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A Spectrochemical Method for the Semiquantitative Analysis of Rocks Minerals, and Ores

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GEOLOGICAL SURVEY BULLETIN 1084-I

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U.S. DEPARTMENT OF THE INTERIOR
March 3, 1849

A Spectrochemical Method for the Semiquantitative Analysis of Rocks Minerals, and Ores

By A. T. MYERS, R. G. HAVENS, *and* P. J. DUNTON

CONTRIBUTIONS TO GEOCHEMISTRY

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CONTENTS

ILLUSTRATIONS

TABLES

CONTRIBUTIONS TO GEOCHEMISTRY

A SPECTROCHEMICAL METHOD FOR THE SEMIQUANTITATIVE ANALYSIS OF ROCKS, MINERALS, AND ORES

By A. T. Myers, R. G. Havens, and P. J. Dunton

ABSTRACT

A visual comparison method for semiquantitative spectrochemical analysis of a powder by d-c arc technique is described. This method has been applied to a wide variety of geological materials, including rocks, minerals, and ores. As 68 elements are routinely looked for, the method has proven useful for the detection of elements not suspected of being present in the samples analyzed. The speed of the analysis and the method of reporting results to ⅓ of an order of magnitude have made this procedure of great value in reconnaissance studies. A total-energy technique is used. Large matrix effects are eliminated between samples and the standards used for comparison, by the addition of graphite to both samples and standards; silica is added to samples only if the samples are low in silica content. The plate-emulsion error is minimized by a light-intensity adjustment for each new batch of plates. The limits of detection and spectral lines used for analysis are shown for 68 elements. The elements are grouped so that only 20 sets of standards are required. Detailed examples for the preparation of the standards are given. A total of 682 comparisons are made between results by this semiquantitative spectrochemical method and by quantitative methods. This comparison shows that the semiquantitative spectrochemical results reported in intervals of ⅓ order of magnitude may be expected to include the quantitative value at least 60 percent of the time.

INTRODUCTION

Many semiquantitative methods of spectrochemical analyses have been described, but only a selected few publications are reviewed for the present discussion.

Waring and Annell (1953) described a semiquantitative method for the determination of 68 elements in minerals, rocks, and ores. Solutions of known concentration were prepared for use as standards. Results were reported to whole orders of magnitudes, that is, 0.0001–0.001, 0.001–0.01, 0.01–0.1, 0.1–1.0, 1.0–10., and 10+. Hodge and Baer (1956) described a rapid matching technique for the determination of 40 elements ranging in concentration from 0.0001 to 30 percent. They used a transparent intensity scale mounted on the screen of a projection comparator. A table of intensities measured by this scale was prepared for the 40 elements. Results were reported to ½ of an order of magnitude, that is, 0.0001, 0.0003, 0.001, 0.003 . . . to 30 percent. Fry and others (1956) have reviewed and classified semiquantitative methods. One of the classifications, "Compare unknown spectra with spectra of synthetic samples," would most nearly describe our method. In our procedure, however, graphite and silica are added to the sample to minimize matrix effects. Buffered external standards are used. A comparator is used for making visual comparison of the unknown line intensity with the standard line intensity.

Since 1950 this semiquantitative method has been used to analyze many thousands of geologic samples for the Division of Raw Materials, U.S. Atomic Energy Commission. It has been applied to uranium-bearing mineralized metamorphic rocks, igneous rocks, igneous minerals, low-grade thorium ores, and soils from above copper mineral deposits. Barnett (1961) has applied this same procedure to National Bureau of Standards standard samples of limestone, iron ore, two phosphate rocks, fluorspar, glass, different glass sands, dolomite, two clays, feldspar, silica brick, various refractory materials, and burned magnesite.

In this procedure, the sample is ground to −100 mesh. A 10-mg sample is weighed, mixed with 20 mg of graphite and packed into a shallow crater electrode. It is burned to completion in a d-c arc and the resulting spectra are compared with reference spectra. Snythetic powders serve as standards for the reference spectra within the general concentration range of 1 ppm to 1.0 percent.

The technique was designed for speed of analysis and is generally accompanied by loss in accuracy as compared with quantitative methods. The loss of accuracy however need not be proportionate to the gain in speed.

ACKNOWLEDGMENT

The authors wish to thank Nancy Conklin and Paul Barnett for many analyses made during the course of this study. The encouragement and advice given by Leonard B. Riley are greatly appreciated. This work was done as part of a program undertaken by the Geological Survey on behalf of the Division of Raw Materials, Atomic Energy Commission.

APPARATUS AND OPERATING CONDITIONS

Spectrograph: A Wadsworth mounted grating spectrograph, equipped with a grating of 15,000 lines per inch and having reciprocal linear dispersion of 5.24 A per mm in the first order.

Electrodes: Lower electrode, ¼-inch diameter with thin wall cavity. United Carbon Products type, preformed electrode No. 3170. Upper electrode, ¼-inch diameter hemispherically tipped, made from graphite rods obtained from National Carbon Company.

Sample and standards: 10 mg of sample or standard mixed with 20 mg of graphite powder. Samples and standards are weighed and arced under identical conditions.

Analytical gap: 5 to 6 mm maintained throughout excitation period. Excitation source: Direct-current arc operated at 12–13 amperes and 300 volts.

Length of exposure: Samples and standards arced to completion for 120 seconds.

Emulsion: Eastman Kodak type III–O X thin plates, developed at 20°C in D–19 for 3½ minutes with continuous agitation. Eastman Kodak type I–N X thin plates developed at 20°C in D–19 for 3 minutes with continuous agitation (alkali determination).

Wavelength region: 2250–4750 A, first order, use III–O plates; 6050–8550 A, first order, use I–N plates.

Densitometer: Direct reading projection comparator microphotometer, split viewing screen with a 20× magnification.

Emulsion calibration: Based on selected iron lines whose relative intensities have been determined. The iron spectra are obtained with a quartz feldspar mixture containing 1 percent Fe_2O_3.

Light intensity: Controlled by neutral filters.

Optics: Arc image focused on the collimator, using a mask to select the central 2-3 mm portion of the arc. A cylindrical quartz lens is used in front of the slit.

PREPARATION OF STANDARDS

The materials used in preparing the powders for the standards are shown in table 9. The details for preparing a few example standards are also given at the end of this report. The method of standard preparation is an outgrowth from methods used by Fleischer and others (1952), as described in the quantitative work done on bauxites from Arkansas. All the matrix materials were tested spectrographically before use, and any that lacked the required purity were discarded. The quartz used was relatively clear crystal quartz from Arkansas. The alumina was a high-purity grade made by Linde Air Products Company. The sodium carbonate, cobalt and iron oxides were of the highest purity supplied by Johnson, Matthey, & Co., Ltd. of London. The feldspars used were chosen on the basis of their low trace-element content. Some of these feldspars were collected with the help of Mortimer H. Staatz and John W. Adams of the Geological Survey. The feldspar (low in lead content) used in the lead standard was supplied by K. J. Murata. Brazilian kyanite was used as a substitute for feldspar in standard 4 M because of its lower trace element content.[1] The elements to be determined were generally added to the standards as the oxides, obtained from Johnson, Matthey, & Co., Ltd.

