Spectrographic Analysis For Selected Minor Elements in Pierre Shale

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By PAUL R. BARNETT

ANALYTICAL METHODS IN GEOCHEMICAL
INVESTIGATIONS OF THE 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 spectro-graphic 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, v, which is computed by the formula:

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

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.
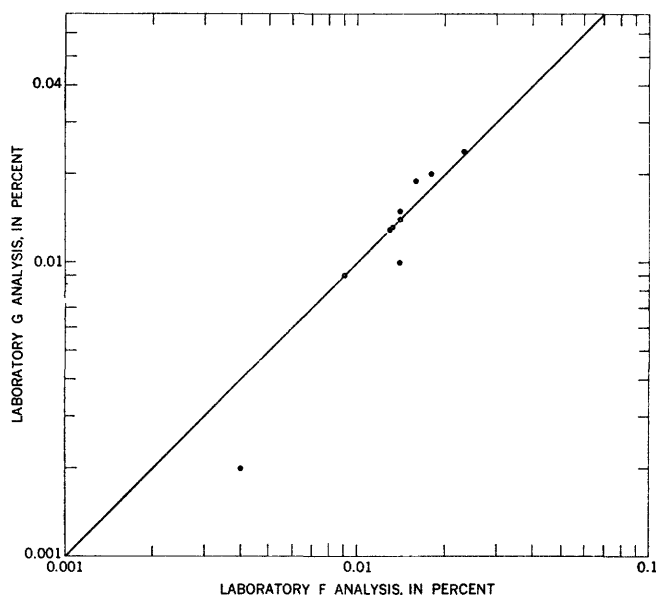

FIGURE 1.—Comparison of determinations of boron in 10 check samples by two spectrographic laboratories.

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

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.

Summary of precision of spectrographic determination of boron

	Number of comparisons	Range of concentration (percent)	Average concentration (percent)	Standard deviation	Coefficient of variatiou
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

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.
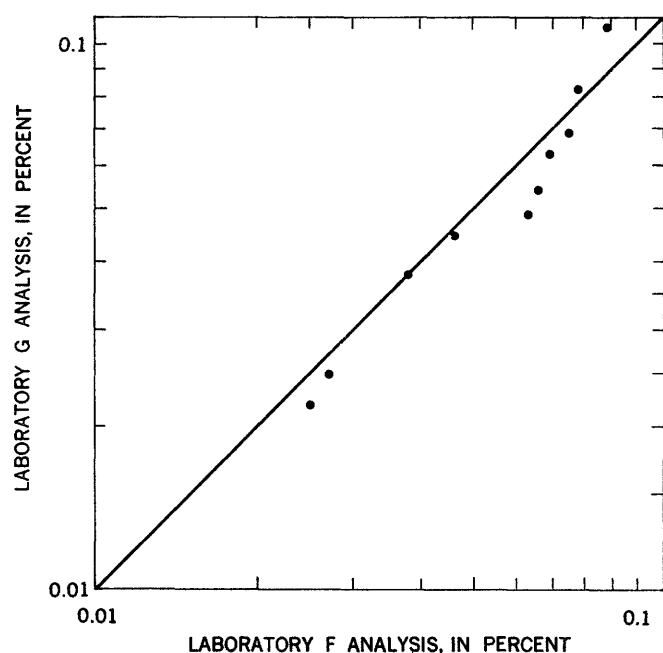

FIGURE 2.—Comparison of determinations of barium oxide (converted from barium) in 10 check samples by two spectographic laboratories.

