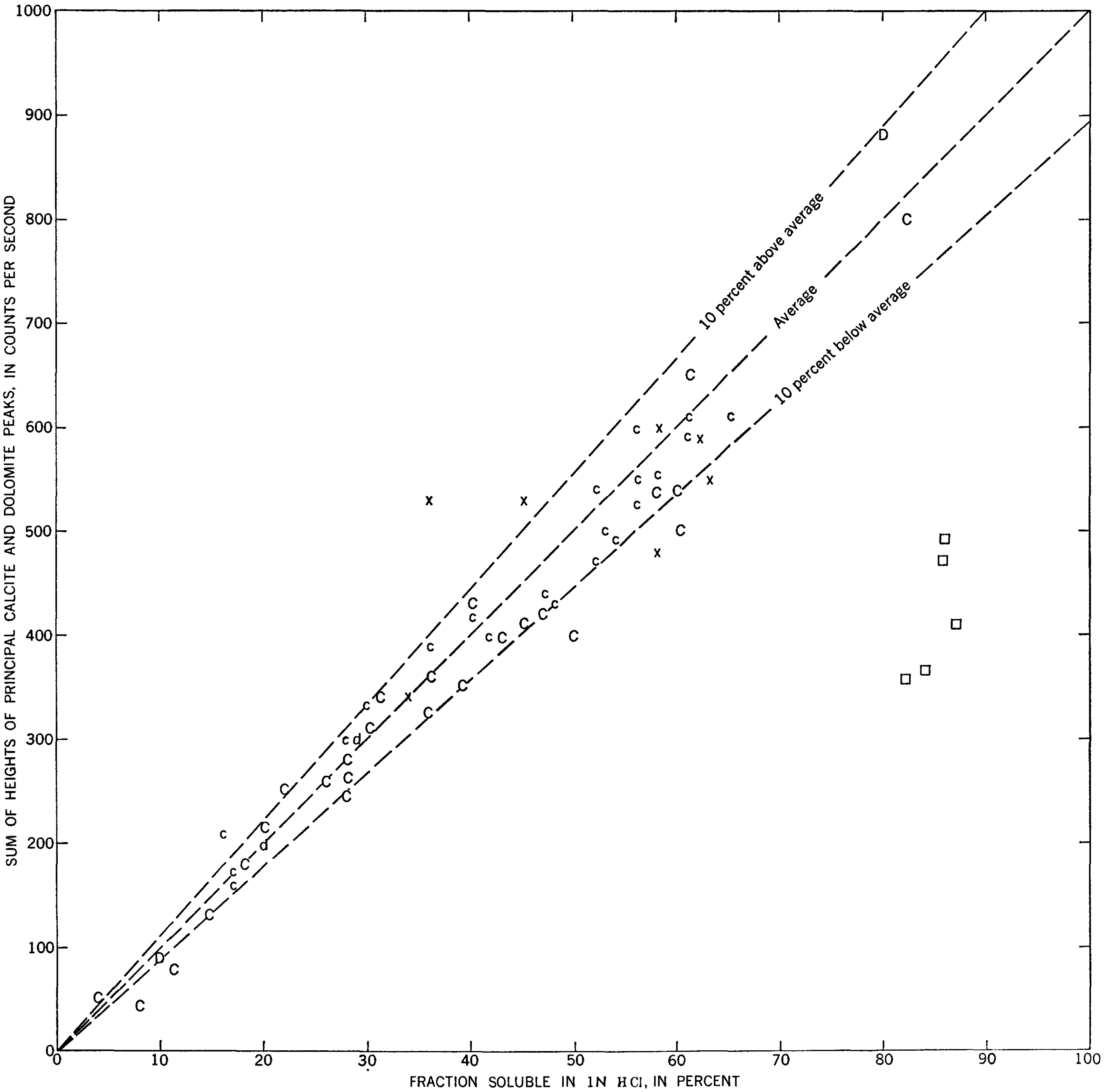

FIGURE 1.—Relation between principal carbonate X-ray peak heights and acid-soluble carbonate for 63 samples from the Pierre Shale. D, dolomite only; d, mostly dolomite; x, dolomite and calcite in about equal amounts; c, mostly calcite; C, calcite only; □, calcite from a concretion with extensive substitution of magnesium, iron, and manganese ions.

acid treatment used. The proportion of calcite and dolomite in each sample estimated from the relative intensities of their principal peaks is indicated by the symbols on figure 1. Regardless of the proportions of calcite and dolomite, the intensity sum of their principal peaks is almost linearly related to the total amount of acid-soluble carbonates. Thus, the fine-grained but pure calcite and dolomite common in many samples of Pierre Shale give principal diffraction peaks of about the same intensity for a given amount of material; with the X-ray equipment used, the intensity of the principal peak can be divided by 1,000 cps (counts per second) to give a carbonate value that generally will be accurate within 10 percent of the amount stated (fig. 1). The fact that the strongest diffraction peaks of calcite and dolomite are of nearly equal intensity agrees generally with the results of Tennant and Berger (1957) and Gulbrandsen (1960).

An intensity factor of 1,000 cps is not applicable to the carbonate minerals composing concretions (fig. 1). The carbonates in concretions gives relatively broad X-ray peaks that are shifted from their normal positions; for a given amount of this mixed carbonate, the height of the principal peak is about half of that expected for a pure calcite (fig. 1). Although this intensity relation for X-ray diffraction peaks of calcite from concretions is shown by only five samples on figure 1, its general applicability is confirmed by observations of many traces of nodules that are composed predominantly (80–90 percent) of carbonate minerals, but for which solubility data are not available. Chemical data indicate extensive substitution of iron, magnesium, and, in some samples, manganese for the calcium in such carbonate. In table 1 and throughout this report, the modifier "mixed" is used to distinguish carbonates having extensive substitution from "pure" carbonates having an ideal chemical composition.

DISORDERED CRISTOBALITE

Cristobalite in the Pierre Shale gives a few broad X-ray peaks close to the strongest peaks of well-crystallized cristobalite. It apparently is similar to the opal of Franks and Swineford (1959, fig. 4) and to the beta cristobalite of Levin and Ott (1933). Yet, the term "opal" seems inappropriate because "opal" generally connotes a hydrous amorphous silica mineral, whereas the material in the Pierre is crystalline and produces a distinct X-ray pattern. Beta cristobalite seems inappropriate because the term "beta," though variously used, generally implies a high temperature form, whereas material like that in the Pierre apparently has not resulted from high temperatures. In this paper, the term "disordered cristobalite" indicates the presence of distortions in the crystal lattice that produce the characteristic broad X-ray peaks. According to Franks and Swineford (1959), the distortions in such material are caused by a small amount of alumina, water, and alkalies stuffed into the cristobalite crystal lattice.

The intensity factor in table 1 for disordered cristobalite in the Pierre Shale was determined empirically, because no pure samples of cristobalite known to be identical with that in the Pierre Shale were available for prepared mixtures. Two considerations were involved in the determination of the intensity factor for cristobalite: (1) the amount of material unaccounted for after percentages of other mineral components had been calculated, and (2) for chemically analyzed samples, the amount of silica left over after an appropriate amount had been assigned to clay and quartz. For example, partial X-ray and chemical analyses of a sample are as follows:

X-ray analysis:	*Percent*
Clay minerals	55
Quartz	7
Plagioclase	1
	63

Chemical analysis:	*Percent*
SiO_2	70.2
Al_2O_3	10.8
	81

The only mineral detected on the X-ray trace other than the three listed is disordered cristobalite, whose principal peak at 21.8° 2θ is 200 cps high. Clay minerals, quartz, and plagioclase constitute 63 percent of the sample; therefore the remaining 37 percent must be mostly disordered cristobalite. The general formula for converting X-ray peak intensity into percent of cristobalite is

$$\frac{\text{peak height (cps)}}{\text{intensity factor (cps) per 100 percent}} = \text{percent cristobalite};$$

for the sample above, the intensity factor (cps) per 100 percent $=\frac{200 \text{ cps}}{37 \text{ percent}}=540.$

The silica and alumina values also can be used to derive an X-ray intensity factor for cristobalite in the following way: The average ratio of weight percent silica to alumina of clays in the Pierre Shale is about 2.6; therefore, in the sample containing 70.2 percent silica, 10.8 percent alumina, and 7 percent quartz, about 28 percent of the silica (10.8×2.6) should be in the clay minerals, 7 percent in quartz, and the remaining 35 percent silica can be assigned to cristobalite. From the inferred amount of 35 percent cristobalite, an X-ray intensity factor of 570 cps $\left(\frac{200 \text{ cps}}{35}\right)$ is calculated.

Both the difference method and the chemical method generally indicate the 570-cps value given in table 1 as an appropriate intensity factor for disordered cristobalite in the Pierre Shale. The amount of cristobalite in one sample, as calculated from X-ray analysis, was subsequently checked by the solubility test of Hashimoto and Jackson (1960). As shown in table 8, the X-ray determination of 35 percent obtained by using the intensity factor of 570 cps is in good agreement with the solubility test in which 34.8 percent dissolved silica and 0.85 percent dissolved alumina are reported. Some solution of components other than cristobalite may have occurred, but the X-ray determination gives a figure that must be nearly correct and that cannot be obtained as conveniently in any other way.

TOTAL CLAY MINERALS

A direct determination of intensity factors for clay minerals in the Pierre Shale was not possible, because all the shale samples contain other components. The only reasonably pure clays are in the bentonites, and diffraction characteristics of these are not typical of the shales in general. There was no assurance that clays used in mixtures intended to approximate the Pierre would be similar to the clays actually in the Pierre. Therefore, the intensity factor for total clay minerals was obtained by difference; samples of Pierre Shale containing in most part only clay and quartz were used. For example, if X-ray data indicated that a sample contained 20 percent quartz and 2 percent feldspar and if no other reflections were perceived except for the clays, then the clay reflections were assumed to represent 78 percent of the sample. A large number of such analyses gave fairly consistent relations between the sizes of the peaks shown on table 1 and the apparent total amount of clays in each sample. Basal reflections were not used because of the considerable effect of any slight preferred orientation on these reflections, a factor which has much less effect on the intensity of the nonbasal reflections. Three nonbasal reflections common to most clay minerals in shale samples from the Pierre were used (see table 1); most significance was given to the amount calculated from the peak at about 19.9° because this peak is the largest of the three and most easily measured. This amount was modified if the 34.6° and 61.9° peaks gave appreciably different but apparently valid amounts of clay. For example, if the 19.9° peak indicated 70 percent clay, but both of the other two peaks indicated 60 percent, then 65 percent clay minerals was reported. Consideration of three peaks also made possible the elimination of any one peak with which reflections from other minerals interfered.

Intensity factors used for total-clay in shales cannot be used for bentonites because the montmorillonite in bentonites generally gives bigger peaks than do the clay minerals in the shales. Therefore, the numbers in parentheses in table 1 were used to evaluate the total amount of clay minerals in bentonites.

The system for determining total clay in samples of Pierre Shale will not be applicable to all possible mixtures of clay. For example, highly kaolinitic samples will give peaks higher than the clay minerals in the Pierre; if factors listed in table 1 were used for such kaolinitic clays, an unrealistic total amount, perhaps 150 percent clay, might be calculated. The particular dual system for shales and bentonites listed in table 1 is appropriate only for material very similar to the Pierre Shale.

Because of the many considerations involved in the determination of the intensity factors for total clay minerals and cristobalite, their quantitative determinations are probably the least accurate. Accordingly, amounts of total clay and cristobalite have been rounded to the nearest 5 percent.

A figure for the total amount of clay minerals in each sample might have been obtained by assuming that clay composed that portion of each sample not assigned to nonclay minerals. This method probably would give a figure for total clay in most samples as accurate or more accurate than could be derived by using the intensity factors listed in table 1. Derivation of total amount of clay by using the X-ray intensity factors in table 1 for all samples has the advantage of indicating which of the hundreds of samples of Pierre Shale analyzed give sums for total minerals present that are so low as to indicate something unusual, such as the presence of amorphous material. Almost all samples give totals between 90 and 105 percent. Sums within this range are interpreted as normal variations caused by the inaccuracies of the methods used and as being free of appreciable amounts of components amorphous to X-rays.

Absorption of X-rays can influence intensity relations greatly in some samples. However, most Pierre samples are composed of reasonably uniform proportions of silicate minerals; the X-ray peak intensity relations observed from most prepared mixtures indicate that absorption has little effect upon the nearly linear relation between mineral percent and diffraction intensities within the concentration ranges in which the different minerals commonly occur in the Pierre Shale. The most extensive variation common in the mineralogy, chemistry, and, thus, in the absorption of Pierre samples probably involves the amount of carbonate minerals, but even in this variation no drastic deviation from linearity is observed (figs. 1 and 6). Exceptions to linearity are provided by samples having high iron contents, in which high absorption of copper radiation by the iron reduces expected intensity for all peaks and adjustments in intensity factors are necessary. Such samples, however, are not common from the Pierre Shale.

CLAY FRACTION DATA

CLAY MINERALS PRESENT

Clay minerals in samples of Pierre Shale analyzed from South Dakota and adjacent areas are classified as kaolinite, chlorite, illite, montmorillonite, and mixed-layer clay. X-ray diffractometer traces of pure clay minerals from or similar to those in the Pierre Shale are shown in figure 2. The following criteria are used to identify the clay minerals:

1. Kaolinite is characterized by a series of basal X-ray diffraction peaks at about 7A, 3.5A, and so forth. Judged from the shape of the 7A peak (Schultz, 1960, fig. 2), kaolinite in the Pierre Shale appears to be of a moderately well crystallized variety.
2. Chlorite is characterized by a series of basal X-ray diffraction peaks at about 14A, 7A, 4.8A, 3.5A, and so forth. Heating at 550°C for half an hour causes a change in the chlorite structure, hence the 14A reflection increases greatly in size and the other basal orders almost disappear.
3. Illite is characterized by a series of X-ray diffraction peaks at 10A, 5A, 3.3A, and so forth that are not appreciably affected by either glycol or heat treatment. Illite is used as a general or group term for the micalike clay of partly uncertain species and undeterminable polymorph that generally gives fewer and broader X-ray reflections than ideal mica, but that shows no significant change in the 10A spacing after mild heat or glycol treatment. The illite in the Pierre Shale is predominantly a dioctahedral aluminous variety. However, materials fitting the above description of illite may include some micalike clays other than the usually dominant disordered muscovitelike clay, and may include a small amount of undetected mixed layers. For example, analyses by optical methods revealed small amounts of glauconite and biotite that were included with illite in the X-ray analyses of some samples.
4. Montmorillonite is characterized by its expanding lattice. When dried under ordinary room conditions, montmorillonite having sodium as the exchange ion frequently has one molecular layer of water and a basal spacing of about 12.5A; when calcium or magnesium is the exchange ion, it frequently has two molecular water layers and a c-axis spacing of about 15.5A (Grim, 1953, p. 57). After glycol treatment, montmorillonite exhibits a series of basal X-ray peaks at 17A, 8.5A, 5.7A, 4.2A, 3.4A, 2.8A, and so forth. When heated at 300°C for half an hour, volatilization of all adsorbed water or ethylene glycol causes a decrease in the basal spacing to about 10A. The montmorillonite in the Pierre Shale gives the X-ray pattern of a dioctahedral aluminous variety.
5. Mixed-layer clay in the Pierre Shale is characterized by a broad basal X-ray diffraction peak near 17A on the trace of the glycolated sample (fig. 2), indicating that montmorillonite layers are most abundant. Complete collapse of the c-axis spacing to about 10A after heat treatment of most samples indicates that the only other common layers are illite, because only illite and montmorillonite give c-axis spacings of about 10A after being heated at 300°C. In only a few samples does a c-axis spacing of greater than 10A after heating indicate presence of a brucitelike interlayered component of moderate thermal stability that prevents collapse to 10A at 300°C but that will collapse at 550°C. The mixed-layer clays of the Pierre Shale are dioctahedral aluminous varieties.

