TOTAL INSTRUMENTAL ANALYSIS

NEVADA BUREAU OF MINES REPORT 6

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VERNON E. SCHEID, DIRECTOR

REPORT 6

TOTAL INSTRUMENTAL ANALYSIS OF ROCKS

PART A

X-RAY SPECTROGRAPHIC DETERMINATION OF ALL MAJOR OXIDES IN IGNEOUS ROCKS, AND PRECISION AND ACCURACY OF A DIRECT PELLETIZING METHOD

PART B

OXYGEN DETERMINATION IN ROCKS BY NEUTRON ACTIVATION

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MACKAY SCHOOL OF MINES
UNIVERSITY OF NEVADA

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A. Volborth

Mackay School of Mines
University of Nevada
Reno, Nevada
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STATE OF NEVADA

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NEVADA BUREAU OF MINES

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PREFACE TO PARTS A, B, AND C

Total instrumental analysis of all major and most minor elements in rocks and minerals can be performed by combining the X-ray emission and the neutron activation techniques. Recent developments in instrumentation permit us to assemble a complete X-ray emission and neutron activation laboratory in a room 15 by 10 feet, with an adjoining shielded room 8 by 5 feet.

In the three parts, A, B, and C, of this report, an attempt is made to show the precision, accuracy, speed, and simplicity of total analysis of rocks by these two combined fully instrumental techniques.

In part A, X-ray emission analysis of seven major oxides, Na_2O, MgO, Al_2O_3, SiO_2, K_2O, CaO, and Fe_2O_3, and two minor oxides, TiO_2 and MnO, is demonstrated on 15 different rocks. By pressing rock-powder pellets against glass, highly reproducible surfaces are obtained.

In part B, analysis of total oxygen by activation with fast neutrons is performed on 11 rocks, and results are compared with equivalent oxygen calculated from the X-ray emission data in Part A. For this analysis, rock powders are simply packed in plastic containers.

Part C, to be published in the near future, will demonstrate trace element analysis of the same 15 rocks analyzed in Part A of this report, using X-rays and pelletized plain rock powders.

The ability to analyze in minutes for practically any single element in rocks or minerals, and to check for the equivalent oxygen, also within minutes, shortens considerably the time required to describe an unknown mixture or mineral, and gives an independent check of totals for such analysis.

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X-RAY SPECTROGRAPHIC DETERMINATION OF ALL MAJOR OXIDES IN IGNEOUS ROCKS, AND PRECISION AND ACCURACY OF A DIRECT PELLETIZING METHOD

By A. Volborth

ABSTRACT

Nondestructive X-ray spectrographic determination of Si, Al, Ti, Fe, Mg, Ca, K, Na, and Mn is performed on pressed rock powders representing fifteen different igneous rocks, including four andesites, two welded rhyolite tuffs, two basalts, three granites, one adamellite, one quartz-monzonite, one diabase, and one syenite. It is shown that by using glass discs as pads, and pressing powders under 37 microns in grain size at 30,000 psi, nearly absolute precision can be achieved in determination of all elements mentioned. The reproducibility of the pellets with glossy surfaces is at least as good as the counting statistics used. The accuracy of this analysis is in all cases equal to the accuracy of conventional methods, and in some cases even a better accuracy could be indicated. The only assumption made in the calibration of the X-ray results is that the intensity ratios of the rocks G-1 and W-1 lie on a straight line, which line is used as calibration curve for all other rock powders. All results are statistically analyzed and the standard deviation S, the standard error $s_{\bar{x}}$, the relative deviation C, and the relative error E calculated. Comparison of the statistical results with corresponding figures of other conventional methods shows that this X-ray method is superior. The method could be called absolute in terms of precision, because no fluxing, dilution, heavy absorber, or even weighing procedures are necessary, and the rock powder is analyzed as such in pellet form. In terms of accuracy it is shown to be at least as accurate as the absolute or other instrumental methods. All calibration points group symmetrically on both sides of the calibration curves. Two little-understood effects are described. The biotite or the mica effect is apparently due to the relative increase of the total mica surface in rock powders upon continued grinding. Micas act as absorbing films influencing mainly the fluorescent intensities of elements present in them in different ratios than in the rocks. This effect can be, therefore, positive or negative, diminishing or even reversing the regular intensity increases upon further grinding. Micas also cause elasticity effects after high-pressure pressing causing some pellets to break. These effects indicate the use of different calibration curves for micaceous, argillaceous, or tuffaceous rocks. It is shown that sodium and silica can be determined in plagioclase with great precision and good accuracy, thus permitting both X-ray diffraction work and nondestructive X-ray spectrographic analysis of the same surface.

INTRODUCTION

X-RAY EMISSION ANALYSIS

Because this publication is not exclusively directed at specialists in the field, it is necessary to include here a brief discussion of the fundamentals of X-ray spectrography.

The basic principles of X-ray spectrographic analysis were developed by physicists in the first two decades of this century, following the discovery of X-rays by Roentgen in 1895. After the relationship of the characteristic X-ray radiation to the atomic number was established by Moseley, von Hevesy and other workers applied this radiation to the analysis of minerals and rocks. Concentrations of different elements down to one part in one hundred thousand parts could soon be measured, and the advantages of the method were demonstrated uniquely by the discovery of the element hafnium.

Despite a very promising and successful start, the widespread application of X-rays to general chemical analysis has developed only very recently, in the period of approximately the last ten - fifteen years. This delay was caused by the high experimental demands of the technique as first applied with demountable tubes and samples used as targets. The main factors which helped to make X-ray emission analysis a universal method were the development of: high intensity sealed X-ray tubes and stable power sources; highly sensitive geiger, scintillation, and proportional counters; large crystals with high diffracting power as dispersion media; reliable, precise and fast electronic counting apparatus and monitoring systems; and finally the development of helium and vacuum path spectrographs. This latter development has extended the range of X-ray analysis to include light elements to atomic number 12 without changing the excitation. During the last three years important improvements in the X-ray techniques, especially valuable to a rock analyst, have been achieved in the ultrasoft X-ray region, making possible the analysis of such light elements as sodium, fluorine, oxygen, nitrogen, carbon, and boron, and improving considerably the intensities obtainable from such elements as magnesium, aluminum, silicon, phosphorous, and sulfur (Henke, 1961; 1962).

Electromagnetic radiation in the wave length region of approximately 100 to 0.1 Angstroms is called X-rays. X-rays are of shorter wave length than ultraviolet rays. Gamma rays which are utilized in Part B of this report, are of shorter wave length than X-rays. When we speak of the electromagnetic spectrum, the use of these terms overlaps to a certain degree so that we may speak, for example, of hard X-rays, meaning gamma rays.

The visible part of the electromagnetic spectrum lies in the 4000 to 7000 Angstrom region. X-rays behave like visible light. They can be refracted and diffracted, and they show interference. Their velocity is that of light.

X-rays are generated when accelerated electrons collide with atoms. X-ray tubes have a filament and a metal target. Electrons emitted from the hot filament hit the positively charged target, producing X-rays with wave length typical of the target metal. These so called primary X-rays in certain cases produce fluorescence, or secondary X-rays, when they strike atoms of other elements. This secondary radiation is used in X-ray spectrography despite the fact that it is weaker than the primary radiation, and mainly because it permits the use of sealed X-ray tubes as excitation sources. This has become possible, however, only with the advances in counter sensitivity and electronics.

The fluorescent X-rays behave exactly as do the primary X-rays when they collide with an atom. Because of their high energy they penetrate the outer electron shells and knock out electrons from the inner two shells, called the K and L shells. When electrons from other shells fill the vacated positions, specific X-ray quanta of energy are emitted. Since there are only two electrons in the K shell and not more than eight electrons in the L shell, the resulting X-ray spectra consist of only a few strong lines, characteristic of each element irradiated. This is the main advantage of the X-ray spectrographic method. In practice, for each element one need seldom consider more than three to four lines, and interferences are relatively few. Another advantage is the relative independence of these lines from the oxidation state or structural relationships of the atom analyzed. This is to be expected, because only the inner electron shells, which do not participate in chemical reactions, are affected. These properties permit nondestructive analysis of complex mixtures.

To disperse or separate the different X-ray radiations caused by different elements in the analyzed material, so called analyzer crystals are used. Here the principle of diffraction is utilized. According to Bragg's law, if X-rays of a certain wave length λ , pass through a crystal with the distance d between two planes of atoms, interference or reinforcement will occur at a certain angle of incidence Θ . This law is expressed in the fundamental equation used in X-ray spectrography as well as in diffraction:

$$n \lambda = 2d \sin \Theta$$

n is here some integer, indicating that various orders of reflection occur only at specific Θ values. It is clear from this that a goniometer or a device to change the position of the crystal in respect to the incident X-ray beam is necessary.

In addition to the analyzing crystal and the goniometer, electronic discrimination or pulse height analysis is used in X-ray spectrography to help separate characteristic lines which occur extremely close to each other in the electromagnetic spectrum. These are devices which can be set to accept for counting only pulses with a certain amplitude distribution, cancelling all other pulses.

Minimum requirements of equipment necessary for X-ray spectrographic analysis from boron to uranium would consist of: 1, two regulated X-ray power sources capable of delivering 50 to 100 kv at 35 ma, and 10 kv at 200 ma, respectively; 2, at least two X-ray tubes, for example one with tungsten target, another with aluminum target; 3, one vacuum spectrograph; 4, a goniometer; 5, a pulse height analyzer; 6, high speed counting electronics; 7, a set of three to five analyzer crystals and molecular films, covering approximately the region of 4 to 100 Angstroms in d spacing; 8, recording and data processing systems.

It is estimated that miniumum cost of such complete system is about $30,000.

DISCUSSION OF PREVIOUS WORK AND PRESENT INVESTIGATION

Part A attempts to show that the X-ray spectrographic analysis of surfaces of pellets produced by the pressing of unfluxed and undiluted finely ground rock powders against glass discs, is precise, accurate, and sensitive for all major and some minor elements in a wide variety of rocks.

The precision of measurement of the major constituents of rocks is seriously affected every time the sample is handled, therefore an analytical method with a minimum of handling steps was sought. The nondestructive nature of X-ray spectrographic analysis provides the best opportunity to study the precision of measurement on the same sample, because, unlike gravimetric or emission spectrographic procedures, the original sample need not be destroyed by dissolving, fluxing, or burning. This eliminates the uncertainty factor of the final splitting and sample preparation, and enables us to study very small changes in composition due to splitting and other factors. The first aim of the present work, therefore, was the development of a nondestructive and highly precise method of measuring percentages of the major rock constituents.

The precision of analysis usually increases with increasing concentration. In silica, which is the major constituent of igneous rocks (40-80%), the highest precision in terms of relative deviation had previously been achieved with gravimetric double HCl method (Fairbairn and others, 1951; Fairbairn, 1953; Stevens and others, 1960). The statistical interpretation of the 60 analyses so performed leaves some doubt as to the reliability and significance of the conventional reporting of silica to four significant figures in gravimetric analysis. Much higher precision is required to justify the reporting of SiO_2 to 0.01 percent in these materials. On the basis of the 60 analyses mentioned above, there is doubt whether gravimetrically one will ever be able to achieve this kind of reproducibility. The main reason for this is that one is trying to "catch and hold" one part of SiO_2 in seven thousand parts.

Baird (1961), Baird and others, (1962, 1963a) using borax fluxing, developed by Claisse (1956), and quartz dilution, have established that high precision can be achieved by X-ray spectrographic methods for all major elements in rocks including Na and Mg.

Chodos and Engel (1961) have shown that good accuracy can be achieved with direct analysis of amphibolite rock powders of basaltic composition for Fe_2O_3, CaO, K_2O, TiO_2, and MnO. Other workers in this field have mostly preferred using different fluxing and dilution methods, as can be seen from the comprehensive literature list on sample preparation methods compiled by Bertin and Longobucco (1962). Recently, La_2O_3 heavy absorber addition technique was introduced in combination with $Li_2B_4O_7$ and boric acid fusion with very good results (Rose and others, 1962). Longobucco (1962) achieved good results in analysis of different minerals and standards using a combined borax - Li_2CO_3 fluxing method at 1350° C, but notes (p. 1264), that "Each of the minerals studied shows a loss on ignition ranging from 0.4 to 17%." To avoid these high losses each "sample material was ignited or calcined at 1350° C before use." It should be clear from this, that the X-ray results can be only as good as the sample preparation methods. In many acid fluxes when water, fluorine, chlorine and some heavy oxides are present, pyrolytic losses are possible. In addition Li_2CO_3, sodium salts, potassium salts and other similar compounds are partly volatilized at high temperatures necessary for fluxing, introducing unknown loss factors and changing dilution ratios. Water-bearing fluxing reagents naturally present the most difficult problems.

In sodium and magnesium analysis by soft X-rays, Baird and others (1962) have used pressed rock powders diluted with quartz-crystal powder with good results.

In December, 1961, and January, 1962, this author adapted Chodos' loose powder method (1961) to the analysis of eleven rock powders, analyzed in this laboratory, with good reproducibility and accuracy for Mn and Ti, but only satisfactory results for Fe, Ca, and K, and unacceptable results for Si and Al. This is apparently due to the variation in density of nonpressed powders, which would naturally affect most the intensity of the major elements.

With the development of a pressed-specimen die (Baird, 1961), direct pressing of rock powders without binders became possible. This author adapted this method immediately. Some improvements to this pressing technique were made in the summer of 1962 by adding a second piston and using a glass disc underneath the powder sample (Volborth, 1963a). Considerable improvement in precision and accuracy was achieved for all elements including silicon and aluminum. The pellet surfaces produced by this technique are extremely smooth and uniform, permitting the high precision of measurement necessary. The importance of good surface reproducibility must be emphasized, especially when working with soft X-rays, as in the case of Na, Mg, Al and Si (Henke, 1962; Baird and others, 1962).

If the present state of X-ray spectrographic analysis is critically examined, one is impressed by the diversity of its uses. Excellent applied work has been done in this field, and there is general agreement that the method offers unprecedented precision in the determination of most elements. When, however, the accuracy of the method is considered, we soon realize that a multitude of problems has developed in the analysis of different substances. Mass absorption effects, enhancement effects, homogeneity effects, grain size effects, and specific mineralogical effects, are the main factors influencing the accuracy of the X-ray determinations. Quantitatively examined these effects can strongly affect the results, even making them meaningless in some cases. Measurements of the magnitude of these effects have been made by different workers in their laboratories, and experimental correction factors have been established for most of them. Unfortunately, when some of these factors are compared, relative differences of several percent and even more are found, and it becomes a matter of choice or intelligent guess which data to use.

A practical analyst is interested in methods that would give him the best possible precision and accuracy with a minimum of work. Every experienced analyst knows that no universal machine exists that will satisfy all his demands. He knows that an efficient laboratory is a combination of instruments that are most suitable to solve his specific problems. He nevertheless strives at all times to restrict his equipment to the necessary minimum, because he knows that he should never attempt to do his work with greater precision and accuracy than are necessary to solve the specific problem.

The present work has evolved from similar considerations. The question to be answered was whether it is at present possible, in the analysis of all major constituents of igneous rocks, to ignore some of the different effects inherent of the X-ray spectrographic method, and still achieve the precision and accuracy of the conventional silicate analysis.

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STATISTICAL TERMINOLOGY

The statistical terminology used in this paper is identical with that used in the U. S. Geological Survey Bulletins 980 and 1113 (Fairbairn and others, 1951; Stevens and others, 1960).

n,	number of pellets analyzed.
$\bar{x}$,	arithmetic mean.
d,	deviation of an observation from the mean.
$S = \sqrt{\frac{\sum d^2}{n-1}}$	standard deviation or the uncertainty of a single observation.

$s_{\bar{x}} = \frac{S}{\sqrt{n}}$ standard error, or the error of the arithmetic mean.

$C = \frac{S}{\bar{x}} \times 100$ relative deviation, or the coefficient of variation.

$E = \frac{C}{\sqrt{n}}$ relative error.

These statistics, suitable for chemical methods, were adapted here instead of counting statistics for a Gaussian distribution, where

$$\sigma\,\% = \frac{100}{\sqrt{n}}$$

σ, standard deviation.
n, total number of counts.

This was done only for comparative reasons, because chemical data were used as base, and it was attempted here to show the analytical reproducibility of pellets at feasible counting times. Thus the counting conditions and statistics for which the expression

$$\sigma = \frac{100}{\sqrt{n}}$$

is valid, were kept constant for each element, and the differences of the pellet's intensities investigated. In all cases, the total counts per pellet are listed, enabling independent checks of counting statistics valid during the experiment. Comparing the counting statistics with the "chemical" statistics in this work one finds that the latter are somewhat better in most cases. Peak to background (P/B) ratios are given in tables.

SAMPLE PREPARATION

The present method* was developed using powders made from 15 typical igneous rocks. Two of the powders, standards W-1 and G-1, were acquired from the U. S. Geological Survey, and were described by Stevens and others (1960). Syenite Rock 1^a was described in a report (1960) of the Nonmetallic Standards Committee of the Canadian Association of Applied Spectroscopy. The quartz monzonite sample Granite 84, was received from Prof. Baird (private communication), and described in a report by Baird and others (1961). The remaining 11 powders were selected from a number accumulated during the past 6 years, which had been gravimetrically analyzed with great care for various laboratory projects. Eight were volcanic rocks analyzed by this author and three granitic rocks analyzed by Mr. H. A. Vincent. These are more fully described in the Appendix.

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* First presented September, 1962, Tenth Annual Norelco Western X-ray Diffraction and Spectrographic School in San Francisco.

The volcanic and granitic rock samples varied in size from 2 kilogram to 15 kilogram, depending on grain size and homogeneity. The rocks were crushed in a jaw crusher, passed through rolls and split into two equal parts with a Jones splitter. The two parts were then pulverized separately in Braun or Bico pulverizers equipped with iron and ceramic (mullite) plates. A representative sample of about 200 grams of each fraction was taken by splitting with the Jones splitter. Thirty grams of each sample were then pulverized in a Fisher mechanical mullite mortar, under lucite cover, allowing one hour per gram of rock powder. In fine powder so obtained biotite flakes (granitic rocks) can only be seen in pelletized form.