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[1] It was possible to lower the trace element content of the kyanite as received from Wards, by crushing and extracting with strong acid (HCl or HNO_3) solution. After repeated washing with distilled water, the product was dried at 110° C and analyzed spectrographically for trace elements Two large batches (300–400 g) have been successfully processed.

The dilution-grinding technique used for preparing these standards is critical. The standard mixtures are ground to an impalpable powder. It is most important that the matrix powder used for dilution should always be prepared as a coarse 10–20 mesh powder to act as a grinding-homogenizing agent when ground with the standard mixture.

As shown in table 9, the 68 elements are so grouped that only 20 sets of standards are required. In each set, the compounds in powdered form containing the elements are diluted with matrix material so that the percentage of each element decreases geometrically by a factor with the value of the reciprocal of the cube root of 10 ($10^{-\frac{1}{3}}$) from 1.0 percent to 0.0001 percent or lower. (See table 3 for values of standards in percentage to 2 significant figures.)

These standards have been cross checked for many elements by quantitative comparisons with other independently prepared standards.

PREPARATION OF PLATES OF STANDARDS

The standard powders are weighed on a small torsion balance in 10-mg amounts, then each 10-mg portion in turn is mixed in a weighing pan with 20 mg of pure graphite by means of a disposable toothpick, and transferred into the electrode cavity. The weighing pan is made from light-weight aluminum sheet and is designed for convenient mixing of powders as well as for delivering the mixture into the electrode cavity without spilling. The standard and graphite mixture is packed into the electrode with an aluminum or graphite tamping rod, sufficient pressure being exerted to pack the charge tightly into the cavity.

It is important that the technique throughout the procedure be the same for the standard powder as for the unknown. Before arcing the standard with the direct-current arc, the electrodes containing the standard are exposed about 15 minutes under an infrared lamp to remove moisture that might prevent complete burning in the arc.

For each set of standards, a photographic record is made of the 20 inches of spectra between 2250 and 4750 A. One long photographic plate would suffice for the purpose, but the problems of obtaining and handling such a plate made preferable the use of two plates, each 10 inches long. Plates 2 inches in width were used in this work because of the comparator available. An example pair of 2- by 10-inch reference plates, designated as *A* and *B*, has the following spectra: iron arc; matrix blank containing 1.0 percent Fe_2O_3; a mixture of 35 elements, called the *X* mixture for aid in finding the sensitive lines of these 35 elements (an R.U. powder commercially available could be used); and dilution series (table 10) of one of the standards. For example, reference plate No. 1 has 13 spectra of the standard dilution series 1 M in addition to spectra for *X*-mix, matrix blank, and iron.

This example includes copper, nickel, cobalt, zirconium, titanium, and manganese in concentrations from 0.0001 (1 ppm) to 1.0 percent. Although this standard is made to cover the range from 0.0001 to 1.0 percent, the limits of detection of these elements vary as follows: Cu, 0.0001; Ni, 0.0003; Co, 0.0005; Zr, 0.001; Ti, 0.0002; and Mn, 0.0002 percent. Depending on the limits of detection of the specific elements, other standard sets may cover such ranges as 0.001 to 1.0 or 0.01 to 10.0 percent, whichever proves most useful for routine analysis. Additional standard plates are made for concentrations above 1 percent.

A large batch of Eastman III–O plates, both 2 by 10 inches and 4 by 10 inches, *X*-thin should be ordered at one time, all of the same emulsion number. The plates of the type used have been found sufficiently uniform throughout any given batch of the same emulsion number. When plates are ordered in large numbers (as a batch of 20 dozen 4 by 10 inches and 10 dozen 2 by 10 inches), the added precaution of storing unused plates at low temperature (−17.8° C or 0° F) is shown by Feldman and Ellenburg (1956) to prevent emulsion fogging with time. When changing from one emulsion number (batch) to a new one, the iron lines of Crosswhite (1950) are used as a control for plate emulsion light response. Several plates from each batch are checked for radiation response by arcing a given weight of Fe_2O_3 (1.0 percent) incorporated in a quartz-feldspar matrix. Plate response is determined by densitometer reading of about 13 selected iron lines. A new batch of plates might require a change in the intensity control filter, that is, from 50 to 64 percent transmission, without re-exposing the complete set of standard plates. By this means a more constant emulsion response may be maintained to element radiation, which in turn results in greater precision. It is usually not necessary to remake plates of standards more than once a year.

SPECTRAL LINES USED AND VISUAL LIMITS OF DETECTION

Table 1 shows the spectral lines useful for this work. The actual line used in any one determination is dependent upon the concentration range, interfering elements, and major elements present. The limits of detection for the elements are shown in table 2. Some combinations of elements affect the detectabilities. Approximate values are given. In unusually favorable materials, concentrations somewhat lower than the values given may be detected. In unfavorable materials the given detectabilities may not be attained for some of the elements.

TABLE 1.—*Spectral lines used in the semiquantitative method*

[Asterisk indicates second exposure is required]

Element	Wavelength (A)	Element	Wavelength (A)
Silver	Ag 3382. 9	Cesium	Cs 8521. 1*
	Ag 3280. 7	Copper	Cu 3274. 0
Aluminum	Al 3092. 7		Cu 3247. 5
	Al 3082. 2		Cu 2824. 4
	Al 2660. 4		Cu 2293. 8
	Al 2652. 49	Dysprosium	Dy 3454. 3
Arsenic	As 2898. 7		Dy 3407. 8
	As 2860. 4		Dy 3393. 6
	As 2780. 2		Dy 3319. 8
	As 2492. 9	Erbium	Er 3385. 1
	As 2349. 8		Er 3372. 8
	As 2288. 1		Er 3220. 7
Gold	Au 3122. 8		Er 3230. 6
	Au 2676. 0	Europium	Eu 4627. 1
	Au 2428. 0		Eu 2906. 7
Boron	B 2497. 7		Eu 2813. 9
	B 2496. 8		Eu 2727. 8
Barium	Ba 4554. 0	Iron	Fe 3441. 0
	Ba 3071. 6		Fe 3440. 6
Beryllium	Be 3321. 3		Fe 3225. 8
	Be 3131. 1		Fe 3222. 1
	Be 3130. 4		Fe 3100. 6
	Be 2348. 6		Fe 3100. 3
Bismuth	Bi 3067. 7		Fe 3099. 97
	Bi 2897. 9		Fe 3099. 9
Calcium	Ca 4226. 7		Fe 3020. 6
	Ca 3179. 3		Fe 3020. 5
	Ca 3158. 9	Gallium	Ga 2943. 6
	Ca 2398. 6		Ga 2874. 2
Cadmium	Cd 3466. 2	Gadolinium	Gd 4262. 1
	Cd 3261. 1		Gd 3423. 9
	Cd 2763. 9		Gd 3422. 5
	Cd 2288. 0		Gd 3362. 2
Cerium	Ce 4296. 7	Germanium	Ge 3039. 1
	Ce 4248. 7		Ge 2691. 3
	Ce 4222. 6		Ge 2651. 6
	Ce 3243. 4		Ge 2651. 2
	Ce 3201. 7	Hafnium	Hf 3134. 7
Cobalt	Co 3462. 8		Hf 3109. 1
	Co 3453. 5		Hf 2904. 7
	Co 3449. 2		Hf 2904. 4
	Co 3412. 6		Hf 2861. 7
	Co 3412. 3	Mercury	Hg 4358. 4
	Co 3405. 1		Hg 3125. 7
Chromium	Cr 4289. 7		Hg 2536. 5
	Cr 4274. 8	Holmium	Ho 3398. 98
	Cr 4254. 4		Ho 3456. 0
	Cr 3021. 6	Indium	In 4511. 3
	Cr 2769. 9		In 3256. 1