COMPARISON OF X-RAY PEAK SIZES

The relative sizes of the X-ray diffraction peaks from the basal planes of the clay minerals in the 7 to 17A range provide the basis for calculating the relative amounts of the different clay minerals. For some calculations, peak area is used and for others, peak height. Methods for measuring peak size and comparing intensities, which were previously derived (Schultz, 1960), are:

1. The peak area is considered to be the sum of five measurements of the height above the baseline. One measurement is at the peak position (called peak height) and the other four are at ½° intervals on either side of the peak position. For example, in the symmetrical peak illustrated in the lower left corner of figure 3, the height above baseline at the peak position is 10 divisions, the height above baseline at ½° and 1° 20 on the left side of the peak position is 1½ divisions and ½ division, and the height above baseline at ½° and 1° on the right side of the peak position is 2 divisions and ½ division; the total of these 5 measurements, 14½ divisions, is considered a measure of the peak area. The size of the divisions is immaterial, because all measurements of the basal clay peaks are used on a relative basis only. In practice, the one-tenth-inch grid on the recorder paper is used as convenient division. For notably asymmetrical peaks (fig. 3, lower left corner), one peak flank measurement is made on the steep side of the peak and three are made on the less steep side. The determination of peak area thus requires consideration of peak shape.
2. The baseline indicates where the trace would be if the mineral producing the diffraction peak were absent. The position of the baseline depends upon the intensity of background radiation and upon radiation reflected from other minerals having closely similar lattice spacings. The exact position of a baseline below critical clay mineral peaks is, to some extent, subject to the personal judgment of the interpreter.
3. After heating at 300°C, all the clay minerals common in the Pierre Shale give X-ray reflections

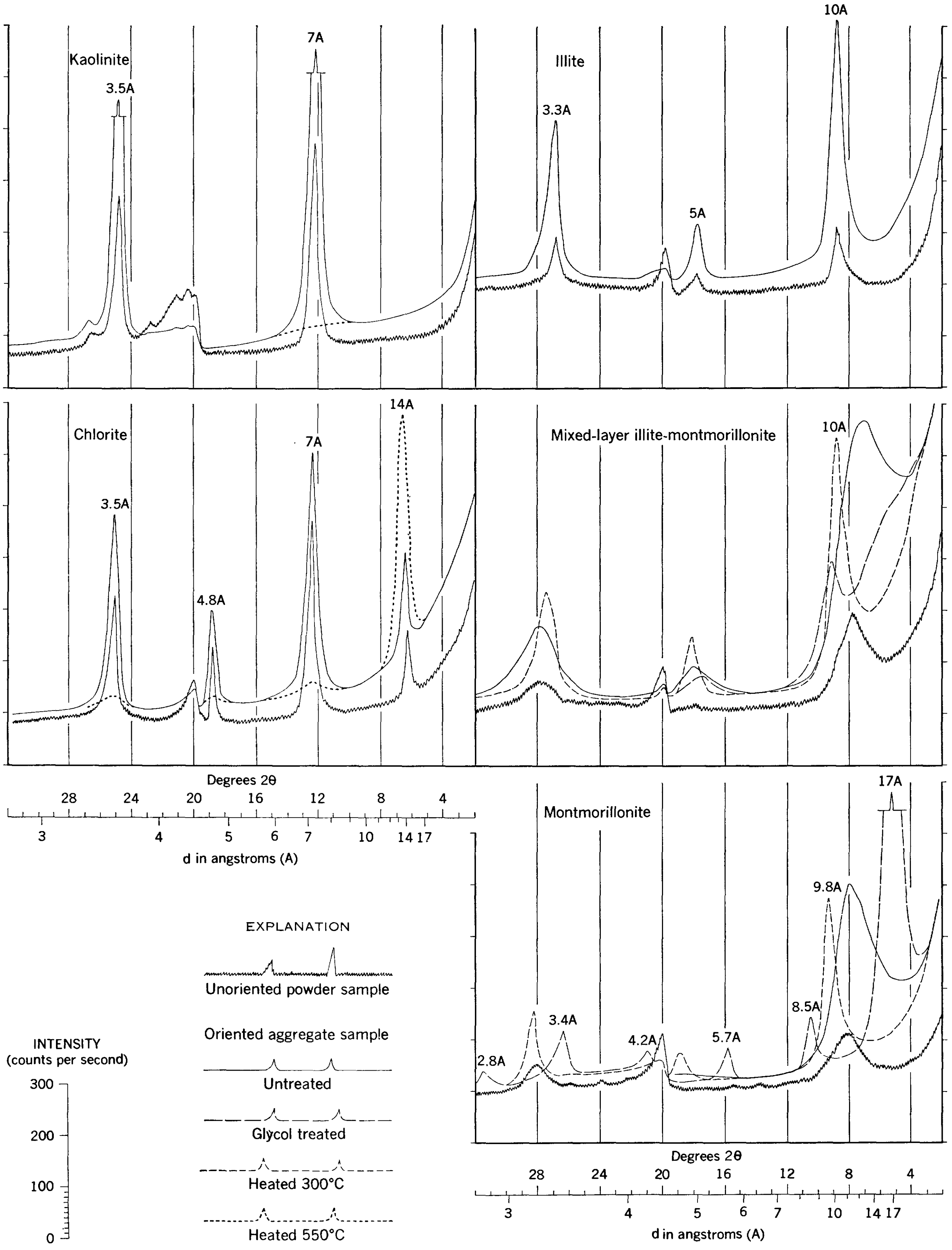

Figure 2.—X-ray diffractometer traces of clay minerals representative of those in the Pierre Shale (CuK α radiation).

from their basal planes at about either 7A (kaolinite and chlorite) or 10A (illite, mixed-layer clay, and montmorillonite) (fig. 2). Therefore, with suitable correction, an initial division into these two groups of clay minerals can be made by comparing the relative areas of the 7A and the 10A peaks after the sample has been heated at 300°C.

4. In their collapsed state after 300°C heating, aluminous illite, montmorillonite, and mixed-layer illite-montmorillonite give 10A X-ray peaks of about the same area for equal weights of material.
5. The ratio of peak areas of the 7A and 10A reflections for equal amounts of kaolinite and collapsed illite, montmorillonite, or mixed-layer illite-montmorillonite ranges from 1:1 for poorly crystallized kaolinite to 2:1 for well-crystallized kaolinite; the ratio for kaolinite of an intermediate degree of crystallinity is intermediate between 1:1 and 2:1. The sharpness of the 7A kaolinite peak as expressed by its area:height ratio can be used to evaluate the crystallinity of kaolinite.
6. The ratio of heights of the 17A peak of glycolated montmorillonite to the 9.8–10A peak of collapsed montmorillonite generally is between 4 and 5 for the sample mounts used; an average value of 4.5 is used.

A relation of peak intensity to crystallinity similar to that for kaolinite may exist also between illite and well-crystallized mica. Well-crystallized mica, however, is not a significant component in the Pierre Shale; thus, only the poorly crystallized illitic type of clay mineral need be considered.

Application of these factors to the quantitative interpretation of X-ray data are discussed on pages C9–C12 and are shown in table 2. The basis and methods of quantitative interpretation of the amounts of kaolinite and chlorite are discussed in the following section.

ESTIMATION OF KAOLINITE AND CHLORITE

Differentiating between kaolinite and chlorite is one of the most common difficulties in X-ray identification of clay minerals. The difficulty arises from coincidence of the basal reflections of kaolinite with those of chlorite at about 7A and 3.5A (fig. 2). The problem is important in this study because the Pierre Shale commonly contains small amounts of both kaolinite and chlorite. The (002) reflection of kaolinite and the (004) reflection of chlorite at about 3.5A are never resolved on diffraction traces of samples from the Pierre Shale; hence, the solution of Grim, Bradley, and White (1957, fig. 2) is not applicable. The thermal stability of the two minerals in the Pierre Shale is such that the intensity changes of the X-ray peaks occur at about the same temperature, and the solution of Johns, Grim, and Bradley (1954) is not applicable. Kaolinite and chlorite in the Pierre Shale commonly occur in such small amounts that the (003) reflections of kaolinite at 2.38A and of chlorite at about 4.8A are not both seen, thus, the solution of Weaver (1958, p. 271) also is not helpful.

The factor for determining the total kaolinite and chlorite was derived in the following manner. In samples containing no chlorite, the shape of the 7A peak indicates that kaolinite in the Pierre Shale has a fairly uniform intermediate degree of crystallinity which should give a 7A peak having an area about 1.4 times that of the 10A peak of the illite and collapsed montmorillonite or mixed-layer illite-montmorillonite (Schultz, 1960, fig. 2; see also item 5, p. C8 of this report). The shape of the 7A peak for samples containing both kaolinite and chlorite is about the same as for samples containing only kaolinite; thus the crystallinity of the kaolinite is apparently similar to that of the chlorite. According to Weaver (1958, p. 271), the 7A peaks of kaolinite and chlorite, which presumably possess similar crystallinity, are of about equal intensity. Therefore, for all Pierre Shale samples the size of the 7A peak was divided by 1.4 and the quotient was then compared with the size of the 10A peak in order to estimate the relative quantities of the minerals producing these two X-ray reflections.

The method formulated for evaluating the relative amounts of kaolinite and chlorite in samples of Pierre Shale is based on a comparison of X-ray traces of oriented aggregates before and after they were treated with warm 6*N* hydrochloric acid for 16 hours and after they were heated at 300° C and 550° C for half an hour. Twenty-eight samples in which chlorite composed more than 5 percent of each were studied. In no sample was a 14A chlorite peak observed after the acid treatment, but in all the samples, a 7A kaolinite peak remained. Because orientation in the aggregates differed in the slides prepared before and after the acid treatment, peak-size comparisons were all relative to the 10A peak after heating at 300°C; minerals causing the 10A peak apparently were not appreciably affected by the acid treatment. For the 28 samples so studied, the amount of the decrease in height of the 7A peak due to removal of chlorite by acid treatment averaged two-thirds (ranged between one-half and one) of the height of the chlorite peak at 14A after heating at 550° C and before treating with hydrochloric acid. Therefore, for a sample of the Pierre Shale, the part of the 7A peak that is attributed to reflections from chlorite is calculated by multiplying the height of the 14A peak obtained after heating the sample at 550° C by the factor two-thirds (or dividing by 1.5). The remainder of the 7A peak height is attributed to kaolinite. For example, if a sample gives a 7A peak that is 12 units high and a 14A peak (after heating at 550°C) 9 units high, then 6 units (9÷1.5) of the 7A peak height would be attributed to chlorite and the other 6 units to kaolinite; the two minerals would be calculated as being equally abundant.

In most samples of the Pierre, kaolinite and chlorite are generally present in small amounts, and one of these minerals is calculated to be no more than twice as abundant as the other. Within this range, differences in the relative abundance of kaolinite and chlorite may be due only to inaccuracy in measuring the usually small 7A and 14A peaks. The differences are considered to be significant only where the total amount of kaolinite and chlorite is more than a few percent and where one mineral is more than twice as abundant as the other.

As the Pierre investigation continues, samples may be found which contain large amounts of either kaolinite or chlorite that is of considerably different crystallinity than that in the fine-grained offshore facies investigated so far. If this happens, appropriate changes can be made in the factors used for the quantitative interpretation of kaolinite or chlorite. In the samples which have been investigated to date (1960), however, kaolinite and chlorite occur in such small amounts and appear to be sufficiently uniform in grain size and crystallinity that a variable comparison factor is not justified.

EXAMPLES OF INTERPRETATION

Figure 3 shows quantitative interpretations of the X-ray diffractometer traces of three samples that illustrate the known range of mineral composition in the Pierre Shale. Sample 259543 (fig. 3*B*) will be discussed in greatest detail because it is most typical of much of the Pierre Shale.

The minerals in sample 259543 for which diffractometer peaks are noted other than the clay minerals are quartz, feldspar, clinoptilolite, and possibly pyrite. By dividing the measured height of the 26.6° quartz peak in counts per second by 2,000 $\frac{\text{cps}}{100\text{ percent}}$ (from table 1), the amount of quartz is determined to be 16 percent. The 2-percent value for feldspar is similarly derived by dividing the measured height of the 28.0° feldspar peak by 1,000 $\frac{\text{cps}}{100\text{ percent}}$. On the basis of the 28.0° peak position rather than the 27.5° one (table 1), the feldspar is determined to be mainly a plagioclase rather than a potassium feldspar. The 1-percent clinoptilolite is interpreted from the small peak at 10.0°; although such a small peak might be considered to be of questionable significance, it is here interpreted as clinoptilolite because the same peak is seen on the X-ray traces of the oriented aggregate and because no other mineral now known to occur in the Pierre Shale gives an X-ray peak in this position. Pyrite is listed as questionably present in this sample because of the very small size of the 33.1° peak and because no other pyrite peak can be distinguished. The value of 75 percent for total amount of clay is derived from the 19.9° clay peak; the values for total clay from the 34.6° peak and the 61.9° peak are in fairly close agreement. The 94-percent total of minerals determined is within the range normally expected. Of the undetermined 6 percent, 1.5 percent is known to be organic matter and the remaining 4.5 percent probably is caused mostly by using a value for total clay that is slightly too low.

Relative amounts of the different clay minerals in sample 259543 are determined by using the procedure listed in table 2. The clay mineral fraction is calculated to be comprised of 4 percent kaolinite, 3 percent chlorite, 17 percent illite, 33 percent montmorillonite, and 43 percent mixed-layer illite-montmorillonite. Each of these relative amounts may be multiplied by 75 percent (the proportion of total clay minerals) to determine their proportion in the total sample.

Amounts and proportions of minerals for samples 259574 (fig. 3*A*) and 259550 (fig. 3*C*) are calculated in a similar fashion. Inasmuch as no 17A peak is shown on the glycol trace for sample 259574 (fig. 3*A*), no montmorillonite is recorded. The very large 17A peak for glycolated sample 259550 (fig. 3*C*) corresponds to an unusually large amount of montmorillonite; although the height of the 17A peak for sample 259550 is twice that for sample 259543, the amount of calculated montmorillonite is not twice as much. The large peaks obtained from the oriented aggregate of sample 259550 are, in part, due to a very high degree of preferred orientation of the clay flakes. The large peaks near 12.5A on the untreated traces for samples 259543 and 259550 indicate that much of the montmorillonite in these samples contains one layer of hydration water, this single layer in turn suggests that sodium probably is the most abundant exchangeable cation.