GRAIN-SIZE DISTRIBUTION OF POWDERS

A grain size distribution test was performed on 1 gram samples of the pelletized iron-plate ground powders of the eight volcanic and two granitic rocks, and the standard powders used in this test. This was done by wet screening in 400, 200, and 100 mesh (37, 74, and 148 microns, respectively) nylon screens, 7 cm in diameter, made by Spex Industries. This test showed that the eight powders of volcanic and the two powders of granitic rocks all consisted of about 95 percent of particles under 37 microns, 1-3 percent under 74 microns, and the remaining 2 percent above. These distribution figures are shown in table 1.

TABLE A1

Grain Size Distribution of Analyzed Samples

Rock Sample (1000 mg)	-37 Microns	+37 -74 Microns	+74 -148 Microns	+148 Microns
16/2 Granite ground 1g/hr	929 mg	18 mg	24 mg	8 mg
16/1 Granite "	985	4	4	2
1 Rhyolitic tuff "	951	20	8	1
2 Andesite "	965	11	7	1
3 Basalt "	967	15	7	1
4 Rhyolitic tuff "	983	10	2	1
5 Andesite "	971	16	11	1
6 Andesite "	974	15	9	0
7 Basalt "	961	25	10	1
8 Andesite "	987	6	5	0
G-1, as received	317	175	400	58
G-1 ground 1.5 g/20 min.	920	50	11	1
W-1, as received	768	166	32	1
W-1 ground 1.5 g/20 min.	939	30	3	1
1^a Syenite, as received	440	213	282	15
1^a Syenite ground 1g/hr	979	18	2	1
84 Granite, as received	157	105	266	446
84 Granite ground 1g/hr	991	4	4	1

Grain size distribution of standards G-1 and W-1 on as received basis (see table 1) varied considerably from the above values, with only 77 percent of the W-1 powder and a mere 32 percent of the G-1 powder passing the 37 micron screen. The G-1 powder still contained 6 percent of grains above 148 microns in size. Of the Syenite Rock 1^a (as received) 44 percent passed the 37 micron screen, and 1.5 percent were still above 148 microns in size.

The powders ground at our laboratory (table 1), were found to contain a much higher percentage of particles of minus 37 micron size, than did the as-received samples of those powders received from other sources (G-1, W-1, Syenite 1^a, and Granite 84). A test was therefore made to show the effect of further grinding on these powders. Grinding was done in a Fisher mechanical mullite mortar. Powders G-1 and W-1 were reground for 20 minutes per 1.5 gram and Granite 84 and Syenite Rock 1^a samples were reground for 1 hour per gram. The grain-size distribution of these reground fractions is also shown in table 1.

EFFECT OF REGRINDING ON X-RAY INTENSITY RATIOS

For the purposes of this analytical work it was rather satisfying to show (table 2) that reproducibility and intensity ratios of silica remained nearly constant, and were not noticeably affected by the large difference in grain sizes of the G-1 and W-1 powders used as received in standard pellets.

Most of the +148 and much of the +74 micron sized powders consisted typically of biotite.

Table 2 shows that if there is an effect of further grinding in mullite mortar on G-1 or W-1 it is very small, and negative in terms of intensity. However, in the two G-1 powders ground 20 and 40 minutes respectively the effect of grinding on SiO_2 percentages was - 0.65 percent (see section entitled "Biotite Effect"). The appearance of the pellet surface and the grain size of the G-1 sample that had been ground for 10 minutes resembled closely that of the four ground granitic rocks, and the appearance of the pellet surface of the W-1 sample that had been ground for 20 minutes resembled that of the eight volcanic rocks here analyzed. Based on these observations, it was assumed safe to pelletize the G-1 and W-1 standards as received without further grinding, which procedure has obviously great advantages if proven reproducible.

TABLE A2

Effect of Grinding on X-ray Intensity Ratios of Standards

Sample	Minutes Ground	Intensity Ratio	C=Relative Deviation	Amount Ground
G-1, mean of 10 pellets, as rec.	0	1.111	0.34	
110-G-1	10	1.113		4.5g, 3x1.5g
111-G-1	10	1.110		4.5g, 3x1.5g
112-G-1	20	1.098		4.5g, 3x1.5g
113-G-1	40	1.098		4.5g, 3x1.5g
W-1, mean of 10 pellets, as rec.	0	0.698	0.33	
114-W-1	20	0.695		4.5g, 3x1.5g

PELLETIZING

A pressed specimen die similar to the one developed by Baird (1961) was machined in our mechanics shop. Buehler Amber bakelite powder 1386 AB was used as backing. Some modifications in materials and additional improvements of this die were found advantageous. The main outer cylinder with its bottom part were made of aluminum. The inner cylinder and the piston were made of stainless steel, because aluminum against aluminum had a tendency to jam when pressed. The sample-loading innermost cylinder was also made of aluminum.

In addition to these parts, a second long piston was built of stainless steel to press the sample powder to a cake of uniform thickness before the removal of the loading cylinder. This is a better way than shaking the powder, which may cause some segregation of magnetic particles and the heavy minerals present in the rock powder. The modified die press used in the investigation is pictured in figure 1.

First the plastic disc (Baird, 1961) was used as a pad between the metal and the powder. Eight Bureau of Standards soda feldspar No. 99 samples were pressed, irradiated and the counting time ratios compared. Relative standard deviation of these eight samples was:

$$C = 0.36$$

which is better than precision achieved by gravimetric methods in analyzing sixty G-1 samples (C = 0.66, Stevens and others, 1960). However, the surfaces of these pellets were found to be very irregular because of the tendency of the mineral grains to cut into the plastic disc and to remain in little clusters and single grains on the plastic when the pellet was removed from the die. Since the surface appeared to the naked eye uneven and unsatisfactory, different plastics were tried but without success. Glass was considered but not tried at first because of the evident prospect of breakage under the 20,000-30,000 psi pressure used. Later a disc was cut from thin plate glass. The glass disc broke as expected but the pellet so received, when compared with previous plastic-pressed pellets, showed a mirror-like surface much superior to the plastic-pressed sample. In terms of relative deviation, precision obtained with glass-pressed samples was three times better than with plastic pads (table 4). Any good plane-parallel glass can be used, but thin projection slide glass was found to be best. Most flashlight glass is of suitable dimensions.

It is my opinion that although not so obvious from the small difference in the relative deviation (different n values), the glass disc has contributed considerably to the precision of this method. The absorption of the soft silicon radiation by a rock powder is so high that the phenomenon can be considered to be practically a surface phenomenon. A mirror-like surface should be in this case of great importance, and may be the main reason for a straight calibration curve obtained for silica (fig. 4).

If these considerations are true, it should make little difference in silicon determination how much powder is used in pelletizing. Three sets of 3 pellets each of Bureau of Standards (BS-99) feldspar standard were prepared with powder quantities of 300, 500, and 1,000 mg, and 614,400 counts taken on each pellet. Arithmetic means of time in seconds required to take this count were:

1,000 mg - 179.8 sec
500 mg - 179.9 sec
300 mg - 180.0 sec

The 300 mg of powder were just enough to cover the one square inch surface of the pellet so that no bakelite particles were visible. In many cases, where only small amounts of

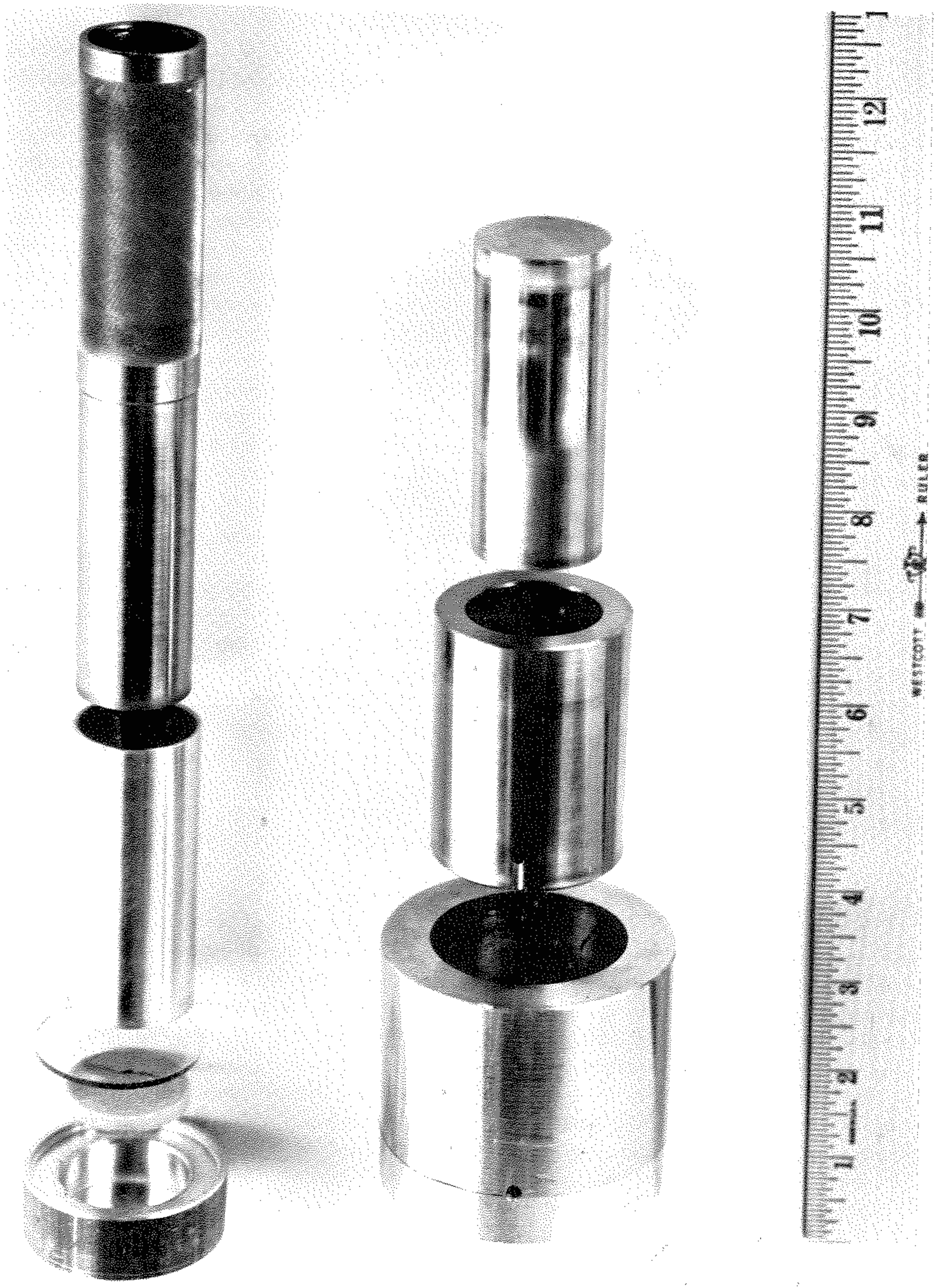


FIGURE A1. Die used for pressing of pellets. Modified from a die developed by Prof. Baird of Pomona College.

pure mineral powder are available, it is an advantage to be able to make large surfaces from 300 mg of sample without fear of loss of intensity of the light elements. This test also shows that no weighing of samples is necessary, therefore a calibrated leveled spoon may be used. In all rock samples made for this work, nevertheless, the exact amount of powder (1,000 ± 10 mg) was pressed, because it was found that the pressure release on the standardized Soiltest 250,000 psi press used (figure 2), was behaving differently with different ratios of rock powder to bakelite powder, and because the ultimate conditions were desired. One gram of fine rock powder consisting of about 95 percent of particles smaller than -400 mesh (37 microns), was used for each pellet during this work. The use of approximately one gram of powder is to be recommended to insure maximum thickness for all major elements to be determined in a rock.

Finally a test of the influence of the pelletizing pressure on the intensity of silicon radiation was made. Three pellets of the same rock powder (2 Alta andesite) were pressed at 10,000 psi, 20,000 psi, and 30,000 psi by increasing the pressure very slowly, waiting at the highest reading for about 30 seconds, then waiting till the pressure was automatically released to below 4,000 psi, and releasing it then slowly manually:

10,000 psi - 793 counts per second
20,000 psi - 795 counts per second
30,000 psi - 793 counts per second

In the preliminary stage of this work, a pressure of about 23,000 psi had been applied to all pellets, until it was discovered that coarser powders and tuffaceous rock powder pellets tended to break up soon after being removed from the die. By increasing the pressure to 30,000 psi this breaking was considerably reduced but not entirely eliminated, especially in the two rhyolitic volcanic tuff powders. Later it was found that addition of a few drops of distilled water to the powder prevented this breakage.

For the precision tests, all pellets of standard samples G-1, W-1, Syenite 1[a], and the secondary standards Granite 84, and four of the ten Mustang Andesite pellets were pressed at 30,000 psi. In the case of the Mustang Andesite powder, no detectable differences in counting time could be observed between the six pellets pressed at 20,000 psi and the four pellets pressed at 30,000 psi.

EQUIPMENT AND INSTRUMENTAL CONDITIONS

The analyses were performed using Norelco equipment similar to that employed for X-ray spectrographic work at Pomona College, Claremont, California (fig. 3), but not including the soft X-ray source, which is now being constructed at this Institution.

Instrumental conditions, including target types, analyzing crystals, vacuum, gas for flow proportional counter, and collimators are listed in table 3.

PRECISION AND STABILITY OF COUNTER ELECTRONICS

A test of the precision and stability of the counter electronics without a permanently positioned reference standard pellet was performed. The main difficulty expected here was the drift phenomenon encountered and elegantly solved by the use of a computer program devised by Baird and others (1962). A similar linear daily drift was first encountered with a narrow PHA window, but when the window was widened the drift diminished

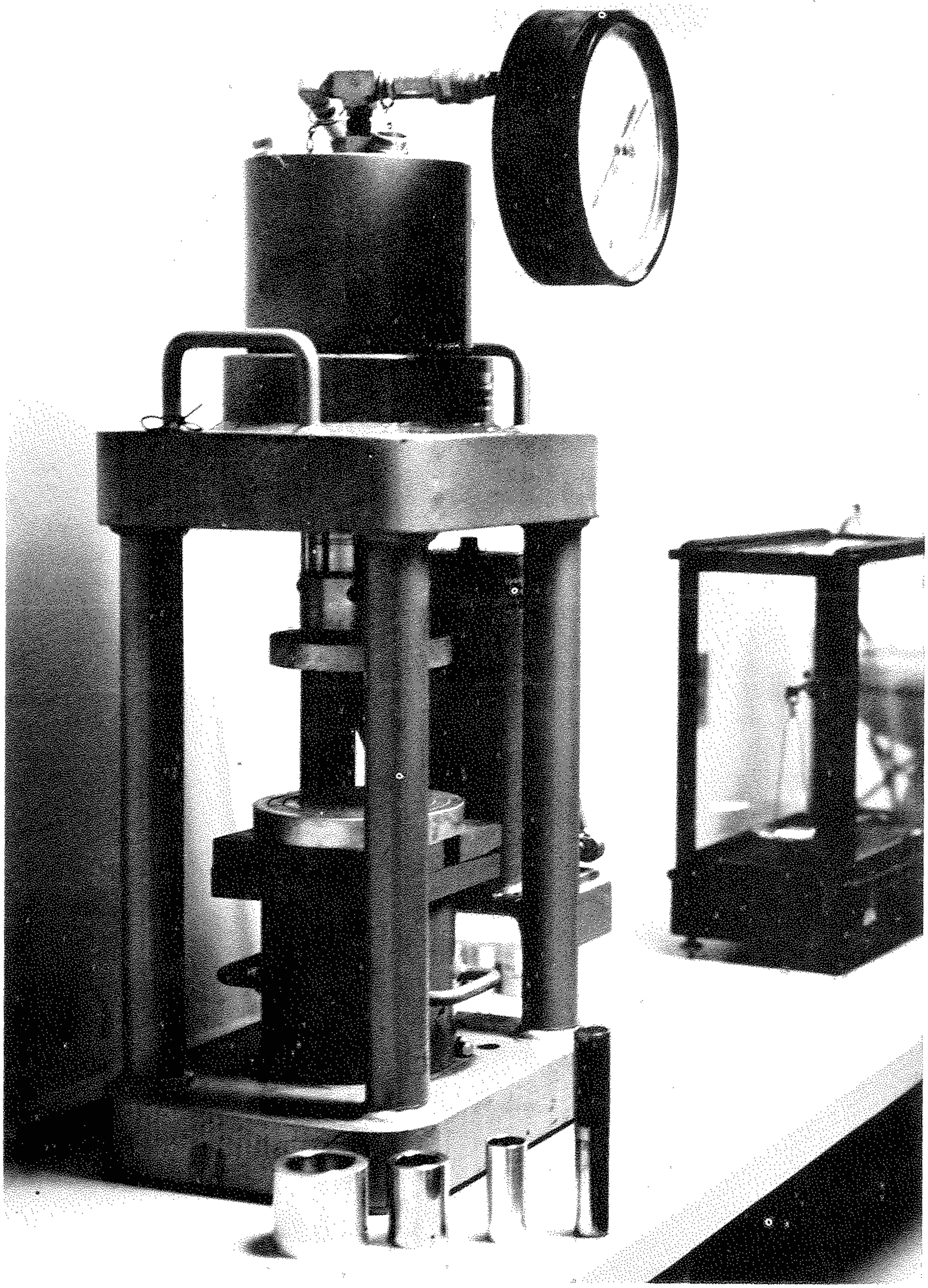


FIGURE A2. Soiltest 250,000 psi press used in pressing of pellets.