TABLE 1.—*Spectral lines used in the semiquantitative method*—Continued

[Asterisk indicates second exposure is required]

Element	Wavelength (A)	Element	Wavelength (A)
Indium	In 3039. 4	Nickel	Ni 3493. 0
Iridium	Ir 3220. 8		Ni 3433. 6
	Ir 3133. 3		Ni 3414. 8
	Ir 2849. 7		Ni 3101. 9
	Ir 2543. 9		Ni 3101. 6
Potassium	K 7699. 0*		Ni 3050. 8
	K 7664. 9*		Ni 2943. 9
	K 4047. 2	Osmium	Os 3301. 6
	K 4044. 1		Os 3058. 7
	K 3446. 7	Phosphorus	P 2554. 9
Lanthanum	La 4429. 9		P 2553. 3
	La 4333. 7		P 2535. 7
	La 3337. 5		P 2534. 0
	La 3245. 1	Lead	Pb 2873. 3
Lithium	Li 8126. 5*		Pb 2833. 1
	Li 6707. 8*		Pb 2802. 0
	Li 6103. 6*		Pb 2663. 2
	Li 4602. 9	Palladium	Pd 3421. 2
	Li 3232. 6		Pd 3404. 6
Lutetium	Lu 3376. 5		Pd 3242. 7
	Lu 3312. 1	Praseodymium	Pr 4223. 0
	Lu 3281. 7	Platinum	Pt 3064. 7
	Lu 3077. 6		Pt 3042. 6
	Lu 2615. 4		Pt 2659. 4
Magnesium	Mg 2852. 1	Rubidium	Rb 7947. 6*
	Mg 2795. 5		Rb 7800. 2*
	Mg 2779. 8	Rhenium	Re 3464. 7
	Mg 2776. 7		Re 3460. 5
Manganese	Mn 2949. 2		Re 3424. 6
	Mn 2939. 3		Re 3405. 9
	Mn 2801. 1	Rhodium	Rh 3434. 9
	Mn 2794. 8		Rh 3396. 8
Molybdenum	Mo 3194. 0	Ruthenium	Ru 3436. 7
	Mo 3170. 4		Ru 3428. 3
	Mo 2816. 2	Antimony	Sb 3267. 5
Sodium	Na 8183. 3*		Sb 2877. 9
	Na 8194. 8*		Sb 2598. 1
	Na 5895. 9*	Scandium	Sc 4246. 8
	Na 5890. 0*		Sc 3353. 7
	Na 3303. 0		Sc 3019. 4
	Na 3302. 3	Silicon	Si 2881. 6
Niobium	Nb 3195. 0		Si 2528. 5
	Nb 3191. 9		Si 2524. 1
	Nb 3163. 4		Si 2516. 1
	Nb 3130. 8		Si 2435. 2
	Nb 3094. 4	Samarium	Sm 4434. 3
Neodymium	Nd 4358. 2		Sm 4433. 9
	Nd 4303. 6		Sm 4424. 3
	Nd 3328. 3		Sm 4329. 0

TABLE 1.—*Spectral lines used in the semiquantitative method*—Continued

[Asterisk indicates second exposure is required]

Element	Wavelength (A)	Element	Wavelength (A)
Samarium	Sm 4244. 7		Tm 3391. 0
Tin	Sn 3262. 3		Tm 3131. 3
	Sn 3175. 0		Tm 3098. 6
	Sn 3034. 1		Tm 3015. 3
	Sn 2863. 3	Uranium	U 4244. 4
	Sn 2840. 0		U 4241. 7
Strontium	Sr 4607. 3		U 3270. 1
	Sr 3464. 6		U 2865. 7
	Sr 3351. 2	Vanadium	V 3185. 4
Tantalum	Ta 3311. 2		V 3184. 0
	Ta 2714. 8		V 3183. 4
	Ta 2653. 3		V 3122. 9
Terbium	Tb 4278. 5		V 3102. 3
	Tb 3324. 4		V 2714. 2
Tellurium	Te 4771. 6		V 2688. 7
	Te 2385. 8	Tungsten	W 4302. 1
	Te 2583. 2		W 4294. 6
Thorium	Th 4381. 9		W 4008. 8
	Th 4019. 1		W 2947. 0
	Th 2942. 9		W 2896. 4
	Th 2870. 4	Yttrium	Y 4374. 9
	Th 2837. 3		Y 3327. 9
Titanium	Ti 3372. 8		Y 3242. 3
	Ti 3248. 6	Ytterbium	Yb 3289. 4
	Ti 3242. 0		Yb 3107. 9
	Ti 3234. 5		Yb 2891. 4
	Ti 3224. 2	Zinc	Zn 3345. 6
	Ti 3168. 5		Zn 3345. 0
	Ti 3152. 3		Zn 3302. 9
	Ti 3088. 0		Zn 3302. 6
Thallium	Tl 3229. 8	Zirconium	Zr 3430. 5
	Tl 2767. 9		Zr 3392. 0
Thulium	Tm 4242. 2		Zr 3279. 3
	Tm 3462. 2		Zr 3273. 1

PREPARATION AND ANALYSIS OF UNKNOWNS

A 10 mg sample, ground to at least 100 mesh, is mixed thoroughly with 20 mg of pure graphite in the weighing pan (as described under Preparation of plates of standards) and transferred to the cavity of an electrode. The unknown samples are arced for 120 seconds, the time found which represents burning to completion for most samples. The same time was then chosen for arcing the standard powders, to provide similar exposures on a pair of 4- by 10-inch type III-0 spectroscopic plates. If the unknown varies widely in composition from the standards, in which silica predominates, a dilution is made by adding pure quartz plus 5 or 10 percent sodium carbonate. This is done to convert the unknown to a sample more closely approximating the synthetic standard matrix. In general, samples estimated or known to contain concentrations above about 2 percent of any of the refractory elements, titanium, zirconium, niobium, tantalum, uranium, thorium, and tungsten, are routinely diluted. The amount of dilution depends upon the analytical problem on hand. Examples of three dilutions frequently used are as follows:

1. One part of the sample is mixed with 1.15 parts of a mixture of 90 percent quartz and 10 percent sodium carbonate. Ten mg of this mixture is used in the spectrochemical procedure by mixing with 20 mg of pure graphite as before. The dilution factor, 1.15, is chosen such that a visual estimate of intensity is shifted by one bracket.
2. By dilution of 1 part of sample with 3.64 parts of 95 percent quartz and 5 percent sodium carbonate, the reading is then shifted by two brackets.

