Method for the Quantitative Spectrochemical Analysis of Rocks, Minerals, Ores, and Other Materials by a Powder D-C Arc Technique

By HARRY BASTRON, PAUL R. BARNETT, *and* K. J. MURATA

CONTRIBUTIONS TO GEOCHEMISTRY

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A quantitative method for the determination of many constituents in a large variety of geologic materials

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CONTENTS

Page

Abstract 165
Introduction 165
Description of method 166
Apparatus 169
    Sample preparation equipment 169
    Spectrographic equipment 170
Standard samples and reference spectra 171
Procedure 174
    Preparation of sample 174
    Electrode system 175
    Excitation 176
    Exposure conditions 176
    Photographic processing 177
    Emulsion calibration 177
    Photometry 178
    Interferences 179
Precision and accuracy 180
Conclusion 181
References cited 181

TABLES

Page

TABLE 1. Selected analysis lines of the elements and useful concentration ranges in a pegmatite matrix 167
2. Iron lines for plate calibration 177
3. Data on precision of method for minor elements in igneous rocks 180

METHOD FOR THE QUANTITATIVE SPECTROCHEMICAL ANALYSIS OF ROCKS, MINERALS, ORES, AND OTHER MATERIALS BY A POWDER D-C ARC TECHNIQUE

By Harry Bastron, Paul R. Barnett, and K. J. Murata

ABSTRACT

A method for the quantitative spectrochemical analysis of rocks, minerals, ores, and other materials by a powder d-c arc technique is given. The method is especially valuable for the determination of those constituents that occur at low concentrations. Matrix effects between samples and standards are minimized by making dilutions with a common base material. The total-energy method is used because of the large number of elements found in the analysis of geologic materials. Plate calibration permits the construction of analytical curves that relate the logarithm of the intensity to the logarithm of the concentration. Analysis lines with the concentration ranges of the analytical curves are given. Examples of precision of the method are included.

INTRODUCTION

Research programs of the U.S. Geological Survey include distribution studies of the chemical elements in geochemical processes. Determinations of major and minor constituents of rocks, minerals, ores, and other materials are required. Major constituents are determined by conventional chemical analysis (Hillebrand and others, 1953) and by rapid chemical methods developed in the U.S. Geological Survey laboratories (Shapiro and Brannock, 1956; Dinnin, 1959). Those constituents amenable to spectrographic analysis, especially where they occur in low concentration, are determined by spectrochemical methods. The method described has been developed in the U.S. Geological Survey laboratories, and its use has contributed to many geochemical studies, examples of which are the study of minor elements in bauxite (Gordon and Murata, 1952), concentration of germanium in the ash of American coals (Stadnichenko and others, 1953), and the geochemical study of serpentines (Faust, Murata, and Fahey, 1956).

Modifications of this method may also be used for the determination of both major and minor constituents of minerals when the amount of sample is too small for chemical analysis, or when conventional chemical analysis is not feasible, as, for example, in the determination of the individual rare-earth elements (Rose, Murata, and Carron, 1954; Robinson, Bastron, and Murata, 1958).

The method outlined is the result of many years of experience in the spectrochemical analysis of a large variety of materials. A special effort has been made to minimize the extraneous effects of other elements and of the physical and chemical differences of a large variety of materials. Chemical and mineralogical data on many materials made available by other U.S. Geological Survey laboratories have aided in the development of this method.

DESCRIPTION OF METHOD

This method provides for the determination of those constituents in rocks, minerals, ores, and other materials that are amenable to spectrochemical analysis, especially where present in low concentration. Constituents present in high concentration are brought into the photometric range of the analytical curves by dilution techniques. The minimum concentration that can be determined for a given element is governed by the spectral sensitivity of this element in the d-c arc. For certain elements the spectral sensitivity can be extended to a lower concentration by using special techniques. Elements and analytical lines together with the concentration range of the working curves are given in table 1. Results are reported in weight percent of the element.

The general steps of procedure for this method follow the conventional d-c arc analysis of powdered material where graphite electrodes are used (Ahrens, 1954). Equal-weight parts of samples and standards are transferred into cupped electrodes of uniform dimensions and completely burned by using a d-c arc stabilized at a point near 16 amperes. The total-energy method (Slavin, 1938, 1939) is used. The relative transmittances of selected analytical lines are determined photometrically; these transmittances are converted to intensities through plate calibration by means of a set of homologous iron lines for which relative intensities have been established (Dieke and Crosswhite, 1943; Crosswhite, 1950). Working curves for the elements are constructed from the spectra of a series of standards by plotting the logarithms of the intensities of the selected analytical lines with the logarithms of the concentrations of the elements in the corresponding standards. The concentrations of the elements in the samples are determined by referring the logarithms of the intensities of the lines in the spectra of the samples to the working curves.

