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UNITED STATES GEOLOGICAL SURVEY
Trace elements investigations report

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

By
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This preliminary report is released without editorial and technical review for conformity with official standards and nomenclature, to make the information available to interested organizations and to stimulate the search for uranium deposits.

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ABSTRACT

The quantity and complex nature of material received for analysis in the spectrographic laboratories of the Geological Survey have emphasized the need for a spectrographic method to determine a maximum number of elements in a limited time with a reasonable degree of accuracy. The semiquantitative method described determines 55 elements in one arcing of a 10-mg sample, requires a minimum of sample handling thus reducing the changes of contamination, detects low concentrations of elements, and is rapid. The method has been used to complete 15,000-20,000 determinations during a nine-month period. Of these determinations 304 were checked chemically and indicated approximately 10 disagreements, in the magnitude of one 10-percent bracket.

INTRODUCTION

The spectrographic laboratories of the Geological Survey receive for analysis each year a very large number of samples of radioactive minerals, rocks and ores in connection with the investigation of radioactive raw materials, a program in which the Survey is engaged for the Atomic Energy Commission. It is desirable to know the trace-elements content of this material and for many purposes it is necessary to gain some knowledge of the amounts of major constituents present without going to the trouble of making chemical analyses.

The quantity and complex nature of the samples received have emphasized the need for a spectrographic method to determine a maximum number of elements in a limited time with a reasonable degree of accuracy. In spectrographic parlance such a method is termed "semiquantitative" and the results are usually reported in orders of magnitude of weight percentages of the elements (not the oxides).

A survey of the literature 1/ reveals that several slightly similar methods are being applied in other laboratories on materials of a different nature. As a starting point, it was decided to use powdered samples in order to eliminate costly dissolution techniques. As it was not intended to provide complete quantitative data, the

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1/ Meggers, W. F., Emission spectroscopy: Anal. Chemistry, vol. 22, no. 1, pp. 18-23, 1950.

internal-standard, buffer, and carrier-distillation methods were not considered, nor could any definite advantage be anticipated in employing the cathode-layer method with its critical optical alinement. Ahrens [2] compared the cathode-layer and anode-excitation methods and found them approximately equally sensitive.

An investigation of the various excitation sources indicates that the direct current arc gives the best sensitivity or produces a higher degree of sample excitation so that lines emitted by elements in low concentrations may be recorded. The interrupted direct-current arc supplied by the Multisource produces a similar degree of sensitivity with the added advantage of simple operation. The nature of the interrupted arc would lead one to expect better control and attack of sample. It was hoped that this source would contribute to the reduction of interference of other elements or matrix effects.

Owing to these advantages the Multisource was selected to excite the graphite-mixed samples, which had been placed in the crater of a graphite electrode at the positive side of the arc. The purpose of the graphite addition was to prevent the formation of mobile beads of molten salts, oxides, or metals, to assist in the volatilization of elements of high boiling points or of elements existing in extremely nonvolatile compounds, and to steady the arc

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[2] Ahrens, L. H., Qualitative spectrochemical analysis of minerals and rocks: Geol. Soc. South Africa Trans. 49, pp. 133-154, 1946.

with a minimum of spraying or mechanical loss of sample.

In the present state of development of spectrochemistry an exact solution is precluded. This paper presents a practical solution that is being studied as it is applied to a wide variety of materials, with the hope that the method either will prove to be sound or will give basic data leading to a more exact solution.

Acknowledgments

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OUTLINE OF METHOD

The guide followed in working out the method and organizing this paper was an unpublished tentative outline for a suggested method of emission spectrochemical analysis, issued about 1948 by Committee E-2 on Spectrographic Analysis, American Society for Testing Materials.

A method is provided for determining 55 elements in one exposure. Table 1 shows the minimum concentration of the elements detectable by the method. Better sensitivity for many of these elements may be obtained by special methods.