TABLE 2.—*Approximate visual detection limits for the elements determined by the semiquantitative spectrographic method*

[Asterisk indicates that a second exposure, using 20 mg of sample, is required for the detectabilities shown in parentheses]

Element	Percent	Element	Percent	Element	Percent
Si	0.002	Cu	.0001	Rb*	10
Al	.001	Dy	0.005		(0.006)
Fe	.0008	Er	.005	Re	.005
Mg	.0005	Eu	.05	Rh	.005
Ca	.005	Ga	.0002	Ru	.01
Na*	.05	Gd	.005	Sb	.01
	(.0005)	Ge	.001	Sc	.0005
K*	.7	Hf	.01	Sn	.001
	(.002)	Hg*	1	Sr	.0002
Ti	.0002		(0.002)	Sm	.01
P	.2	Ho	.01	Ta	.02
Mn	.0002	In	.001	Tb	.1
Ag	.0001	Ir	.01	Te*	.1
As*	.1	La	.002		(.01)
	(.01)	Li*	.02	Th	.02
Au	.002		(.00006)	Tl	.01
B	.002	Lu	.01	Tm	.01
Ba	.0002	Mo	.0005	U	.05
Be	.0001	Nb	.001	V	.001
Bi	.001	Nd	.01	W	.01
Cd	.005	Ni	.0003	Y	.001
Ce	.02	Os	.01	Yb	.0005
Co	.0005	Pb	.001	Zn	.02
Cr	.0001	Pd	.0003	Zr	.001
Cs*	2	Pr	.05		
	(.02)	Pt	.003		

3. By dilution of 1 part of sample with 9 parts of 95 percent quartz and 5 percent sodium carbonate, the reading is shifted by three brackets.

The method can be extended to the red region of the spectrum, 6050–8550 A, by making an extra exposure with a second prepared electrode on 1–N plates. This is necessary for the determination of lower concentrations of the alkalies, cesium, lithium, potassium, rubidium, and sodium, as shown in parentheses in table 2.

Spectra of (a) iron arc, (b) an *X*-mix (or R.U. powder), and (c) a feldspar matrix containing 1 percent ferric oxide are recorded on each plate for analytical work with the same technique as was used for the plates for standards. There is room enough for 35 to 38 exposures of unknown samples on each pair of 4- by 10-inch plates.

The processed plates to which unknown samples have been exposed are compared with the previously described plates for standards in an optical comparator which allows the analyst to bring images of spectra of unknowns adjacent to images of the standard spectra for direct comparison of line intensity. A comparator giving an image of 20× magnification on a screen is convenient for this work.

The actual operation of reading a plate consists of locating the position of the specific lines of an element (table 1) in the unknown's spectrum and noting whether the element is present. If present, the line intensities are visually compared with corresponding line intensities on the standard plates to find lines of next lower and next higher concentration. Spectra from *X*-mix samples included on both standard and sample plates are used for orientation. After an element's concentration is bracketed, it is reported following the scheme shown in table 3. The number thus reported represents a concentration lying between two concentrations taken from line intensities on the standard plate. If a line of the sample apparently matches a line of the standard, the arbitrary convention is followed of reporting the greater concentration bracket.

Interference with the analytical line used by nearby element lines is normally checked by reference to wavelength tables (Massachusetts Institute of Technology, 1939). While this interference is not very common for geologic materials, the possibility should always be checked. When analyzing for trace elements in minerals, especially of uranium or thorium minerals, precaution is required to avoid line interference.

METHOD OF REPORTING RESULTS

The numbers used for reporting semiquantitative results and the concentration ranges they represent are shown in table 3. The two significant figures in the second column refer to the concentration of the standard. They should not be confused with the precision of the method, which is more properly shown by the method of reporting results given in the first column.

An estimate of the concentration of an element is thus based on an estimate of a line intensity for the unknown as falling between the intensities of the same line in two adjacent reference spectra.

RESULTS AND DISCUSSION

Table 4 shows the analytical data for Ag, Co, Cu, Mn, Mo, Ni, Pb, U, V, and Zn in 30 samples of veins and mineralized metamorphic rocks and compares the semiquantitative ⅓ of an order results with quantitative chemical results. Data are given in table 5 on 8 samples of igneous minerals and 2 samples of igneous rocks in which quantitative spectrochemical results for Co, Cr, Mn, Ni, and Ti are compared with semiquantitative spectrochemical results obtained independently by four different analysts. More than 100 soil samples from the Malachite mine area, Jefferson County, Colo., were analyzed for copper by this semiquantitative method, and the results are compared with quantitative chemical results in table 6. In table 7 the semiquantitative results on low-grade thorium ores obtained by two analysts are compared with an average of results from three independent quantitative methods (radiochemical, X-ray fluorescence, and quantitative spectrochemical).

TABLE 3.—*Concentration ranges of reported semiquantitative spectrographic results based on one-third order of magnitude*

Number reported (percent)	Limits of concentration defined by standards (percent)
7	10 - 4.6
3	4.6 - 2.2
1.5	2.2 - 1.0
.7	1.0 - .46
.3	.46 - .22
.15	.22 - .10
.07	.10 - .046
.03	.046 - .022
.015	.022 - .010
.007	.010 - .0046
.003	.0046 - .0022
.0015	.0022 - .0010
.0007	.0010 - .00046
.0003	.00046 - .00022
.00015	.00022 - .00010

In addition to the above the following symbols are used in reporting results: M: major constituent greater than 10 percent. Tr: barely detected and concentration uncertain. O: looked for but not found (for limits of detection see table 2). —: not looked for. < with number: less than number shown; here standard detectabilities do not apply.