The method of differentiating montmorillonite and mixed-layer clay may be unrealistic, because all the material producing the broad 17A peak in samples like no. 259543 (fig. 3) might be interpreted as entirely mixed-layer clay rather than as a combination of montmorillonite and mixed-layer clay. Pure, unmixed montmorillonite having a 17A reflection as strong as that shown for sample 259543 should produce a series of reasonably sharp basal reflections at submultiples of the 17A(001) spacing—8.5A(002), 5.7A(003), 4.2A(004)

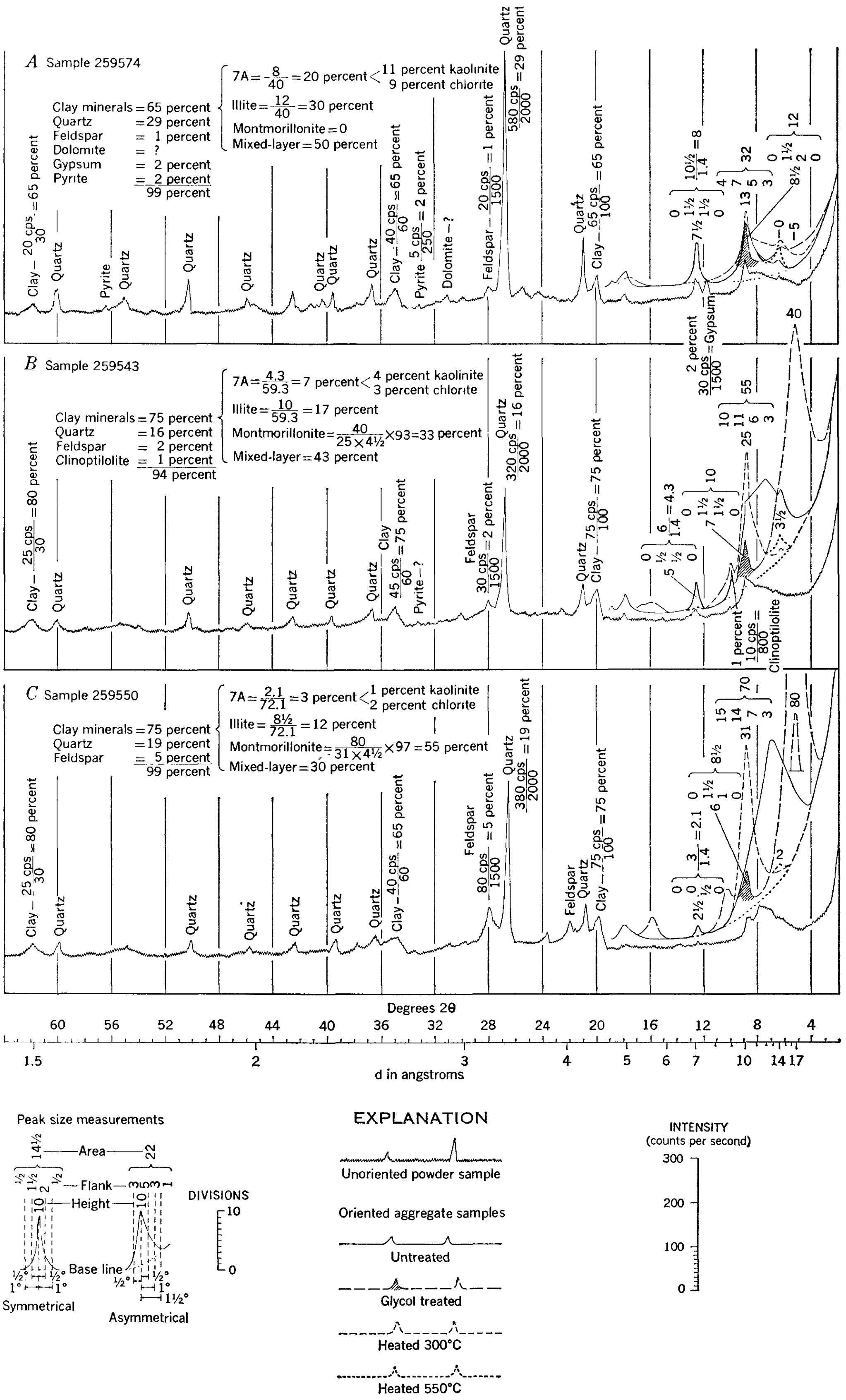

FIGURE 3.—Examples of quantitative evaluation of X-ray diffractometer traces of three samples of Pierre Shale (CuK α radiation). Illite peak at 10A is shaded.

TABLE 2.—*Procedure for calculation of relative amounts of clay minerals in the Pierre Shale*

General procedure	*Calculations for sample 259543 (fig. 3B)*
1. Measure the areas of the 7A, the 10A glycol, and the 10A 300°C peaks; measure the heights of the 7A, the 10A 300°C, the 14A 550°C, and the 17A glycol peaks	7A peak height=5; peak area=6. 10A glycol peak area=10. 10A 300°C peak height=25; peak area=55. 14A 550°C peak height=3½. 17A glycol peak height=40.
2. Corrected 7A peak area $=\frac{\text{7A peak area}}{1.4}$	Corrected 7A peak area $=\frac{6}{1.4}=4.3$.
3. Kaolinite+chlorite (percent) = $\frac{\text{corrected 7A peak area}}{\text{corrected 7A peak area}+\text{10A 300}^\circ\text{C peak area}}\times 100$	Kaolinite+chlorite $=\frac{4.3}{4.3+55}\times 100=7$ percent.
4. Chlorite (percent) = (kaolinite+chlorite) $\times\frac{\text{14A 550}^\circ\text{C peak height}}{1.5\times\text{7A peak height}}$	Chlorite = 7 percent $\times\frac{3\frac{1}{2}}{1.5\times 5}=3$ percent.
5. Kaolinite (percent) = (kaolinite+chlorite) − chlorite	Kaolinite = 7 percent − 3 percent = 4 percent.
6. Illite (percent) = $\frac{\text{10A glycol peak area}}{\text{corrected 7A peak area}+\text{10A 300}^\circ\text{C peak area}}\times 100$	Illite $=\frac{10}{4.3+55}\times 100=17$ percent.
7. Montmorillonite (percent) = $\frac{\text{17A glycol peak height}}{4\frac{1}{2}\times\text{10A 300}^\circ\text{C peak height}}\times(100-\text{kaolinite}-\text{chlorite})$	Montmorillonite $=\frac{40}{4\frac{1}{2}\times 25}\times 93=33$ percent.
8. Mixed-layer clay (percent) = 100 − (kaolinite + chlorite + illite + montmorillonite)	Mixed-layer clay = 100 − (4+3+17+33) = 43 percent.

and so forth. Such higher order basal reflections, though commonly noted for bentonite samples, are generally not observed for the shale samples, or, if present, they are very broad, small, and shifted slightly from their theoretical positions. According to Weaver (1956, fig. 1), interlayering of 10–20 percent of nonexpanding layers with montmorillonite produces very little shift in the first basal reflection at 17A. Such scant mixed-layering apparently shifts the higher order basal reflections more than the 17A (001) reflection. Probably the most notable effect, however, is the broadening and decrease in intensity of all the basal reflections. If mixed-layering is accompanied by dilution with several other minerals as it is in the Pierre Shale, the higher order basal reflections commonly are not clearly seen. Thus, the first basal reflection at 17A is the only consistently usable criterion for evaluating the expandable clay. However, if only the position of the 17A reflection is considered and is interpreted as evidence that all the expanding clay is unmixed montmorillonite, then the quantitative values give no indication of any difference between the expanding clay in shale samples like 259543 or 259550 (fig. 3) and the montmorillonite in the bentonite samples (fig. 2). In contrast to the shales, the bentonites generally produce a series of sharp basal reflections at 17A, 8.5A, 5.7A, and so forth. On the other hand, if broadness of the 17A reflection peak and weakness or slight shifting of higher order basal reflection peaks are interpreted as indicating that all the expandable clay is mixed layered, then the interpretation provides no basis for differentiating the expanding clay in a sample like 259543 from that in sample 259574 (fig. 3), even though the diffractometer patterns for the two samples are quite different. Both samples would be reported as containing abundant mixed-layer clay but no montmorillonite.

The sharpness and relative height of the 17A reflection are the most notable differences observed between most X-ray patterns from samples of Pierre Shale; in some manner the quantitative X-ray interpretation should express these differences. The means by which they have been expressed is by reporting both mixed-layer montmorillonite-illite and theoretically pure montmorillonite in relative amounts that depend on the sharpness or relative size of the 17A reflection. If no distinct 17A reflection is perceived, as in sample 259574 (fig. 3), then no montmorillonite is reported, and all the increase in size of the 10A reflection after heating at 300°C is attributed to mixed-layer clay. Relatively large 17A reflections, as in samples 259543 and 259550 (fig. 3), result in proportionately large amounts of reported montmorillonite; nevertheless, in both these samples some reported mixed-layer clay serves to differentiate the partially expanding clay in these samples from the completely expanding montmorillonite common in the bentonite beds.

Some discretion must be used in calculating the ratio of montmorillonite to mixed-layer clay, because several factors may affect the 17A:10A ratio of 4.5:1 normally expected for montmorillonite in the Pierre Shale. First, the 4.5:1 ratio is an average; thus, for example, if a 4.0:1 ratio is measured but the X-ray pattern shows a good, sharp sequence of basal orders all in the proper positions for montmorillonite, then the expanding clay is interpreted as being entirely montmorillonite, regardless of the deviation of peak heights from the ideal 4.5:1 average. Second, a very thin oriented aggregate of pure montmorillonite produces a 17A:10A ratio considerably in excess of the expected 4.5:1 ratio, because, as the diffraction angle increases from the 17A to the 10A positions, increasingly more of the X-ray beam penetrates through the sample instead of being diffracted by it. In such an example, however, the thinness of the sample is readily observed and a fairly good sequence of basal orders is still produced by the glycol-treated slide; the clay can therefore be reasonably interpreted as montmorillonite, regardless of the abnormally high 17A:10A ratio. Third, a thick oriented aggregate of exceptionally well oriented montmorillonitic clay will produce extremely strong X-ray reflections which saturate the geiger counter for the 17A peak and cause an abnormally low 17:10A peak-height ratio. In such instances, the sharpness and relative intensities of the higher order basal reflections can be used to estimate the extent of mixed-layering in the montmorillonite; moreover, the intensity of the X-ray beam reaching the sample can be reduced in order to reduce the intensity of the diffracted beam until it is within the linear range of the detector.

REPRODUCIBILITY

Four variables affect the reproducibility of quantitative values as determined from the X-ray diffractometer studies. They are:

1. Interpretation: inconsistencies in measurement of peak size.
2. Machine: variations in response of the X-ray diffractometer equipment.
3. Sample preparation: variations in packing of the unoriented powder and in the degree of preferred orientation of the oriented aggregates.
4. Sampling: differences in pieces of sample selected for analysis.

Repeated analyses that are intended to indicate the importance of each of these four variables are given in table 3.

Quantitative values determined from X-ray traces of powders of five different pieces of the same sample are recorded in column 1 of table 3, and the clay-mineral analyses from the oriented aggregates prepared from the same five pieces are recorded in column 2; all four variables enter into the values in columns 1 and 2. The oriented aggregates used for columns 3, 4, and 5 of the table are made from the same minus-2 micron fraction from each of the three different samples in order to eliminate any sampling error. Data in column 3 are from five oriented aggregates prepared from the same clay-water slurry; the first three variables enter into the tabulated quantitative values. Data in column 4 are from five different groups of X-ray traces made from a single oriented aggregate; the first two variables enter into these values. Data in column 5 are from five different interpretations of the same diffractometer traces made over a period of several days; only the first variable (interpretation) enters into these values.

The means, standard deviations $\left(\sqrt{\frac{n\Sigma x^2-(\Sigma x)^2}{n(n-1)}}\right.$; n=number of determinations; x=calculated value), and coefficients of variation $\left(\frac{\text{standard deviation}\times 100}{\text{mean}}\right)$ from each group of five determinations are also given in table 3. In the lower part of the table, the standard deviations and coefficients of variation are totaled for each of the clay minerals and for all five clay minerals combined.

The standard deviations for the five determinations of each of the individual clay minerals in each of the three samples vary considerably (table 3). The total of the three standard deviations for each clay mineral, however, generally decreases from column 2 to column 5 of the table, and the total of the standard deviations for all five clay minerals decreases consistently. The magnitude of this decrease is an approximate measure of the influence of each of the four previously mentioned variables on the reproducibility of the quantitative values. Each of the four variables introduces some uncertainty, but inconsistent interpretation of peak size seems to cause the largest variation in the calculated values.

Part of the inconsistency of interpretation is caused by slight differences in placement of the baseline below

Table 3.—*Repeated X-ray analyses, in percent, of three samples of Pierre Shale*

[?, presence doubtful, calculated as zero. Variables: a, interpretation; b, X-ray machine; c, sample preparation; d, sampling]

Sample	Whole sample												
	1 (variables a–d)							2 (variables a–d)					
	Total clay	Quartz	Feldspar	Pyrite	Dolomite	Gypsum	Clinoptilolite	Kaolinite	Chlorite	Illite	Mixed-layer	Montmorillonite	Total
259547	65	30	1	?	?	1	--------	9	7	29	55	--------	--------
	65	30	1	0	?	0	--------	10	7	30	53	--------	--------
	70	31	2	?	?	0	--------	11	7	30	52	--------	--------
	65	31	1	3	2	0	--------	8	8	27	57	--------	--------
	70	30	2	4	?	?	--------	8	7	27	58	--------	--------
Mean	67	30.4	1.4	1.4	.4	.2	--------	9.2	7.2	28.6	55.0	--------	--------
Standard deviation	2.7	.6	.6	2.0	.9	.5	--------	1.3	.4	1.5	2.6	--------	--------
Coefficient of variation	4	2	43	140	225	250	--------	14	6	5	5	--------	--------
259543	80	14	2	?	--------	--------	1	6	5	19	43	27	--------
	75	14	2	1	--------	--------	?	3	6	19	46	26	--------
	70	17	1	0	--------	--------	0	5	4	18	47	26	--------
	75	15	2	?	--------	--------	0	5	3	18	45	29	--------
	75	16	2	0	--------	--------	2	6	3	17	45	29	--------
Mean	75	15.2	1.8	.2	--------	--------	.6	5.0	4.2	18.2	45.2	27.4	--------
Standard deviatiou	3.5	1.3	.5	.4	--------	--------	.9	1.2	1.3	.8	1.5	1.5	--------
Coefficient of variation	5	9	28	200	--------	--------	150	24	31	4	3	5	--------
259550	75	20	5	--------	--------	--------	--------	3	2	14	31	50	--------
	80	16	3	--------	--------	--------	--------	2	2	15	33	48	--------
	80	16	3	--------	--------	--------	--------	2	1	11	32	54	--------
	75	17	9	--------	--------	--------	--------	2	2	12	32	52	--------
	80	18	10	--------	--------	--------	--------	2	2	12	29	55	--------
Mean	78	17.4	6.0	--------	--------	--------	--------	2.2	1.8	12.8	31.4	51.8	--------
Standard deviation	2.7	1.7	3.3	--------	--------	--------	--------	.5	.5	1.6	1.5	2.9	--------
Coefficient of variation	.3	10	55	--------	--------	--------	--------	23	28	13	5	6	--------
Total of standard deviations for three samples								3.0	2.2	3.9	5.6	4.4	19.1
Total of coefficients of variation for three samples								61	65	22	13	11	172

Sample	Minus-2 micron fraction																	
	3 (variables a–c)						4 (variables a–b)						5 (variable a)					
	Kaolinite	Chlorite	Illite	Mixed-layer	Montmorillonite	Total	Kaolinite	Chlorite	Illite	Mixed-layer	Montmorillonite	Total	Kaolinite	Chlorite	Illite	Mixed-layer	Montmorillonite	Total
259574	7	5	24	64	------	--------	8	5	21	66	------	--------	7	6	25	62	------	------
	8	5	25	62	------	--------	8	6	24	62	------	--------	8	5	24	63	------	------
	8	6	23	63	------	--------	7	7	22	64	------	--------	7	6	24	63	------	------
	7	6	25	62	------	--------	7	6	25	62	------	--------	7	7	25	61	------	------
	6	7	21	66	------	--------	7	6	25	62	------	--------	7	6	24	63	------	------
Mean	7.2	5.8	23.6	63.4	------	--------	7.4	6.0	23.4	63.2	------	--------	7.2	6.0	24.4	62.4	------	------
Standard deviation	.8	.8	1.7	1.7	------	--------	.5	.7	1.8	1.8	------	--------	.5	.7	.5	.9	------	------
Coefficient of variation	11	14	7	3	------	--------	7	12	8	3	------	--------	7	12	2	1	------	------
259543	3	2	11	49	35	--------	2	3	14	47	33	--------	3	2	13	46	36	------
	4	2	11	49	34	--------	3	2	13	47	35	--------	2	3	14	45	36	------
	3	2	10	49	36	--------	3	2	13	47	35	--------	3	3	15	44	35	------
	3	2	11	49	35	--------	3	3	13	45	36	--------	2	3	15	47	33	------
	2	3	14	47	33	--------	3	2	13	46	36	--------	2	3	14	45	36	------
Mean	3.0	2.2	11.4	48.6	34.6	--------	2.8	2.4	13.2	46.4	35.0	--------	2.4	2.8	14.2	45.4	35.2	------
Standard deviation	.7	.4	1.5	.9	1.1	--------	.4	.5	.4	.9	1.2	--------	.5	.4	.8	1.1	1.3	------
Coefficient of variation	23	18	13	2	3	--------	14	21	3	2	3	--------	21	14	6	2	4	------
259550	1	1	10	30	58	--------	1	1	12	27	59	--------	1	1	11	30	57	------
	1	1	11	30	57	--------	2	?	10	29	58	--------	1	2	10	31	56	------
	1	1	8	36	54	--------	1	0	10	30	59	--------	1	1	9	31	58	------
	1	0	9	33	57	--------	1	1	9	30	58	--------	1	1	8	32	58	------
	1	1	12	27	59	--------	1	1	11	30	57	--------	1	2	10	32	55	------
Mean	1.0	0.8	10.0	31.2	57.0	--------	1.2	0.6	10.4	29.2	58.2	--------	1.0	1.4	9.6	31.2	56.8	------
Standard deviation	.0	.4	1.6	3.4	1.9	--------	.4	.5	1.1	1.3	.8	--------	.0	.5	1.1	0.8	1.3	------
Coefficient of variation	0	50	16	11	3	--------	33	83	11	4	1	--------	0	36	11	3	2	------
Total of standard deviations for three samples	1.5	1.6	4.8	6.0	3.0	16.9	1.3	1.7	3.3	4.0	2.0	12.3	1.0	1.6	2.4	2.8	2.6	10.4
Total of coefficients of variation for three samples	34	82	36	16	6	174	54	116	22	9	4	205	28	62	19	6	6	121

1. Five different splits, unoriented powder.
2. Five different splits, oriented aggregate.
3. Five different oriented aggregates from one split.
4. Same oriented aggregate, rerun five times.
5. Same X-ray diffractometer traces, interpreted five times.

the X-ray peaks being measured. Figure 4 illustrates the importance of baseline placement in repeated analyses of the same set of X-ray traces; the two interpretations are the first and second listed for sample 259543 in column 5 of table.