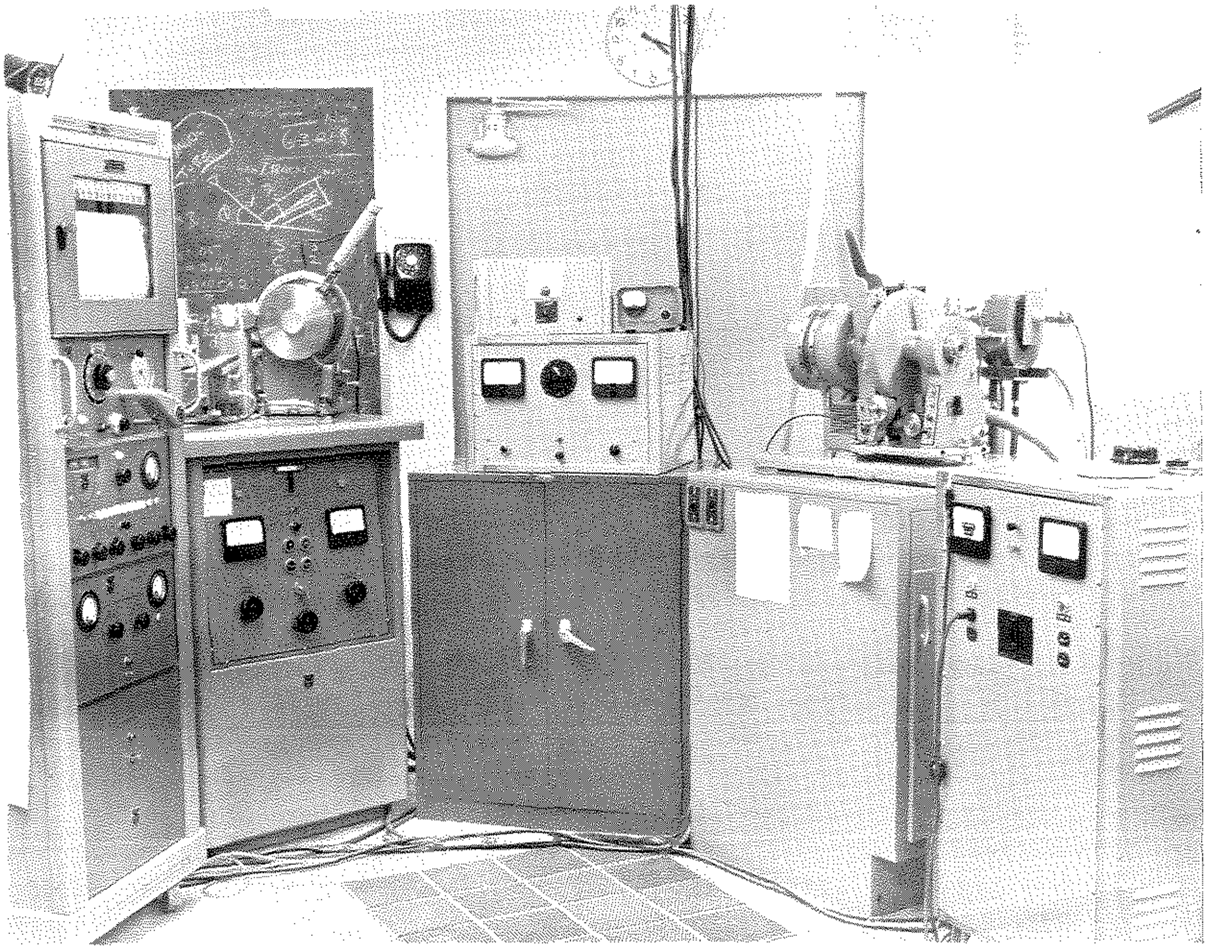


FIGURE A3. Equipment used for X-ray spectrographic analysis of rocks. Photograph shows equipment in the laboratory of the Geology department, Pomona College. Similar equipment, but minus soft X-ray source, was used in the present investigation. Equipment, left to right, includes: electronic circuit panel; X-ray power supply for diffraction and conventional W- and Cr-target spectrograph tubes; power supply for Vacion pump used with soft X-ray source, and gauges for measurement of X-ray tube and spectrograph vacuum (apparatus resting on steel cabinet, center); Universal Philips vacuum spectrograph containing the Al-target X-ray tube (top front) designed by Prof. B. L. Henke and Vacion system (right rear), and mechanical pumps for both spectrograph and Vacion system in cabinet beneath; power supply for soft X-ray tube. Published with permission of Professor D. B. McIntyre, Pomona College, Claremont, California.

and finally could not be noticed over a period of 5 days with a 30 volt (open) window. Under these conditions it became feasible to determine the reproducibility of the permanently positioned reference standard, disregarding the possible drift and other fluctuations in the system.

Over a period of five days, 31 readings were taken and statistically analyzed:

$$C = 0.63 \ (n = 31)$$
$$E = 0.11 \ (n = 31)$$

This shows that despite of a greater number of observations the precision in this case is less than with a permanently positioned standard when used as reference each time a reading is taken. Nevertheless, it should be emphasized that this relative deviation

TABLE A3. Instrumental Conditions for Complete Analysis of Igneous Rocks by X-ray Spectrography

Element	Characteristic Radiation	2θ	Target Excitation	Analyzing Crystal	Vacuum Path	Base Volts PHA	Window Volts PHA	Amplifier Voltage	Gas Flow, Prop. Counter 90% Ar + 10% CH_4 SCF H/air	Total Counts	Peak to Background	Collimator Mils
Si	K_α	107.98°	W 50KV 35MA	EDDT	0.4 mm Hg	4.2	30.0	1570	0.4	3x204800	86-140	20
Ti	K_α	36.37°	W 50KV 35MA	EDDT	0.4 mm Hg	9.0	21.0	1470	0.4	2x25600	8-14	20
Al	K_α	142.40°	W 50KV 35MA	EDDT	0.4 mm Hg	0.6	10.8	1470	0.5	3x25600	23-53	20
Mg	K_α	81.12°	Al 10KV 150MA	Gysum	0.3 mm Hg	5.4	21.0	1615	0.5	1x32000	7-35	500
Ca	K_α	44.84°	W 50KV 35MA	EDDT	0.4 mm Hg	4.8	22.2	1470	0.4	2x204800	15-34	20
K	K_α	50.28°	W 50KV 35MA	EDDT	0.4 mm Hg	3.0	21.0	1470	0.4	2x25600	11-98	20
Na	K_α	103.09°	Al 10KV 150MA	Gysum	0.3 mm Hg	6.0	18.0	1635	0.5	1x32000	6-16	500
Mn	K_α	27.61°	W 50KV 35MA	EDDT	0.4 mm Hg	1.8	18.0	1410	0.4	2x25600	4-9	20
Fe	K_α	25.39°	W 50KV 35MA	EDDT	air	18.0	30.0	1510	0.4	2x204800	7-47	20

already compares well with that for gravimetric and spectrographic determinations of SiO_2 in G-1 (Fairbairn and others, 1951; Fairbairn, 1953; Stevens and others, 1960). One is therefore tempted to suggest that this method can be used if reproducibility equal to but not better than obtainable by gravimetric procedures is desired.

Since this work attempts to show the best precision obtainable with the original equipment and the pelletizing method described, with the purpose of enabling a comparison with wet chemical analysis, the same permanently positioned rock sample (G-1 in most cases) was retained as reference, and all results were obtained from the ratio:

Standard sample counting time/sample counting time

ANALYTICAL DATA

SILICON AS SiO_2

Gravimetric procedure for determination of silica consisted of double dehydration with HCl, and recovery of SiO_2 in the R_2O_3 group. Each dehydration was performed overnight on waterbath and lasted a minimum of 16 hours. After the second dehydration, the dry residue was heated on a sand bath for 5 to 10 minutes. The SiO_2 was filtered and washed after each dehydration, the precipitates ignited at 1000° C to standard weight, combined, treated with $HF + H_2SO_4$, and the residue subtracted from the total.

Instrumental settings for the X-ray spectrographic determination of silicon are listed in table 3.

Silica, as a major constituent of igenous rocks, requires the best possible instrumental stability in order to obtain the ultimate precision, therefore, the experiment was conducted at night between 1 and 2 a.m. at which time the least disturbance in the electrical net system occurs. Ten glass-pressed albite BS-99 pellets and eight plastic-pressed albite BS-99 pellets were analyzed during this time with a fine-ground G-1 standard pellet as reference in permanent position. During this time intermittently 2,048,000 total counts were accumulated for the standard and 614,400 total counts for each of the pellets. Percentages in SiO_2 were read from intensity ratios of each pellet separately and these percentages statistically treated in table 4.

The relative deviation of ten glass-pressed pellets (in percent SiO_2 units) was:

$C\% = 0.07\%$

$\bar{x} = 68.64\%\ SiO_2,$

then $$68.64\% \times \frac{0.07\%}{100} = 0.05 \text{ weight percent } SiO_2$$

thus, with 95 percent confidence ($\pm$ 2 C)

$$\text{weight percent } SiO_2 = 68.64\% \pm 0.10\%,$$

or a range of 0.20 percent SiO_2.

This precision nearly warrants the reporting of silica in X-ray spectrographic analysis of albite to the nearest 0.01 percent.

A similar test was performed on ten ceramic-ground Andesite-5 pellets, giving a relative deviation of

$C\% = 0.09\%$

$\bar{x} = 56.46\%\ SiO_2$

TABLE A4

Precision of X-ray Spectrographic Determination of SiO_2

Sample	Pellet No.	SiO_2 Percent	Deviation from Mean	Statistical Data (2,048,000 cts.)	Remarks
Albite, BS-99	26	68.67	0.03	n=10	Pressed same day.
glass disc	28	68.67	0.03	$\bar{x}$=68.64	
"	29	68.55	0.09	S=0.048	
"	31	68.58	0.06	$s_{\bar{x}}$=0.015	
"	32	68.66	0.02	C=0.07	
"	33	68.62	0.02	E=0.02	
"	23	68.70	0.06		
"	24	68.67	0.03		
"	25	68.60	0.04		
"	30	68.66	0.02		
Albite, BS-99	16	67.95	0.16	n=8	Decrease in total intensity due to rougher surface.
plastic disc	17	67.83	0.28	$\bar{x}$=68.11	
"	18	68.13	0.02	S=0.162	
"	19	68.19	0.08	$s_{\bar{x}}$=0.057	
"	12	68.15	0.04	C=0.24	
"	21	68.05	0.06	E=0.08	
"	20	68.19	0.08		
"	22	68.36	0.25		
Andesite 5, Mustang,	68	56.38	0.08	n=10	Pressed on different days.
1 hr. ground	69	56.43	0.03	$\bar{x}$=56.46	
"	70	56.51	0.05	S=0.053	
"	71	56.48	0.02	$s_{\bar{x}}$=0.017	
"	72	56.48	0.02	C=0.09	
"	73	56.52	0.06	E=0.03	
"	96	56.45	0.01		
"	97	56.38	0.08		
"	98	56.43	0.03		
"	95	56.52	0.06		
W-1, as received	41	52.48	0.145		Pressed on different days.
"	42	52.49	0.135	n=13	
"	43	52.57	0.055	$\bar{x}$=52.625	
"	76	52.82	0.195	S=0.11	
"	77	52.73	0.105	$s_{\bar{x}}$=0.03	
"	78	52.70	0.075	C=0.21	
"	75	52.50	0.125	E=0.06	
"	79	52.53	0.095		
"	80	52.55	0.075		
"	82	52.70	0.075		
"	83	52.70	0.075		
"	84	52.68	0.055		
"	81	52.68	0.055		
G-1, as received	85	72.75	0.10	n=10	
"	87	72.64	0.01	$\bar{x}$=72.65	
"	88	72.43	0.22	S=0.17	
"	89	72.52	0.13	$s_{\bar{x}}$=0.05	
"	90	73.00	0.35	C=0.23	
"	91	72.52	0.13	E=0.07	
"	92	72.75	0.10		
"	93	72.61	0.04		
"	94	72.75	0.10		
"	86	72.48	0.17		

In this case

$$56.46\% \times \frac{0.09}{100} = 0.05 \text{ weight percent } SiO_2$$

thus, with 95% confidence (± 2 C)

$$\textit{weight percent } SiO_2 = 56.46\% \pm 0.10\%,$$

or a range of

$$0.20 \text{ percent } SiO_2$$

This precision for silica in this andesite is equivalent to the precision of silica in the albite feldspar, thus nearly warranting the reporting of SiO_2 in rocks to one hundredth of one percent. Coarser powders of G-1 and W-1 on which similar tests were performed, give somewhat inferior precision. The plastic-pressed albite BS-99 powder also gives precision almost four times inferior in terms of relative deviation, proving the superiority of the glass pressing for best possible reproducibility.

Standard errors in all the rocks so investigated vary in the region of 0.01-0.06 percent, which fact already shows that the reporting to the nearest one hundredth of a percent would be desirable and on the verge of being statistically meaningful in X-ray spectrographic analysis of rocks.

The results for silica, obtained by *assuming a straight calibration curve between* G-1 and W-1, figure 4, are compiled in table 5 for comparison with the gravimetric data.

ACCURACY OF THE X-RAY SPECTROGRAPHIC METHOD BASED ON GRAVIMETRIC DETERMINATION OF SILICA

The results of standardization of G-1, W-1, Syenite Rock 1[a], and Granite 84, where plotted on millimeter paper versus recommended gravimetric values - on as received basis (Stevens and others, 1960, p. 78), and a two point curve drawn between G-1 and W-1, (fig. 4). Eight volcanic and three granitic rock powders ranging from 52 to 77 percent SiO_2 were ground by iron plates, pelletized, and the intensity ratios for each powder determined on three pellets for six volcanic rocks and one pellet for the others. *These 11 new points fall closer than within 1 percent SiO_2 on the calibration curve when* plotted against the gravimetric values (fig. 4). SiO_2 values so determined appear in table 5 in comparison with gravimetric data, number of pellets analyzed, relative deviation, and sample description. Gravimetric data on volcanic rocks are by this author, granitic rocks have been analyzed by Mr. H. A. Vincent (see Volborth, 1962a, p. 826).

To provide a measure of the accuracy of these X-ray spectrographic analyses, the minus or plus deviations from the chemical data were taken in percent:

Sample No.	1	2	3	4	6	7	8
d (% SiO_2)	+0.33	0.00	-0.49	+0.81	-0.15	-0.78	-0.85

Sample No.	10	11	15	16	17	18	19
d (% SiO_2)	+1.00	+0.27	-0.21	+1.07	0.00	+0.19	-0.32

Deviations were squared, and assuming the chemical data to be accurate and to represent the arithmetic means, the standard deviation calculated:

$$S = 0.61$$

$$s_{\bar{x}} = 0.16$$

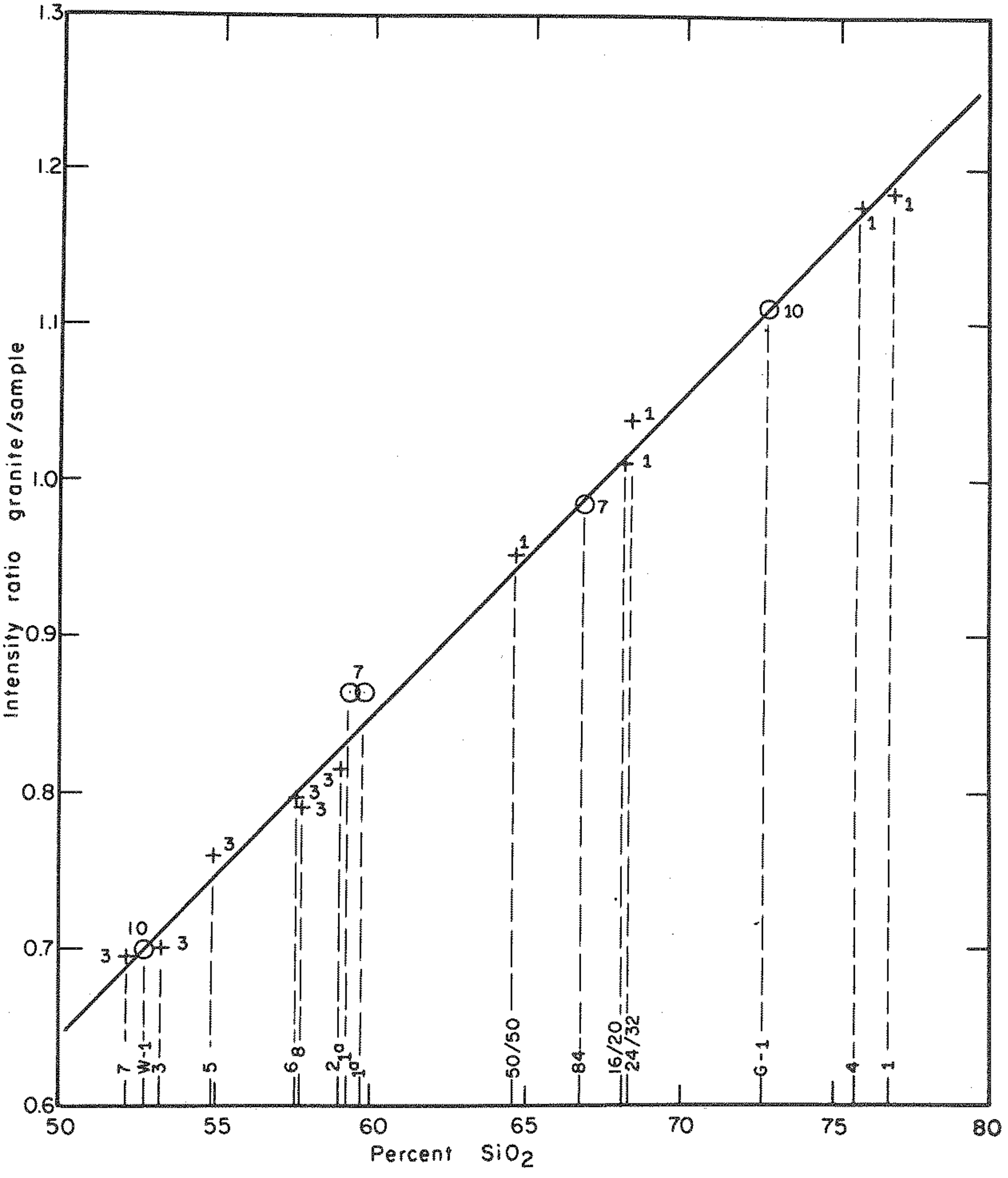


FIGURE A4. Calibration curve for X-ray spectrographic determination of SiO_2, based on gravimetric data on rock powders ground by iron plates. Identifying numbers of the rocks are indicated above the abscissa. The points representing rocks G-1, W-1, Granite 84, and Syenite 1^a are marked with circles. Syenite 1^a is shown by two points, one corresponding to the mean of the determinations given in the report of the Nonmetallic Standards Committee of the Canadian Association for Applied Spectroscopy (1961), the other corresponding to the highest value given in that report. Both were shown because of the usual negative bias in gravimetric determinations of silica. The points representing rocks analyzed in this laboratory are marked by plus signs; numbers beside the signs indicate number of pellets spectrographically analyzed.