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.
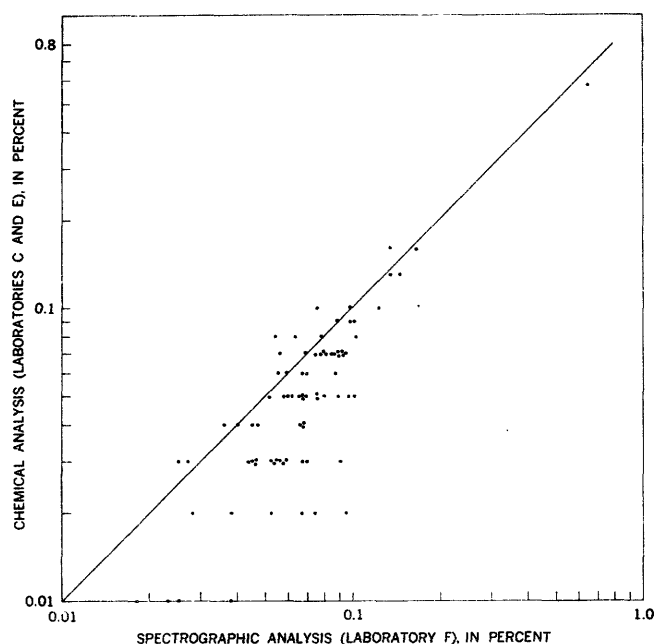

FIGURE 3.—Comparison of spectrographic with chemical determinations of barium in 80 samples.

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.
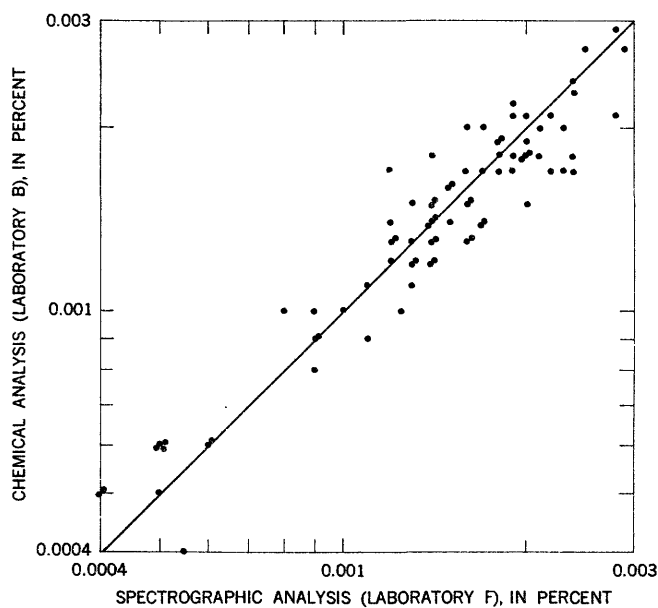

FIGURE 4.—Comparison of spectrographic with chemical determinations of cobalt in 80 samples.

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.
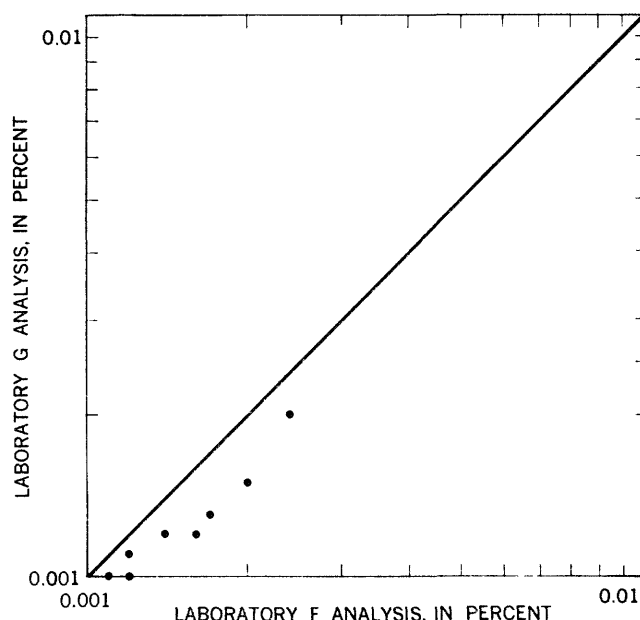

FIGURE 5.—Comparison of determinations of cobalt in 10 check samples by two spectrographic laboratories.