The long baseline below the 7A, the 10A-300°C, and the 17A-glycol peaks is constructed by use of a french curve. Even if the low-angle portions of the glycol and the 300°C traces do not exactly coincide as shown on figure 4, the 300°C trace is still a useful parallel guideline for construction of a baseline for the glycol trace. Nevertheless, the baseline was placed slightly lower in the first than in the second interpretation and resulted in differences in measured sizes of the 7A, 10A-300°C, and 17A-glycol peak sizes. The baselines below the 10A-glycol peak and the 14A-550°C peak are sketched in freehand. Differences in the measured peak sizes of the two interpretations are small, but nevertheless they are large enough to explain much of the variability reported in column 5 of table 3.

Coefficients of variation in table 3 fluctuate much more than the standard deviations. The very small amounts of kaolinite and chlorite in some of the samples cause most of this variation. For example, the coefficient of variation of 50 percent for chlorite in sample 259550, column 3, is caused by a difference of only 1 percent in one of the determinations. In such a case, the coefficient of variation has little meaning.

High variation in determinations for pyrite, dolomite, gypsum, and clinoptilolite in column 1 of table 3 indicates that in small amounts these minerals are not consistently detected.

The importance of the amount of material sampled to the consistency of the X-ray quantitative determinations is illustrated in figure 5 by plotting the coefficients of variation for total clay, quartz, feldspar, and the clay minerals in columns 1, 2, and 3 of table 3 as functions of the average amount of each component calculated to be present. For minerals composing more than 15 percent of the sample, any one single determination likely will be within 10 percent of the average of five repeated determinations. The reproducibility is less for amounts smaller than 15 percent.

This generalization will apply to most, but not all, samples of Pierre Shale. For example, some bentonite and some highly bentonitic shale samples contain rela-

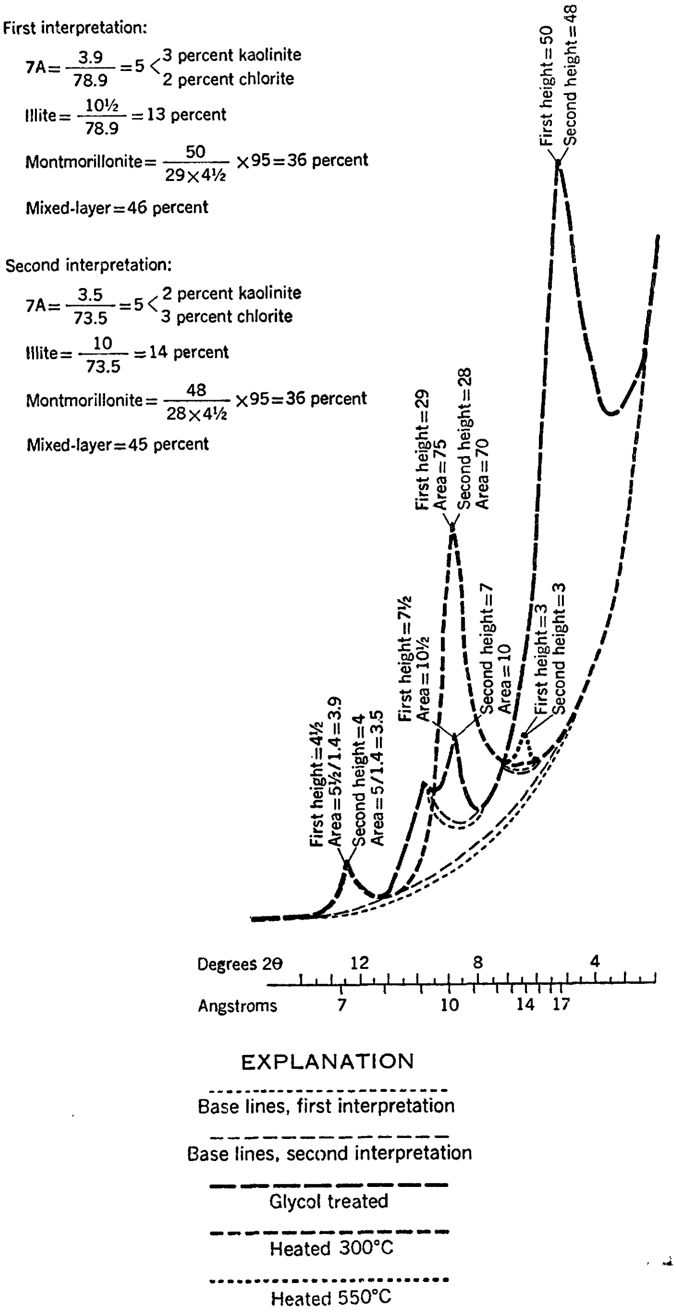

FIGURE 4.—The effect of baseline position on quantitative interpretation of X-ray diffractometer traces. The two interpretations illustrate derivations of the percentages in first two horizontal rows for sample 259543, column 5, table 3.

tively large particles of feldspar that in the powder samples readily orient parallel to cleavage faces. The reproducibility of X-ray intensity relations for feldspar in these samples may be considerably outside the expected limits unless the samples are especially ground or unless averages of several repeated runs are used. Sample 259550 (table 3) illustrates this. The general similarity of most values in table 3, however, shows that most minerals in the Pierre Shale are sufficiently fine-grained that they behave like ideal powders for diffraction studies. This fine-grained characteristic is also illustrated by the uniform results from repeated analyses made for calcite and quartz each in 11 samples, as shown in table 4.

An additional indication of the consistency of the X-ray quantitative mineralogical determinations is shown by the eight sets of duplicates in table 5. At the time the samples were analyzed, the duplicates were not known as such. The consistency of the mineralogical values is generally what would be expected from the standard deviation and coefficients of variation from tables 3 and 4 and from figure 5. As in table 3, the values given in table 5 indicate that small amounts of nonclay minerals are not consistently detected in the X-ray analyses—for example, alunite in sample 259549 and its duplicates, and calcite and pyrite in sample 259568 and its duplicate.

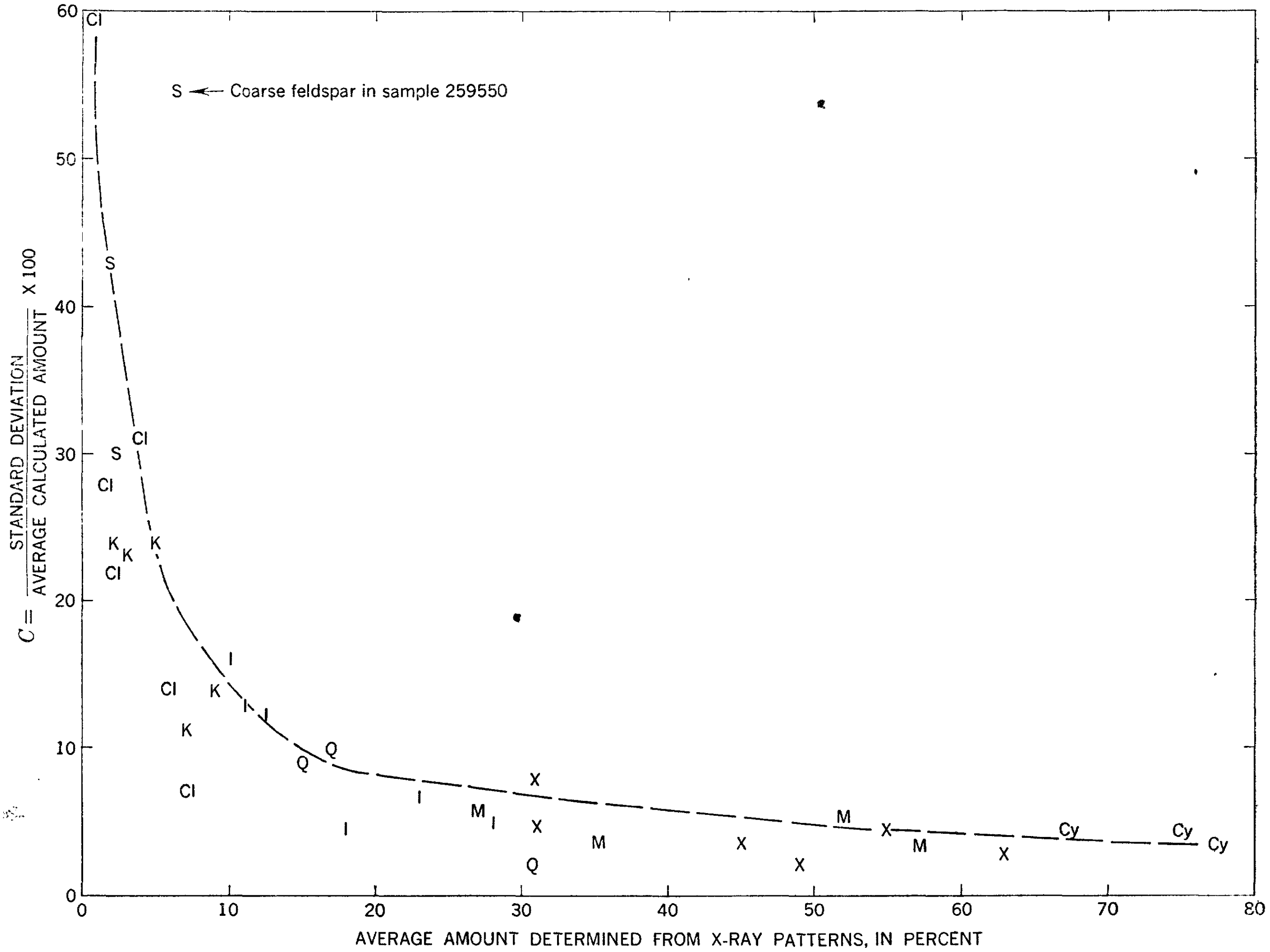

FIGURE 5.—Relation between coefficient of variation (C) and the average amount of each mineral determined from X-ray patterns. Cy, total clay minerals; Q, quartz; S, feldspar; K, kaolinite; Cl, chlorite; I, illite; X, mixed-layer clay; M, montmorillonite. Data from table 3.

TABLE 4.—*Repeated X-ray analyses, in percent, for calcite and quartz in samples of Pierre Shale*

Sample	Determinations	Calculated values ± standard deviation (range of determinations in parentheses)	Coefficient of variation
Calcite			
S57-32-6	5	55±3.0 (53-60)	5.5
S57-35A-2	11	43±1.5 (41-45)	3.5
S57-35A-3	11	42±1.0 (41-44)	2.4
S57-35C-1	11	44±1.0 (41-44)	2.3
S57-34-1	11	28±2.2 (26-32)	7.8
S57-34-2	6	41±1.9 (39-43)	4.6
S57-34-3	6	21±1.3 (20-23)	6.2
S57-35D-5N	6	47±1.5 (44-48)	3.2
S57-35E-2	6	47±5.0 (40-50)	10.5
S57-30-7	6	88±3.5 (84-93)	4.0
To57-1-3	5	65±2.0 (62-66)	3.1
Average			4.8
Quartz			
S57-35B-1	5	12±1.8 (11.0-12.5)	15.0
S57-35A-2	6	6±0.4 (5.5- 6.5)	6.7
S57-35A-6	6	18±1.0 (17.0-19.5)	5.6
S57-34-3	6	13±0.8 (12.0-14.0)	6.2
S57-35D-3	5	19±1.5 (17.5-21.0)	7.9
S57-35D-5	6	16±0.8 (15.0-16.5)	5.0
S57-35D-6	6	21±1.0 (19.5-22.5)	4.8
S57-35E-2	6	12±0.3 (11.5-12.0)	2.5
S57-35E-3	6	12±0.5 (11.5-12.5)	4.2
G57-4-26L	5	37±1.0 (35.0-37.5)	2.7
S57-35A-3	6	1±0.2 (1.0- 1.5)	[1] 20.0
Average			6.1

[1] Not included in average.

LONG-TERM REPRODUCIBILITY

Results illustrated in table 3 were obtained from carefully prepared samples having good orientation of the oriented aggregates; all samples were treated in exactly the same manner and run on the same Norelco X-ray machine during a 3-month period in late 1958 and early 1959. In contrast, X-ray data for the Pierre study, as a whole, have been obtained over a period of several years by using two different machines and three goniometers. To determine if the reproducibility indicated in table 3 could be maintained under these conditions, three additional sets of analyses of the same group of three samples were obtained under less ideal conditions (table 6). The first set of analyses were run in November 1957 on one X-ray machine, and the two additional sets were run in 1960 on each of two goniometers mounted on another machine. Even when pyrite, dolomite, gypsum, and clinoptilolite are excluded from consideration because they occur as such small amounts and when an average of the standard deviations for each mineral in the three samples is used (table 7), less than half of the determinations are within one standard deviation of the mean for each mineral reported in table 3. Because maintenance of the same degree of reproducibility requires that two-thirds of the values be within one standard deviation, the short-term reproducibility was not maintained under the conditions in which data for the Pierre study have been accumulated.