TABLE A5

Comparison of X-ray Spectrographic Data with Gravimetric Data for SiO_2

No.	SiO_2% Gravimetric analysis as rec.	Times Analyzed	SiO_2% Spectrographic analysis	Pellets Analyzed	Relative deviation (C) grav.	Relative deviation (C) X-ray	Sample Number	Gravimetric Analyst or source
1.	52.12	1	52.45	3			7 Basalt Fe plate	Volborth
2.	52.64	7	52.64	10	0.91	0.33	W-1 USGS	Chodos *in* Stevens and others, 1960, p. 78
3.	53.24	1	52.75	3			3 Basalt Fe plate	Volborth
4.	54.79	1	55.60	3			5 Andesite, Fe plate	Volborth
5.	None		56.50	10		0.13	5 Andesite, Ceramic plate	Volborth, X-ray only
6.	57.60	1	57.45	3			6 Andesite, Fe plate	Volborth
7.	57.83	1	57.05	3			8 Andesite, Fe plate	Volborth
8.	59.05	1	58.20	3			2 Andesite, Fe plate	Volborth
9.	59.29	3	60.65	7		0.29	Syenite 1^a, mean value	Non-metallic Standards Committee Report, 1961
10.	59.65	1	60.65	3			Syenite 1^a, highest value	Non-metallic Standards Committee report, 1961
11.	64.63	1	64.90	3			Biotite adamellite 50, Fe plate	Vincent *in* Volborth, 1962, p. 826
12.	None		66.77				Quartz monzonite (Granite 84) Fe plate	Baird, X-ray only
13.	None		66.60	7		0.36	Quartz monzonite (Granite 84) Fe plate, reground	Volborth, X-ray only
14.	None		68.55	3			Quartz monzonite (Granite 84) 4-min Pica ground, as received	Volborth, X-ray only

Table A5 - Continued

15.	68.06	1	67.85	1			Granite, 16/20, Fe plate	Vincent *in* Volborth, 1962, p. 826
16.	68.23	1	69.30	1			Granite, 24/36, Fe plate	Vincent *in* Volborth, 1962, p. 826
17.	72.65	7	72.65	10	0.81	0.34	G-1 USGS	Stevens and others, 1960 p. 78
18.	75.66	1	75.85	1			4 Rhyolitic tuff, ceramic plate	Volborth
19.	76.77	1	76.45	1			1 Rhyolitic tuff, Fe plate	Volborth

The highest gravimetric value for Syenite 1[a] was selected here because of the usual negative bias in silica determination. Relative deviations of these X-ray results from the gravimetric values were calculated, assuming $\bar{x} = 52\%$, $\bar{x} = 65\%$, and $\bar{x} = 77\%$ SiO_2, to cover the range of actual rocks covered by this investigation:

$$C_{52\%} = 1.17$$
$$C_{65\%} = 0.94$$
$$C_{77\%} = 0.79,$$

and accordingly relative errors:

$$E_{52\%} = 0.31$$
$$E_{65\%} = 0.25$$
$$E_{77\%} = 0.21$$

A graph (fig. 18) has been prepared which indicates the relative deviation of X-ray spectrographic silica from gravimetric silica for this type of rocks. It is fully realized that we are not dealing with homogeneous populations. This curve is only intended as an approximate guide.

The experiments above were all performed on the iron-plate ground powders (with one exception) from which the gravimetric SiO_2 was determined. Ten ceramic-ground powders were now similarly analyzed for SiO_2 contamination in each rock separately (column 3, table 6). Three pellets were made in each case. All X-ray data are expressed in this table to the nearest 0.05 percent. Figure 5 shows the relation of composition of these two different powders. In this graph the points corresponding to the iron-plate-ground material were placed in their proper positions according to intensity. All but two of these samples showed higher, but variable silica. Both deviating samples are biotite-rich granites, which explains their anomalous behavior. The arithmetic mean of the eight positive deviations was found to be:

$$\bar{x}_{+d} = 0.46\% \ SiO_2,$$

TABLE A6

Comparison of all SiO_2 Determinations on Powders in Weight Percent

	SiO_2 Content (wt. percent)						
Sample	Gravimetric	X-ray Fe Plates	X-ray Cer. Plates	column 3 minus 2	Fe Plates X-ray coarse powder	Cer. Plates X-ray coarse powder	Anal. powders X-ray
	1	2	3	4	5	6	7
7 Basalt	52.12	52.45	53.20	+0.75	54.05	52.90	53.55
W-1 Diabase	52.64				52.64		52.50 (20 min)
3 Basalt	53.24	52.75	53.10	+0.35	53.35	53.80	53.55
5 Andesite	54.79	55.60	56.45	+0.85	54.70	54.60	56.75
6 Andesite	57.60	57.45	58.10	+0.65	57.10	57.00	57.15
8 Andesite	57.83	57.05	57.50	+0.45	57.95	58.30	58.00
2 Andesite	59.05	58.20	58.40	+0.20	57.15	57.90	57.85
50 Adamellite	64.63	64.90	63.85	-1.05	66.45	no pellet	no pellet
16/20 Granite	68.06	67.85	68.20	+0.35	70.55	no pellet	no pellet
24/36 Granite	68.23	69.30	69.05	-0.25	70.75	70.80	no pellet
G-1 Granite	72.65	72.00 (40 min)	72.65 (10 min)		72.65		72.00 (20 min)
4 Rhyolite tuff	75.66	no pellet	75.85		76.60	76.90	no pellet
1 Rhyolite tuff	76.77	76.45	76.55	+0.10	no pellet	no pellet	78.60
Syenite 1[a]	59.65	60.65			60.70		
Albite BS-99	68.66	68.55					
9 Andesine	56.10	56.20					

indicating possible introduction of silica to the samples. However, part of the relative increase of intensity may be due simply to the absence of metallic iron in this case.

Since most of these positive deviations are much above four relative deviations of the method, it can be assumed here with 95 percent confidence that they represent true variations in intensity due to different types of contamination introduced by the mullite plates versus steel plates used in the Braun or Bico pulverizer. These variations would be characteristic of each rock, the distance of rotating plate surfaces, the rotating speed, grinding time, and finally the plate material.

Two more analytical tests were performed. The coarse powders of both grinding procedures were pelletized directly without the 1 hour per gram grind. These coarse powders are difficult to press and break easily, and biotite flakes about 1mm in diameter can be seen on the surfaces of the granitic powders. As a result, SiO_2 content given in columns 4 and 5 of table 6 shows a somewhat larger scatter, but agrees in general. It has to be emphasized that these data represent only one coarse grained pellet and one series of counts, so that occasional larger deviations from the gravimetric results are to be expected. The largest single deviation from gravimetric percentage was observed in this group, and amounted to 2.57 percent SiO_2 (sample 24/36, a granite with over 6 percent biotite).

Finally, the remains of some of the iron-plate-ground powders originally used for gravimetric analysis of these rocks, and retained for control, also were pelletized and analyzed. These powders were almost as coarse as the powders in columns 4 and 5 in table 6, and were pulverized by this author for only about 5 minutes per gram by hand in an agate mortar to avoid possible oxidation of ferrous iron. Only one pellet was made of each of the 7 powders so available. Column 6 in table 6 contains these analyses. Considering the single nature of these determinations, they compare satisfactorily with the

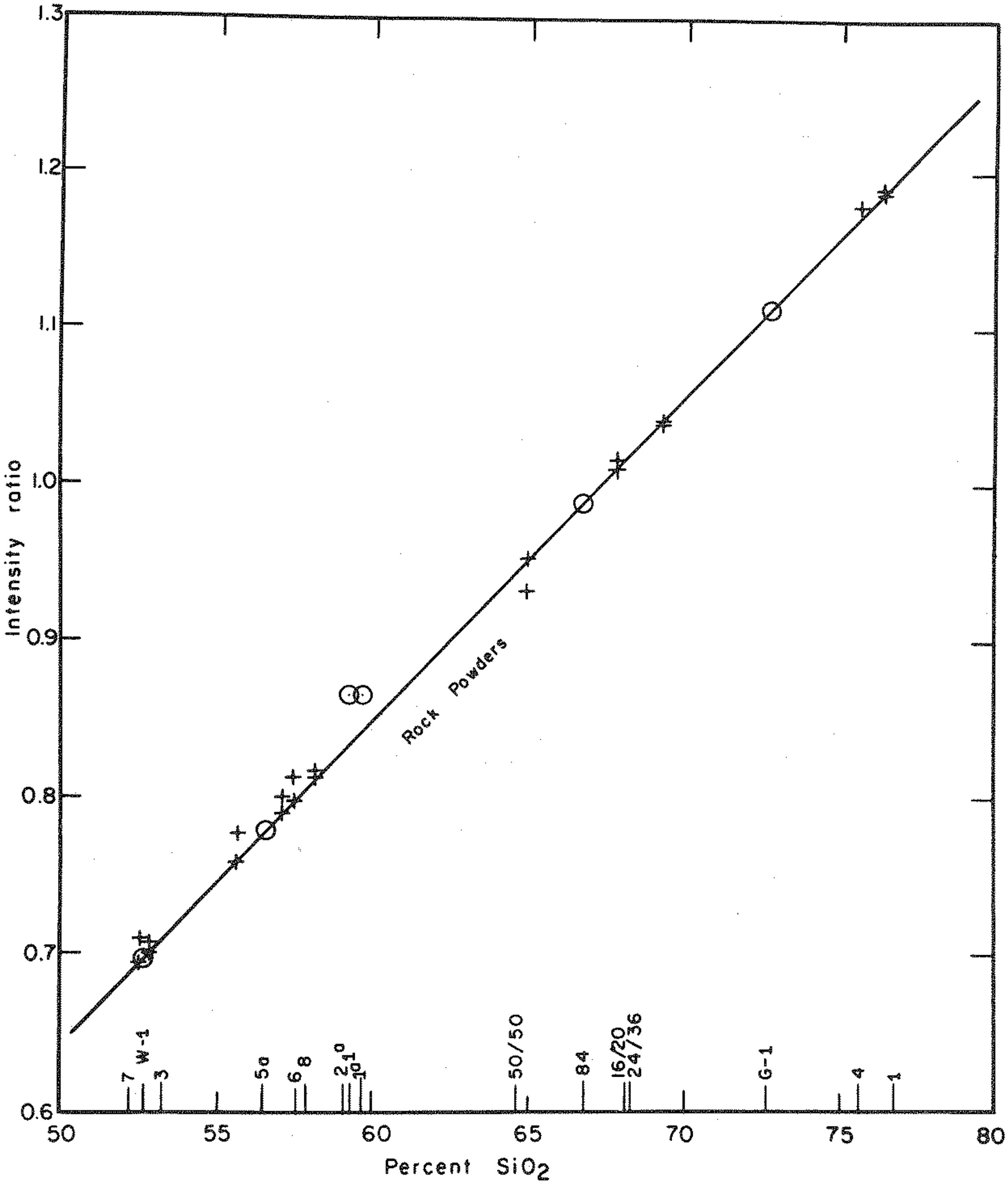


FIGURE A5. Same calibration curve as Figure 4, but with the points corresponding to rocks ground by iron plates moved horizontally to coincide with the calibration curve, and the points corresponding to rocks ground by ceramic plates moved a corresponding distance horizontally. Distance between the pairs of points demonstrates the SiO_2 contamination due to grinding by ceramic plates.

other data, proving that representative splits of the same powders were used originally for the gravimetric work. Powders of samples 1, 2, and 4 in this group have been treated with a hand magnet to remove the iron and, therefore, are not directly equivalent to the other members in their row.

Two hundred and thirteen different rock pellets representing 56 different rock and mineral powders were analyzed for silica during this study, none were discarded because of "high" or "low" readings, and only those with broken surfaces were abandoned. Therefore, in evaluating this experiment, table 6 should provide the best proof of the reproducibility and accuracy of silicate analyses of different rock powders by one person using this method, and give perhaps an indication of the accuracy of such procedures as compared with gravimetric work.

Because of the vacuum used, it was first considered necessary to recalculate all values on a moisture-free basis. This would require, however, a change in the position of the "as received", recommended G-1 and W-1 standard points. Since no recommended values on moisture-free basis were provided by Stevens and others (1960), and because the arithmetic means of preferred values given on moisture-free basis are less than the recommended "as received" values, this recalculation would have made little sense. Since the distribution of analyzed rock points is random, and is equal on both sides of the calibration curve, this recalculation could not have had much significance. Besides, better confidence in chemical results on rocks analyzed in this laboratory would be required.

A statistical test of precision and accuracy, disregarding the effects of grain size and of contamination introduced by different grinding procedures, was based on 56 different powders represented in table 6. In this test powders ground by different media, powders of different grain size, as well as powders of standards and secondary standards, were considered to be different rock powders. All the gravimetric analyses available were assumed to represent the arithmetic means, and the negative or positive deviations for each of the 56 powders were calculated (table 7). Pellets representing the powders were selected at random.

TABLE A7

Deviations of SiO_2 Percentages from the Gravimetric Percentages in Table 6.
Columns numbered as in Table 6.

Sample	2	3	5	6	7
7 Basalt	+0.33	+1.08	+1.93	+0.78	+1.43
W-1 Diabase	-	-	0.00	-	-0.14
3 Basalt	-0.49	-0.14	+0.09	+0.56	+0.31
5 Andesite	+0.81	+1.66	-0.09	-0.19	+1.96
6 Andesite	-0.15	+0.50	-0.50	-0.60	-0.45
8 Andesite	-0.78	-0.33	+0.12	+0.47	+0.17
2 Andesite	-0.85	-0.65	-1.90	-1.15	-1.20
50 Adamellite	+0.27	-0.78	+1.82	-	-
16/20 Granite	-0.21	+0.14	(+2.49)	-	-
24/36 Granite	+1.07	+0.82	(+2.52)	(+2.57)	-
G-1 Granite	-0.65	0.00	0.00	-	-0.65
4 Rhyolite tuff	-	+0.19	+0.94	+1.24	-
1 Rhyolite tuff	-0.32	-0.22	-	-	+1.83
Syenite 1[a]	+1.00	-	+1.05	-	-
BS-99, Albite	+0.11	-	-	-	-
9 Andesine	+0.10	-	-	-	-

In the case of the standards G-1 and W-1, the intensity ratios of pellets chosen coincided on our calibration curve with the preferred values given in Stevens and others (1960).

This test gives us a general picture of the kind of results to be expected from this method if all the different varying factors of grinding contamination and grain size distribution are disregarded.

Only five percent (three analyses) of the 56 performed, deviated more than 2 percent (+2.49, +2.52, +2.57 percent, table 7) from the gravimetric percentages. All of these pellets were composed of coarse biotite-rich rocks. A clearly detectable positive bias in table 7 is unquestionably due to the above described introduction of SiO_2 from the ceramic plates, the slightly higher intensity of pressed coarser rock powders (table 2), and because the gravimetric analysis was originally performed on iron plate ground material.

The three analyses were discarded as unacceptable, and the remaining 53 deviations (in percent) were treated statistically (n = 53):

$$S = 0.89$$

$$s_{\bar{x}} = 0.12,$$

and accordingly the relative deviations and errors representing the SiO_2 percentages encountered are:

$$C_{52\%} = 1.71 \qquad E_{52\%} = 0.24$$

$$C_{65\%} = 1.37 \qquad E_{65\%} = 0.19$$

$$C_{77\%} = 1.15 \qquad E_{77\%} = 0.16$$

This permits us to conclude that if contamination introduced by grinding, and intensity changes due to different grain sizes, are disregarded, the uncertainty of a single observation in 95 percent of all analyses made, would be 0.89 (in percent), in relation to gravimetric data, which were here assumed to be correct. This is an indication of the accuracy of this method when applied to a heterogeneous group of rock powders, and based only on standards G-1 and W-1.

The symmetrical distribution of all points on both sides of the calibration curve, indicates a greater accuracy of X-ray work based on G-1 and W-1, than the accuracy of single gravimetric determinations.

ALUMINUM AS Al_2O_3

The determination of aluminum presents several problems as expected. In gravimetric procedure, alumina is determined by difference from the R_2O_3 group. Errors made in the titration of Fe, precipitation of P_2O_5, colorimetric determination of TiO_2, and in the determination or omission thereof of some other constituents, such as zirconium and the lanthanides, all are contributing factors to the uncertainty of the gravimetric alumina determination. When X-ray spectrographic determinations of this oxide are done, one has to be aware of these facts, and not accept the uncorrected gravimetric data.

Instrumental conditions used in the spectrographic determination of alumina are listed in table 3.