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

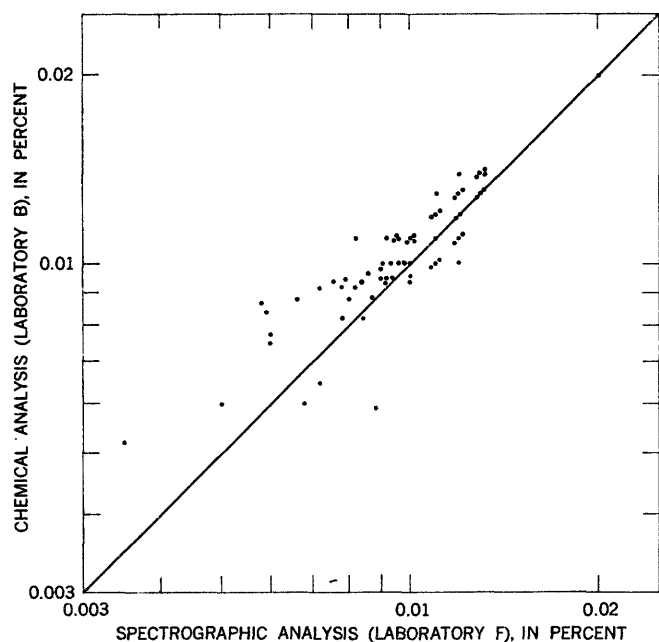| Number of comparisons	Range of concentration (percent)	Average concentration (percent)	Coefficient of variation
36	0.010 – 0.020	0.012	9.0
33	.001 – .010	.0073	12.1
5	.0004 – .001	.00076	45.9
74	.0004 – .020	.0096	10.3

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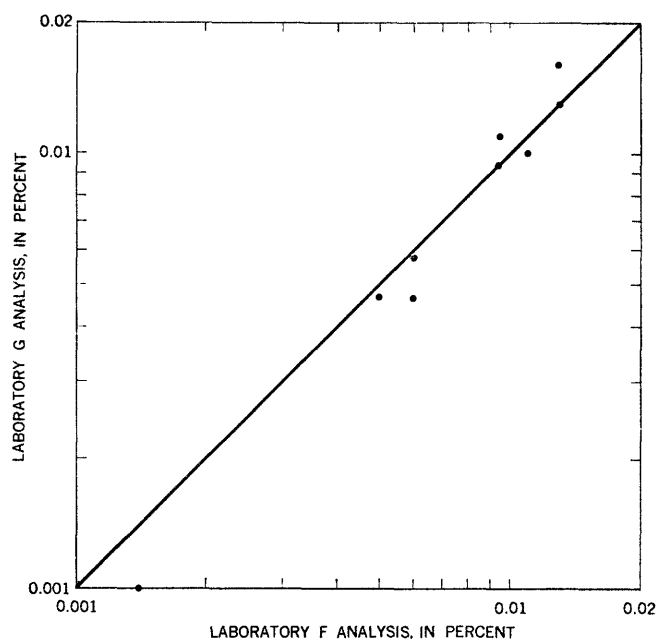

FIGURE 7.—Comparison of chromium determinations in 10 check samples by two spectrographic laboratories.

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.
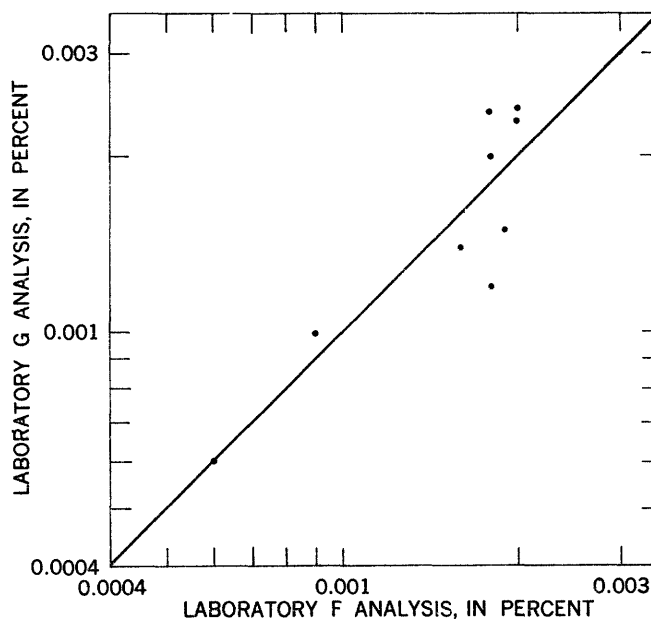