TABLE 1.—*Selected analysis lines of the elements and useful concentration ranges*

[Asterisk indicates line-width or comparison methods]

Element	Wavelength, A	Range of concentration (percent)
Silver	Ag 3280.68	0.0001- 0.01
Do	Ag 3382.89	.0001- .01
Aluminum	Al 3082.16	.001 - .1
Do	Al 2660.39	.02 - 1
Do	Al 2652.49	.03 - 1
Arsenic	As 2349.84	.05 - .5
Do	As 2780.20	.1 - 1
Gold	Au 2675.95	.002 - .1
Do	Au 3122.78	.01 - .1
Boron	B 2496.78	.001 - .05
Do	B 2497.73	.001 - .05
Barium	Ba *4554.04	.0002- .3
Beryllium	Be 2348.61	.0001- .001
Do	Be 3130.42	.0005- .02
Do	Be 3131.07	.001 - .05
Bismuth	Bi 3067.72	.001 - .1
Do	Bi 2897.98	.03 - .5
Calcium	Ca *4226.73	.0001- 1
Do	Ca *4283.01	.01 - 5
Do	Ca 3158.87	.01 - 1
Cadmium	Cd 3261.06	.005 - .1
Do	Cd 3466.20	.01 - .3
Cerium	Ce *4222.60	.02 - .2
Do	Ce 3201.71	.05 - 5
Cobalt	Co 3453.50	.0002- .01
Do	Co 3449.17	.001 - .1
Chromium	Cr *4274.80	.0001- .1
Do	Cr *4254.35	.0005- .5
Do	Cr 3021.56	.001 - .1
Cesium	Cs *4593.18	.8
Do	Cs 3347.44	.8
Copper	Cu 3247.54	.0001- .01
Do	Cu 3273.96	.0005- .01
Dysprosium	Dy 3407.80	.003 - .1
Do	Dy 3319.89	.01 - .5
Erbium	Er 3230.58	.001 - .5
Do	Er 3220.73	.01 - .5
Europium	Eu 2813.95	.003 - .3
Do	Eu 2906.68	.01 - .5
Fluorine	CaF 5291.0	.01
Iron	Fe 3020.64	.001 - .2
Do	Fe 3025.84	.01 - 1
Do	Fe 3286.76	.05 - 5
Do	Fe 3083.74	.1 - 5
Do	Fe 3175.45	.5 -10
Gallium	Ga 2943.64	.0005- .05
Do	Ga 2944.18	.005 - .3
Gadolinium	Gd 3350.48	.003 - .1
Do	Gd 3027.61	.01 - .5
Do	Gd 3331.39	.01 - .5
Germanium	Ge 2651.18	.001 - .05
Do	Ge 3039.06	.002 - 1
Hafnium	Hf 2866.37	.005 - .2
Do	Hf 3109.12	.03 - .5
Do	Hf 3134.72	.03 - .5
Mercury	Hg 2536.52	.1
Holmium	Ho 3398.98	.003 - 3
Do	Ho 3474.25	.005 - .1

TABLE 1.—*Selected analysis lines of the elements and useful concentration ranges*—Continued

Element	Wavelength, A	Range of concentration (percent)
Indium	In 3039. 36	0. 001 -0. 05
Do	In 3051. 25	. 01 - . 1
Iridium	Ir 3220. 78	. 006 - . 1
Potassium	K 3774. 70	. 1
Do	K *4044. 14	. 5
Lanthanum	La 3337. 49	. 003 - . 2
Do	La *4333. 73	. 003 - . 2
Do	La 3245. 12	. 01 -1
Lithium	Li 3232. 61	. 05 -1
Lutetium	Lu 2615. 42	. 003 - . 03
Do	Lu 2911. 39	. 003 - . 1
Magnesium	Mg 2852. 13	. 0001- . 1
Do	Mg 2776. 69	. 005 - . 5
Do	Mg 2782. 97	. 005 - . 1
Do	Mg 3329. 93	. 05 -3
Manganese	Mn 2801. 06	. 0001- . 05
Do	Mn 2949. 20	. 005 - . 3
Do	Mn 3070. 27	. 1 -1
Molybdenum	Mo 3170. 35	. 0002- . 03
Do	Mo 3193. 97	. 003 - . 1
Sodium	Na 3302. 32	. 1 -5
Do	Na 3302. 99	. 2 -3
Niobium	Nb 3163. 40	. 001 - . 05
Do	Nb 3194. 98	. 001 - . 05
Neodymium	Nd *4303. 57	. 01 -1
Do	Nd 3328. 27	. 05 -3
Do	Nd 3134. 90	. 2 -5
Nickel	Ni 3414. 76	. 0002- . 01
Do	Ni 3050. 82	. 001 - . 1
Do	Ni 3101. 55	. 001 - . 1
Do	Ni 3064. 62	. 01 - . 5
Osmium	Os 3301. 56	. 005
Do	Os 3262. 29	. 01
Phosphorus	P 2553. 28	. 1 -1
Do	P 2554. 93	. 1 -1
Do	P 2534. 01	. 5 -5
Lead	Pb 2833. 07	. 001 - . 05
Do	Pb 2663. 17	. 02 - . 5
Palladium	Pd 3404. 58	. 0003- . 01
Do	Pd 3242. 70	. 001 - . 03
Praseodymium	Pr 3245. 46	. 05 -2
Do	Pr 3121. 57	. 3 -5
Platinum	Pt 2659. 45	. 001 - . 1
Do	Pt 3064. 71	. 001 - . 1
Rubidium	Rb 3350. 89	10
Rhenium	Re 3464. 72	. 001 - . 05
Do	Re 3460. 47	. 005
Rhodium	Rh 3396. 85	. 0003- . 03
Do	Rh 3434. 89	. 0003- . 01
Ruthenium	Ru 3436. 74	. 001
Do	Ru 2965. 12	. 03
Antimony	Sb 2598. 06	. 01 - . 2
Do	Sb 2877. 92	. 03 - . 5
Scandium	Sc *4246. 83	. 0001- . 2
Do	Sc 3353. 73	. 0005- . 05
Selenium	Se 2413. 52	
Silicon	Si 2881. 58	. 001 - . 5
Samarium	Sm 3254. 38	. 003
Do	Sm 3408. 67	. 02 - . 5