X-ray spectrographic determination of alumina in silica-rich matrix with varying silica content presents a problem due to the enhancement of aluminum radiation by silicon and the biotite effect in G-1. The calibration curve corrected for this effect is given in figure 6. This enhancement effect interferes with the accuracy of alumina determination in plutonic rocks because, as a rule, the more siliceous members carry less alumina and

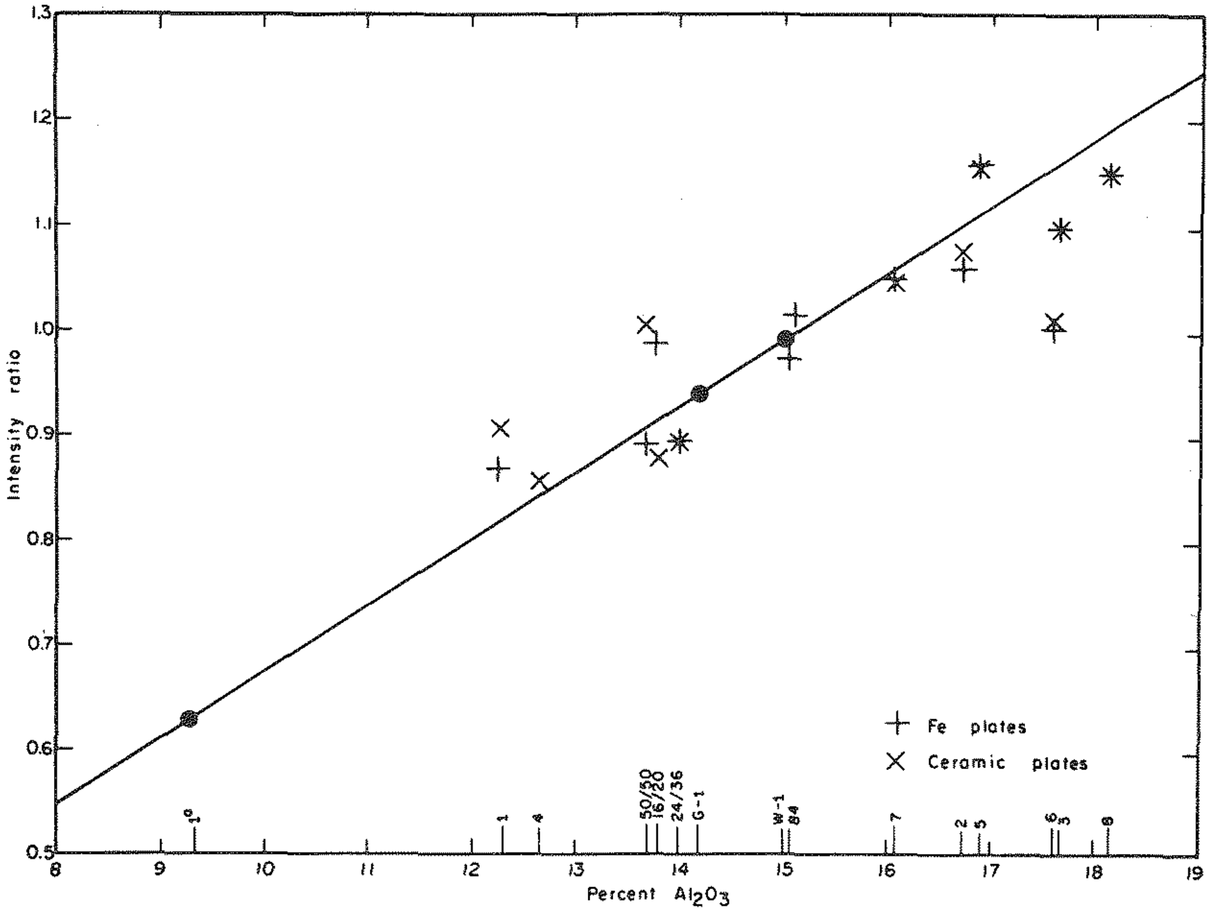


FIGURE A6. Calibration curve for X-ray spectrographic determination of Al_2O_3, corrected for silicon enhancement and biotite effect. For graphic correction see Figure 8. Standards W-1, G-1, and Syenite 1^a are shown as solid circles.

the more mafic carry more alumina. In addition, although the silica content in these rocks varies from 80 to 40 percent, the alumina content varies only from 10 to 20 percent. Thus the larger and reversely proportional variation of silica percentage increases the enhancement effect on aluminum. This is demonstrated by the fact that in the calibration curve uncorrected for silicon enhancement and biotite effect (figure 7) all points representing silica-rich rhyolitic and granitic rocks occur above the calibration curve, whereas all points representing the silica-poor andesitic and basaltic rocks fall beneath the calibration curve, which is based on W-1 and Syenite Rock 1^a standards, both with comparable amounts of silica (53 and 59 percent respectively). *In the case of finely ground standards G-1 and* W-1, the fact that alumina varies only 0.77 percent, but the silica 20.01 percent, causes a negative almost horizontal calibration curve to emerge (figure 8) in powders with the same grain size distribution.

Before attempting to correct for these interferences, the precision of determination of alumina by X-ray spectrography will be demonstrated. Three rock powder standards, W-1, G-1, and Syenite Rock 1^a, were selected for this purpose. Because of comparable *amounts* of silica in W-1 and Syenite 1^a, and only insignificant biotite, it was assumed that a straight line could be drawn between the intensity ratio points, obtained by counting ten different W-1 pellets and three Syenite 1^a pellets, all pressed from powders as received.

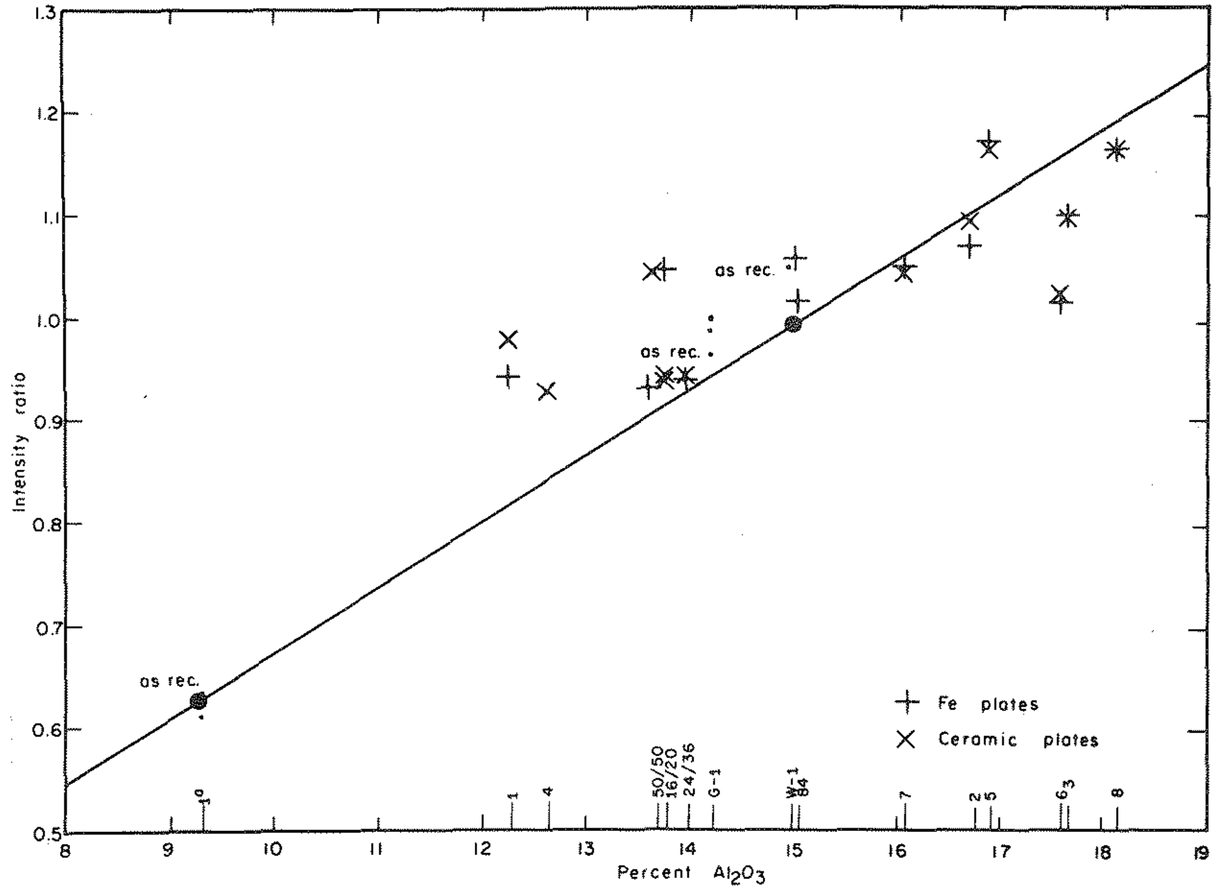


FIGURE A7. Calibration curve for X-ray spectrographic determination of Al_2O_3. Not corrected for Si enhancement and biotite effect. Points marked "as is" represent standard powders as received. Grinding of G-1 for 10, 20, and 40 minutes enhances the intensity, mostly due to biotite effect, as shown by ascending row of dots. In Syenite 1^a further grinding has very little effect, and in W-1, grinding for 40 minutes decreases the intensity. Note that if these three powders, each with widely varying grain-size distribution, are analyzed as received, no correction appears necessary for Si, and one would use an actually incorrect calibration line slope.

Similarly ten G-1 pellets were counted independently and a straight line was drawn through points representing the Syenite 1^a and G-1. From the graphs so obtained the composition of each pellet was determined, and results compiled in table 8 and treated statistically. In terms of relative deviation, these results show much better precision than previously achieved by gravimetric or emission spectrographic methods for alumina (Stevens and others, 1960, p. 71).

With a precision as high as here demonstrated, single determinations on single pellets have great significance, and a study of enhancement, homogeneity, and absorption effects becomes possible.

The flattening effect and reversal of calibration curve of alumina due to enhancement by silica and the biotite effect in G-1, is demonstrated in figures 7 and 8. To correct for this effect, two powders of W-1 and G-1 rocks with 95 percent of particles below 37 microns were counted and intensity ratios plotted versus chemical composition. With the help of a calibration curve drawn to pass through the W-1 and the Syenite 1^a points, the approximate influence of the enhancement of the known difference of 20 percent in silica of W-1 and G-1 was found to be 0.88 percent. Using this figure approximated to one

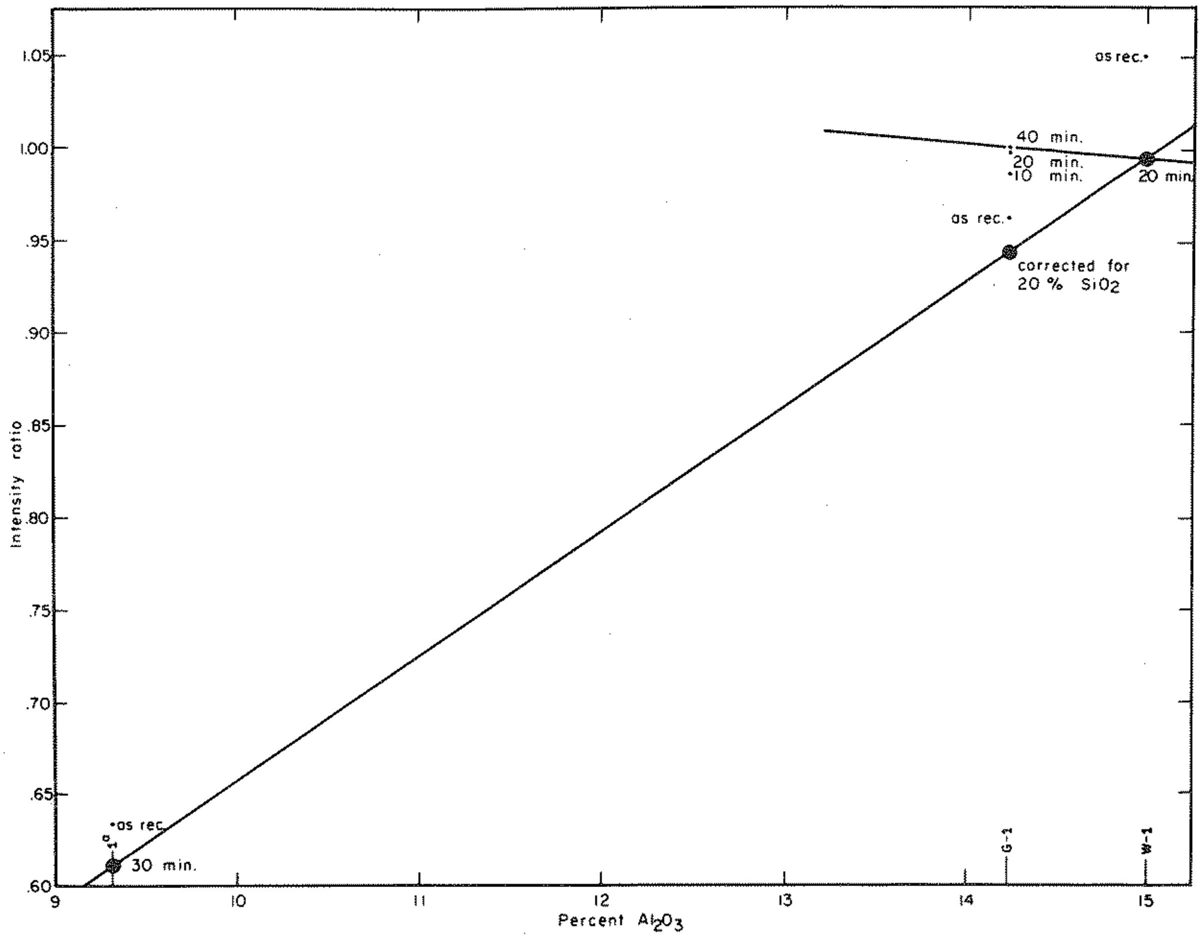


FIGURE A8. Calibration curve for Al_2O_3 showing graphic correction for silica enhancement and biotite effect in rock G-1. See explanation to Figure 7.

percent and assuming a linear relationship, the position of all the other rocks here analyzed was corrected using the ratio of the known difference in percent SiO_2 to the 20 percent between W-1 and G-1 (SiO_2 (G-1) - SiO_2 (W-1) = 20.01% SiO_2).
Example:

$$\frac{6}{20} \times 1 = 0.30 \text{ (Syenite } 1^a\text{)}$$

A comparison of figures 6 and 7 shows the improvement achieved by this procedure. For silica percentages used see table 9 which gives the corrected results for Al_2O_3 in the 26 rock powders so analyzed. In this table, G-1 point has been corrected by 1 percent and not the calculated 0.88 percent for the purposes of consistency only. These results can be regarded as satisfactory when all the factors influencing the alumina determination are taken in account. Twenty-one determinations out of the 24 made are within 1.5 percent of the chemical values. Considering that the chemical values in all but three cases are single determinations by Mr. Vincent and this author, no specific significance should be attributed to them. With additional gravimetric data and mass absorption corrections for Fe and Ca, this picture will improve further. From the distribution of the SiO_2 - corrected points in figure 6, one can see the mass absorption effect in the negative bias of the iron- and calcium-rich mafic rocks. This correction, if introduced, will force these points

TABLE A8

Precision of X-ray Spectrographic Determination of Al_2O_3

Pellets No.	Percent Al_2O_3	Statistical Data
	Syenite Rock 1[a] - 9.32% Al_2O_3	
55	9.31	$\bar{x} = 9.30\%$
56	9.28	$S = 0.021$
57	9.32	$s_{\bar{x}} = 0.01$
		$C = 0.23$
		$E = 0.13$
	W-1 - 15.00% Al_2O_3	
75	14.93	$\bar{x} = 14.99\%$
76	14.85	
77	14.93	$S = 0.12$
78	14.83	
79	15.07	$s_{\bar{x}} = 0.04$
80	14.86	
81	15.14	$C = 0.82$
82	15.07	($C = 4.16$ Stevens and others, 1960)
83	15.10	$E = 0.26$
84	15.13	
	G-1 - 14.23% Al_2O_3	
85	14.08	$\bar{x} = 14.23\%$
86	14.10	
87	14.28	$S = 0.09$
88	14.40	
89	14.27	$s_{\bar{x}} = 0.03$
90	14.25	
91	14.27	$C = 0.63$

closer to the calibration line and should have little or no effect on the granitic rocks. The true magnitude of the Si enhancement can not be here estimated because of the biotite effect.

The iron-rich syenite and diabase points would in this case also move closer to the line, causing a more symmetrical distribution of points on both sides of the calibration curve. These corrections would, however, improve the picture significantly only after more gravimetric data are available; therefore, they were not attempted at present.

The precision achieved should make possible the distinction of contamination effects introduced by ceramic and iron plate grinding, and indeed in the majority of cases (fig. 6 and table 9) the intensities for aluminum are greater or equal for the mullite ground powders, but the relatively poor accuracy, due to the multitude of interfering factors, obscures the contamination effects. Mass absorption corrections for iron and calcium are apparently necessary to bring out the slight contamination differences.

Homogeneity effects due to variations in grain size of different minerals are clearly detectable in the mica-rich rocks and in the effects of grinding demonstrated in figure 8.

TABLE A9

Comparison of X-ray and Gravimetric Data for Al_2O_3 and Corrections Introduced

Rock (Fe)-iron plates (Cer)-cer. plates	Al_2O_3 Percent		Corrections Applied	SiO_2 Percent	Analyst, Chemical
	Chemical	X-ray			
Syenite 1[a]	9.32	9.30	-0.30	59	Nonmetall. Std. Comm. Report, 1961
Rhyolite 1 (Fe)	12.29	13.05	-1.15	76	Volborth
Rhyolite 1 (Cer.)		13.70	-1.15	76	
Rhyolite 4	12.67 (Fe)	12.90 (Cer.)	-1.15	76	Volborth
Adamellite 50 (Fe)	13.71	13.40	-0.60	65	Vincent
Adamellite 50 (Cer.)		15.20	-0.60	65	
Granite 16/20 (Fe)	13.79	14.95	-0.75	68	Vincent
Granite 16/20 (Cer.)		13.25	-0.75	68	
Granite 24/36 (Fe)	13.99	13.47	-0.75	68	Vincent
Granite 24/36 (Cer.)		13.47	-0.75	68	
G-1	14.23	14.15	-1.00	73	Stevens and others, 1960
W-1	15.00	15.00	0.00	53	Stevens and others, 1960
Granite 84 (Fe)	(15.06)	15.37	-0.70	67	April, 1962 (Baird, X-ray)
Granite 84 (Fe)	(15.06)	14.70	-0.70	67	August, 1962 Pica (Baird, X-ray)
Basalt 7 (Fe)	16.08	16.00	+0.05	52	Volborth
Basalt 7 (Cer.)		15.90	+0.05	52	
Andesite 2 (Fe)	17.05	16.00	-0.25	58	Volborth
Andesite 2 (Cer.)		16.32	-0.25	58	
Andesite 5 (Fe)	17.53	17.70	-0.15	56	Volborth
Andesite 5 (Cer.)		17.57	-0.15	56	
Andesite 6 (Fe)	17.58	15.15	-0.20	57	Volborth
Andesite 6 (Cer.)		15.30	-0.20	57	
Basalt 3 (Fe)	17.66	16.70	0.00	53	Volborth
Basalt 3 (Cer.)		16.62	0.00	53	
Andesite 8 (Fe)	18.32	17.48	-0.20	57	Volborth
Andesite 8 (Cer.)		17.48	-0.20	57	

TITANIUM AS TiO_2

Titanium was determined colorimetrically by the peroxide method.