FIGURE 8.—Comparison of gallium determinations in 10 check samples by two spectrographic laboratories.

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.
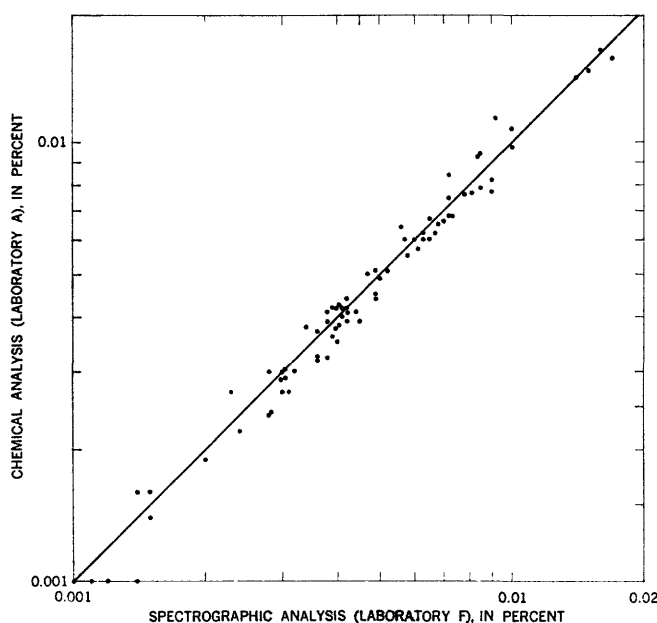

FIGURE 9.—Comparison of spectrographic and chemical determinations of nickel in 80 samples.

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
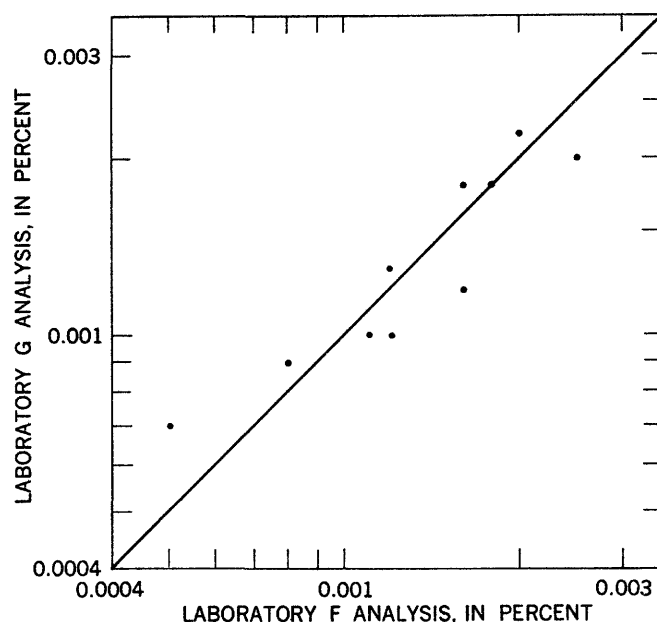

FIGURE 10.—Comparison of determinations of scandium in 10 check samples by two spectrographic laboratories.

paired values are graphed in figure 10. Scandium was not determined chemically.