TABLE 1.—*Selected analysis lines of the elements and useful concentration ranges*—Continued

Element	Wavelength, A	Range of concentration (percent)
Tin	Sn 2839.99	0.001 -0.1
Do	Sn 3175.02	.001 -.1
Strontium	Sr *4607.33	.0001-.2
Do	Sr 3464.46	.01
Tantalum	Ta 2714.67	.01 -5
Do	Ta 3311.16	.05 -5
Terbium	Tb 3324.40	.004 -.3
Do	Tb 3219.95	.01 -.5
Do	Tb 3293.07	.03 -.5
Tellurium	Te 2385.76	.05 -1
Thorium	Th 2870.41	.05 -5
Titanium	Ti 3372.80	.0005-.02
Do	Ti 3168.52	.005 -.5
Do	Ti 3261.60	.005 -.5
Do	Ti 3152.25	.05 -3
Thallium	Tl 2767.87	.003 -.3
Do	Tl 3229.75	.3 -1
Thulium	Tm 3131.26	.001 -.1
Do	Tm 3462.20	.001 -.05
Uranium	U *4244.37	.05 -1
Do	U 3270.12	.1
Vanadium	V 3183.98	.0005-.05
Do	V 3185.40	.001 -.05
Do	V 3102.30	.002 -.3
Do	V 3183.41	.002 -.2
Tungsten	W 2896.45	.02 -1
Do	W *4294.61	.02 -1
Yttrium	Y 3242.28	.001 -.05
Do	Y 3327.88	.001 -.1
Do	Y 3195.62	.005 -2
Ytterbium	Yb 3289.37	.0001-.01
Do	Yb 2970.56	.005 -.3
Zinc	Zn 3345.02	.02 -.5
Do	Zn 3302.59	.05
Zirconium	Zr 3273.05	.001 -.1
Do	Zr 3391.98	.001 -.1
Do	Zr 2752.21	.01 -.1

APPARATUS

SAMPLE PREPARATION EQUIPMENT

Large rocks are crushed to about walnut-size in a commercial rock crusher, put through a commercial roller mill, and reduced to about 8-mesh size. Mechanical grinders equipped with agate mortars and pestles reduce samples to fine powders of about 200-mesh size. Samples may also be reduced to 100-mesh size, without contamination, by a new high-alumina ceramic buckboard and muller (Bloom and Barnett, 1955)—the speed of grinding is faster than that of an agate mortar. Iron plates and tool-steel mortars are also used for reducing the particle size of some samples. Boron carbide mortars are used for samples requiring analysis for silicon. Precision balances are used in sample dilution and electrode-loading operations. Standard chemical laboratory equipment including an analytical balance, an electric furnace, a drying oven, porcelain and platinum crucibles, and chemical glassware are used when needed.

Auxiliary equipment for making mineral separations in preparing samples for the study of the distribution of the elements in geochemical processes include a petrographic microscope, a binocular microscope, and an isodynamic separator. Other equipment can be used that takes advantage of a difference in physical property. The short-wavelength ultraviolet light of a mercury-arc lamp is useful in checking for the presence of fluorescent minerals, such as scheelite and zircon (Cannon and Murata, 1944). The visible light of such a lamp is valuable in identifying and separating certain rare earth minerals because of color differences arising from the intense absorption band of neodymium in the yellow (Murata and Bastron, 1956).