Table 1.--Threshold or visual detection limits of the 55 elements included in the semiquantitative spectrographic method

Based on 10 mg of sample

Element		Minimum conc. detectable (in percent)	Element		Minimum conc. detectable (in percent)
As		0.1	Mo		0.001
Al		0.0001	Mg		0.0001
Ag		0.001	Mn		0.001
B		0.001	Na	(0.0001)1/	0.1
Ba		0.001	Ni		0.001
Be		0.001	Nd		0.01
Bi		0.001	P		0.1
Ce		0.1	Pt		0.01
Co		0.001	Pb		0.01
Cb		0.01	Pr		0.01
Cd		0.01	Rb		10.0
Cu		0.0001	Re		0.01
Ca		0.0001	Sb		0.001
Cr		0.001	Sr		0.01
Cs		1.0	Sn		0.01
Dy		0.01	Sm		0.1
Er		0.01	Si		0.0001
Fe		0.001	Sc		0.1
Ga		0.01	Th		0.1
Ge		0.001	Tl		0.1
Gd		0.01	Ti		0.001
Hf		0.1	Ta		0.1
Hg		0.1	U		0.1
In		0.001	V		0.01
K	(0.0001)1/	0.1	W		0.1
La		0.01	Y		0.001
Li	(0.0001)1/	0.1	Zr		0.001
			Zn		0.001

1/ A second exposure is necessary to produce the high sensitivity listed.

The method is applicable when samples must be inspected previous to quantitative spectrographic or chemical analysis. For many purposes the semiquantitative results are sufficient, and eliminate the expense of quantitative tests. The selection of a few samples from a large quantity of materials for more accurate tests is one of the most important applications of the semiquantitative spectrographic method. All of the elements listed in table 1 may be checked in one exposure, except the alkalies, Li, Na, and K, at concentrations of **less than 0.1 percent**, which require a second exposure in the red region of the spectrum (5500-8000 A).

The method has been applied to the analysis of the following: phosphate rocks, clays, sandstones, limestones, slags, coal ash, sulfur ore, sphene, allanite, apatite, zircon, microlite, galena, idocrase, carnotite, hewettite, sphalerite, thorite, vanoxite, uranothorite, brannerite, davidite, bastnaesite, miscellaneous precipitates, tap- and mine-water residues, leach products, and other types of materials.

A powdered sample is weighed, mixed with graphite, and placed in a prepared electrode, which is subjected to an interrupted direct-current arc. A grating spectrograph permits a range from 2250 to 4750 A to be covered on two adjacent spectrographic plates. After processing the plates, the quantities of unknown elements are estimated by visual comparison of certain lines of the elements in question with those on standard plates. A standard plate is prepared for each element, with the percentage of the elements decreasing from 10 to 10^{-4}. In preparing the standard plates, an inorganic-solution technique is employed. Standard solutions are prepared from the purest chemicals obtainable. These solutions are added to the electrode cups, and evaporated before arcing.

Apparatus

Excitation source - Applied Research Laboratories, Multisource interrupted direct-current arc.

Spectrograph - Jarrell-Ash 21-foot, Wadsworth-mounted grating.

Intensity control - Applied Research Laboratories neutral filters.

Viewing box - Jarrell-Ash.

Developing equipment - Applied Research Laboratories rocking developing tank, plate washer, and drier.

Electrode cutters
  A - Lower electrodes, designed to cut 1/4-inch electrodes (outside diameter 0.22 inch, inside diameter 0.19 inch, depth of crater 0.12 inch, depth of shoulder 0.12 inch).

  B - Upper electrodes, hemispherical 0.06-inch radius.

Miscellaneous glassware, etc.

Procedure

Preparation of standard plates

Standard solutions are prepared from "C.P." and "Specpure" chemicals, usually 10 mg of the element per milliliter of solution (see appendix 1 for the composition and preparation of standard solutions). These solutions are diluted until 0.1 ml of each equals 10.0, 1.0, 0.1, 0.01, 0 001, and 0.0001 percent based on a 10-mg sample.

A 0.1-ml aliquot is added to the sealed 3/ electrode cups from a micropipette and permitted to dry on an asbestos-covered hot plate (temperature approximately 100°C.). A few milligrams of pure graphite are added to the remaining salts in the electrodes. The electrodes are arced for 60 seconds. The following Multisource conditions and plate-processing conditions are used:

Capacitance	60 microfarads
Inductance	400 microhenries
Resistance	15 ohms
Initiator	high
Phase	0
Strike	strike position
Amperes	12
Spectrograph	Jarrell-Ash
Distance from electrode to slit	53.5 cm
Slit	25 microns
Optics	arc image focused on grating
Emulsion	1-L (Eastman)
Development	4 minutes at 18°C. ± 1/2°C., D-19
Gap	5-6 mm
Transmission	64 percent

3/ Seal is made of 1 percent parafin + benzine solution.