TABLE 4.—*Comparison of semiquantitative spectrochemical results with quantitative metamorphic rocks from*

(In

[O, looked for but not found; <, less than percentage shown,

Sample	Ag		Co		Cu		Mn		Mo	
	Fire assay [1]	Spectrochemical [2]	Wet chemical [2]	Spectrochemical [2]	Wet chemical [4]	Spectrochemical [2]	Wet chemical [1]	Spectrochemical [2]	Wet chemical [3]	Spectrochemical [2]
1	0.00014	0.00015	<0.005	0.003	0.03	0.03	0.15	0.15	0.04	0.07
2	.00054	.0015	<.005	.007	.15	.15	.20	.3	.22	.3
3	.00014	.0015	<.005	.003	.14	.15	.17	.3	.038	.03
4	---------	0	<.005	.003	.0095	.015	1.80	3.	.018	.015
5	.0046	.007	.018	.015	.15	.15	.63	.7	.60	.7
6	---------	.0003	<.005	.007	.02	.015	1.45	1.5	.060	.07
7	.0014	.0015	<.005	.007	.09	.07	.56	.7	.18	.15
8	.00068	.0015	<.005	.007	.08	.07	.50	.7	.072	.07
9	Tr.	Tr.	<.005	.003	.03	.03	4.12	3.	.062	.07
10	.00014	.0003	<.005	.003	.03	.03	.59	.7	.060	.07
11	.0062	.007	.017	.015	.87	1.5	.08	.15	.56	.7
12	.0042	.007	.008	.015	.14	.15	.10	.07	.43	.3
13	.00014	.0007	<.005	.003	.11	.15	.05	.07	.04	.03
14	.0015	.003	.012	.015	.19	.3	.08	.15	.14	.15
15	---------	Tr.	<.005	.003	.03	.03	.12	.15	.006	.007
16	.0062	.007	.021	.015	.23	.3	.09	.15	.31	.7
17	.0048	.007	.007	.015	.09	.15	.47	.7	.42	.7
18	Tr.	.0015	<.005	.003	.09	.07	1.8	3.	.058	.07
19	.0178	.015	.04	.03	1.07	1.5	.22	.15	.22	.3
20	Tr.	.0015	<.005	.007	.22	.3	.09	.15	.054	.15
21	.0056	.015	.018	.015	.95	1.5	.12	.15	.21	.3
22	.0095	.015	.016	.015	.62	.7	.05	.07	.15	.3
23	.0012	.003	.006	.007	.46	.7	.02	.03	.07	.15
24	.0120	.015	.016	.015	1.16	1.5	.04	.03	.22	.3
25	.0241	.015	.05	.03	.89	1.5	.21	.3	.84	.7
26	.0036	.007	.012	.015	.32	.3	.28	.3	.17	.15
27	.00068	.003	<.005	.007	.10	.15	.18	.15	.092	.15
28	.0031	.003	.013	.015	.16	.15	.58	.7	.14	.3
29	.0016	.003	<.005	.007	.43	.7	.41	.3	.17	.3
30	.0066	.007	.018	.015	.85	1.5	.06	.15	.95	.7

[1] Analyst, D. L. Skinner.
[2] Analyst, N. M. Conklin.
[3] Analysts, R. F. Dufour and Claude Huffman, Jr.
[4] Analyst, W. D. Goss.

results by other methods for 10 elements in 30 samples of vein material and mineralized the Front Range, Colorado

percent)

standard detectability does not apply; leaders, not looked for]

Ni		Pb		U		V		Zn	
Wet chemical[3]	Spectrochemical[2]	Wet chemical[5]	Spectrochemical[2]	Wet chemical[6]	Spectrochemical[2]	Wet chemical[5]	Spectrochemical[2]	Wet chemical[7]	Spectrochemical[2]
0.0065	0.007	0.10	0.07	0.63	0.7	0.02	0.015	0.013	<0.03
.010	.015	.46	.7	.58	.7	.03	.07	.014	<.03
.0075	.007	.06	.07	.26	.3	.03	.03	.012	<.03
.0065	.007	.009	.007	.017	<.07	.03	.01	.020	Tr.
.006	.03	.81	.3	5.57	7.	.03	.07	.086	.07
.002	.007	.21	.15	.33	.3	.04	.05	.027	<.03
.011	.007	.23	.3	.58	.3	.08	.03	.030	<.03
.0075	.007	.08	.07	.66	.7	.03	.03	.023	<.03
.0085	.003	.05	.015	.067	.07	.02	.015	.019	<.03
.008	.007	.07	.03	.084	.07	.04	.03	.022	<.03
.022	.03	1.05	1.5	.79	.7	.03	.03	.19	.07
.011	.015	.46	.7	1.95	1.5	.02	.03	.056	.03
.0065	.007	.11	.07	.033	.07	.01	.015	.062	.03
.016	.015	.63	.7	.72	.7	.02	.015	.16	.15
.009	.007	.03	.03	.009	<.07	.02	.015	.11	.07
.039	.03	.73	.7	1.59	1.5	.03	.03	.088	.07
.022	.03	.69	.3	4.59	7.	.05	.03	.020	<.03
.009	.007	.13	.07	.50	.3	.03	.03	.046	Tr.
.035	.03	.62	.7	3.61	3.	.05	.07	.11	.07
.0085	.015	.06	.07	.28	.3	.03	.03	.044	.03
.018	.015	.29	.3	.58	.7	.03	.03	.092	.07
.018	.03	.37	.7	1.15	1.5	.02	.03	.082	.07
.014	.015	.08	.15	.11	.15	.02	.03	.076	.07
.016	.015	.70	.7	2.79	3.	.03	.03	.089	.07
.053	.07	.60	.7	3.70	3.	.08	.07	.10	.03
.017	.015	.16	.3	1.11	.7	.04	.03	.045	Tr.
.009	.007	.10	.15	.29	.3	.03	.03	.041	.03
.016	.015	.28	.3	2.49	3.	.05	.03	.16	.07
.019	.03	.73	.7	1.37	1.5	.03	.03	.16	.15
.041	.07	1.45	1.5	6.36	7.	.06	.07	.084	.07

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[5] Analysts, H. M. Nakagawa and C. E. Thompson.
[6] Analysts, H. H. Lipp, J. P. Schuch, and J. S. Wahlberg.
[7] Analyst, J. S. Wahlberg.

TABLE 5.—*Comparison of semiquantitative spectrochemical results (in percent) igneous rocks*

[Leaders indicate element

Sample	Description	Mn					Ni				
		Quantitative average[1]	Semiquantitative[2]				Quantitative average[1]	Semiquantitative[2]			
			A	B	C	D		A	B	C	D
1	Olivine	0.12	0.15	0.15	0.15	0.15	0.25	0.7	0.3	0.3	.3
			.15	.15	.15	.15		.7	.3	.3	.3
2	Olivine	.13	.15	.15	.15	.15	.26	.7	.15	.3	.3
			.15	.15	.15	.15		.7	.15	.3	.3
3	Enstatite	.10	.15	.15	.15	.15	.08	.15	.15	.15	.15
			.15	.15	.15	.15		.15	.15	.15	.15
4	Enstatite	.14	.3	.15	.15	.15	.049	.07	.07	.07	.07
			.3	.15	.15	.15		.07	.07	.07	.07
5	Diopside	.08	.07	.07	.07	.15	.025	.07	.07	.07	.07
			.07	.07	.07	.15		.03	.015	.03	.03
6	Diopside	.09	.07	.07	.07	.15	.035	.07	.07	.07	.07
			.07	.07	.07	.15		.07	.07	.07	.07
7	Spinel	.17	.15	.15	.15	.3	.13	.15	.15	.15	.15
8	Spinel	.28	.15	.15	.15	.3	.056	.07	.07	.15	.07
9	Granite (G-1)	.025	.03	.015	.015	.015	--------	------	------	------	------
10	Diabase (W-1)	.13	.07	.15	.15	.15	.0073	.007	.015	.007	.007

[1] Average of quantitative spectrochemical and wet chemical results. Analysts, P. R. Barnett, A. A. Chodos, M. D. Foster, and A. T. Myers.