SPECTROGRAPHIC EQUIPMENT

A spectrograph having a reciprocal linear dispersion of 5 Angstrom units per millimeter is used in the region 2250 to 4750 A. A series of neutral quartz filters mounted in a self-contained unit controls the intensity of the light that reaches the slit of the spectrograph. A direct-current excitation source capable of maintaining a steady current of 16 amperes between the electrodes is used. Resistors in series control the current and are connected in such a way that a rapid change from low to high current can be made by means of a switch while the arc is burning.

Commercially available purified cupped graphite electrodes and graphite rods are used. Prior to the availability of the preformed electrodes, all electrodes were machined in the laboratory on a lathe employing a special cutting tool (Myers, 1951) or a specially designed commercial electrode cutter.

The spectra are photographed on two 10-inch plates placed end to end and record the region from 2250 to 4750 A. Kodak type III–O plates (extra thin) are usually used for this purpose.

A nonrecording projection microphotometer, incorporating a phototube, an amplifier, and a galvanometer, is used for measuring the optical density or transmittance of the analytical lines. Continuous scanning must be provided by such an instrument when line-width measurements are made.

Apparatus that permits the entire operation of developing, fixing, and washing spectrographic plates at a controlled constant temperature is used. Means for continuous agitation during the developing process are provided. Plates are dried on an electric drier equipped with an air circulator.

STANDARD SAMPLES AND REFERENCE SPECTRA

Two rock samples, designated as G–1 and W–1 (Fairbairn and others, 1951), are used as reference standards for the major as well as for most of the minor constituents. Mixtures of these two samples in various proportions furnish additional standards. A series of National Bureau of Standards powdered samples serve as additional reference standards for many of the major constituents, but unfortunately very few analyses for minor constituents are available. Samples analyzed in the U.S. Geological Survey chemical laboratories are also used as reference standards, although analyses for minor constituents again are limited.

Analytical curves are established from a series of synthetic standards, each containing known amounts of several elements in a common matrix. It is important that the base material should approximate the samples as closely as possible, because the chemical composition and physical form of the matrix are factors which affect the burning qualities of the arc and the intensities of the spectral lines. Such a matrix, called pegmatite base, has been developed (Gordon and Murata, 1952). It consists of 60 parts quartz, 40 parts microcline, and 1 part ferric oxide. Large quartz crystals are broken up by heating in a furnace to about 1,000°C and then quenching in distilled water. After reduction to about 80-mesh size in an agate mortar, the quartz is washed with hot acid (HCl, 1:1). The resulting product is a purified quartz, free of practically all other elements except traces of the major constituents of the common rocks. The microcline crystals are isolated by handpicking, if necessary, and reduced to 80-mesh size in an agate mortar. The cleaned material is checked spectrographically for elements other than potassium, sodium, aluminum, and silicon. Microcline samples are then reserved in lots according to the minor element content. For example, a quantity of microcline from the Bearpaw Mountains area in Montana was found to be very low in lead; accordingly, it is reserved for base material in the preparation of the lead standard. Microcline that is low in barium and strontium is reserved for the barium and strontium standard. Only a few minor elements are found in microcline, usually in very low concentration. Ferric oxide is not added to a matrix used for the preparation of a standard for iron. The ferric oxide provides a series of iron lines in a spectra of the standards that are used for plate calibration.

The synthetic standards in a pegmatite matrix are used for all elements except potassium, sodium, aluminum, and silicon because these elements are the constituents of the base material. Synthetic standards in a silica matrix are used for potassium, sodium and aluminum. Silicon is determined by the use of synthetic standards in a carbon matrix. Special standards are also made for suites of samples in which the matrix is quite different from pegmatite base; for example, a barium sulfate matrix is used in standards for the study of minor-element distribution in barites.

Synthetic standards are made by using specially purified chemicals (usually as the oxides) to contain the individual element at a definite concentration. Volatile elements such as boron, lead, arsenic, lithium, rubidium, and cesium are incorporated into the synthetic standard in the form of analyzed minerals or certain standard glass samples of the National Bureau of Standards. By successive dilutions with pegmatite base, a series of standards is obtained that covers a wide concentration range. The dilutions are made to give concentrations varying on a logarithmic scale, whereby the relationship between line intensity and concentration is matched. A convenient series results when successive dilutions are made by using the reciprocal of the cube root of 10 (0.4642) as the factor. The preparation of such a series of synthetic standards in use in this laboratory is given in detail as an example. As starting material, mixture A is made to contain exactly 5.00 percent of each element for which analyses are desired; chemicals of the highest purity are used. The following elements have been incorporated into this series of standards:

Element	Compound used	Gravimetric factor	Weight of compound used (gram)
Co	Co_3O_4	1.362	0.1362
Cr	Cr_2O_3	1.461	.1461
Cu	CuO	1.252	.1252
Ga	Ga_2O_3	1.344	.1344
Ge	GeO_2	1.440	.1440
La	La_2O_3	1.173	.1173
Mo	MoO_3	1.500	.1500
Ni	NiO	1.273	.1273
Sn	SnO_2	1.270	.1270
Ti	TiO_2	1.668	.1668
V	V_2O_5	1.785	.1785
Y	Y_2O_3	1.270	.1270
Zn	ZnO	1.245	.1245

Total weight of compounds used	1.8043
Weight of pegmatite base added	.1957
Total weight of mixture A	2.0000

The compounds and matrix are weighed on an analytical balance and mixed to a fine homogeneous powder by grinding together in a clean agate mortar. Agate mortars and pestles are cleaned by scrubbing with a stiff brush and pumice soap, which removes any loose material, then by grinding successive portions of clean sand to a fine powder, which takes up the last traces of impurities. The mortar is again scrubbed, rinsed, and dried before use. Occasionally it is necessary to clean a mortar with hydrochloric acid.

A 1.00 percent standard A–1 is made by mixing 0.700 gram of the standard mixture A with 2.800 g of pegmatite base. Successive standards are made by using the reciprocal of the cube root of 10 (0.4642) as the dilution factor. Thus, if 1.000 g of standard A–1 is diluted to 2.154 g by using 1.154 g of pegmatite base, a standard A–2 results which contains 0.464 percent of each element. Next, 1.000 g of standard A–2 is diluted to 2.154 g by using 1.154 g pegmatite base; this step results in standard A–3, which contains 0.215 percent of each element. Upon diluting standard A–3 in the same way, standard A–4 is made, which contains 0.100 percent of each element. Dilutions are continued until a standard is reached that is below the limit of detectability for all the elements, usually to below the 0.0001 percent level.

The amount of material desired for each standard of the series may be altered by an appropriate factor. In actual practice the amounts used for the preparation of the standards following standard A–1 are increased by a factor of 1.5. To improve the burning qualities of all standards and samples, one-quarter of their weight of spectrographically pure graphite powder (200 mesh or finer) is mixed with them by grinding in an agate mortar. Each standard is stored in a clean stoppered vial.

Spectrographic plates composed of a complete series of one or more of the synthetic standards are used as reference spectra. They prove valuable when used in a projection comparator to estimate concentrations of the elements semiquantitatively by comparing the blackness or width of lines on the standard plate with the corresponding lines on a sample plate. The validity of the comparison depends upon the degree of reproducibility of the process of exposing and developing the plates as well as upon the uniformity in photographic response of the emulsions.

A reference spectra that aids in quickly locating spectral regions and line positions is produced by exposing a mixture of compounds designated as "X-Mix" on each plate. This mixture contains several selected elements having simple spectra at concentrations that will produce a few intense guide lines in different spectral regions. Other elements, especially those having complex spectra, are present in low concentrations, so that only the most sensitive lines will appear on the plate.

PROCEDURE

PREPARATION OF SAMPLE

A small homogeneous split that is representative of the original material serves as the sample for spectrographic analysis. All the original material is crushed to about 8-mesh size, then mixed and quartered to about one-half of a pound; care is taken to prevent segregation. This material is then reduced to a fine powder of less than 200-mesh size in a mechanical grinder—a clean agate mortar and pestle is used. After grinding, the material is again thoroughly mixed and quartered to about 5 grams, and this split is placed in a stoppered vial and reserved for analysis.

When the amount of material is limited or when lengthy mineral separations are required to obtain a sample, a minimum of 50 milligrams is desirable for analysis by the procedure as outlined. Small samples are reduced to a fine powder by hand grinding in an agate mortar to guard against loss.

Some types of material that contain much water of crystallization or other volatile matter must be ignited before spectrographic analysis to guard against loss of sample during the burning procedure. An ignition factor is obtained, which is applied to the spectrographic results to express concentrations on the basis of the original material. Ordinarily, ignitions are carried out at 800°–1,000° C in porcelain crucibles. These temperatures insure the destruction of carbonates, which may also give trouble in the burning procedure. Organic matter is usually destroyed by ashing at 450° C. Special procedures must be used for materials that contain volatile elements which may be lost during ignition.

The sample is prepared for excitation by the following procedure. A 100-mg portion is weighed on the pan of a precision-type balance and transferred to an agate mortar. To this sample a 100-mg portion of a mixture consisting of 10 parts pure sodium carbonate and 90 parts pure quartz is added, together with 50 mg of spectroscopically pure graphite powder. After thoroughly grinding and mixing to a homogeneous powder, 25-mg portions of the prepared sample are weighed in duplicate on the appropriate precision balance and loaded into cupped electrodes by means of a special plastic or stainless steel funnel, which facilitates loading without loss of sample. The charge is firmly packed in the electrode with a glass rod, and the electrode is placed into a numbered position in an electrode box. The remainder of the mixed material is reserved for further dilutions or for possible repeat exposures by folding into a clean 3- by 5-inch paper, or by placing into any other suitable container. The electrode position, the identity of the sample, and the extent of dilution are recorded on a 4- by 6-inch card. Other pertinent information is added when the exposures are made, and the card furnishes a permanent record of the complete spectrographic plate.