TABLE 5.—*X-ray mineralogical analyses in percent, of unknown duplicate samples*

[Figures in parentheses are calculated from chemical analyses and are not included in total. ?, presence of the mineral doubtful]

Constituent	Set 1		Set 2				Set 3		Set 4		Set 5		Set 6		Set 7		Set 8	
	259533	259597 (duplicate)	259549	259596 (duplicate)	259599 (duplicate)	259603 (duplicate)	259553	259604 (duplicate)	259565	259598 (duplicate)	259568	259601 (duplicate)	259580	259600 (duplicate)	259582	259602 (duplicate)	259586	259605 (duplicate)
Clay minerals:																		
Montmorillonite	43	41	7	---	---	---	34	35	35	30	22	19	24	25	25	28	35	30
Mixed-layer	37	37	39	49	48	43	29	34	28	34	38	39	39	42	40	37	48	53
Illite	17	16	42	35	36	41	21	17	25	26	21	23	25	22	22	22	12	11
Chlorite	?	4	?	---	---	---	6	6	6	7	9	7	7	5	5	8	---	---
Kaolinite	3	2	12	16	16	16	10	8	6	3	10	12	5	6	8	5	5	6
Whole rock:																		
Total clay minerals	45	45	45	40	40	35	40	35	70	70	70	65	70	70	65	60	80	80
Quartz	4	5	12	14	13	9	9	6	22	21	25	21	19	22	19	21	19	19
Cristobalite	35	30	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Feldspar:																		
Predominantly potassium feldspar	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Predominantly plagioclase	---	---	---	---	---	---	---	---	4	4	---	3	3	4	2	2	2	3
Undertermined	1	1	---	?	?	---	?	1	---	---	2	---	---	---	---	---	---	---
Calcite	---	---	---	---	---	---	35(40)	42(40)	---	---	2(2½)	?(2)	---	---	---	2(1)	---	---
Dolomite	---	---	---	---	---	---	---	---	0(½)	?(1)	?	---	3(5)	8(5)	?(1½)	2	---	---
Rhodochrosite	13(14)	10(13)	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---	---
Gypsum	---	---	6(4)	3(4)	3	5	---	---	---	---	---	---	---	---	---	---	---	---
Jarosite	---	---	8(2)	5(15)	5	5	---	---	---	---	---	---	---	---	---	---	0(1)	?(1)
Alunite	---	---	?	?	2	?	---	---	---	---	---	---	---	---	---	---	---	---
Pyrite	1(1)	2(1)	15(18)	20(7)	20(4)	20(4)	4(4)	2	---	---	0(1)	1	---	---	10(8)	15(3)	---	---
Clinoptilolite	---	---	---	---	---	---	---	1?	---	---	---	---	---	---	---	---	---	---
Total	99	93	[1] 86	82	83	74	88	87	96	95	99	90	95	104	96	102	101	102

[1] Also contains 12 percent organic matter.

The probable increase in variability due to lapse of time and use of different apparatus was estimated by trial and error adjustment of the standard deviations to the point that the required two-thirds of the determinations for each mineral in table 6 came within one empirical standard deviation on each side of the mean-values given in table 3. Significant differences between the empirical and average standard deviations (table 7) are the larger empirical standard deviations for montmorillonite, mixed-layer clay, and, to a lesser extent, illite. The empirical standard deviation for total clay seems to be fortuitously and unrealistically low. The other empirical standard deviations, however, are believed to be more applicable to the quantitative mineralogical data for the Pierre Shale than are the generally lower standard deviations from table 3. The empirical standard deviations, however, still generally give coefficients of variation that are close to the 10 percent figure previously mentioned in reference to figure 5.

The high empirical standard deviations for some of the clay minerals (table 7) probably result mostly from slight differences in goniometer alinement. Variations in the electronic circuits and X-ray tubes probably are not important because these factors should cause increased variability for all minerals equally, not mostly for montmorillonite, mixed-layer clay, and illite. In fact, inasmuch as quantitative determinations of the different clay minerals depend on relative peak sizes all determined within one or two days, long-term variation in electronic components should have the least effect on determinations for these clay minerals. On the other hand, slight variations in goniometer alinement have the greatest effect in the low-angle region of the measured montmorillonite, illite, and mixed-layer clay reflections. Thus, goniometer alinement would seem to be the most important cause of the increased variability in table 6, as compared with that in table 3. Increase in variability of interpretation over a long period of time also may have some effect.

TABLE 6.—*Repeated X-ray analyses, in percent, of three different splits each of three samples of Pierre Shale over a period of 2 years*

Sample	Date run	Whole sample												Minus-2 micron fraction				
		Unoriented powder							Oriented aggregate					Oriented aggregate				
		Total clay	Quartz	Feldspar	Pyrite	Dolomite	Gypsum	Clinoptilolite	Kaolinite	Chlorite	Illite	Mixed-layer clay	Montmorillonite	Kaolinite	Chlorite	Illite	Mixed-layer clay	Montmorillonite
259574	Nov. 1957	65	29	1	2	?	2	------	11	9	30	50	------	6	7	32	56	------
	Jan. 1960	65	32	2	1	4	2	------	10	8	31	51	------	9	7	26	58	------
	do	65	31	1	?	2	2	------	8	7	30	55	------	9	5	21	65	------
259543	Nov. 1957	75	16	2	?	------	------	1	4	3	17	43	33	3	2	15	47	33
	Jan. 1960	75	16	3	?	------	------	2	4	3	14	40	32	4	2	10	58	26
	do	75	16	2	?	------	------	1	3	4	17	47	36	3	2	10	54	31
259550	Nov. 1957	75	19	5	------	------	------	------	1	2	12	30	55	1	?	12	30	64
	Jan. 1960	80	17	3	------	------	------	------	1	1	14	29	54	1	1	7	32	59
	do	80	17	2	------	------	------	------	2	1	10	41	46	1	1	8	37	53

TABLE 7.—*Different standard deviations derived from repeated analyses of three samples of Pierre Shale*

	Total clay	Quartz	Feldspar	Kaolinite	Chlorite	Illite	Mixed-layer clay	Montmorillonite
Average standard deviation (from table 3)	3.0	1.2	1.4	0.8	0.6	1.4	1.9	1.9
Empirical standard deviation (for long-term use)	2.5	1.0	1.0	1.0	1.0	2.0	5.0	5.0

ACCURACY—COMPARISON WITH CHEMICAL ANALYSIS

The reproducibility of quantitative values derived from X-ray diffractometer traces is not, of course, an indication of the accuracy of the values. However, the accuracy of the quantitative X-ray analyses of some of the minerals can be checked by calculations from chemical analyses.

SULFIDE, SULFATE, AND CARBONATE MINERALS

In samples of Pierre Shale, acid-insoluble sulfur reported as sulfide sulfur probably is present in pyrite; acid-soluble sulfur reported as sulfur trioxide may be present in gypsum, jarosite, or rarely alunite; and carbon dioxide may be present in calcite, dolomite, or rarely siderite, or rhodochrosite. X-ray patterns determine which of the possible minerals is present. Relations between the values derived from X-ray data and values calculated from chemical analyses are shown in figure 6; duplicate samples (table 5) are not included. Minerals recorded as questionably present from the X-ray analyses are plotted at 0.5 percent, and chemically derived values of less than 0.5 percent are plotted together as 0.0–0.25 percent. Of the three mineral groups represented in figure 6, the X-ray and chemical determinations are in best agreement for the carbonates. Agreement of values for the sulfate and sulfide minerals is not good, but where these minerals are present in appreciable amounts, the chemical and X-ray determinations generally agree within a factor of two.

The lack of agreement between amounts of sulfate and sulfide minerals determined by X-ray methods and amounts calculated from chemical analyses (fig. 6) may also be due to error in the chemical analyses. The value

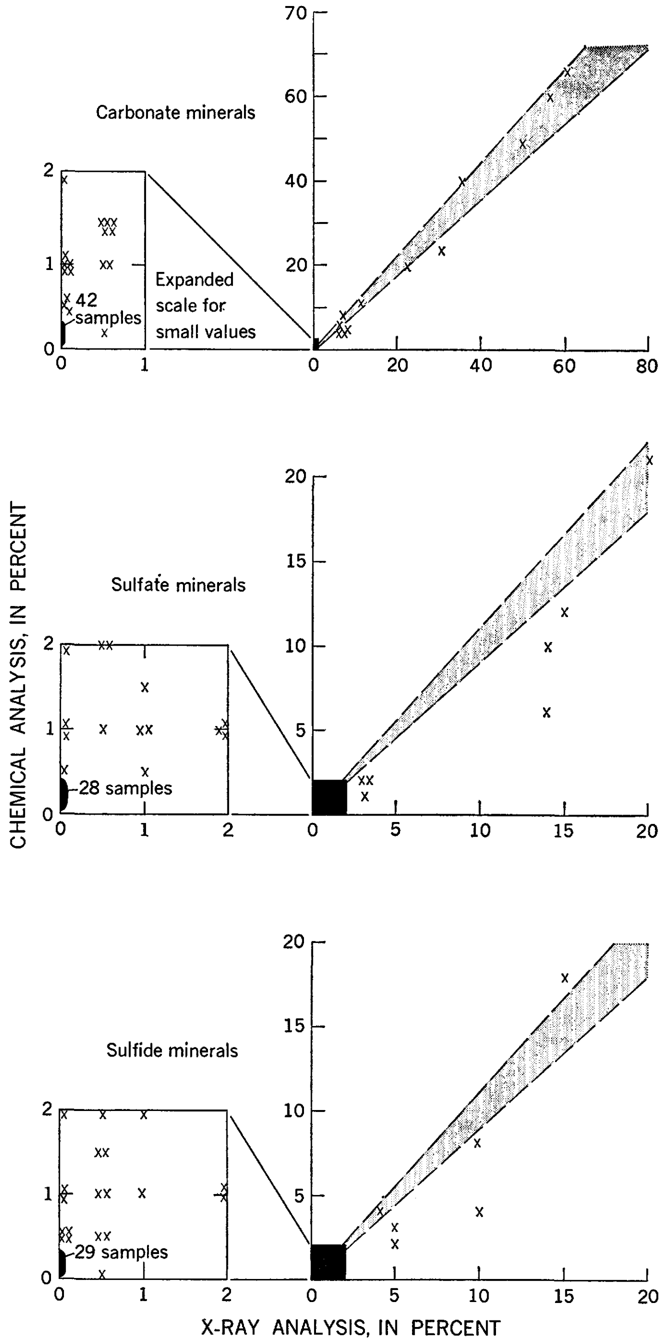

FIGURE 6.—Comparison of quantitative determinations of carbonate, sulfate, and sulfide minerals derived by X-ray methods and by chemical analysis. Points that fall within shaded areas on graphs represent differences of less than 10 percent between amounts determined by X-ray and chemical methods.

determined for ferrous oxide in the presence of organic matter such as occurs in most samples of Pierre Shale is uncertain, and the amount of ferric iron is assumed to be the difference between total iron and ferrous iron. These less dependable chemical determinations may limit the amount of pyrite and jarosite that can be calculated from the chemical analyses (such as sample 259549 and its duplicates, table 5). Therefore, only the graph of the carbonate minerals (fig. 6) may reflect the accuracy of the X-ray determinations.

ALUMINA

Nearly all of the alumina in samples of Pierre Shale occurs in the clay minerals. Feldspar is the only other alumina-containing mineral found in most samples, and it rarely exceeds a few percent of any sample; in such amounts of feldspar, the alumina content is less than 1 percent. The chemical composition of the different clay minerals is not the same. However, the proportions in which the clay minerals occur are fairly constant for most samples of Pierre Shale. Kaolinite and chlorite compose only a few percent of the clay-mineral fraction of most samples although kaolinite may constitute as much as 10 to 15 percent of this fraction in a few samples. Illite commonly composes 15 to 25 percent of the clay-mineral fraction. Montmorillonite and mixed-layer clay are the dominant clay minerals. The montmorillonite, illite, and mixed-layer clays are the common aluminous varieties. Therefore, theoretically, the amount of alumina should bear a fairly consistent relation to the total clay content in each sample and should provide a rough check on the reliability of the X-ray-determined values for total clay.

Values for total clay and alumina are compared in figure 7. If the middle dashed line in figure 7 represents the average alumina content for a given percentage of total clay in the Pierre Shale, most of the points plot outside the limits expected from either the 3.0-percent average or the 2.5-percent empirical standard deviation for total clay shown in table 7. However, about two-thirds of the samples plot within the 10 percent coefficient of variation indicated by figure 5. Furthermore, some of the scatter of points on figure 7 may be caused by different clay-mineral composition of the samples. Of the clay minerals in the Pierre Shale, the relative amounts of kaolinite and montmorillonite should have the most pronounced effect on the alumina content (fig. 7). Samples having unusually high montmorillonite: kaolinite ratios should have relatively low alumina content, because kaolinite contains 40 percent alumina, whereas montmorillonite like that in the Pierre probably contains only about 16 to 20 percent. As expected (fig. 7), the more kaolinitic samples (low montmorillonite: kaolinite ratio) are generally plotted above the average alumina content, and the more montmorillonitic samples are plotted below the average.

Figure 8 shows an evaluation of the relative importance of errors in total clay values and of the effect of different proportions of the clay minerals as causes for

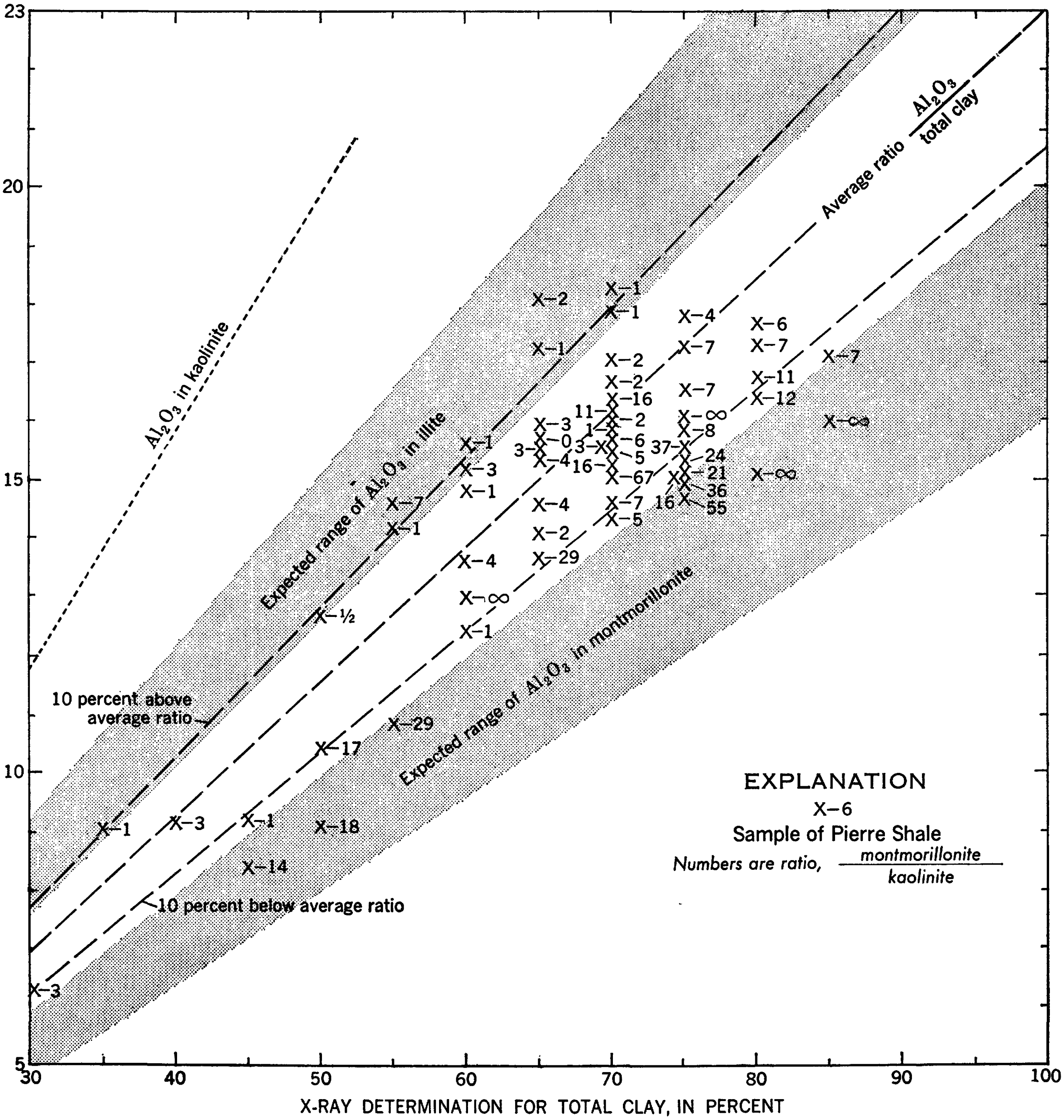

FIGURE 7.—Comparison of chemical determinations for alumina and determinations for total clay derived from X-ray diffractometer data for the Pierre Shale.

scatter of points on figure 7. A theoretical amount of alumina for each sample is calculated by multiplying the determined amount of each significant alumina-bearing mineral by an alumina content assumed to be reasonable for that mineral. The amount of each clay mineral in the sample is the product of its proportion in the clay fraction and the amount of total clay in the sample. For example, the alumina content shown in figure 8 for sample 259543 (fig. 3) is calculated as follows:

Calculation of alumina from X-ray data

[Total clay is 75 percent (rounded) of whole sample]

Mineral	Percent of total clay (1)	Percent of whole sample (2; 1×75 percent)	Alumina	
			Percent of mineral (3)	Percent of whole sample (2×3)
Clay minerals:				
Montmorillonite	33	24	18	4.46
Mixed-layer clay	43	32	20	6.45
Illite	17	13	27	3.44
Chlorite	3	2	17	.38
Kaolinite	4	3	40	1.20
Feldspar	----------	2	22	.44
Total	100	----------	----------	16.37
Total alumina determined from chemical analyses	----------	----------	----------	15.92

The points on figure 8 are scattered much less than they are on figure 7, and they more realistically portray the probable accuracy of determinations for total clay. Even if all the scatter of points on figure 8 is attributed to error in the total clay determinations, the indicated accuracy clearly is within the coefficient of variation of 10 percent previously mentioned in reference to figure 5.