Analysis of unknowns

A 10-mg sample is weighed, mixed thoroughly with two parts of pure graphite in the weighing pan, and placed in the electrode cup through a small glass funnel drawn from pyrex tubing. The unknowns are arced for a period of 60 seconds. Spectra of iron 4/ and also of an aluminum alloy are recorded on each plate, along with the spectra of the unknowns. Reference points for locating lines and a general index of exposure, plate sensitivity, and development thus are obtained. The aluminum alloy of known composition also serves as a standard, when arced for 120 seconds at 32-percent transmission, with no change in the other conditions. The above conditions for recording the aluminum spectra were determined experimentally. After the plates are processed, the quantities of unknown elements are estimated by visual comparison of certain lines of the elements in question (table 2) with those on standard plates. The results are reported in the following brackets: over 10.0 percent, 1.0-10.0 percent, 0.1-1.0 percent, 0.01-0.1 percent, 0.001-0.01 percent, and 0.0001-0.001 percent. Work has been planned to include a lower percentage bracket (0.00001-0.0001 percent), as a few of the elements are detectable in concentrations of less than 0.0001 percent.

4/ Lower electrode is 1/4-inch iron rod, upper electrode is carbon (0.06-inch hemispherical radius). Arcing time 60 seconds, 4-5 amperes, 300 volts, transmission 64 percent.

Table 2.—Arc lines used in the semiquantitative method

Element	Wave lengths (in A)	Element	Wave lengths (in A)	Element	Wave lengths (in A)
As	2780.2 2349.84 2288.12	**Cb**	3358.4 3094.2 2875.5	**Ge**	3039.1 2691.4 2651.2
Al	3092.7 3082.2 3059.9 2660.4 2652.5 2575.1 2568.0	**Cd**	3466.2 3261.1 2763.9 2288.0	**Gd**	3671.2 3646.2 3358.6 3082.0
Ag	3382.9 3280.7	**Cu**	3274.0 3247.6 2824.4 2492.2 2293.9	**Hg**	4358.3 3650.2 3125.6 2536.5
B	2497.8 2496.7	**Ca**	4456.6 4226.7 3179.3 3158.9	**In**	4511.3 3256.09 2710.3
Ba	5535.55 4554.04 3071.6	**Cr**	4289.7 4274.8 4254.3 2780.7 2769.9 2731.9	**K**	7698.9 7664.9 4047.2 4044.1 3447.7 3446.4
Be	3321.3 2348.6	**Cs**	4593.0 4555.5 3347.4 3247.5	**La**	4429.9 4333.8 3380.9 3337.5
Bi	3067.7 2897.9	**Dy**	3645.42 3454.33 3407.8 3393.58	**Li**	6707.9 3232.7 2741.3
Ce	4222.6 4186.6 4040.7 4012.4	**Fe**	3100.31 3099.97 3099.9 3020.65 2599.4 2598.38	**Mo**	4251.9 3194.0 3170.4 2816.1
Co	3465.8 3453.5 3449.2 3405.1 3283.5 3243.8			Ga	2944.2 2874.2
Er	[illegible] 3499.1 3372.8			Hf	3134.7 3072.8

Table 2.—Continued

Element	Wave lengths (in A)	Element	Wave lengths (in A)	Element	Wave lengths (in A)
Mg	4351.9 2852.1 2795.5 2779.9 2776.7	Pr	4241.0 4225.3 4206.7	Tl	3775.7 3529.4 3519.2 2767.9 2379.6
Mn	2798.3 2605.7 2593.7 2576.1	Rb	4215.6 4201.8 3350.9	Ti	3372.8 3242.0 3239.0 3234.5 3224.2
Na	5895.9 5890.0 3302.9 3302.3	Re	3460.5	Ta	4574.3 3642.1 3311.2
Ni	3492.9 3433.6 3414.8 3002.5 2320.1	Sb	3267.5 2877.9 2598.1 2528.5 2311.5	U	4287.9 4241.7 3566.6 2837.328 2837.187
Nd	4325.8 4303.6 3328.3	Sr	4607.3 3464.5 3351.3 2569.5	V	4379.2 3185.4 3184.0 3183.4
P	2554.9 2553.3 2535.7 2534.0	Sn	3262.3 2863.3 2839.9	W	4302.1 4294.6 3049.7
Pt	4442.6 3064.7 3042.6 2659.4	Si	2987.7 2881.6 2528.5 2524.1 2516.1 2435.2	Y	3242.3 3195.6
Pb	2873.3 2833.1 2663.2 2614.2	Sc	3911.8 3907.5 3369.0 3019.3 2552.4	Zr	3556.6 3438.2 3391.9
Sm	4424.4 4256.4	Th	4619.5 4019.1 2837.3	Zn	4680.1 3345.0 3302.6 3282.3