Instrumental conditions for determination of titanium by X-ray emission are listed in table 3.

On four pellets, 51,200 counts were taken in two intervals for the standards, corresponding to a total of 204,800 counts for each determination, and on three pellets for the volcanic rocks, corresponding to 153,600 counts for each determination. For granitic rocks only one pellet was available for analysis in most cases.

Precision of the method was established by the analysis of seven different powders of rocks G-1, W-1, Syenite 1[a], Andesite 5, and Granite 84 (table 10). In all of these cases, the precision was found to be superior to that of the colorimetric or spectrographic methods used in analyzing standards G-1 and W-1 (table 10). Even when compared with

TABLE A10

Precision of the X-ray Spectrographic Determination of TiO_2

Rock	Pellet No.	Percent TiO_2	Statistical Data						Source and Chemical Data
			S	$s_{\bar{x}}$	C X-ray	P/B	E	C Chem.	
W-1 as is	75	1.05				19		4.31	Stevens and others, 1960, p. 80
"	76	1.05	0.01	0.005	0.5		0.2	22.56	Fairbairn and others, 1951
"	77	1.05						18.34	Stevens and others, 1960
"	78	1.07						6.54	Preferred value - Stevens and others, 1960
								15.0	Spectrographic - Stevens and others, 1960
G-1 as is	85	0.19				9		9.23	Stevens and others, 1960, p. 80
"	87	0.21	0.01	0.006	5.0		2.9	23.20	Fairbairn and others, 1951
"	88	0.20						16.59	Stevens and others, 1960
								5.76	Preferred value - Stevens and others, 1960
								12.9	Spectrographic - Stevens and others, 1960
Syenite 1^a	64	0.39				8			Ground
"	65	0.40	0.005	0.003	1.3		0.6		Ground
"	66	0.39							Ground
"	67	0.39							Ground
Andesite 5	96	1.03							Cer. pl.
"	97	1.04							Cer. pl.
"	98	1.03							Cer. pl.
"	95	1.04	0.008	0.003	0.7		0.3		Cer. pl.
Andesite 5	74	1.03							Fe plates
"	75	1.05							Fe plates
"	76	1.04							Fe plates
Granite 84	68	0.52				14			Pica, reground 1 hr.
"	69	0.52	0.005	0.003	1.0		0.5		"
"	70	0.52							"
"	71	0.53							"
Granite 84	61	0.55							Received coarse, 1 hr. ground
"	62	0.54	0.008	0.004	1.5		0.8		"
"	64	0.53							"
"	63	0.54							"
Syenite 1^a	55	0.31							as is
"	56	0.32	0.005	0.003	1.5		0.9		as is
"	57	0.32							as is

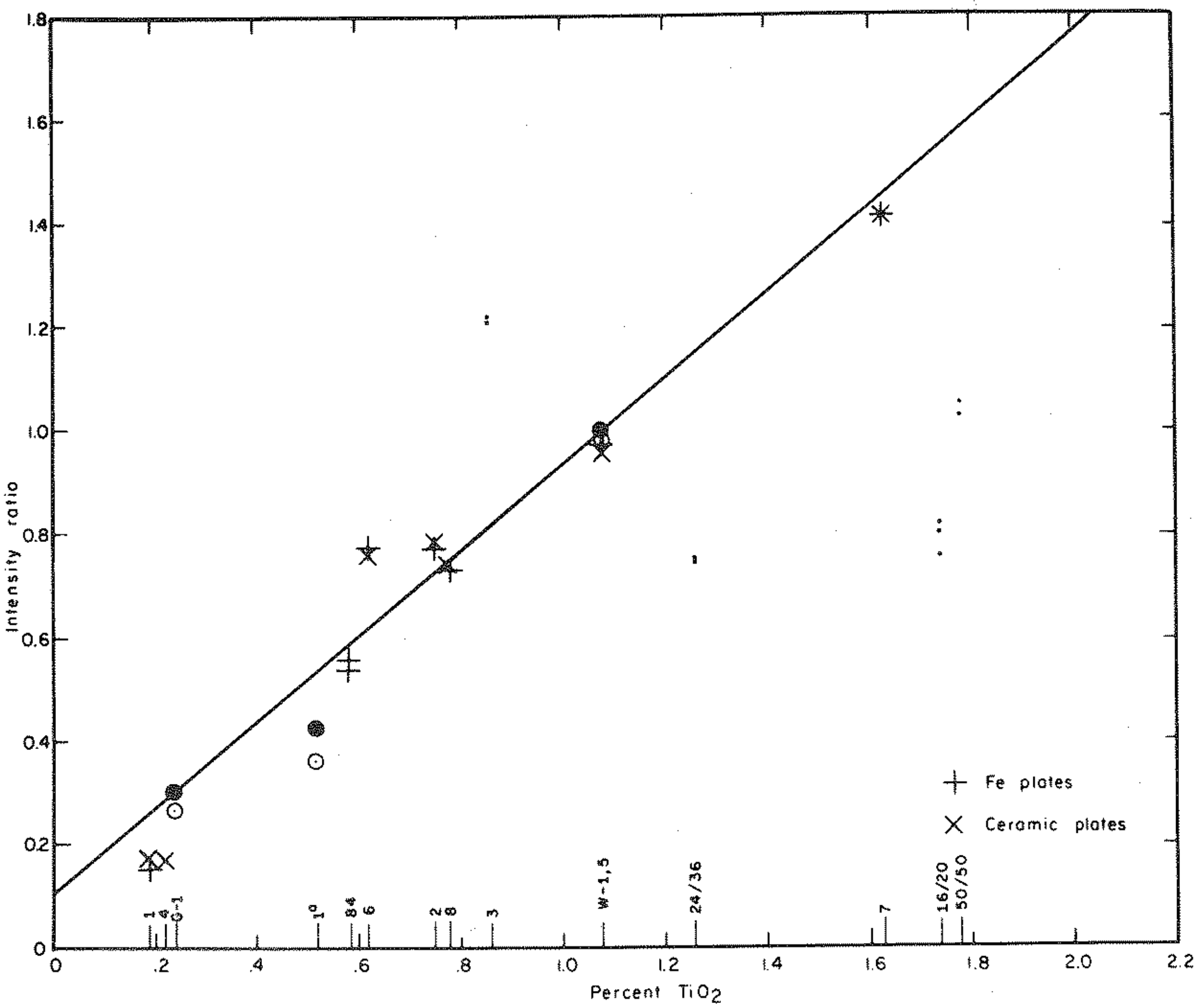


FIGURE A9. Calibration curve for X-ray spectrographic determination of TiO_2. The deviations in intensities shown for the granitic rocks are probably due to an error in colorimetric procedure; see text.

the precision of the direct reading A.R.L. quantometer data of Matocha and Tingle (Stevens and others, 1960), this X-ray spectrographic method gives twice the precision, in terms of relative deviation, for G-1 and eight times better precision for W-1. Here one must emphasize that it takes only five minutes to press the powder, and thirty seconds to one minute repeated twice, to obtain these data for each pellet.

The X-ray spectrographic data obtained from the calibration curve (fig. 9) are compared in table 11 with the colorimetric results. In this table the accepted values are grouped first, and the four rocks with unusually divergent colorimetric values at the end. Critical evaluation of these last data shows consistently high precision of iron- and ceramic ground powders, therefore excluding the possibility of a mixup in samples. Therefore, the negative bias of the colorimetric basalt-3 analysis could be explained by overcorrection for the eight percent of iron present in this rock. The positive bias of the TiO_2 values in all three granite analyses must be due to an analytical or calculating error. Here it is interesting to note that in the modal analysis of granite 16/20 (Volborth, 1962, p. 826) this author has calculated 0.6 percent for TiO_2, which fits much closer to the present X-ray spectrographic result (table 11).

TABLE A11

Comparison of X-ray Spectrographic and Gravimetric Data for TiO_2

Rock Fe-iron plate Cer-cer. plate	TiO_2 Content		Deviation	Analyst, Chemical	Remarks
	Chem.	X-ray			
Rhyolite 1 (Anal.)	0.19	0.13	-0.06	Volborth	Fe removed with magnet, loose powder.
Rhyolite 1 (Fe)		0.06		Volborth	
Rhyolite 1 (Cer.)		0.09			
Rhyolite 1 (Anal.)	0.24	0.11	-0.13	Volborth	Fe removed with magnet, loose powder.
Rhyolite 4 (Cer.)	0.24	0.08		Volborth	
G-1	0.24	0.24	0.00	Stevens and others, 1960	Ground 40 min.
G-1	0.24	0.20	-0.04	"	as received
Syenite 1[a]	0.52	0.40	-0.12	Nonmetall. Std. Comm., Report 1961	Ground 1 hr.
Syenite 1[a]	0.52	0.31	-0.21	"	as received
Granite 84	(0.59)	0.55	(-0.04)	Baird, X-ray	X-ray only, April, 1962.
Granite 84	(0.59)	0.53	(-0.06)	"	Pica, reground, Sept., 1962.
Andesite 6 (Anal.)	0.62	0.80	+0.18	Volborth	Loose powder.
Andesite 6 (Fe)		0.80			
Andesite 6 (Cer.)		0.79			
Andesite 2 (Anal.)	0.75	0.72	-0.03	Volborth	
Andesite 2 (Fe)	0.75	0.80		Volborth	
Andesite 2 (Cer.)		0.81			
Andesite 8 (Fe)	0.78	0.76	-0.02	Volborth	
Andesite 8 (Cer.)		0.77			
Andesite 5 (Fe)	1.08	1.04	-0.04	Volborth	
Andesite 5 (Cer.)		1.03			
W-1	1.08	1.08	0.00	Stevens and others,1960	Ground 20 min.
W-1		1.06			as received.
Basalt 7 (Fe)	1.63	1.58	-0.05	Volborth	
Basalt 7 (Cer.)		1.58			
Basalt 3 (Fe)	0.86	1.32	+0.46	Volborth	colorimetric error?
Basalt 3 (Cer.)		1.34			
Granite 24/36 (Fe)	1.26	0.78	-0.48	Vincent	colorimetric error?
Granite 24/36 (Cer.)		0.78			
Granite 16/20 (Fe)	1.74	0.84	-0.90	Vincent	colorimetric error?
Granite 16/20 (Cer.)		0.86			0.6% TiO_2, modal analysis.
Granite 16/10 (Cer.)		0.79			Different split.
Adamellite 50 (Fe)	1.78	1.14	-0.64	Vincent	colorimetric error?
Adamellite 50 (Cer.)		1.11			

IRON AS Fe_2O_3

Iron is the only element for the determination of which no vacuum was used. Instrumental conditions are listed in table 3. For each pellet, 409,600 counts were accumulated.

Reproducibility figures on some of the rocks analyzed are compared in table 12. Comparison with data by Stevens and others (1960) shows double to tenfold precision in terms of relative deviation. Fine powders give considerably better precision and intensity, therefore the calibration curve in figure 10 was based on fine powders with a dotted line for powders similar to G-1 and W-1 in grain size. Intensity ratios were used, as elsewhere in this paper, to provide workers with the best comparative data possible.

There is little doubt, when comparing the X-ray data with the titrimetric data in table 13, that the X-ray method is actually more accurate when based solely on rocks G-1 and W-1. The deviations of titrimetric determinations are actually equal or even greater than the deviations between the X-ray results and titrimetric results (Syenite 1^a). In one case where double titrimetric analyses were done (Basalt 3), the mean coincides perfectly with the X-ray results. One can therefore say that the scatter of points in figure 10 is more an indication of poor precision and accuracy of the titrimetric procedure, than an indication of the inaccuracy of the X-ray results. The twelve points representing ceramic-ground material group symmetrically on both sides of the calibration curve, indicating no bias in the chemical work. The iron-plate-ground powders show a definite positive bias indicating the introduction of about one percent of iron in terms of iron oxide (1 percent Fe_2O_3) by use of the Braun plates. All of the volcanic rocks are shown to have been contaminated by a nearly equal amount of iron. The granitic rocks are much less contaminated, amounting to about 0.20 percent of iron in terms of iron oxide Fe_2O_3. The precision of this method is so high that these figures may be regarded as guides when grinding similar rocks. This method clearly permits the correction of analyses for introduced iron, based on the dual grinding method presently under study by this author.

The influence of biotite on the iron determination of biotite-rich rocks is treated separately.

MAGNESIUM AS MgO

Magnesium was determined with the Al-target X-ray tube developed by Prof. Burton L. Henke at Pomona College, Claremont, California. Instrumental settings (table 3) were: target excitation 150 milliamperes at 10 kilovolts, flow proportional counter detector chamber voltage 1615 volts, pulse height analyzer base voltage 5.4 volts with a 21 volt window. All blades of the collimator in the Philips Universal Vacuum X-ray Spectrograph were removed as described by Baird and others (1962).

In the first group of analyses the daily decrease in intensity of the Mg radiation accepted by the discriminator necessitated a dedrifting procedure for each count before

TABLE A12

Reproducibility of X-ray Spectrographic Determinations of Fe_2O_3

Rock	Pellet No.	Percent Fe_2O_3	P/B	X-ray Statistical Data (409,600 cts)	Comparative Statistical Data
Rhyolite 1, ground 1 hr.	49	0.40		$S = 0.006$	
	50	0.41		$s_{\bar{x}} = 0.003$	
	51	0.40		$C = 1.4$	
G-1, as rec.	85	1.93	7.3	$n = 9$	G-1, spectrometric
	87	2.03		$\bar{x} = 1.964$	Stevens and others (1960, p. 80.)
	88	1.93		$S = 0.031$	$n = 32$
	89	1.97		$s_{\bar{x}} = 0.010$	$S = 0.055$
	90	1.95		$C = 1.60$	$s_{\bar{x}} = 0.010$
	91	1.97		$E = 0.53$	$C = 2.96$
	92	1.95			$E = 0.52$
	93	1.98			G-1, all anal., Stevens and others (1960)
	94	1.97			$C = 13.90$
Granite 84, ground 1 hr.				$n = 4$	G-1, spectrometric, Stevens and others (1960)
	68	3.72		$\bar{x} = 3.708$	$C = 2.5$
	69	3.70		$S = 0.0096$	
	70	3.71		$s_{\bar{x}} = 0.0048$	
	71	3.70		$C = 0.26$	
				$E = 0.13$	
Andesite 5, ground 1 hr.	95	6.96		$n = 8$	
	96	6.97		$\bar{x} = 6.93$	
	97	6.91		$S = 0.029$	
	98	6.92		$s_{\bar{x}} = 0.010$	
	68	6.91		$C = 0.42$	
	69	6.96		$E = 0.15$	
	70	6.92			
	71	6.89			
Syenite 1[a], ground 1 hr.				$n = 4$	
	64	8.09		$\bar{x} = 8.095$	
	65	8.09		$S = 0.01$	
	66	8.11		$s_{\bar{x}} = 0.005$	
	67	8.09		$C = 0.12$	
				$E = 0.06$	
W-1, as rec.	75	11.03	47.2	$n = 10$	W-1, spectrometric, Stevens and others (1960, p. 80)
	76	11.08		$\bar{x} = 11.10$	$n = 32$
	77	11.15		$S = 0.056$	$S = 0.27$
	78	11.03		$s_{\bar{x}} = 0.018$	$s_{\bar{x}} = 0.05$
	79	11.15		$C = 0.50$	$C = 2.38$
	80	11.15		$E = 0.16$	$E = 0.42$
	81	11.15			W-1, all anal., Stevens and others (1960)
	82	11.15			$C = 2.49$
	83	11.08			W-1, spectrometric, Stevens and others (1960)
	84	11.03			$C = 5.91$

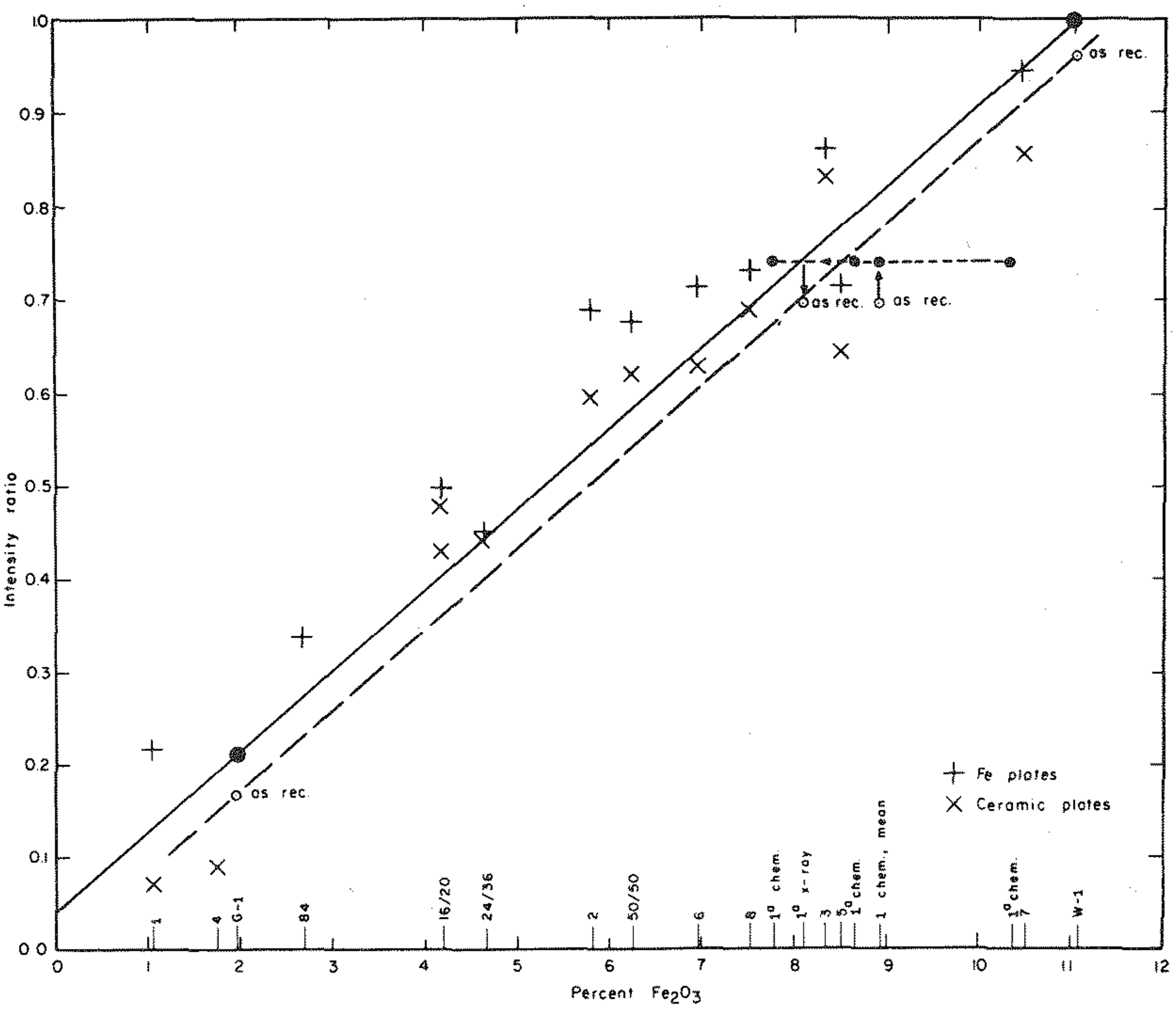


FIGURE A10. Calibration curve for X-ray spectrographic determination of Fe_2O_3. All powders ground by means of iron plates show greater intensity due to contamination by the plates. Medium size solid circles to upper right represent Syenite 1^a standard. Three of these represent independent gravimetric determinations given in the report (1960) of the Nonmetallic Standards Committee of the Canadian Assoc. for Applied Spectroscopy. Another circle represents the mean of those results, and the intensity ratio for finely powdered rock, while the circle beneath represents the intensity ratio for the same rock on an as-received basis. Arrows show the displacement of the last named point if the X-ray values are assumed to be correct. This was done to show the regularity of the grain-size effect on the standards G-1, Syenite 1^a, and W-1. Open circles have for this purpose been connected by a dashed line. The positive bias is apparently due partly to the biotite effect. A good measure of the relative precision of the X-ray spectrographic method is the fact that all four independent values for Syenite 1^a represent a total spread of data equivalent to 0.03 percent, and fall within the circle diameter shown, whereas the gravimetric - colorimetric determinations spread over 2.50 percent.