An additional conclusion may be derived from figure 8, namely, that errors in total clay values probably cause the greatest observed deviations from the ideal 1:1 ratio of chemically determined alumina and alumina calculated from X-ray data. Two of the three samples that give alumina values of more than 10 percent in excess of the chemically determined alumina (plot below shaded area, fig. 8) have a total of minerals calculated from X-ray that is in excess of 100 percent; obviously, for some mineral in these samples the determination is too large. In these samples, inasmuch as determined feldspar is only 1 to 2 percent, determined amounts cannot possibly exceed the true amounts sufficiently to explain the abnormally high alumina calculated from X-ray data. The determinations that must be high are those for the only other common alumina-bearing minerals in these samples, the clays.

On the other end of the scale, the total amount of minerals determined for the four samples that are plotted farthest above the ideal 1:1 ratio (fig. 8) is 88 to 90 percent. The 10 to 12 percent of these samples not determined probably is not amorphous silica, for silica alone would not affect the alumina calculations. It probably is not feldspar either, because, if it were, the 2 to 4 percent feldspar determinations for these samples would correspond to true values of 12 to 16 percent; an error of this magnitude for all four samples is extremely unlikely. The only remaining common alumina-bearing minerals that can be responsible for the 10 to 12 percent deficiency in the total sample and the deficiency of about 2 percent in alumina calculated from X-ray data are the clays.

LOWER LIMITS OF DETECTION

Data in table 3 and figure 5 suggest that generally a mineral must be uniformly distributed in a sample in amounts of 2 percent or more before it is consistently detected in the X-ray analyses. In no sample is the mineral detected if present in amounts of less than 0.5 percent. These lower limits of detection depend to some extent upon the inherent diffracting ability of the different minerals (see table 1). To be consistently detected, a mineral must give a peak height of about 5 to 10 cps above background. Quartz, for example, tends to give large peaks and may be consistently detected in amounts of only 1 percent, whereas the lower limit of detection for pyrite generally is 2 percent or greater. Interference of X-ray reflections from other minerals also may raise the lower limit of detection. For example, either plagioclase or clinoptilolite could mask the main X-ray peak for a small amount of cristobalite, and a combination of X-ray diffraction peaks from illite and gypsum can hide the two main peaks of jarosite.

MINERALOGICAL OCCURRENCE OF PRINCIPAL CHEMICAL ELEMENTS

CALCULATIONS DESCRIBED IN THE LITERATURE

Calculation of the mineralogical composition of a rock from its chemical composition was first proposed by Cross, Iddings, Pirsson, and Washington (1903). By their system, generally known as the CIPW System, a chemical analysis is used to calculate a theoretical mineral composition called the norm of the rock. The norm includes minerals of simple chemical composition that may have crystallized from a magma having the chemical composition of the rock. Minerals having complex and variable chemical compositions like the micas, garnets, and aluminous amphiboles and pyroxenes are not included as norm minerals. The calculated norm may or may not agree closely with the actual (modal) mineralogical composition of the rock. CIPW normative calculations have been widely applied to igneous rocks.

Krumbein and Pettijohn (1938, p. 490–492) indicated the possible value of chemical analyses in identifying minerals in fine-grained sedimentary rocks and gave an example of the calculation of the norm of a graywacke. They assumed that the constituents occurred in minerals like kaolinite or amesite to which they ascribed simple, fixed chemical compositions. They also pointed out that the calculations were only as appropriate as were the assumptions underlying them.

Such an approach has been more fully explained by both Miesch and Nicholls. Miesch (1962) calculated the possible range of the gross mineral composition of

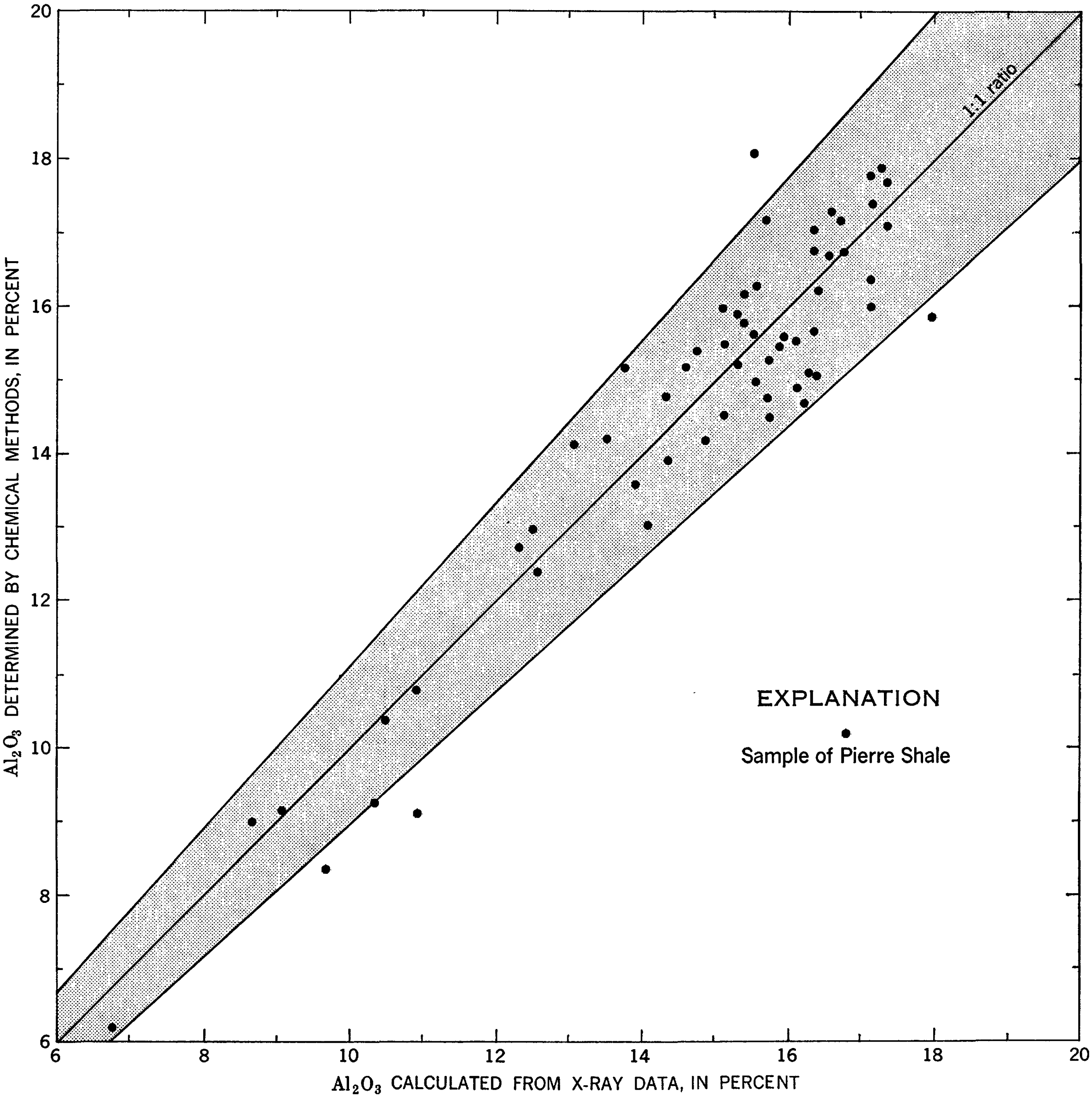

FIGURE 8.—Comparison of chemical determinations for alumina and calculations for alumina from X-ray data. Points that fall within shaded area represent differences of less than 10 percent between amounts determined by X-ray and chemical methods.

rocks from chemical composition and known mineral occurrence of some of the chemical constituents. Nicholls (1962) proposed a scheme for recalculating chemical analyses first into normative formulae representing ideal muscovite, paragonite, kaolinite, magnesian antigorite, and iron antigorite, which in turn may be regrouped into normative minerals of more probable chemical composition such as illite, chlorite, and kaolinite.

Imbrie and Poldervaart (1959) described a method for the calculation of mineral composition from chemical analyses of sedimentary rocks which contain minerals of complex and variable composition, including montmorillonite, illite, and chlorite. In the shale studied by them, these minerals were carefully determined, using several analytical techniques. Once the norm minerals were determined and the chemical compositions of these minerals were assumed, the amounts of each norm mineral in the individual samples were determined by rigidly following a sequence of steps and allotting the chemical elements to the different norm minerals. This method obtained a good agreement between norm values, amounts of insoluble residues, and X-ray quantitative values for percent of carbonates, quartz, and total clay minerals (Imbrie and Poldervaart, 1959, tables 5 and 6). However, there was little agreement between the norm calculations and X-ray values for the various clay minerals.

A good agreement between X-ray mode and chemical norm for a sample containing mainly muscovite, chlorite, and plagioclase was obtained by Zen (1960, p. 135). The investigated rocks were sufficiently coarse grained that optical properties and chemical composition of individual minerals could be determined. Such is not true for samples of Pierre Shale.

PIERRE SHALE

The objective of the chemical-mineralogical calculations for the Pierre Shale is to allot the chemical constituents as realistically and accurately as possible to minerals known to occur in each sample. This objective allows a comparison of X-ray and chemical data to make sure they are not conflicting, and facilitates a study of compositional similarities and differences between groups of samples.

Most of the chemical constituents in the Pierre Shale can occur in several minerals, and many of these minerals in the Pierre may vary in composition. For example, alumina occurs in feldspar, in all five of the clay minerals, and also in clinoptilolite or alunite in a few samples. In fact, all the chemical components that commonly amount to more than 1 percent in the analyses of Pierre Shale have multiple mineralogical occurrences. Therefore, X-ray data are used to help assign the proper amount of the more common elements to minerals; the X-ray data are used not only to help identify minerals present in individual samples, but also to determine the amounts of several of the minerals calculated from the chemical analysis.

The moderate variation in the mineralogical composition of the Pierre Shale permits some procedures and assumptions about chemical composition of minerals that would not be justified for all sedimentary rocks. The composition of minerals which make up only a minor part of the Pierre Shale does not need to be known as accurately as does the composition of the major mineral constituents.

BASIS OF CALCULATIONS

Minerals in the Pierre Shale are divided into three groups on the basis of the method used for calculating their amounts and compositions.

In the first group, a unique constituent in the chemical analysis is the primary basis for calculating the abundance of the mineral. This group contains minerals such as pyrite, apatite, and the carbonate minerals. X-ray data aid in determining exactly the composition of the minerals in this group that are somewhat variable, such as apatite and the carbonates, but the X-ray determinations have little or no relation to the amount of the minerals calculated.

The second group includes minerals, such as kaolinite, the feldspars, illite, and chlorite, that have no unique chemical constituent to determine their abundance. Compositions of some of the minerals are almost unvariable, but the compositions of others may be highly variable, and assumptions have to be made. Because most of the minerals in this group that vary considerably in composition are present in Pierre samples only in small amounts, the effect of assumed chemical formulae in the overall calculations is small. The X-ray data provide the only basis for distributing the chemical elements in such minerals.

The third group of minerals contains montmorillonite and mixed-layer illite-montmorillonite, both of which may vary considerably in chemical composition. These minerals commonly make up half or more of most samples of Pierre Shale, and any errors in assumed chemical composition would have considerable effect on the overall chemical calculations. Therefore these two minerals are grouped together, and all chemical elements not assigned to other minerals are assigned to them.

Frequent reference to plate 1 may help the reader to understand the following discussion of the individual minerals.

CHEMICAL COMPOSITION OF MINERALS

MINERALS CALCULATED PRIMARILY FROM CHEMICAL ANALYSES

APATITE

Apatite is the principal mineral in some concretions in the Pierre Shale, but in the shale itself, apatite is detected only rarely by X-ray techniques. Petrographic examination of thin sections and heavy mineral separates reveals apatite in some shale samples in amounts too small to be detected by X-ray analysis. Small amounts of phosphate also may be adsorbed on the clay minerals.

In the Pierre Shale, the common range for chemically determined phosphorous pentoxide is about 0.05 to 0.30 percent, and most determinations are in the smaller end of this range. For the chemical-mineralogical calculations, phosphorous pentoxide in amounts less than 0.5 percent is disregarded because it is of uncertain mineralogical occurrence, and because if phosphorus having appropriate amounts of other constituents is calculated as apatite, the remaining amount of calcium in many samples is insufficient for other determined calcium-bearing minerals. In amounts of 0.5 percent or greater, phosphorous pentoxide is calculated as apatite. X-ray and chemical data indicate that apatite in the Pierre Shale is a carbonate-fluorapatite similar to that described by Altschuler, Clarke, and Young (1958, p. 49). In chemical calculations for the Pierre Shale, apatite is assumed to contain 55 percent calcium oxide, 38 percent phosphorous pentoxide, 4 percent fluorine, and 3 percent carbon dioxide. Errors introduced by this procedure will not significantly affect most calculations, as apatite generally is at most a very minor component in the Pierre Shale.

PYRITE (FeS_2)

Pyrite has a relatively simple and unvarying chemical formula. It is the only sulfide mineral known to occur in the Pierre Shale; thus, the amount of pyrite can be calculated from the amount of acid-insoluble sulfur reported as sulfide sulfur, in the chemical analysis, unless there is reason to consider the effects of barite on the determination of insoluble sulfur.

BARITE ($BaSO_4$)

Most sulfate minerals are soluble under the conditions by which acid-soluble sulfur is determined. The amount of acid-soluble sulfur is subtracted from the amount of total sulfur to give a value for acid-insoluble sulfur. Barite, however, is insoluble under conditions by which acid-soluble sulfur is determined and, therefore, if barite is present, its sulfur is reported with acid-insoluble sulfur as sulfide sulfur. Unless suitable corrections are made, the amount of sulfur in barite will be used in calculating the amount of pyrite.

Although in a few places barite occurs as nodules in the Pierre Shale, in the shale itself it has not been recognized either petrographically or on X-ray traces. The commonly reported range for barium oxide in the Pierre Shale is 0.02 to 0.2 percent; most determinations are in the smaller end of this range. In such small amounts, barium oxide is disregarded in the chemical-mineralogical calculations. If reported in amounts of 0.5 percent or greater, barium oxide is calculated as barite and an appropriate correction is made in the amount of acid-insoluble sulfur. In the great majority of samples, the amount of barium is so small that errors in this procedure will not appreciably influence the calculations.