DISCUSSION

The choice of lines to be employed for estimating concentrations of the elements is guided by the major components of the sample and by possible interferences. For example, when inspecting a spectrogram for zinc, the zinc line (3302.6 A) cannot be used if the sample contains greater than 1.0 percent of sodium, because of sodium (3302.3 A) interference. The zinc lines, 3345.0 A and 4680.1 A are used instead. More than 10 percent of uranium interferes with thorium, 2837.3 A; therefore thorium, 4619.5 A or 4019.1 A, should be employed. Titanium, 3242.0 A, in amounts more than 0.1 percent will interfere with yttrium, 3242.3 A.

When the sample contains more than 0.1 percent chromium, the 2780.7 A chromium line has an undesirable effect on arsenic 2780.2 A. Chromium, 2731.9 A, and arsenic, 2349.84 A, are substituted. Cerium lines, 4186.6, 4040.7, 4012.4 A, below a 1.0-percent concentration are masked by the cyanogen band. The cerium line, 4222.6 A, occurs in a clearer part of the spectrum, and has a detectable limit of 0.1 percent.

The presence of 5 percent or more of calcium fluoride has a general enhancing effect on aluminum. The spectrum of aluminum in concentration of about 0.01 percent then appears ten times too intense. This effect was not observed in phosphate-rock samples. In feldspar samples a depressing effect was observed on aluminum to the extent that a percentage estimation of this element could be incorrect by one bracket.

Table 1 shows the threshold values or visual detection limits of the elements included in the method. The method is not designed for maximum sensitivity, but is applicable rather for a general treatment by which 55 elements may be checked on one exposure. Experimental data suggest that increased sensitivities can be obtained for some elements by increasing the arcing time to 120 seconds, thus insuring complete consumption of the sample. This conversion is planned when time becomes available to prepare the proper standard plates.

RESULTS AND TABLES

The method has been employed to complete 15,000-20,000 determinations during a nine-month period. Of these determinations 304 were checked by chemical methods and indicated approximately 10 disagreements, in the magnitude of one bracket, with the spectrographic results. Comparison of chemical and spectrographic analyses are shown in tables 3-8. Some of the results were borderline cases in the sense that there was some doubt as to which of two adjacent brackets they belonged. This, however, is true of any procedure which involves assigning the results to one of a series of arbitrary categories. Because no particular element was the chief offender, the sampling and segregation may be at fault, and not the method.

Table 3.--Comparison of chemical and spectrographic analyses of samples of Florida phosphate rock

(TWS-61, TWC-908, Lot 524)

Element	No. 1		No. 2		No. 3		No. 4		No. 5	
	chem 1/	spec	chem 1/	spec	chem 1/	spec	chem 1/	spec	chem 1/	spec
P	11.3	a	12.6	a	12.7	a	15.8	a	15.5	a
Ca	19.6	a	18.3	a	17.7	a	19.4	a	19.8	a
Fe	1.26	c	1.19	c	0.46	c	0.87	c	1.25	c
Al	0.32	c	0.44	c	0.66	c	0.33	c	0.07	c
Si	4.1	b	3.9	b	7.6	b	4.0	b	2.9	b
Na	0.75	c	0.82	c	0.39	c	0.22	c	0.16	c
K	0.25	c	0.28	c	0.025	d	0.033	d	0.016	d
Mg	0.63	b	0.69	b	0.09	d	0.16	c	0.14	c
Mn	0.023	d	0.023	d	0.023	d	0.031	d	0.108	d
V	0.0056	d	0.0056	d	0.0056	d	0.011	d	0.014	d
Ti	0.036	d	0.012	d	0.006	d	0.018	d	0.036	d
Cr	0.00	e	0.00	e	0.00	e	0.00	e	0.00	e

a = 10.+, b = 1.0-10.0, c = 0.1-1.0, d = 0.01-0.1, e = 0.001-0.01

1/ Chemical results = oxides reduced to elements

Table 4.--Comparison of chemical and spectrographic analyses of samples of Florida phosphate rock