TABLE A13

Comparison of X-ray Spectrographic and Titrimetric Data for Fe_2O_3

Rock Cer - ceramic ground Fe - iron ground	Fe_2O_3 Content (Percent) Chem.	X-ray	Deviation	Analyst, chemical	Remarks
Rhyolite 1, Cer.	0.74	0.35	-0.39	Volborth, $KMnO_4$	
Rhyolite 1, Fe	1.07	0.84	-0.23		Loose Powder
Rhyolite 1, Fe		2.06			
Rhyolite 4, Cer.	1.05	0.58	-0.47	Volborth, $KMnO_4$	
Rhyolite 4, Fe	1.76	1.84	+0.08	Volborth, $KMnO_4$	Loose Powder
G-1	1.96	1.96	0.00	Stevens and others (1960)	
Granite 84a, Fe	(2.69)	3.46	(0.77)	Baird, X-ray	rec. May, 1962.
Granite 84b, Fe	(2.69)	3.71	(1.02)	Baird, X-ray	rec. Aug., 1962, reground.
Granite 84c, Fe	(2.69)	3.02	(0.33)	Baird, X-ray	rec. Aug., 1962, Pica, as is.
Granite 16/20, Cer.	4.20	5.08	+0.88	Vincent, $KMnO_4$	
Granite 16/20, Fe		5.33			
Granite 16/10, Cer.		4.54			
Granite 24/36, Cer.	4.66	4.68	+0.02	Vincent, $KMnO_4$	
Granite 24/36, Fe		4.72			
Andesite 2, Cer.	6.47	6.42	-0.05	Volborth, $KMnO_4$	
" "	5.82		+0.40	Volborth, $KMnO_4$	
Andesite 2, Fe	5.80	7.47	+1.67	Volborth, $KMnO_4$	
Adamellite 50/50, Cer.	6.26	6.70	+0.44	Vincent, $KMnO_4$	
Adamellite 50/50, Fe		7.36			
Andesite 6, Cer.	6.95	6.79	-0.16	Volborth, $KMnO_4$	
Andesite 6, Fe	6.91	7.78	+0.87	Volborth, $KMnO_4$	
Andesite 8, Cer.	7.52	7.51	-0.01	Volborth, $KMnO_4$	
Andesite 8, Fe	7.42	8.03	+0.61	Volborth, $KMnO_4$	
Syenite 1^a, Fe	7.75		+0.35		
Syenite 1^a, Fe	8.66	8.10	(0.56)	Nonmetall. Std. Comm. report,(1961)	
Syenite 1^a, Fe	10.37		(2.27)		
Basalt 3, Cer.	10.01	9.16	-0.85	Volborth, $KMnO_4$	
" "	8.34		+0.82	Volborth, $KMnO_4$	
Basalt 3, Fe	8.36	9.50	+1.14	Volborth, $KMnO_4$	
Andesite 5, Cer.	8.51	6.96	-1.55	Volborth, $KMnO_4$	
Andesite 5, Fe	8.94	7.80	-1.14	Volborth, $KMnO_4$	
Basalt 7, Cer.	10.50	9.46	-1.04	Volborth, $KMnO_4$	
Basalt 7, Fe	10.56	10.48	-0.08	Volborth, $KMnO_4$	
W-1	11.10	11.10	0.00	Stevens and others (1960)	

it could be plotted on the calibration curve. In the case of magnesium and sodium, this was done graphically by determining the total percentage of the daily drift, and plotting this percentage on the y-axis and the time in minutes on the x-axis of a coordinate net. This, of course, required a time reading simultaneous with each count. Results so obtained are obviously less accurate than the results obtained by the intensity ratio procedure used in this work for other elements. These dedrifted results appear in parentheses in table 15. It should be emphasized that the equipment used was experimental, and the increasing contamination of the Al-target caused a linear decrease in intensity, necessitating periodical cleaning of the target. Two additional reasons for the drift encountered may have been the shifting of the base voltage, and the use of a relatively narrow PHA window. This could be avoided by widening the window.

Two calibration curves were prepared using the intensity ratio procedure. Figure 11 shows concentration of magnesium in the range of 0.2-1.4 percent MgO, and figure 12 the higher concentration in the range of 2.5-4.5 percent. Because in each of these cases only one reliable standard point was available, the calibration curves were drawn so as to fit the path of the least squares passing through the standard point.

The precision of the magnesium analysis was established in rocks W-1 and G-1. Table 14 is a comparison of the precision of this method with other commonly used methods. In W-1, precision is clearly improved in fine-ground samples.

This analytical method for magnesium, in terms of precision and speed, is unquestionably superior to all other conventional methods known to this author. It may be of special significance to people working with cements, limestones, and magnesite, because none of the fast conventional methods have yet been able to give very good results. For example, flame photometric magnesium determination is unsatisfactory; emission spectrographic determination of more than a few percent is unfeasible; gravimetric precipitation as magnesium ammonium phosphate is difficult and tedius when much calcium is present; and finally, the EDTA titration, although fast and satisfactory, requires a knowledge of the amount of calcium present. None of the methods mentioned even remotely approaches the speed of the X-ray spectrographic procedure.

The effect of smaller grain size on the increase of intensity is in the case of magnesium normal, as expected, because here the biotite with its larger surface is contributing to the increase. In addition, most of the magnesium in the diabase W-1 is not in biotite but in pyroxene, but in the granites G-1, 16, 24, and 50, most of the magnesium is contained in biotite. To demonstrate this increase of Mg intensity in biotite-bearing rocks upon further grinding, coarse rock powders of granites 24 and 16 were pelletized and intensity ratios plotted in fig. 11, marked "as received".

Table 15 gives the comparison of X-ray data with the gravimetric results. Magnesium gives the least satisfactory results if the chemical data are considered accurate, and the calibration curve can be regarded as straight line only over a relatively short composition range of 2-3 percent, and the large deviations remain to be explained. In this case the results are of such nature that one can not simply assume the X-ray results to be more accurate. It appears, however, on the basis of the very good coincidence in the low percentage region, and on the basis of the queries of Prof. R. L. Rose, who earlier questioned, on the basis of his petrographic studies, the relatively low MgO percentages obtained by gravimetric methods for the andesites, Nos. 2 and 6, that also in this case the X-ray data are more accurate than the gravimetric data obtained by this author.

Magnesium emits fluorescent radiation of long wave length, which is absorbed by the thinnest surface layers of rock powders or films (Henke, 1961). The main consideration

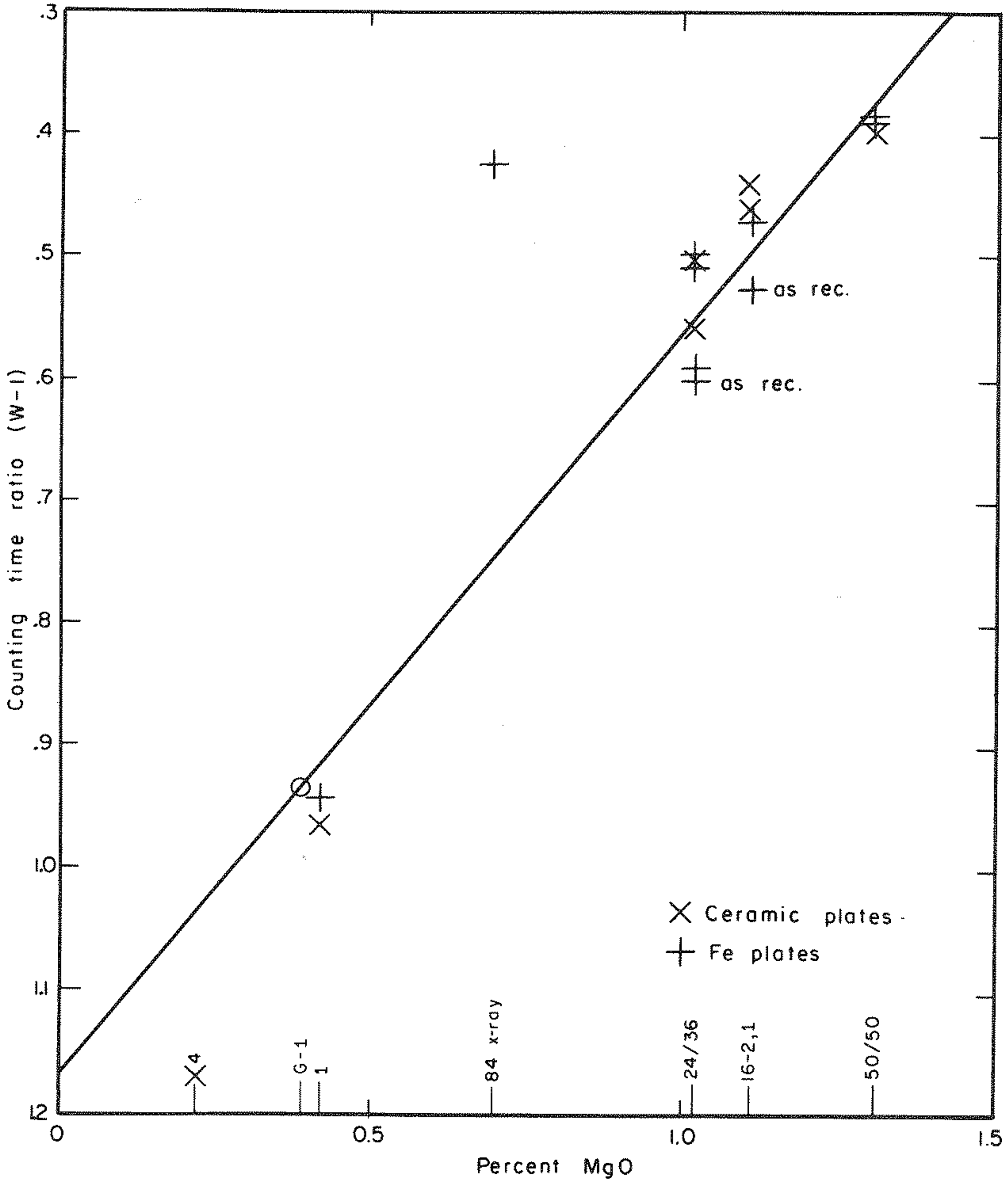


FIGURE A11. Calibration curve for the X-ray spectrographic determination of MgO in the range of 0.2-1.4 percent. The only strongly deviating point is that of Granite 84, which is based not on gravimetric data, but on independent X-ray data of Prof. Baird.

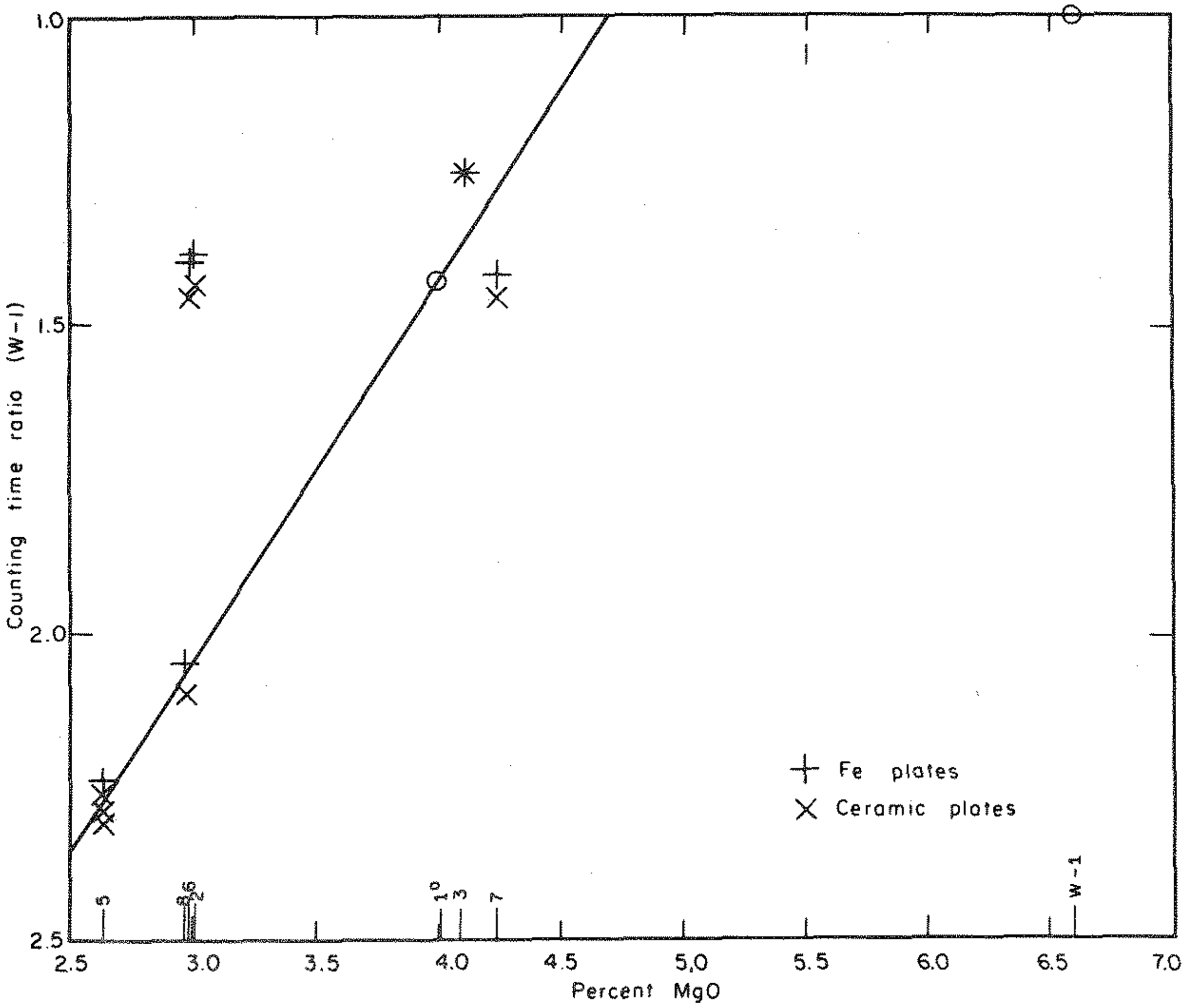


FIGURE A12. Calibration curve for X-ray spectrographic determination of MgO in the 2.5-4.3 percent region. In Andesites number 2 and 6, petrographic evidence indicates more magnesium than gravimetrically determined by this author.

with magnesium, as well as with sodium, is the achievement of perfectly reproducible surfaces, which makes the glass disc pelletizing technique, as described here, of great importance. Equal distribution of grain sizes for all samples analyzed can not be overemphasized in this case.

CALCIUM AS CaO

Instrumental conditions for the X-ray spectrographic determination of calcium are listed in table 3. As can be seen from tables 16 and 17, excellent precision and very good accuracy were obtained for calcium in the range of 0.4 to 11.0 percent, based on single chemical determinations. Figure 13 shows, however, a slight negative bias of gravimetrically-determined(?) calcium in rocks with higher percentages, which could be due to incomplete precipitation as oxalate, because of the necessarily shorter precipitation time allotted (4 instead of 12 hours) for the purpose of avoiding the co-precipitation of magnesium.