GYPSUM ($CaSO_4 \cdot 2H_2O$)

Unless X-ray or other data indicate presence of other sulfate minerals, all acid-soluble sulfur reported as sulfur trioxide in the chemical analyses and the necessary amounts of calcium oxide and water are assigned to gypsum. Where calculated to be present in amounts of 2 percent or more, gypsum is invariably indicated by the X-ray patterns.

JAROSITE

Jarosite is not present in most samples of Pierre Shale, but where present, it may compose several percent of the sample. In small amounts, it is best detected by the presence of a yellow powder on the hand specimen.

The theoretical chemical formula of jarosite is $KFe_3(OH)_6(SO_4)_2$. Within it, extensive substitutions are possible (Hendricks, 1937); sodium and hydrogen most commonly substitute for potassium, and aluminum may substitute for the iron.

X-ray patterns of the jarosite in the Pierre Shale show c-axis measurements slightly smaller than those reported by Warshaw (1956) for jarosite, indicating that the jarosite in the Pierre contains some sodium or hydrogen substituting for potassium. Furthermore, several samples of Pierre having abundant jarosite contained only one-third to two-thirds of the potassium oxide needed to explain the sulfate reported in the chemical analysis as ideal jarosite. In a semiquantitative spectrographic analysis of a nearly pure jarosite separated from the Pierre Shale, 1 to 2 percent sodium oxide was reported; this is not enough sodium to make up for the deficiency in potassium in most jarosite-bearing samples. The fact that only samples containing jarosite have determinations for water-soluble sulfate in excess of 1 percent indicates that jarosite in the Pierre is slightly soluble in water. Yet, these same samples yield not enough water-soluble potassium and sodium to explain the water-soluble sulfate as a sodium jarosite. All the dissolved solutions, however, give a pH of 2 to 4, which is lower than any of the pH values determined for samples without jarosite. Apparently, appreciable numbers of hydrogen or hydronium (H_3O^+) as well as sodium ions substitute for potassium ions in jarosite in the Pierre Shale.

For chemical calculations of the Pierre Shale, jarosite is assumed to have the composition $(K_{1/2}Na_{1/6}H_{1/3})Fe_3(OH_6)(SO_4)_2$. Inaccuracies in this assumed composition may cause considerable error in the chemical calculations for a few samples, but inasmuch as most samples contain no jarosite, the assumption only rarely enters into the calculations.

ALUNITE [$KAl_3(OH_6)(SO_4)_2$]

Alunite, the aluminous analogue of jarosite, is found in a few samples of Pierre Shale. Its X-ray pattern closely matches that of a pure alunite. Where alunite is indicated by X-ray or other data, it is calculated as having the ideal chemical composition.

WATER-SOLUBLE SALTS

Amounts of water-soluble calcium, magnesium, sodium, potassium, sulfate, and iron were determined for 65 samples. The most abundant soluble ions commonly are sodium and sulfate. A good correlation between reported water-soluble calcium and the presence of gypsum reflections on X-ray traces indicates that water-soluble calcium comes from gypsum; it is so assigned in the calculations. If water-soluble sulfate, potassium, and sodium apparently come from jarosite, they are so assigned. Water-soluble salts in amounts over 0.5 percent that have no obvious mineral affinity are listed simply as water-soluble ions. In amounts below 0.5 percent, which are most common, the water-soluble components are disregarded. For most samples, errors caused by using such a procedure will be small.

CARBONATE MINERALS

Calcite ($CaCO_3$) and dolomite [$CaMg(CO_3)_2$] in samples of shale from the Pierre have compositions near those of the ideal end members. Unless a carbonate other than calcite is indicated by the X-ray data, all carbon dioxide reported in the chemical analysis is calculated as calcite. If both calcite and dolomite are indicated, carbon dioxide is calculated as calcite and dolomite in proportions indicated by the X-ray analysis.

All siderite and rhodochrosite in the Pierre, as well as calcite in nodules or concretions from the Pierre, are mixed carbonates having extensive substitutions of calcium, magnesium, ferrous, and manganese ions. Chemical analyses indicate that ratios of weight percents of CaO:MgO:FeO are generally about 35:2:3 for the mixed calcite and about 3:2:15 for siderite.

All fresh shale samples from the Pierre having manganese oxide values of over 0.1 percent contain appreciable carbon dioxide, and X-ray data usually indicate either siderite, calcite, or rhodochrosite. Therefore, although small amounts of manganese may occur in the clay mineral structures, amounts in excess of 0.1 percent probably occur as carbonate and they are so assigned. Rhodochrosite in the Pierre is of a highly mixed variety. Most of the rhodochrosite is composed of slightly more than half maganese carbonate; the remaining part is composed of calcium and iron carbonate in about equal amounts and magnesium carbonate in smaller amounts. In siderite, amounts of manganese oxide range from 0.5 percent to nearly 10 percent, and, in mixed calcite, amounts of manganese oxide are as high as 5 percent. Therefore, no common or general ratio for manganese oxide in these minerals can be given.

The procedure adopted for mixed carbonates in the chemical-mineralogical calculations for the Pierre Shale is to assign manganese oxide below 0.1 percent to the clay minerals, and to assign manganese oxide in excess of 0.1 percent to the carbonate mineral indicated to be present by X-ray data. The carbon dioxide not combined with manganese is combined with calcium, magnesium, and ferrous iron oxide in the ratios of 2:1:2 for rhodochrosite, 3:2:15 for siderite, and 35:2:3 for mixed calcite. Where necessary, these ratios are adjusted to accommodate the chemical analyses of the individual samples.

The aforesaid procedures for pure calcite and dolomite should cause little error in the chemical-mineralogical calculations. The procedures for the mixed carbonates can cause greater error. Fortunately, pure calcite and dolomite are the common carbonates in most shale samples from the Pierre; mixed carbonates are rare.

MINERALS CALCULATED PRIMARILY FROM X-RAY DATA

FELDSPAR

Assignment of chemical elements to feldspar is dependent on the X-ray data. Where the composition of plagioclase in the Pierre can be determined, it is commonly 20–40 percent anorthite. Therefore, if plagioclase is determined to be the dominant feldspar, the elements are assigned in ratios corresponding to a composition of 30 percent anorthite which is comprised of 61 weight-percent silica, 25 weight-percent alumina, 6 weight-percent calcium oxide, and 8 weight-percent sodium oxide. If potassium feldspar is dominant, the elements are assigned in the ratios of 65 percent silica, 18 percent alumina, and 17 percent potassium oxide, a composition corresponding to the ideal formula of $KAlSi_3O_8$. If the dominant type of feldspar is not determined, as commonly happens where only 1 to 2 percent feldspar is indicated, then half is assumed to be plagioclase and half is assumed to be potassium feldspar, and the elements are assigned in ratios of 63 percent silica, 22 percent alumina, 3 percent calcium oxide, 4 percent sodium oxide, and 8 percent potassium oxide.

Because most feldspar values are small, errors due to inappropriate assumptions for chemical composition will also be small.

CLINOPTILOLITE ($Na_4KAl_{5.5}Si_{30.5}O_{72} \cdot 19H_2O$)

The assumed formula for clinoptilolite is simplified from a formula—$(Mg_{.12}Ca_{.19}Na_{3.78}K_{1.08})_{5.18}Al_{5.49}Si_{30.5}O_{72} \cdot 19H_2O$—given by Mason and Sand (1960, p. 346). Inasmuch as this mineral is generally present only in small amounts in the Pierre Shale, slight deviations from the assumed composition will not seriously affect the chemical calculations.

QUARTZ

Quartz (SiO_2) is present in all samples of Pierre Shale. Amounts of silica assigned to quartz are determined from the X-ray data. Errors in the X-ray value for quartz can be of considerable importance because quartz is fairly abundant (15 to 20 percent of most samples), occurs in all shale samples, is a notably troublesome mineral in quantitative X-ray analysis, and because all the error is concentrated in one chemical constituent. Errors of even a few percent are significant.

CRISTOBALITE

Cristobalite of the disordered variety that occurs in the Pierre Shale probably contains small amounts of alkalies, alumina, and water (Franks and Swineford, 1959). Because the impurities probably compose only 1 to 2 percent of the cristobalite, they are disregarded in the chemical calculations. Of considerable significance, however, is the absolute accuracy of the X-ray-determined value for percentage of cristobalite. As for quartz, all the error is concentrated in one constituent—silica. Cristobalite, however, occurs only in a tenth of the chemically analyzed samples.

KAOLINITE

Kaolinite [$Al_4Si_4O_{10}(OH)_8$] contains about 40 weight-percent alumina, 46 percent silica, and 14 percent water. Because of its nearly invariable chemical composition and the small amounts in which it occurs, kaolinite probably causes very little error in the chemical calculations.

CHLORITE

Chlorite varies widely in chemical composition. The most common variation is in the amount of aluminum substitution and in the relative amounts of iron and magnesium.

Theoretically, alumina may compose from zero to eight ions per unit cell of trioctahedral chlorite. However, "chlorite" minerals such as antigorite and amesite having a minimum and maximum amount of aluminum substitution, respectively, have been shown to have a 7A c-axis spacing corresponding to the kaolinite structure, and, therefore, they are not true chlorites. The chlorite in the Pierre has the 14A c-axis spacing of a true chlorite, and therefore, has a quantity of aluminum between the theoretical maximum or minimum amount. Chlorite in the Pierre is assumed to have a median number of four aluminum ions per unit cell.

The relative intensities of the basal reflections indicate that chlorite in the Pierre is not a highly ferruginous variety (Brindley, 1951, p. 187). Yet, if no ferrous iron is assumed to substitute for magnesium, when mineralogical-chemical calculations are made, most samples containing more than average amounts of chlorite have deficiencies of magnesia and unusually large excesses of ferrous iron; the anomalies thus created disappear if ferrous iron oxide and magnesia are assumed to occur in equal weight percents. Inasmuch as ferrous iron oxide commonly amounts to only 1 to 2 percent in most analyses of Pierre Shale, this oxide is particularly sensitive to errors in assumed composition, even of minerals that, like chlorite, rarely exceed 5 percent of the sample.

The assumed composition of chlorite in the Pierre Shale is 29 percent silica, 17 percent alumina, 21 percent magnesia, 21 percent ferrous iron oxide, and 12 percent water; it corresponds approximately to a structural formula of $(Mg_5Fe_3Al_2)(Al_2Si_6)O_{20}(OH)_{16}$.

ILLITE

The composition of illite is of considerable importance in the chemical calculations, because it commonly composes 10 to 15 percent of the samples of Pierre Shale. The composition of illite is variable (Grim, 1953, p. 372). However, X-ray patterns and petrographic data show clearly that most illite in the Pierre is a dioctahedral aluminous muscovitelike variety; the number of possible variations in the chemical composition are therefore greatly reduced. The formula used for illite in the Pierre Shale—

$$K_{1.2}(Al_{3.0}Ti_{0.1}Fe^{+3}_{0.4}Fe^{+2}_{0.1}Mg_{0.4})_{4.0}(Al_{1.1}Si_{6.9})O_{20}(OH)_4\text{—}$$

is an average from the literature (Grim, 1953, p. 372, table D, Nos. 1, 2, 5, 6, 7; Whitehouse and McCarter, 1958, p. 86, e and f; Foster, 1954, p. 390) for illites apparently similar to that in the Pierre Shale; the composition also reflects the preponderance of magnesia and ferric iron over ferrous iron in most samples of Pierre Shale. The assumed chemical formula for illite corresponds to 7 weight-percent potassium oxide, 2 percent magnesia, 1 percent ferrous iron oxide, 4 percent ferric iron oxide, 1 percent titanium dioxide, 27 percent alumina, 53 percent silica, and 5 percent water.

MINERALS CALCULATED FROM CHEMICAL CONSTITUENTS NOT OTHERWISE ASSIGNED

Montmorillonite and mixed-layer illite-montmorillonite in the Pierre Shale can have variable chemical composition, particularly in the interlayer cations. Because these two clays are quantitatively the most important in Pierre Shale, even small errors in their assumed chemical compositions would cause significant errors in the chemical calculations. Furthermore, these two clays calculated from the X-ray analyses may actually represent a single entirely mixed-layered entity, the proportions of the different types of layers varying from one sample to the next. (See discussion on p. C9–C11.) Therefore, instead of using a fixed chemical formula for either mineral, all chemical elements not assigned to other minerals are assumed to occur in one of these two clay minerals. The chemical elements so assigned to montmorillonite and mixed-layer illite-montmorillonite are then calculated into a combined structural formula according to the method of Ross and Hendricks (1945). This method has been explained clearly by Kelley (1955) and is briefly illustrated under "Example of chemical-mineralogical calculations."

The calculated structural formulas for montmorillonite and mixed-layer illite-montmorillonite in the Pierre Shale are useful not only as a check on the overall accuracy of the X-ray data and the approximate validity of assumptions in the chemical calculations, but also as a basis for evaluating the variations in composition of these minerals through the Pierre Shale. The second use, of course, presupposes satisfactory results from the first.

EXAMPLE OF CHEMICAL-MINERALOGICAL CALCULATIONS

The chemical-mineralogical calculations used for the Pierre Shale are illustrated by the worksheet reproduced as plate 1. Data for sample 259543 were used for plate 1 and were used also for figure 3*B* and table 2. The worksheet includes space for tabulating chemical analysis, water soluble ions, pH, and X-ray quantitative data; chemical compositions assumed for minerals in the Pierre Shale are listed, and spaces are provided for assignment of chemical constituents to the different minerals. Not all the spaces are needed for recording data obtained from sample 259543, but all may be necessary for recording data from other samples of Pierre Shale. Most of the calculations are performed on the basis of weight percentages instead of the usual molar proportions because X-ray quantitative values used in parts of the calculations were made in terms of weight percents. The structural formula for montmorillonite and mixed-layer illite-montmorillonite is calculated using the last five columns and is entered in the skeletal formula at the top of the worksheet.

On plate 1, the numbers in parentheses represent the amount of each constituent remaining after calculation of each successive mineral; for example, in the third column, 1.43 percent ferrous iron oxide remains after 0.94 percent is assigned to pyrite. No apatite, barite, or water-soluble ions were calculated because amounts of phosphorous pentoxide, barium oxide, and determinations of water-soluble cations were all below the 0.5 percent limit previously mentioned. No jarosite, alunite, or dolomite were calculated, because these minerals were not detected in the X-ray analysis. Amounts of pyrite, gypsum, and calcite were calculated by multiplying the chemical determinations for sulfide sulfur, sulfur trioxide, and carbon dioxide, respectively, by the factors listed at the top of the columns for each of these minerals (for example, FeO in pyrite$=1.12\times0.84=0.94$ percent). For pyrite, the sum of the constituents do not equal the total amount of the mineral calculated, because the oxygen of the ferrous oxide does not occur in the pyrite. Amounts of oxides assigned to the feldspars, clinoptilolite, quartz, cristobalite, kaolinite, chlorite, and illite are the products of the X-ray modes for these minerals (listed in the row below the mineral names) and their assumed chemical compositions (listed at the top of each column). The amounts of the clay minerals are the products of the relative amounts of each clay and the total clay (for example, kaolinite$=0.04\times75=3$ percent).

Chemical constituents not assigned after calculation of illite are assumed to occur in the only two minerals in the Pierre Shale not yet calculated—montmorillonite and mixed-layer illite-montmorillonite. A combined structural formula for these two clay minerals is calculated in the columns to the right as follows:

1. Cation equivalents are calculated by dividing the weight percent of each oxide by the result of the molecular weight of the oxide divided by the cations per molecule (pl. 1, fifth column from the right).
2. Charge equivalents are the product of the cation equivalents multiplied by the valence of each cation. Charge equivalents are totaled at the bottom of the column. A total of 44 positive charges is needed to balance the 44 negative charges $[O^{-2}{}_{20}(OH^{-1}, F^{-1})_4]$ in each unit cell of montmorillonite or mixed-layer illite-montmorillonite. A factor (*f*) was derived by dividing 44 by the sum of the charge equivalents ($44/3.156=13.94$). (Note: If hydrogen ions are subsequently calculated in interlayer positions, the factor (*f*) must be adjusted to compensate for the charge on the H^{+1} ions; $f'=\dfrac{44-H^{+1}}{\text{sum of charge equivalents.}}$)
3. The number of each of the cations per unit cell is the product of the factor (*f*) and the cation equivalents.
4. Cations are assigned to the three different structural positions as indicated at the top of plate 1, with enough Al^{+3} ions substituting for Si^{+4} to fill all eight tetrahedral positions. Possible occurrence of aluminum, magnesium, or hydrogen in interlayer positions is discussed later.