The initial dilution described above is made with the quartz and sodium carbonate mixture to form a high-silica matrix. A good natural quartz is practically free of all minor elements and therefore is ideal for this purpose. The added alkali stabilizes the arc, and the graphite causes the elements to distill more uniformly. Matrix differences between samples and synthetic standards are usually minimized by this dilution, although some sensitivity is sacrificed. The matrix of samples that do not contain much aluminum, one of the major constituents of the standards matrix, can be adjusted for this element by the addition of spectroscopically pure Al_2O_3 with the quartz and sodium carbonate mixture when an analysis for this element is not desired. Elements in very low concentrations are determined from the spectrograms of this first dilution. This first dilution, except for the addition of the proper amount of graphite powder, can be omitted when samples are known to contain the same major elements that occur in the standards matrix and in about the same proportion.

Elements present in concentrations higher than the upper limit of the working curve (which can be easily identified by inspection of the first dilution spectrogram) are brought within range by a further appropriate dilution of the first mixture with pegmatite base and graphite. The matrix of the sample is thus made even more nearly like that of the standards, which further minimizes matrix effect. Elements having less sensitive analytical lines can be frequently determined without further dilution. For instance, in most rock analyses the concentration of manganese is such that the sensitive arc line Mn 2801 cannot be used without further dilution. Instead, the less sensitive lines Mn 2939 or Mn 2949 are used.

ELECTRODE SYSTEM

A commercially available cupped graphite electrode is used for the lower sample-containing electrode, which is made the anode. These electrodes are highly purified after being machined from graphite rods ¼ inch in diameter and 1⅝ inches in length. The cup has an inner diameter of 0.144 inch, a wall thickness of 0.015±0.001 inch, and a crater depth of 0.240±0.002 inch; the crater has a 60° truncated cone ending in a 0.031-inch-diameter bottom. A highly purified graphite rod ⅛ inch in diameter and 1½ inches in length is used for the upper electrode, which is made the cathode. High-purity electrodes are used because tests have shown that impurities occasionally show up when less pure material is used.

EXCITATION

All samples and standards are excited in the same manner in the d-c arc. After the shutter is opened, the arc is started at 5 amperes, and after 10 seconds the current is instantly raised to 16 amperes by means of a switch. The peak current varies slightly during the burning period; it is also affected by large differences in the composition of the materials being burned, but usually remains quite steady between 16 and 17 amperes. The exposure is continued until the sample is completely consumed, during which time a constant electrode gap of 4–5 millimeters is maintained. When the sample is completely vaporized, a definite change occurs in the burning characteristics of the arc. The hissing of the pure-graphite arc is noted, accompanied by a slight drop in current. Ten seconds after this point is reached, the shutter is closed and the current is switched off.

The spectral lines produced by the 1 percent Fe_2O_3 in a series of synthetic standards that have been recorded on each plate are used for plate calibration. Thus no special exposure is required for this purpose.

EXPOSURE CONDITIONS

Spectral region……A	2250–4750
Slit width……μ	25
Slit length……mm	2
Arc preburn……	None
Arc exposure……	Complete consumption of sample

The light from the arc is focused on the collimator of the spectrograph by a condensing lens placed in front of the slit. The collimator is masked at the top and bottom to exclude the image of the glowing electrodes. The intensity of the light that enters the spectrograph is controlled by a system of neutral quartz filters mounted between the source and the slit. An image of the electrodes formed on a target with an auxillary light source permits the electrodes to be positioned before the arc is struck. A lens that focuses an image of the arc on a graduated target permits the desired electrode gap to be maintained for the duration of the exposure period by manipulation of the electrode-holder control knobs.

All precautions are taken to keep operative procedures and instrument settings exactly the same after the light intensity has been adjusted for a particular batch of plates, all of which carry the same emulsion number. Because all photographic emulsions deteriorate with time, no more than an 8- or 9-month supply of type III–O plates is obtained at one time and stored in a refrigerator. The intensity is adjusted so that some background is produced to assure the recording of very light lines. The background is of optimum intensity when the iron line at 3225.8 A, produced by the 1 percent Fe_2O_3 in the low concentration standards, has a transmittance reading of about 3.5 percent on a microphotometer.