The results of the analyses of the 149 samples and the 682 comparisons are summarized in table 8. These comparisons show that 69.3 percent of the semiquantitative results included the quantitative results within the reported ⅓ order of magnitude. The percent missed by ⅓ of an order is 29.9 percent, while only 0.7 percent is missed by more than ⅓ of an order. These results are shown graphically in figure 1. A diagonal line is drawn through the squares in which the results of the two methods are in the same order of magnitude. There are 133 misses by ⅓ of an order above the corresponding quantitative result and 71 misses by ⅓ of an order below the quantitative value. This small positive bias has not been resolved.

The samples used for the data presented in this report have been selected to show the effects on accuracy and precision caused by various factors within the method. Several years of experience in applying this method to many routine determinations indicate that similar precision and accuracy are obtained for all the elements included in this procedure, that is, the assigned ⅓-order of magnitude includes the quantitative value at least 60 percent of the time.

with quantitative results by other methods for 5 elements in 8 igneous minerals and 2 (G–1 and W–1)

was not looked for].

Cr					Co					Ti				
Quantitative average ¹	Semiquantitative ²				Quantitative average ¹	Semiquantitative ²				Quantitative average ¹	Semiquantitative ²			
	A	B	C	D		A	B	C	D		A	B	C	D
0.014	0.015	0.015	0.015	0.015	0.015	0.03	0.015	0.015	0.03	0.003	0.0015	0.003	0.003	0.003
	.015	.015	.015	.015		.03	.015	.015	.03		.0015	.003	.003	.003
.016	.015	.015	.015	.015	.018	.03	.015	.015	.03	.0025	.0015	.003	.003	.003
	.015	.015	.015	.015		.03	.015	.015	.03		.0015	.0015	.0015	.003
.49	.7	.3	.7	.3	.0065	.007	.007	.003	.007	.08	.07	.07	.07	.15
	.7	.3	.7	.3		.007	.003	.003	.007		.07	.07	.07	.15
.34	.3	.3	.3	.3	.0085	.007	.007	.007	.007	.015	.015	.015	.015	.015
	.3	.3	.3	.3		.007	.007	.007	.007		.015	.015	.015	.015
.49	.7	.3	.7	.7	.0036	.003	.003	.003	.003	.014	.015	.03	.03	.03
	.3	.3	.3	.3		.003	.003	.003	.003		.015	.03	.03	.03
.64	.7	.7	.7	.7	.0042	.003	.003	.003	.003	.23	.15	.3	.3	.3
	.7	.7	.7	.7		.003	.003	.003	.003		.15	.3	.3	.3
---------	------	------	------	------	.021	.03	.03	.03	.03	.21	.15	.15	.15	.15
---------	------	------	------	------	.045	.07	.07	.07	.07	.08	.07	.07	.07	.07
.0024	.0015	.003	.003	.003	---------	------	------	------	------	.16	.15	.15	.15	.15
.013	.03	.015	.015	.015	.0047	.007	.007	.007	.007	.64	1.5	.7	1.5	1.5

[2] Analysts, P. R. Barnett, N. M. Conklin, P. J. Dunton, and R. G. Havens.

PREPARATION OF POWDER STANDARDS

A complete list of each of the standards used, showing the composition of the matrix and the concentration range, is given in table 9 Examples of preparation of 8 standards (1, 2, 4, 5, 10, 13, 17, and 18) are given in table 10. These standards have also been used for quantitative analysis. Data for preparing the dilutions of these standards are given in table 11.

TABLE 6.—*Comparison of semiquantitative spectrochemical results with wet chemical results (in percent) for copper in 104 soil samples from the Malachite mine area, Colorado*

Sample	Wet Chemical[1]	Semiquantitative Spectrochemical[2]	Sample	Wet Chemical[1]	Semiquantitative Spectrochemical[2]	Sample	Wet Chemical[1]	Semiquantitative Spectrochemical[2]
31	0.032	0.03	66	.052	.03	101	.005	.007
32	.032	.03	67	.030	.015	102	.11	.07
33	.043	.03	68	.020	.015	103	.079	.07
34	.040	.03	69	.015	.015	104	.058	.03
35	.024	.015	70	.020	.015	105	.042	.03
36	.032	.03	71	.018	.015	106	.024	.03
37	.076	.03	72	.030	.03	107	.016	.015
38	.032	.03	73	.038	.03	108	.017	.015
39	.008	.007	74	.026	.015	109	.0065	.007
40	.008	.007	75	.026	.015	110	.0040	.007
41	.007	.007	76	.027	.015	111	.0050	.007
42	.007	.007	77	.0065	.007	112	.0060	.007
43	.0065	.007	78	.007	.007	113	.0055	.007
44	.007	.007	79	.006	.007	114	.0050	.007
45	.0085	.007	80	.0055	.007	115	.009	.015
46	.007	.007	81	.0055	.007	116	.008	.007
47	.008	.007	82	.006	.007	117	.005	.007
48	.008	.007	83	.013	.015	118	.007	.007
49	.04	.03	84	.017	.015	119	.0055	.007
50	.064	.03	85	.025	.015	120	.0045	.007
51	.032	.03	86	.044	.03	121	.0050	.007
52	.026	.03	87	.052	.03	122	.0040	.007
53	.044	.03	88	.032	.03	123	.0045	.007
54	.044	.03	89	.13	.07	124	.0050	.007
55	.035	.03	90	.0055	.007	125	.0070	.007
56	.030	.03	91	.0065	.007	126	.0055	.007
57	.007	.007	92	.0065	.007	127	.0065	.007
58	.005	.007	93	.0045	.007	128	.0095	.015
59	.005	.007	94	.0040	.003	129	.0050	.007
60	.0065	.007	95	.0050	.007	130	.0040	.007
61	.007	.007	96	.0050	.007	131	.0055	.007
62	.007	.007	97	.0060	.007	132	.0045	.007
63	.019	.015	98	.0040	.007	133	.0040	.007
64	.024	.03	99	.007	.007	134	.0045	.007
65	.025	.015	100	.007	.007			

[1] Analyst, C. E. Thompson.
[2] Analyst, N. M. Conklin.

TABLE 7.—*Comparison of semiquantitative spectrochemical results (in percent) with quantitative results by other methods for thorium in five miscellaneous low-grade thorium type ores from Colorado and New Mexico*

Sample	Quantitative results[1]	Semiquantitative results[2]	
		A	B
1	0. 12	0. 15	0. 15
2	. 18	. 3	. 3
3	. 70	. 7	. 7
4	. 48	. 7	. 7
5	. 98	1. 5	1. 5

[1] Average of results by P. J. Dunton and A. King (X-ray fluorescence), by John Rosholt (radiochemical), and by P. J. Dunton (quantitative spectrochemical).