(TWS-86, TWC-780, Lot 2-23)

Element	BP-1		BP-2		BP-3		BP-5		BP-6		BP-7		BP-8	
	chem 1/	spec	chem 1/	spec	chem 1/	spec	chem 1/	spec	chem 1/	spec	chem 1/	spec	chem 1/	spec
Si	25.4	a	18.6	a	23.8	a	28.8	a	36.8	a	38.2	a	38.8	a
P	4.8	b	5.7	b	5.1	b	3.1	b	1.1	b	1.4	b	1.5	b
Al	9.5	a	12.8	a	10.7	a	8.8	a	5.3	a	4.2	a	3.6	a
Zr	0.08	c	0.08	c	0.1	c	0.1	c	0.09	c	0.1	c	0.1	c
Ca	0.68	c	0.64	c	0.05	d	0.08	d	0.29	c	0.16	d	0.05	d
Fe	1.8	b	2.0	b	1.7	b	1.5	b	1.2	b	1.7	b	1.5	b
Mn	0.00	e	0.00	e	0.00	e	0.01	e	0.00	e	0.01	e	0.01	e
Mg	0.18	c	0.23	c	0.29	c	0.17	c	0.15	c	0.12	c	0.13	c
Na	0.21	c	0.30	d	0.25	d	0.045	e	0.13	d	0.19	d	0.12	d
Ti	0.44	c	0.69	c	0.50	c	0.40	c	0.24	c	0.21	c	0.20	c
Cr	0.03	d	0.11	d	0.13	d	0.06	d	0.06	d	0.03	d	0.04	d
V	0.01	e	0.01	e	0.00	e	0.01	e	0.00	e	0.00	e	0.00	e

a = 10.+, b = 1.0-10.0, c = 0.1-1.0, d = 0.01-0.1, e = 0.001-0.1

1/ Chemical results = oxides reduced to elements

Table 5.--Comparison of chemical and spectrographic analyses of red and gray clays from the Colorado Plateau

(TWS-118, Lot 0-20)

Element	Red clay chem 1/	Red clay spec	Gray clay chem 1/	Gray clay spec
Ca	1.7	1.0-10.0	1.8	1.0-10.0
Si	28.0	10.+	30.0	10.+
Fe	3.84	1.0-10.0	1.7	1.0-10.0
Al	5.6	1.0-10.0	4.7	1.0-10.0
Mg	2.46	1.0-10.0	2.42	1.0-10.0
Cu	1.37	1.0-10.0	1.45	1.0-10.0
Na	0.03	0.1-1.0	0.07	0.1-1.0
K	5.0	1.0-10.0	4.6	1.0-10.0
Ti	0.35	0.1-1.0	0.36	0.1-1.0
V	0.04	0.01-0.1	0.04	0.01-0.1

1/ Chemical results = oxides reduced to elements

Table 6.--Comparison of chemical and spectrographic analyses of samples of Idaho phosphate rock

(TWS-124, Lot 1202; TWS-125, Lot 1204; TWS-126, Lot 1205; TWS-127, Lot 1206)