Complete sets of standards are recorded in duplicate on separate plates, and working curves for suitable lines of the various elements (table 1) are constructed. These working curves are used until the supply of plates is exhausted. Samples are exposed in duplicate on the same plate in a random order together with 5 or 6 single exposures of a set of synthetic standards that contain many of the elements usually determined. Single exposures of G–1 and W–1 or suitable mixtures of these standards are recorded on all plates. For the usual rock analysis the use of G–1 without dilution (except for the required addition of graphite) and of W–1 (diluted with an equal part of a 5 percent sodium carbonate in quartz mixture together with the required amount of graphite) is recommended. Forty exposures may be recorded on a single plate; this procedure permits 16 samples to be exposed in duplicate, together with the standards.

PHOTOGRAPHIC PROCESSING

Emulsion	Eastman Kodak III–O (extra thin) plate.
Developing	Eastman D–19 developer at 68°F for 4 min with constant agitation, followed by a water rinse at 68°F.
Fixing	Eastman acid fixer at 68°F for 5 min with agitation.
Washing	Running water at 68°F for 15 min.
Drying	Sponge, heater with blower.

EMULSION CALIBRATION

Calibration is accomplished by measuring the percent transmission of a series of spectral lines produced by the 1 percent Fe_2O_3 in the low-concentration synthetic standards which have been recorded on each plate. The lines chosen for calibration purposes have been selected from a list of homologous lines (Crosswhite, 1950) and are given with their relative intensities in table 2. The calibration curve is determined by plotting percent transmission versus intensity on logarithmic coordinates. Intensity values of some lines are adjusted whenever points for these lines consistently fall above or below the best fitting curve. After the shape of the curve for a particular

TABLE 2.—*Iron lines for plate calibration*

Fe *line*	*Intensity*	Fe *line*	*Intensity*
3157.89	73	3217.38	165
3166.44	64	3222.07	625
3175.45	125	3225.99	770
3178.02	94	3239.44	285
3196.93	430	3251.24	62
3205.40	210	3268.24	29
3215.94	225		

emulsion has been established, not all the lines need be used for calibrating future plates. This calibration curve serves for the entire region of the lower wavelength plate, 2250–3500 A. The type III-O emulsion was chosen for quantitative analysis by the d-c arc technique because it has a very uniform response throughout the entire wavelength region for which it is used and an adequate sensitivity with high contrast and low granularity. The higher wavelength plate, 3500–4750 A, is not calibrated because the lines in this region are rather wide and dark. Line-width methods are used to determine the few elements having lines in this region of the spectrum that do not have usable lines at lower wavelengths.

PHOTOMETRY

Relative transmittance measurements for analytical lines and lines of the calibration spectra are made on a projection comparator microphotometer. The lines appropriate to the concentration range are selected from the list in table 1.

For densitometry the clear-plate reading (100 percent transmittance) is adjusted in the wavelength region of the line to be measured on an unexposed part of the emulsion; the line is then moved into position and scanned. The minimum percent transmittance of the line and the percent transmittance of the background are recorded. The percent transmittances of the analytical lines and background are converted into intensities by means of the calibration curve. The intensity value of the background is subtracted from the intensity value of the analytical line. For low concentrations an overcorrection usually results when a full background correction is made. Experience with materials of known composition where background is high has shown that there is better agreement with a working curve when a background correction of one-half the measured intensity value is used. When this procedure is carried through for a series of standards, it serves to establish analytical curves for the elements by plotting intensities and concentrations on logarithmic coordinates. Intensities of the lines of the elements for which analytical determinations are desired are converted into concentrations by reference to the appropriate analytical curve.

The use of line widths as a measure of concentration (Ahrens, 1950) is applied especially to those lines in the 3500- to 4750-A region of the spectrum. Measurements are made on a microphotometer equipped with a constant speed scanning device. Line widths are determined by measuring the scanning time at constant speed through the line by means of a stop watch. Full-scale deflection is adjusted in the background at an appropriate position in the spectrum near the line to be measured. The time required to scan the line is then measured by clocking the interval during which the percent transmittance remains below a given value. For intense, wide line the time for which the transmittance remains below 5 percent is used. For light lines the time for which the transmittance remains below 50 percent is used. Analytical curves are constructed by plotting the scanning times and the corresponding concentrations of a series of standards on a semilogarithmic scale.

If a constant-speed continuous-scanning instrument is not available, a comparison plate consisting of a series of iron spectra is made in which the line intensity varies with the total exposure time. This plate can be made by using a step-sector in which the successive steps vary by a constant factor—for example, a sector having a step ratio of 1 to 1.5. An iron line that shows a difference in width for successive steps is chosen, and working curves for the elements are constructed by relating the width of an analytical line at a given concentration to the step of the iron spectra it most nearly matches. The comparison plate can also be made without the use of a step sector by successively exposing iron spectra for which the lengths of the exposure times vary by a constant factor. A shutter that accurately controls exposures to fractions of a second is necessary.