[2] N. M. Conklin and R. G. Havens participated in semiquantitative spectrochemical analysis.

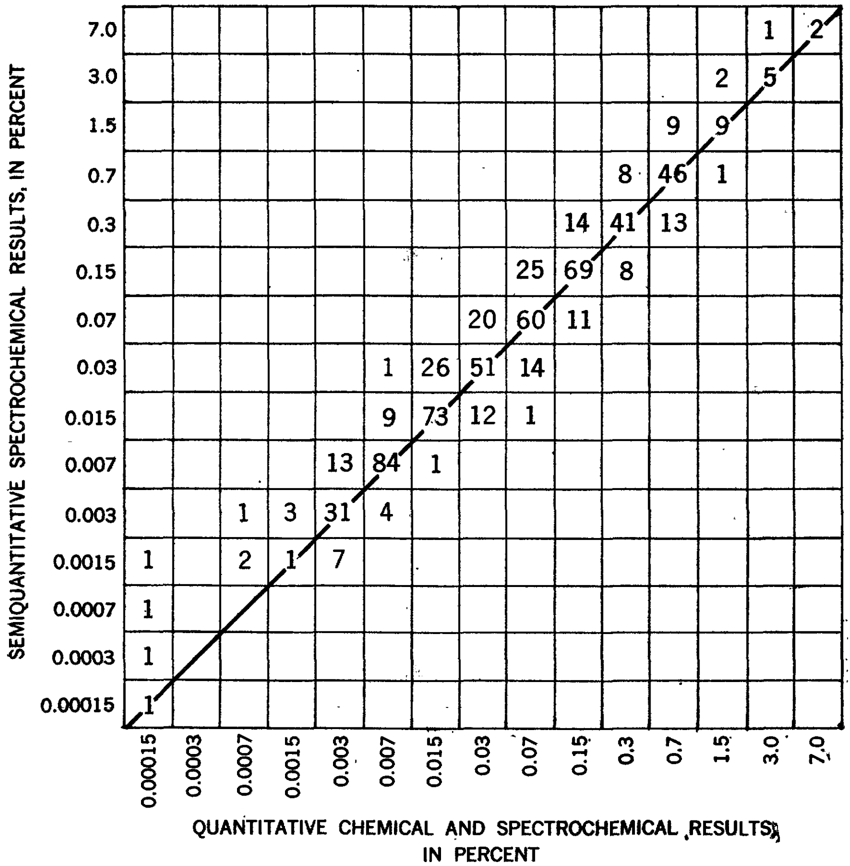

FIGURE 31.—Comparison of semiquantitative spectrochemical results with chemical and spectrochemical quantitative results. Elements determined: Ag, Co, Cr, Cu, Mn, Mo, Ni, Pb, Th, Ti, U, V, and Zn. Source of samples analyzed: veins, mineralized metamorphic rocks, igneous minerals, and soils. Total number of paired results, 682; in agreement, 473; missed by ⅓ order, 204; missed by more than ⅓ order, 5.

TABLE 8.—*Summary of results (in percent)*

Element	Agreement within ⅓-order	Miss by ⅓-order	Miss by ⅔-order	Miss by 1-order	Total number of comparison
30 samples of veins and mineralized metamorphic rocks [1]					
Ag	41. 7	45. 8	8. 3	4. 2	24
Co	80. 0	20. 0	0	0	15
Cu	73. 3	26. 7	0	0	30
Mn	56. 7	43. 3	0	0	30
Mo	66. 7	33. 3	0	0	30
Ni	73. 3	23. 3	3. 3	0	30
Pb	66. 7	30. 0	3. 3	0	30
U	85. 2	14. 8	0	0	27
V	66. 7	33. 3	0	0	30
Zn	61. 1	38. 9	0	0	18
Average	67. 1	30. 9			
Total					264
8 samples of igneous minerals and 2 samples of igneous rocks [2]					
Co	68. 3	31. 7	0	0	60
Cr	80. 4	19. 6	0	0	56
Mn	78. 1	21. 9	0	0	64
Ni	51. 7	48. 3	0	0	60
Ti	70. 3	29. 7	0	0	64
Average	69. 8	30. 2			
Total					304
104 samples of soils from the Malachite mine [3]					
Cu	75	25	0	0	104
5 samples of low-grade thorium type ores [4]					
Th	60	40	0	0	10

[1] See table 4.

[2] See table 5.

[3] See table 6.

[4] See table 7.

TABLE 9.—*List of ⅓ order standards and materials used for analysis of 68 elements*

Number	Elements	Composition of matrix [1]	Concentration range (percent)
1M	Cu, Ni, Co, Zr, Ti, and Mn.	Quartz;[2] Canadian microcline; Fe_2O_3.	0.0001– 1.00
2M	Na, K, and Li	Quartz; Al_2O_3; Fe_2O_3	.01 – 4.64
3M	P, Hg, Te, Tl, and As	Quartz;[2] Bigger pertbite; Fe_2O_3	.01 – 4.64
4M	Sr, Ba, Ca, La, and Ce.	Quartz; kyanite; K_2CO_3; Fe_2O_3	.0001– 1.0
5M	V, Cr, Re, Be, Mo, and Sn.	Quartz;[2] Canadian microcline; Fe_2O_3.	.0001– 1.0
6M	Cd, Bi, Sb, Zn, and In	Quartz;[2] Hugo perthite; Fe_2O_3	.0001– 1.0
7M	Fe	Quartz; Al_2O_3; Co_3O_4	.001 –10.00
8M	Mg	Quartz;[2] Hugo perthite; Fe_2O_3	.001 –10.00
9M	Ag, Au, Rh, Pd, and Pt.	Quartz;[2] Bigger perthite; Fe_2O_3	.0001– 1.0
10M	U	Quartz;[2] Bigger perthite; Fe_2O_3	.01 –10.00
11M	Pb, Sc, Ge, Ga, and B	Quartz;[2] Sandy Creek microcline; Fe_2O_3.	.0001– 1.0
12M	Th	Quartz;[2] Bigger perthite; Fe_2O_3	.01 –10.0
13M	K, Li, Cs, and Rb	Quartz; Al_2O_3; Na_2CO_3 (Na constant) Fe_2O_3.	.0001– 1.00
14M	Ta and Nb	Quartz;[2] Bigger perthite; Fe_2O_3	.001 – 4.64
15M	Y, Dy, Er, Yb, and Gd.	Quartz;[2] Bigger perthite; Fe_2O_3	.0001– 1.00
16M	Sm, Pr, Ce, La, and Nd.	Quartz;[2] Bigger perthite; Fe_2O_3	.001 – 1.00
17M	Al	Quartz;[2] Na_2CO_3; $CaCO_3$; FE_2O_3	.001 –10.00
18M	Si	Al_2O_3; Na_2CO_3; Fe_2O_3	.001 -10.00
19M	Ru, Ir, Os, Hf, and W	Quartz;[2] Bigger perthite; Fe_2O_3	.001 – 1.00
20M	Ho, Eu, Lu, Tm, and Tb.	Quartz;[2] Bigger perthite; Fe_2O_3	.0010– .215

[1] Sources of materials used in the matrix are as follows:

Quartz	Clear Arkansas quartz, Hot Springs, Ark.
Fe_2O_3	Johnson, Matthey, and Co., Ltd., London.
$CaCO_3$	Do
Co_3O_4	Do.
Na_2CO_3	Do.
Al_2O_3	Linde Air Products, New York City.
Bigger perthite	Bigger mine, Tinytown, Colo.
Hugo perthite	Hugo mine, near Keystone, S. Dak.
Canadian microcline	Parry Sound, Ontario, Canada (from Ward's Natural Science Establishment, Rochester, N.Y.).
Sandy Creek microcline	Sandy Creek, Bearpaw Mountains, Mont.
Kyanite	Brazil (from Ward's Natural Science Establishment, Rochester, N.Y.).