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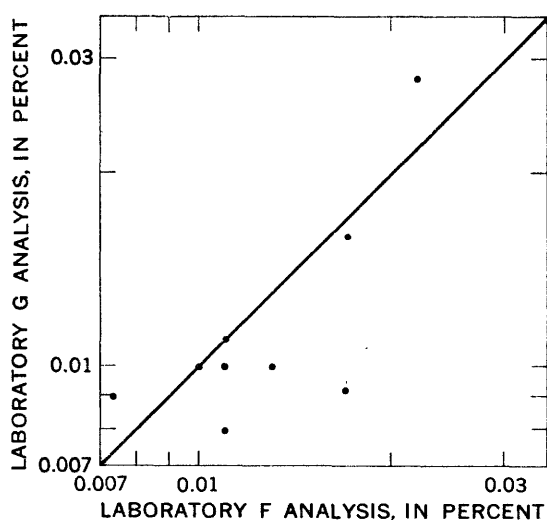
FIGURE 11.—Comparison of strontium determinations in 10 check samples by two spectrographic laboratories.

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.
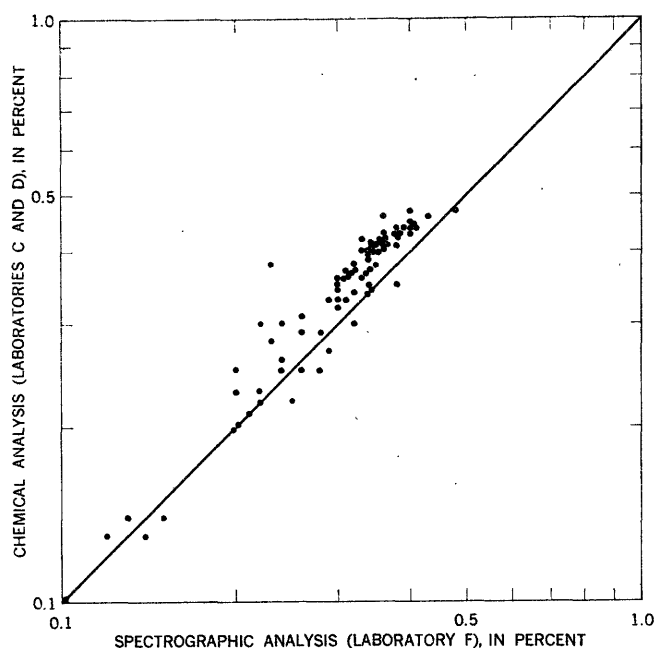

FIGURE 12.—Comparison of spectrographic and chemical (hydrogen peroxide) method of determination of titanium in 80 samples.
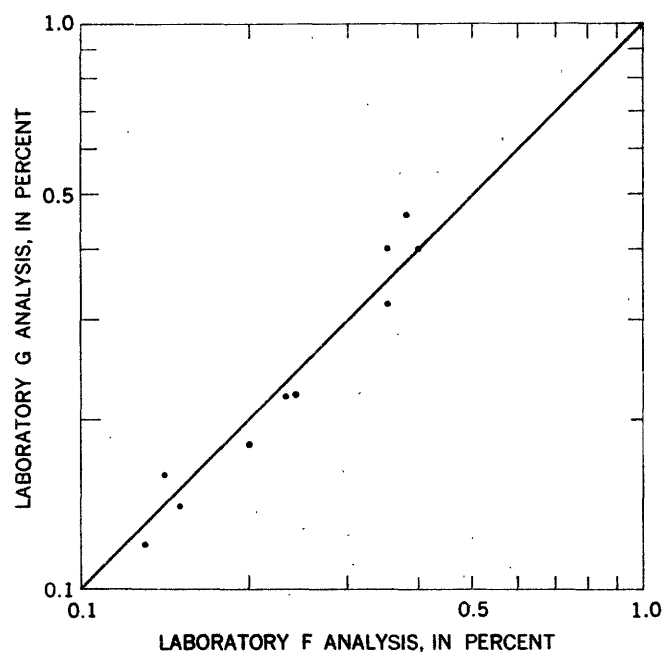

FIGURE 13.—Comparison of determinations of titanium in 10 check samples by two spectrographic laboratories.

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

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

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).

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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