INTERFERENCES

The problem of interference is ever present in the spectrochemical determination of any element. The relatively high reciprocal linear dispersion (5 A per mm) of the spectrograph permits the use of many lines whose wavelengths differ by as little as 0.1 A without interference. The procedure as outlined permits high resolution of the spectral lines, yet with sufficient width for densitometry. Because the intensity and the width of spectral lines are a function of the amount of an element present in the arc, the degree of interference depends upon the concentration of the interfering element. Interference is often circumvented by using another suitable spectral line. For example, the line Ag 3382.89 is used for traces of silver in the presence of high amounts of manganese, because Mn 3280.76 would interference with Ag 3280.68. When no other suitable line is available for analysis, a correction for the amount of interference may be made (Ahrens, 1950). In the analysis for zirconium, for instance, the most sensitive line Zr 3391.98 is not resolved from Fe 3392.01. An adjacent more sensitive iron line Fe 3392.31 is used to determine the amount of correction. The spectra of a series of standards containing varying amounts of iron but no zirconium are recorded, and the intensities of Fe 3392.01 are determined and plotted versus Fe 3392.31. From this curve the amount of intensity to be subtracted from Zr 3391.98 due to iron is determined by measuring the intensity of Fe 3392.31 found in the sample. If the interfering line and the correction line belong to the same multiplet, their intensity ratio is constant for various concentrations; this factor, when multiplied by the intensity of the correction line, indicates the amount of correction to be subtracted from the intensity of the analysis line.

PRECISION AND ACCURACY

Data on precision of the method, especially for minor elements in rock analysis, are given in table 3. The success of the method depends primarily upon the reproducibility of the d-c arc. The addition of graphite to the samples and standards results in a smoother burning arc and a more even rate at which the various elements are volatilized. The high current of 16 amperes minimizes wandering of the arc, and thus the arc's reproducibility is improved. Exposures are made in duplicate, and the time for complete volatilization is recorded and serves as an additional check on reproducibility. Loss of sample from the electrode during the excitation procedure results in a shorter time for complete burning. Exposure times for duplicates in which there is complete volatilization usually do not vary by more than 5 percent. A preliminary inspection of the processed plate immediately reveals any major difference in the spectra of duplicates. The procedure is repeated whenever complete volatilization of the sample is not obtained. Because no internal standards are used, all precautions are taken to perform each step of the procedure in exactly the same way for every sample and standard. Long-term differences and major errors are controlled by recording the standard samples G–1 and W–1 on every plate.

TABLE 3.—*Data on precision of method for minor elements in igneous rocks*

Element	Range of concentration (percent)	Average concentration (percent)	Number of pairs of determinations	Coefficient of variation of the average
Ba	0.003 –0.1	0.05	103	11.0
Co	.0002– .003	.001	80	6.7
Cu	.0001– .008	.002	102	9.0
Cr	.0001– .04	.004	88	11.9
Fe	.3 –4.4	1.7	90	5.7
Ga	.0005– .0013	.0007	85	8.8
La	.004 – .006	.005	20	10.3
Mn	.004 – .08	.036	88	5.3
Nb	.001 – .004	.0017	43	10.2
Ni	.0002– .025	.003	73	7.5
Pb	.0013– .0055	.002	51	10.2
Sc	.0004– .002	.002	75	10.2
Sr	.001 – .09	.02	66	12.3
Ti	.04 – .8	.2	91	4.9
V	.0005– .013	.004	80	9.9
Y	.001 – .004	.002	90	11.4
Yb	.0001– .0004	.0002	65	11.5
Zr	.0025– .0215	.011	101	7.2

Confidence in the accuracy of the method has been established by making many comparisons with chemical analyses of the same samples. It is difficult to obtain good chemical data for many of the minor elements, because the concentrations usually involved are below the best chemical range.

CONCLUSION

A general spectrographic method that is especially valuable for the detection and determination of the minor chemical elements in rocks, ores, and minerals has been described. The d-c arc source of excitation provides good detectability of elements present in very small amounts because a relatively large sample, as compared with spark techniques, is consumed for an analysis. Most geochemical investigations involve nearly all the chemical elements, and this method has proved particularly valuable because of its applicability to the determination of more than 50 of them. The method is based on the measurement of the integrated intensities of spectral line images recorded photographically during the time in which a sample is completely volatilized. Analytical curves constructed from a series of synthetic standards that relate the intensity of a spectral line of an element to its concentration provide for determining unknown concentrations. Elements present in high concentration are brought into the best analytical range by dilution of the samples with matrix material similar to that which is used in the preparation of the standards; this dilution further minimizes matrix effects. The method has also been used for the analysis of major constituents in cases where an insufficient sample makes a chemical analysis difficult and where a chemical analysis is not feasible, as is true in the determination of the individual rare-earth elements.

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