[2] These materials have been mixed in the following proportions throughout: 6 parts quartz, 4 parts feldspar, and 0.1 part Fe_2O_3.

TABLE 10.—*Examples of preparation of standards*

[Dilution follows details given in table 11]

Compound	Source	Gravimetric factor	Amount weighed		Composition of matrix (constituents and ratio)
			Compounds (grams)	Matrix (grams)	
Standard 1M: Copper nickel cobalt, zirconium, titanium, and manganese (8 g, 1.0 percent basis)					
CuO	(1)	1.2517	0.100		Quartz,[2] Canadian microcline,[3] Fe_2O_3.[1] 6:4:0.1
NiO	(1)	1.2726	.102		
Co_3O_4	(1)	1.3620	.109		
ZrO_2	(1)	1.3508	.108		
TiO_2	(1)	1.6681	.133		
Mn_3O_4	(1)	1.3884	.111		
Total			.663	7.337	
Standard 2M: Sodium, potassium, and lithium (8 g, 1.0 perecnt basis)					
Na_2CO_3	(1)	2.3051	0.184		Quartz,[2] Al_2O_3,[4] Fe_2O_3[1]. 9.12:0.884:0.1
K_2CO_3	(1)	1.7673	.141		
Li_2CO_3	(1)	5.3235	.426		
Total			.751	7.249	
Standard 4M: Barium, calcium, strontium, cerium, and lanthanum (8 g, 1.0 percent basis)					
$BaCO_3$	(1)	1.4369	0.115		Quartz,[2] kyanite,[5] K_2CO_3,[1]. Fe_2O_3[1]. 8.15:1.25:0.5:0.1
$CaCO_3$	(1)	2.4973	.200		
$SrCO_3$	(1)	1.6848	.135		
CeO	(1)	1.2284	.098		
La_2O_3	(1)	1.1728	.094		
Total			.642	7.358	

See footnotes at end of table.

TABLE 10.—*Examples of preparation of standards*—Continued

Compound	Source	Gravimetric factor	Amount weighed: Compounds (grams)	Amount weighed: Matrix (grams)	Composition of matrix (constituents and ratio)
Standard 5M: Vanadium, chromium, rhenium, beryllium, molybdenum, and tin (8 g, 1.0 percent basis)					
V_2O_5	(1)	1.7851	0.143	--------	Quartz,[2] Canadian microcline,[3] Fe_2O_3 [1]. 6:4:0.1
Cr_2O_3	(1)	1.4614	.117	--------	
NH_4ReO_4	(1)	1.5944	.128	--------	
BeO	(6)	2.7738	.222	--------	
MoO_3	(1)	1.5003	.120	--------	
SnO_2	(1)	1.2696	.102	--------	
Total			.832	7.168	
Standard 10M: Uranium (8 g, 1.0 percent basis)					
U_3O_8	(6)	1.1792	0.943	--------	Quartz,[2] Bigger perthite,[7] Fe_2O_3 [1]. 6:4:0.1
Total			.943	7.057	
Standard 13M: Lithium, potassium, rubidium and cesium (Na_2CO_3 in matrix—8 g 1.0 percent basis)					
Li_2CO_3	(1)	5.3235	0.426	--------	Quartz,[2] Al_2O_3,[4] Na_2CO_3,[1] Fe_2O_3 [1]. 8.12:0.884:1.0:0.1
KCl	(1)	1.9068	.152	--------	
RbCl	(1)	1.4148	.113	--------	
CsCl	(1)	1.2668	.101	--------	
Total			.792	7.208	
Standard 17M: Aluminum (8 g, 10 percent basis)					
Al_2SiO_5	(8)	3.061	2.449	--------	Quartz,[2] $CaCO_3$,[1] Na_2CO_3,[1] Fe_2O_3 [1]. 8.33:0.567:1.0:0.1
Total			2.449	5.551	

See footnotes at end of table.

TABLE 10.—*Examples of preparation of standards*—Continued

Compound	Source	Gravimetric factor	Amount weighed		Composition of matrix (constituents and ratio)
			Compounds (grams)	Matrix (grams)	
			Standard 18M: Silicon (8 g, 10 percent basis)		
SiO_2	(1)	2.1404	1.712		Al_2O_3,[4] Na_2CO_3,[1] Fe_2O_3 [1] 4.4:0.5:0.1
Total			1.712	6.288	

Sources of materials used in the standards are as follows:

[1] Johnson, Matthey, and Co. Ltd., London.

[2] Clear Arkansas quartz, Hot Springs, Ark.

[3] Parry Sound, Ontario, Canada (from Ward's Natural Science Establishment, Rochester, N.Y.).

[4] Linde Air Products, New York City.

[5] Brazil (from Ward's Natural Science Establishment, Rochester, N.Y.).

[6] U.S. National Bureau of Standards, Washington, D.C.

[7] Bigger mine, Tinytown, Colo.

[8] Clear kyanite, Brazil (from Ward's Natural Science Establishment, Rochester, N.Y.).

TABLE 11.—*Dilution data for standards* [1]

[Resulting standards have concentrations of each of the elements varying in a geometric series, the common factor of which is the $\sqrt[3]{10}$]

Dilution No.	Metal concentration in percent	
	Initial standard mixture diluted with matrix	Resulting standard mixture
1	(2)	1.000
2	1.000	.464
3	.464	.215
4	.215	.1000
5	.1000	.0464
6	.0464	.0215
7	.0215	.01000
8	.01000	.00464
9	.00464	.00215
10	.00215	.001000
11	.001000	.000464
12	.000464	.000215
13	.000215	.0001000
14	.0001000	.0000464
15		(3)

[1] For successive dilutions 3.712 g (8×0.464) the initial standard mixture is added to 4.288 g of matrix to produce 8 grams of the next lower standard mixture.

[2] X g of metal compounds plus Y g of matrix, the values of the two components depending on the standard mixture to be made, i.e., in this instance a 1.000 percent standard mixture resulted as shown above.

[3] Matrix used as blank for each standard.

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