Element	Lab. No. 35832 S. No. RAH-47-10		35859 RAH-47-46		35863 LES-47-36		35894 VEM-47-253	
	chem 1/	spec	chem 1/	spec	chem 1/	spec	chem 1/	spec
Si	7.06	1.0-10.0	8.28	1.0-10.0	2.21	1.0-10.0	4.10	1.0-10.0
Cr	0.11	0.1-1.0	0.13	0.1-1.0	0.07	0.1-1.0	0.11	0.1-1.0
V	0.09	0.1-1.0	0.04	0.01-0.1	0.01	0.01-0.1	0.02	0.01-0.1
Ti	0.09	0.01-0.1	0.11	0.01-0.1	0.02	0.01-0.1	0.04	0.01-0.1
P	11.5	1.0-10.0	12.2	10.+	15.3	10.+	10.4	1.0-10.0
Mn	0.04	0.001-0.01	0.03	0.001-0.01	0.01	0.001-0.01	0.06	0.01-0.1
Ca	26.6	10.+	29.0	10.+	35.0	10.+	32.3	10.+
Mg	0.20	0.1-1.0	0.22	0.1-1.0	0.15	0.1-1.0	0.55	0.1-1.0
Fe	0.70	1.0-10.0	0.55	0.1-1.0	0.44	1.0-10.0	0.49	0.1-1.0
Al	1.46	1.0-10.0	1.44	1.0-10.0	0.42	1.0-10.0	0.75	1.0-10.0

1/ Chemical results = oxides reduced to elements

Table 7.--Comparison of chemical and spectrographic analyses of Colorado Plateau uranium- and vanadium-bearing ores for lead

(TWS-175, Lot 0-21)

Sample no.	(Percent Pb) chem 1/	(Percent Pb) spec
LRS-6-48	0.10	0.1-1.0
LRS-7-48	0.16	0.1-1.0
LRS-21-48	0.11	0.1-1.0
LRS-22-48	0.003	0.1-1.0
LRS-26-48	0.013	0.01-0.1
LRS-32-48	0.004	0.01-0.1
LRS-33B-48	0.010	0.01-0.1
LRS-34-48	0.22	0.1-1.0
LRS-35A-48	0.004	0.01-0.1
LRS-39A-48	0.10	0.1-1.0
LRS-43-48	0.12	0.1-1.0
LRS-60-48	0.045	0.01-0.1
LRS-67-48	0.11	0.1-1.0
LRS-69-48	0.011	0.01-0.1

1/ Chemical results = oxides reduced to elements

Table 8.--Comparison of chemical and spectrographic analyses of miscellaneous samples

Element	Montroseite 1/		Hummerite 2/		Ore 3/		Idocrase 4/		Hewettite 5/	
	chem 6/	spec	chem 6/	spec	chem 6/	spec	chem 6/	spec	chem 6/	spec
Mg			5.5	1.0-10.0					0.96	0.1-1.0
Al			0.10	0.1-1.0	0.054	0.1-1.0			0.07	0.1-1.0
K			3.6	1.0-10.0						
V	51.7	10.+	37.4	10.+	10.9	1.0-10.0			45.9	10.+
Fe	6.8	1.0-10.0			0.007	0.01-0.1	3.3	1.0-10.0		
Si			0.31	0.1-1.0	0.014	0.01-0.1	17.3	10.+	0.23	0.1-1.0
Ca			0.03	0.01-0.1	3.88	1.0-10.0	24.4	10.+	4.6	1.0-10.0
Mn							0.047	0.01-0.1		
U					47.5	10.+				
Sr					0.072	0.1-1.0				
Ba					0.25	0.1-1.0				

1/ Bitter Creek mine, Montrose County, Colo.
2/ Jo Dandy mine, Montrose County, Colo.
3/ Hand-picked sample from ore-bearing sandstone, May Day mine, Mesa County, Colo.
4/ Olmstedville, Essex County, N. Y.
5/ Jo Dandy mine, Montrose County, Colo.
6/ Chemical results = oxides reduced to elements

APPENDIX 1

Composition of standard solutions

The following standard solutions were made from compounds and elements available in the laboratory. Many of the compounds and elements used were Johnson, Matthey and Co. "Specpure" grade (J and M). The compounds were dissolved in distilled water unless otherwise noted.

Element standardized	Compound used	Solution
Ag	$AgNO_3$, reagent	
Al	$AlCl_3 \cdot 6H_2O$, C.P.	Compound dried in oven at 140°C. and dissolved in cold acidified H_2O.
As	As_2O_3, Nat. Bur. St. No. 83a	1:1 HNO_3, heated. Diluted to volume with H_2O.
B	H_3BO_3, C.P.	
Ba	$BaCl_2 \cdot 2H_2O$, C.P.	
Be	Be, metal, J and M	Dilute HCl.
Bi	Bi, metal, J and M	1:1 HNO_3. Diluted to volume with H_2O.
Ca	$CaCl_2 \cdot 2H_2O$, anal. reag.	
Cb	Cb, metal, J and M	48 percent HF. Diluted to volume with HNO_3, conc.
Cd	$CdCl_2 \cdot 2\frac{1}{2}H_2O$, C.P.	
Ce	CeO_2, J and M	H_2SO_4, conc., heated to form amber, $Ce(SO_4)_2$. 6 percent H_2SO_3 added to form colorless $Ce_2(SO_4)_3$. Diluted to volume with H_2O.