DISCUSSION

The structural formula calculated in plate 1 is typical of the formulas calculated for montmorillonite and mixed-layer clay in the Pierre Shale. The formula is close to that expected for a dioctahedral, aluminous montmorillonitic clay. For all samples calculated, the most consistent discrepancy is that the determinations for total octahedral cations are commonly slightly below 4 per unit cell; in a very few samples silicon ions exceed the theoretical limit of eight per unit cell. Both discrepancies could result from assigning too much silica to the montmorillonitic clay. Significantly, the calculated total of octahedral cations for bentonites, which contain no quartz, generally is very close to 4. At least part of the deficiency of octahedral cations in montmorillonite and mixed-layer clay of the shale samples may result from assignment of insufficient SiO_2 to quartz, and a consequent excess of SiO_2 assigned to the clay. Possibly, the fine-grained quartz in the Pierre Shale is surrounded by poorly crystallized layers of silica. Gordon and Harris (1955) suggested that such silica coatings would cause X-ray modes for quartz that are about 12 percent too low. For the Pierre Shale, such an error would result in quartz determinations that generally are about 2 percent low (that is, a determination of 16 percent quartz would probably represent about 18 percent silica).

Several analyses for amorphous silica in samples of Pierre Shale were made using the method of Hashimoto and Jackson (1960). The first two samples in table 8 seemed to contain excess amorphous silica, because the calculated structural formula for their montmorillonite and mixed-layer illite-montmorillonite had more than 8 silica molecules per unit cell. The third sample in table 8 was analyzed to determine the approximate accuracy of the cristobalite determination. The last group of samples in table 8 includes two of shale and one of bentonite (259537). These three samples were assumed to be controls having little or no amorphous silica because they caused no difficulties in the chemical-mineralogical calculations.

The dissolved silica and alumina for the control samples may be in part due to solution of crystalline silicates; for sample 259569 the silica-alumina ratio is about that expected for the clays in the Pierre Shale. The important fact shown by the table is that, although a few percent amorphous silica may be undetected (as possibly in sample 259535), the chemical-mineralogical calculations are sufficiently precise to identify samples like 259561 and 259563 that apparently contain fairly large amounts of material amorphous to X-rays.

TABLE 8.—*Amorphous silica and alumina, in percent, in Pierre Shale*

[Analyses by E.C. Mallory using method of Hashimoto and Jackson (1960; sample boiled 2½ minutes in ½*N* NaOH, leachate analyzed by light transmission)]

Sample	Dissolved SiO_2	Dissolved Al_2O_3
Shale samples apparently containing amorphous SiO_2 assigned to clay minerals		
259561	17.40	0.68
259563	9.76	.61
Shale sample containing 35 percent cristobalite determined by X-ray		
259529	34.80	0.85
Control samples		
259535	4.48	0.39
259537	2.60	.39
259569	1.68	.58

The theoretical interlayer charge of an ideal mica is 2 per unit cell. The interlayer charge of montmorillonite and mixed-layer clays, like those in the Pierre Shale, theoretically should be from a third to about two-thirds or possibly three-fourths of the interlayer charge of mica. The total of the charge on the potassium, sodium, and calcium ions calculated to occur in interlayer positions of mixed-layer clay and montmorillonite from samples of Pierre Shale are plotted as dots and squares on figure 9. Most of the Pierre samples plot within the theoretically reasonable field that is represented by the shaded area on figure 9. Other samples plot outside the shaded area for several reasons. For example, the bentonite sample having a calculated total of 1.17 interlayer charges per unit cell contains several percent biotite for which no correction was made. The abnormally high calculated interlayer charge results from 0.35 potassium ion per unit cell, most of which actually occurs in biotite. Therefore, the shaded area is not extended to include this sample. Some of the other samples of shale that are plotted above the shaded area contain unusually small amounts of montmorillonite and mixed-layer clay; others plotted above the shaded area contain water-soluble cations or sulfate in unknown quantities. Calculated structural formulas for these samples therefore are less reliable than most, and they are not included in the shaded area on figure 9. If the shaded area had been extended to include them, its projected upper limit would exceed the maximum possible interlayer charge of 2 per unit cell.

A considerable group of samples also are plotted below the shaded area on figure 9. For example, three of the bentonite samples, which are composed almost entirely of montmorillonite and therefore afford very little room for errors in chemical constituents assigned to other minerals, have totals of interlayer charge from 0.17 to 0.42 per unit cell. Such totals are much below the reasonably expectable minimum. The low totals for interlayer charge plotted on figure 9 generally are related to two features: the occurrence of interlayer brucite- or gibbsite-like structures in the clay minerals and the pH of the sample slurry.

Brucite- or gibbsitelike layers in some of the clays represented on figure 9 are indicated in the X-ray traces by incomplete collapse of the first basal reflections after the samples are heated at 300°C for half an hour (fig. 10). Additional heating at 550°C for half an hour generally causes these interlayer structures to break down, and the clay layers collapse to a 10A spacing. Thus, the interlayer structures are not as stable as the brucite layer of chlorite which maintains a basal spacing near 14A after heating at 550°C for half an hour.

The method used to calculate structural formulas (pl. 1) assigns all magnesium and aluminum to octahedral or tetrahedral positions within the clay lattice. If some magnesium or aluminum actually occurs in interlayer positions, the usual procedure would produce an abnormally high total for cations in octahedral positions and also an abnormally low total for interlayer cations and the charge on those cations. These high and low totals occur for several of the Pierre samples. For example, the bentonite sample having only 0.33 positive interlayer charge per unit cell (fig. 9) has a calculated total of 4.31 octahedral cations as compared with an ideal number of 4.0 octahedral cations. Therefore, in the chemical-mineralogical calculations

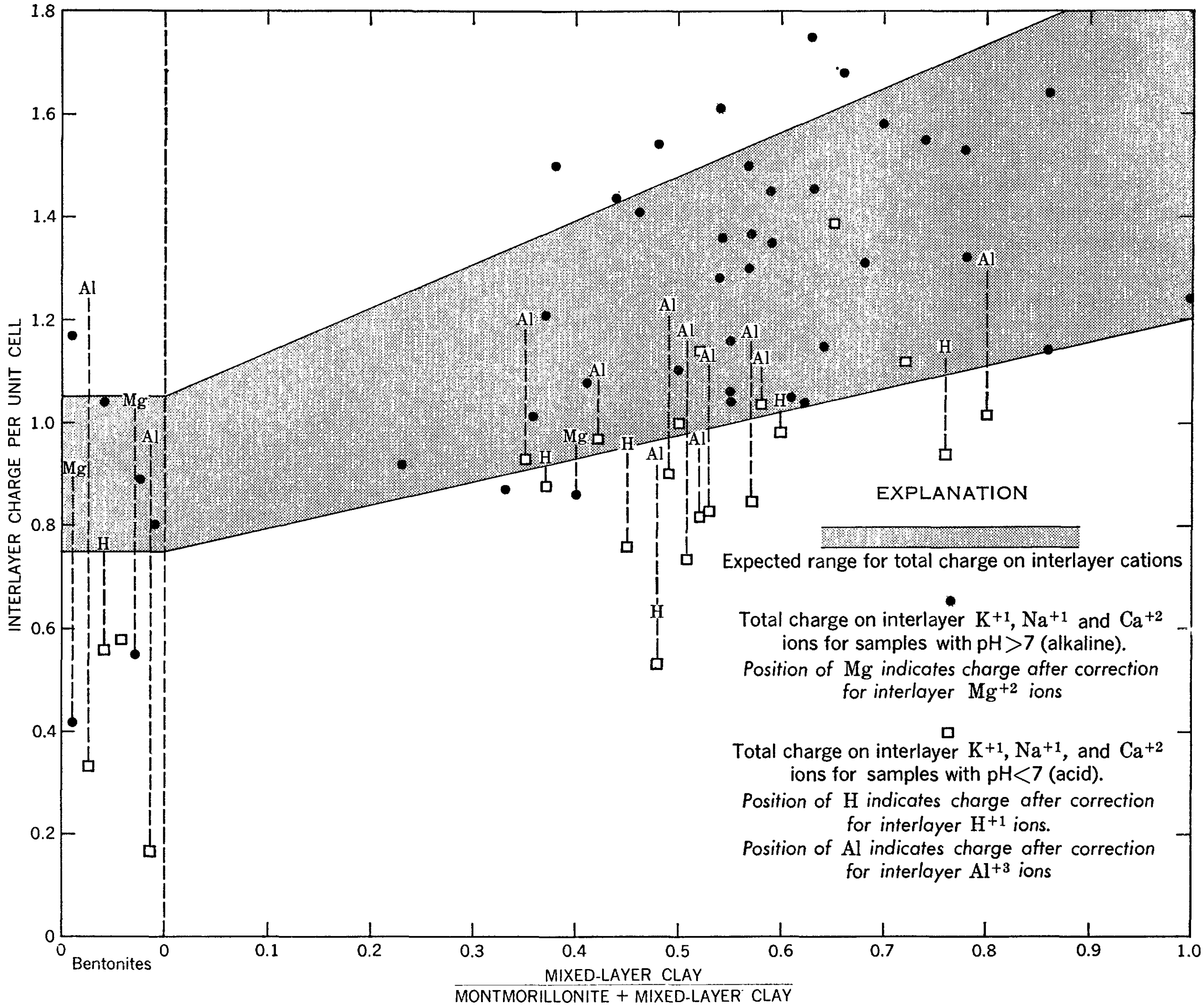

FIGURE 9.—Total charge on interlayer cations of montmorillonite and mixed-layer clay in the Pierre Shale.

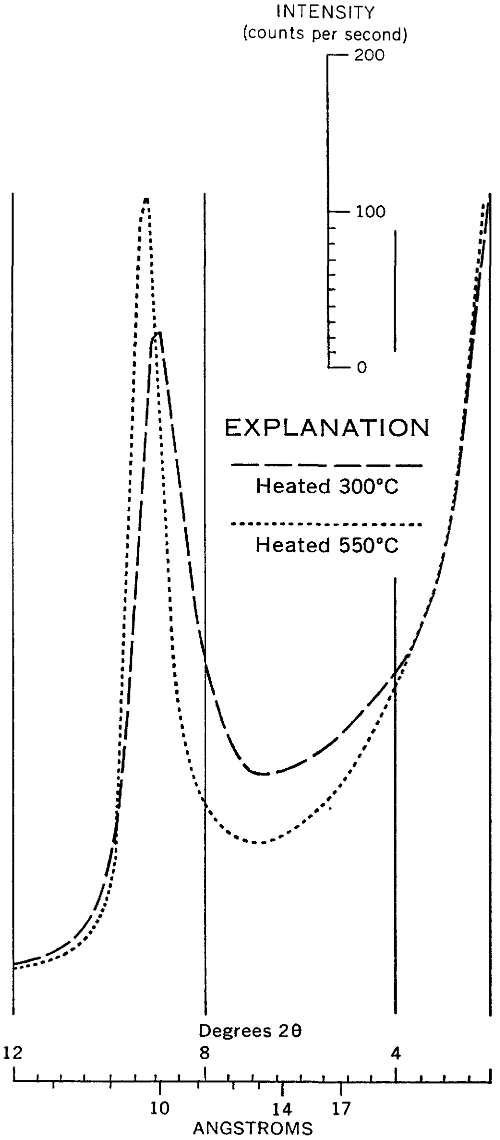

Figure 10.—Effect of brucite- or gibbsitelike interlayers on the X-ray diffractometer traces of montmorillonitic clay.

for the Pierre Shale, if a sample contains detectable brucite- or gibbsitelike interlayers, and if the calculated total of octahedral cations exceeds 4.0, enough magnesium or aluminum is transferred into interlayer positions to reduce the total of octahedral cations to 4.0.

Both interlayer hydrogen (or hydronium) and aluminum ions may occur in clays having a low pH; the hydrogen ions are the cause and the aluminum ions are the effect of the acid condition. However, only the aluminum will form gibbsitelike interlayer structures that prevent complete collapse to a basal spacing of about 10A after heating at 300°C for half an hour. Therefore, if X-ray data indicate an interlayer structure and if a low pH denotes that the clay is acid, then aluminum ions are transferred in the structural formula to interlayer positions. If the pH shows that the clay is alkaline, the interlayer structure is assumed to be brucitelike and magnesium is transferred to interlayer positions. Such transfers generally increased the total interlayer charge until they were within the expected range shown on figure 9. For one bentonite sample, the aluminum transfer caused the total interlayer charge to exceed the expected range, probably because the charges on some of the interlayer aluminum ions are balanced by interlayer OH^{-1} ions for which no attempt was made to compensate.

All but one of the samples that showed no evidence of brucitelike or gibbsitelike interlayers, but which were plotted below the shaded areas of figure 9, have low pH. These samples probably contained interlayer hydrogen (or H_3O^+) ions that were not included when the structural formula was calculated by the usual method. The amount of the interlayer hydrogen was determined by assuming sufficient interlayer hydrogen to increase the interlayer charge to the minimum expected total indicated by the shaded area on figure 9.

The aforesaid procedures for the calculation of interlayer magnesium, aluminum, and hydrogen ions will not produce corrections in every situation where small amounts of these ions actually occur in the exchange positions. Scant available data indicate that magnesium ions frequently compose about 10 percent of the total exchangeable cations. Because no magnesium generally is calculated in interlayer positions, exchangeable magnesium in small amounts is assigned to octahedral positions. However, in the one sample having calculated interlayer magnesium for which exchange data are available, magnesium ions composed 41 percent of the exchangeable cations. Thus, the adopted procedure generally will indicate the presence of interlayer magnesium, aluminum, and hydrogen ions where they compose a major proportion of the interlayer cations, and the resulting structural formulas will give a more accurate picture of the occurrence of elements in the minerals of the Pierre Shale.

The calculated structural formulas for montmorillonite and mixed-layer clay are by no means perfect. They contain a residuum of all errors made in the chemical analysis, the interpretation of the X-ray data, and the assignment of chemical elements to other minerals, as well as small errors in assignment of the remaining cations to the three structural positions of the montmorillonite and mixed-layer clay. Nevertheless, the formulas are still useful for comparison among samples handled by uniform methods, and they indicate the major features of distribution of elements in the clay lattices.

CONCLUSIONS

The accuracy and the reproducibility that can be expected for the quantitative determinations of mineral abundance derived from X-ray diffraction traces of samples of the Pierre Shale seem to be of the same order of magnitude. Most determinations, if greater than about 15 percent, are accurate within 10 percent of the stated value. However, unless precautions are taken, a few errors in determinations can be made that are considerably greater than the usual limits of error. Poor reproducibility of the feldspar determination in one sample illustrated the need for careful hand grinding and homogenization or repeated analyses of samples containing relatively coarse particles. Machine grinding produced uniformity, but also produced a considerable change in crystallinity and diffraction properties of some minerals. In making comparisons, consideration must be given to which minerals in which types of samples are likely to be most in error. Comparisons are best made on the basis of groups of samples rather than between individual samples. If determined values for amounts of minerals in groups of samples are consistently different, then differences smaller than 10 percent probably are significant.

Structural formulas calculated for the montmorillonite and mixed-layer clay also should be interpreted with caution, and due regard should be given to the many factors which enter into their calculation. They also are best compared as groups rather than as individual samples.

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