Element standardized	Compound used	Solution
Co	$CoCl_2 \cdot 6H_2O$, C.P.	
Cr	$K_2Cr_2O_7$, C.P.	
Cs	CsCl, C.P.	
Cu	CuO, reagent	Dilute HCl.
Dy	Dy_2O_3, J and M	1:1 HCl. Diluted to volume with H_2O.
Er	Er_2O_3, J and M	1:1 HCl. Diluted to volume with H_2O.
Fe	Fe, metal, J and M	Dilute H_2SO_4.
Ga	Ga, metal, C.P.	Aqua regia. Diluted to volume with H_2O.
Ge	GeO_2, C.P.	HF, 48 percent. H_2SO_4, conc., added and heated to drive off HF. Diluted to volume with H_2O.
Gd	Gd_2O_3, J and M	Dilute HCl.
Hf	HfO_2, J and M	Dilute H_2SO_4, heated, and H_2O_2, 3 percent, added until dissolved. Diluted to volume with H_2O.
Hg	$HgCl_2$, reagent	
In	In, metal, J and M	HNO_3, conc. Diluted to volume with H_2O.
K	$HKC_8H_4O_4$, Nat. Bur. Stand.	
La	La_2O_3, J and M	Dilute HCl.
Li	Li_2CO_3, reagent	Dilute HCl.
Mg	Mg, metal, J and M	Dilute HCl.
Mn	$MnCl_2 \cdot 4H_2O$, C.P.	

Element standardized	Compound used	Solution
Mo	Mo, metal, J and M	Aqua regia, heated. Diluted to volume with H_2O.
Na	NaCl, reagent	
Nd	Nd_2O_3, J and M	1:1 HCl. Diluted to volume with H_2O.
Ni	Ni, metal, J and M	1:1 HNO_3, heated. Diluted to volume with H_2O.
P	$NaH_2PO_4 \cdot H_2O$ C.P.	
Pb	$Pb(NO_3)_2$, C.P.	
Pr	Pr_6O_{11}, J and M	1:1 HCl. Diluted to volume with H_2O.
Pt	Pt, sheet	Aqua regia. Boiled down several times with HCl, conc., to drive off HNO_3. Diluted to volume with H_2O.
Rb	RbCl, J and M	
Re	Re, metal, J and M	HNO_3, conc. Diluted to volume with H_2O.
Sb	SbI_3, C.P.	Acetone + HCl, dil.
Sc	$Sc_2(SO_4)_3 \cdot 5H_2O$, J and M	
Si	SiO_2, pure	Na_2CO_3 fusion. Diluted to volume with H_2O.
Sm	Sm_2O_3, J and M	Dilute HCl.
Sn	$SnCl_2 \cdot 2H_2O$, reagent	
Sr	$SrCO_3$, reagent	Dilute HCl.
Ta	Ta, metal, J and M	48 percent HF + HNO_3, conc. Diluted to volume with H_2O.

Element standardized	Compound used	Solution
Th	$Th(NO_3)_4 \cdot 4H_2O$, C.P.	
Ti	TiO_2, C.P.	48 percent HF + H_2O_2. H_2SO_4, conc., added and heated to drive off HF. Diluted to volume with H_2O.
Tl	$TlNO_3$, C.P.	
U	$(UO_2)(C_2H_3O_2)_2 \cdot 2H_2O$, C.P.	
V	NH_4VO_3, C.P.	Hot H_2O.
W	W, metal,	48 percent HF + HNO_3, conc., heat. Diluted to volume with H_2O.
Y	Y_2O_3, J and M	1:1 HCl and heat. Diluted to volume with H_2O.
Zn	ZnO, reagent	Dilute HCl.
Zr	$ZrOCl_2 \cdot 8H_2O$, C.P.	