TABLE A14

Precision of X-ray Spectrographic Determination of MgO

Rock	Pellet No.	MgO%	X-ray Statistical Data (64,000 total counts)	P/B	Comparative Statistical Data Direct Reading spectrometric	 All grav. anal.:
					Stevens and others (1960)	
W-1, ground			$n = 3$	35	$n = 32$	
95% < 37 micron	38	6.61	$\bar{x} = 6.63$		$\bar{x} = 6.74$	$n = 60$
"	39	6.63	$S = 0.012$		$S = 0.15$	$C = 5.29$
"	40	6.64	$s_{\bar{x}} = 0.007$		$s_{\bar{x}} = 0.027$	spectrogr.:
			$C = 0.17$		$C = 2.28$	
			$E = 0.10$		$E = 0.40$	$C = 3.0$
			$n = 3$			
W-1, as received	41	6.28	$\bar{x} = 6.17$			
"	42	6.14	$S = 0.075$			
			$s_{\bar{x}} = 0.043$			
"	43	6.08	$C = 1.21$			
			$E = 0.70$			
G-1, ground			$n = 3$	7	$n = 32$	$n = 60$
95% < 37 micron	35	0.390	$\bar{x} = 0.389$		$\bar{x} = 0.38$	
"	36	0.385	$S = 0.0004$		$S = 0.008$	$C = 32.15$
			$s_{\bar{x}} = 0.0002$		$s_{\bar{x}} = 0.001$	spectrogr.:
"	37	0.393	$C = 0.11$		$C = 2.03$	
			$E = 0.06$		$E = 0.36$	$C = 6.6$
G-1, as received	47	0.383	$\bar{x} = 0.384$			
"	48	0.385				

In biotite-rich rocks, where most of the calcium is concentrated in plagioclase and sphene, the relative increase, upon grinding, of the surface of biotite, (which usually contains only traces of CaO), causes a decrease of the calcium intensity, as explained in the chapter on the biotite effect. This effect is clearly detectable, and in the case of G-1, where it is most pronounced, it amounts to a difference of 0.11 percent CaO affecting, however, the calibration curve only insignificantly. In single determinations of high accuracy, this biotite effect has to be taken in account in deciding what calibration curve to use, and the knowledge of modal percentage of biotite would be desirable.

The superiority of the X-ray spectrographic determination of calcium as compared to other conventional methods is obvious.

In terms of relative deviation the X-ray method is five to twenty times more precise than any of the conventional methods for determination of calcium.

POTASSIUM AS K_2O

Instrumental settings for the X-ray spectrographic determination of potassium are listed in table 3. The ratio of counting time of permanently positioned G-1 powder to that of the unknown powder, was plotted on the calibration curve. This curve was made by counting four pellets for each of the standards G-1, W-1, and Syenite 1^a, pressed as received (total counts: 409,600). The Syenite 1^a point deviated only by 0.07 percent

TABLE A15. Comparison of X-ray Spectrographic and Gravimetric Data for MgO

Rock, Fe, Cer. - ground	MgO Content (percent) Chemical	MgO Content (percent) X-ray	Deviation	Analyst, Chemical
Rhyolite 4, Cer.	0.22	(0.22)	(0.00)	Volborth
		0.22	0.00	
Rhyolite 1, Fe	0.42	(0.40)	(-0.02)	Volborth
		0.38	-0.04	
Rhyolite 1, Cer.		(0.39)		
		0.34		
G-1	0.39	(0.39)	(0.00)	Stevens and others (1960)
		0.39		
Andesite 5, Fe	2.66	(-1.80)	(-0.86)	Volborth
		2.66	0.00	
		2.68	+0.02	
Andesite 5, Cer.		(1.40)		
		2.66		
		2.60		
		2.58		
Andesite 8, Fe	2.97	(2.50)	(-0.47)	Volborth
		3.00	+0.03	
Andesite 8, Cer.		(1.43)		
		2.93		
Andesite 6, Fe	2.99	(5.00)	(+2.01)	Volborth
		4.05	+1.06	
Andesite 6, Cer.		(4.80)		
		3.95		
Andesite 2, Fe	3.01	(4.95)	(+1.94)	Volborth
		4.08	1.07	
Andesite 2, Cer.		(4.70)		
		3.98		
Basalt 3, Fe	4.08	(5.60)	(+1.52)	Volborth
		4.30	+0.22	
Basalt 3, Cer.		(5.50)		
		4.30		
Basalt 7, Fe	4.24	(4.95)	(+0.71)	Volborth
		4.03	-0.21	
Basalt 7, Cer.		(4.92)		
		3.95		
W-1	6.61	(6.61)	(0.00)	Stevens and others (1960)
Granite 24/36, Fe	1.02	1.11	+0.09	
	1.02	1.09	+0.07	
	1.02	0.96	-0.06	
Granite 24/36, Fe, as is	1.02	0.94	-0.08	
Granite 24/36, Cer.	-	1.10		
	-	1.01		
Granite 16/20, Fe	1.11	1.15	+0.04	
Granite 16/20, Fe, as is		1.06		
Granite 16/20, Cer.		1.20		
		1.17		
Granite 50, Fe	1.31	1.30	-0.01	Volborth
	1.31	1.28	-0.03	Volborth
Granite, 84		1.23		Volborth
		0.70		Baird, X-ray
Syenite 1[a]	4.02	4.02	0.00	Nonmetall. Std. Comm. (1960)

TABLE A16. Precision of the X-ray Spectrographic Determination of CaO

Rock	Pellet No.	CaO Percent	X-ray Statistical Data (409,600 cts)	P/B	Comparative Statistical Data; Remarks
G-1, as rec.	85	1.46	$n = 4$	15	Stevens and others (1960, p. 80.), spectr.:
	87	1.46	$\bar{x} = 1.458$		$n = 32$
	88	1.46	$S = 0.005$		$S = 0.080$
	89	1.45	$s_{\bar{x}} = 0.0025$		$s_{\bar{x}} = 0.014$
			$C = 0.34$		$C = 5.92$
			$E = 0.17$		$E = 1.04$
Andesite 5	95	7.14		32	Pellets 95-98 and 68-71 were pressed and counted on different days.
	96	7.16	$n = 8$		
	97	7.16	$\bar{x} = 7.145$		
	98	7.15	$S = 0.017$		
	68	7.15	$s_{\bar{x}} = 0.006$		G-1, Stevens and others (1960), all anal.:
					$C = 8.95$, $n = 60$.
	69	7.16	$C = 0.24$		pref. values:
					$C = 5.05$.
	70	7.12	$E = 0.08$		
	71	7.12			
Syenite 1^a	64	9.34	$n = 4$	34	G-1, Stevens and others (1960), spectr.:
					$C = 13.0$
	65	9.37	$\bar{x} = 9.36$		
	66	9.37	$S = 0.014$		
	67	9.36	$s_{\bar{x}} = 0.007$		W-1, Stevens and others (1960), all anal.:
					$C = 1.46$, $n = 60$.
			$C = 0.15$		pref. values:
					$C = 0.74$
			$E = 0.08$		spectr. $C = 6.3$
W-1, ground	114	10.94		34	
W-1, as rec.	75	10.91	$n = 10$		Stevens and others (1960, p. 80.), spectr.:
W-1, as rec.	76	10.94	$\bar{x} = 10.939$		$n = 32$
W-1, as rec.	77	10.93	$S = 0.014$		$S = 0.25$
	78	10.96	$s_{\bar{x}} = 0.005$		$s_{\bar{x}} = 0.04$
	79	10.94	$C = 0.13$		$C = 2.28$
	80	10.94	$E = 0.04$		$E = 0.40$
	81	10.93			
	82	10.96			
	83	10.94			

K_2O from the straight calibration line drawn between G-1 and W-1 on as received basis, figure 14. The three powders, G-1, W-1, and Syenite 1^a, were also further ground and intensity ratio plotted on the same diagram (circles). In all cases a slightly lower intensity was obtained. It was immediately obvious that reproducibility of pellets was so high that only four pellets were necessary to arrive at an identical mean for K_2O. To prove this, four pellets of five rocks, G-1, W-1, Syenite 1^a, Andesite 5, and Granite 84, were counted and the results statistically interpreted in table 18. One can see that this X-ray spectrographic method is superior to the gravimetric and spectrographic methods used in analyzing the G-1 and W-1 powders. In terms of relative deviation in G-1 and W-1, the reproducibility is ten times better. Even if only the preferred values of Stevens and others (1960, p. 76) are considered, the X-ray spectrographic method is superior.

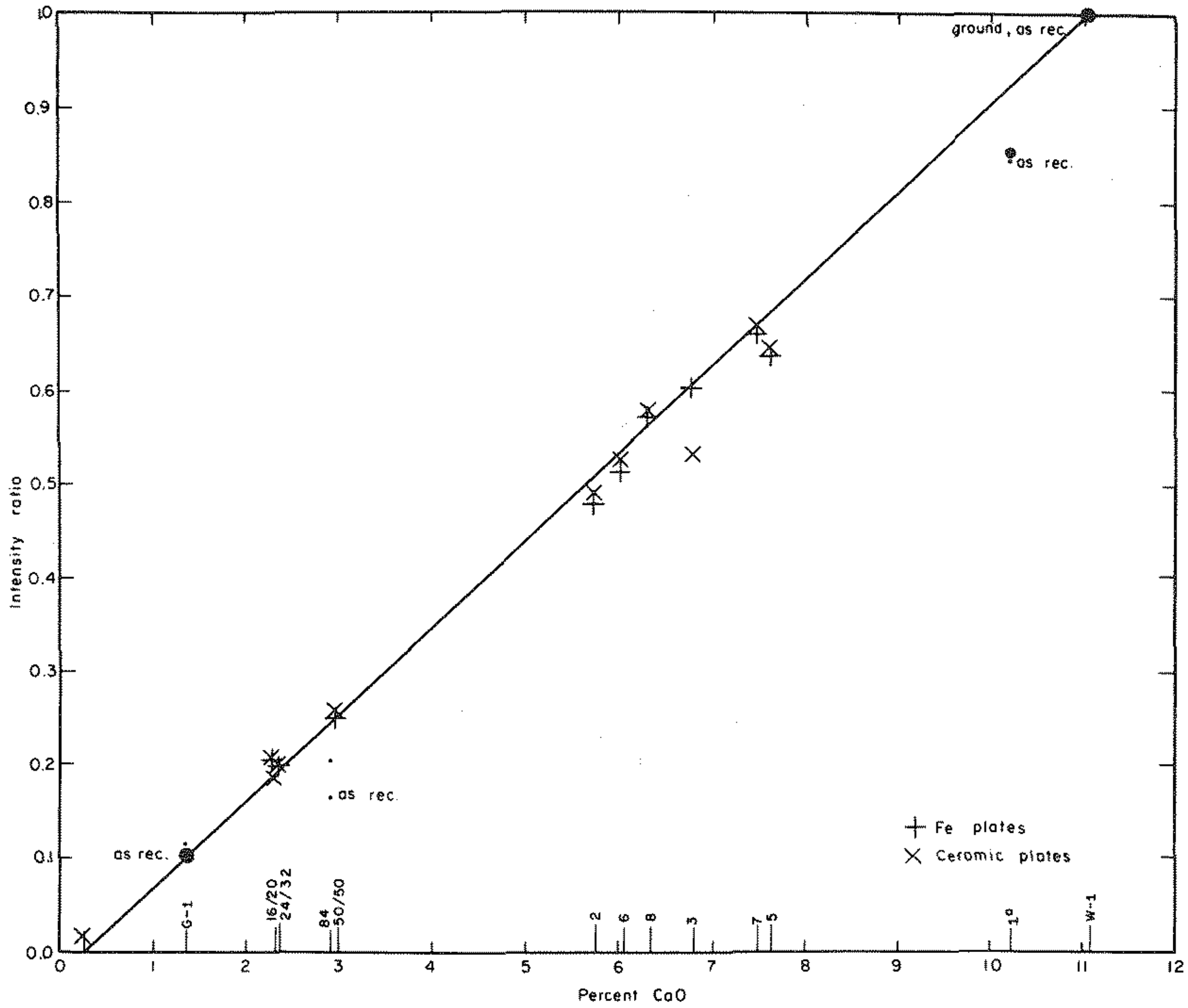


FIGURE A13. Calibration curve for X-ray spectrographic determination of CaO. Two dots corresponding to the Granite 84 are based on X-ray analysis by Prof. Baird. These two samples come from entirely different grinds and have been received in May and August, 1962, respectively.

Twenty seven different powders, usually pressed in three pellets each (307,200 total count), were counted and intensity ratios plotted on the calibration curve, figure 14, with results represented in table 19. The symmetrical distribution of all calibration points on figure 14 may indicate gravimetric and flame photometric errors due to dilution, contamination, fluxing, and the multiple handling necessary in these procedures, rather than inaccurate X-ray data. It is the author's opinion that with the improvement of the absolute methods, and with additional chemical analyses of these rocks, closer agreement will be achieved between the gravimetric and flame photometric percentages and the X-ray spectrographic data. On this basis, it seems to be possible to assume at least equal accuracy for the X-ray spectrographic determination of K_2O as compared to the conventional methods, when based on rocks G-1 and W-1. As an indication of the accuracy of these X-ray spectrographic data, the positive and negative deviations of the actual rock powders analyzed, were treated statistically assuming the gravimetric and flame photometric data to be correct. The gravimetric results on twelve samples obtained by precipitating K_2PtCl_6 and $KClO_4$, were separated from the flame photo-

TABLE A17. *Comparison of X-ray Spectrographic and Gravimetric Data for CaO*

Rock Cer. - ceramic plates Fe - iron plates	CaO Content (percent)		Deviation	Analyst, Chemical
	Chemical	X-ray		
Rhyolite 1, Fe	0.27	0.42	+0.15	Volborth
Rhyolite 1, Cer.		0.42		
G-1, ground	1.36	1.36	0.00	Stevens and others (1960)
G-1, as rec.	1.36	1.47	+0.11	Stevens and others (1960)
Granite 16/20, Cer.		2.48		
Granite 16/20, Fe	2.32	2.45	+0.13	Vincent
Granite 16/10, Cer.		2.27		
Granite 24/36, Cer.		2.38		
Granite 24/36, Fe	2.36	2.40	+0.04	Vincent
Granite 84, Fe	(2.92)	2.00		Baird, X-ray; May, 1962.
Granite 84, Pica	(2.92)	2.43		Baird, only Pica ground, Aug., 1962.
Adamellite 50/50, Cer.		3.00		
Adamellite 50/50, Fe	2.98	2.94	-0.04	Vincent
Andesite 2, Cer.		5.40		
Andesite 2, Fe	5.76	5.47	-0.29	Volborth
Andesite 6, Cer.		5.87		
Andesite 6, Fe	6.04	5.75	-0.29	Volborth
Andesite 8, Cer.		6.42		
Andesite 8, Fe	6.36	6.34	-0.02	Volborth
Basalt 3, Cer.		5.82		
Basalt 3, Fe	6.82	6.71	-0.09	Volborth
Basalt 7, Cer.		7.40		
Basalt 7, Fe	7.51	7.29	-0.22	Volborth
Andesite 5, Cer.		7.14		
Andesite 5, Fe	7.65	7.06	0.41	Volborth
Syenite 1[a]	10.24	9.37	0.87	Nonmetall. Std. Comm. report, (1961); ground
Syenite 1[a]	10.24	9.27		Nonmetall. Std. Comm. report, (1961); as received
W-1, as received	10.94	10.94	0.00	Stevens and others (1960)
W-1, ground	10.94	10.94	0.00	Stevens and others (1960)

metric results by Harold A. Vincent, done on five samples (table 20), this table shows that when the precision and accuracy of a comparative method improve, the coincidence of X-ray data increases, indicating a possibility that the use of additional standards would result in still greater accuracy.

SODIUM AS Na_2O

Sodium oxide was determined with the prototype Al-target X-ray tube developed by Prof. Burton L. Henke at Pomona College (Henke, 1961, 1962; Baird and others, 1962). The Philips Universal Vacuum X-ray Spectrograph, pulse height analyzer, and panel were used. Excitation, dispersion, and detection conditions were 150 ma and 10 kv for the target, with 1635 volts for the flow-proportional detector tube, and 6 volt base with 18 volt window of the pulse height analyzer. A gypsum crystal was used as dispersing medium. Sodium K_α was measured at $2\theta = 103.09°$ (table 3).

As shown previously by Baird (1962) and Henke (1961, 1962), the soft sodium radiation is mainly a surface phenomenon, and therefore should be greatly affected by the reproducibility of the irradiated surface. For this purpose a statistical study was conducted to

TABLE A18

Precision of X-ray Spectrographic Determination of K_2O

Rock	Pellet No.	Percent K_2O	Statistical Data S	$s_{\bar{x}}$	C	E	P/B	Chem. C	Source and Chemical Data
G-1, as rec.	87	5.43							
G-1, as rec.	85	5.48	0.04	0.020	0.74	0.37	98	8.41	Fairbairn and others (1951)
G-1, as rec.	88	5.40						7.26	Stevens and others (1960)
G-1, as rec.	89	5.40						2.74	Stevens and others (1960), pref. values
W-1, as rec.	75	0.64						11.7	Stevens and others (1960), spectrogr.
W-1, as rec.	76	0.64	0.01	0.005	1.6	0.8	11	24.61	Fairbairn and others (1951)
W-1, as rec.	77	0.64						19.00	Stevens and others (1960)
W-1, as rec.	78	0.62						4.68	Stevens and others (1960), pref. values
Syenite 1^a, as rec.	64	2.68							
"	65	2.71	0.015	0.008	0.6	0.3	36		
"	66	2.68							
"	67	2.68							
Andesite 5	95	2.37							
Andesite 5	97	2.35	0.15	0.008	0.6	0.3			
Andesite 5	98	2.38							
Andesite 5	96	2.35							
Granite 84	68	3.59							
Granite 84	69	3.52	0.03	0.015	0.84	0.42			
Granite 84	70	3.59							
Granite 84	71	3.58							

determine the reproducibility of Albite BS-99 pellets pressed against glass as compared with those pressed against plastic. From the data in table 21, one can conclude that in terms of relative deviation the glass-pressed pellets are at least four times as reproducible as the plastic-pressed pellets. However, the reproducibility of surfaces of the plastic-pressed pellets is itself much better than that achieved by other conventional methods known to this author. Compared to the direct reading data of Matocha and Tingle (Stevens and others, 1960, p. 79-81) X-ray spectrographic determination of sodium is about 25 times superior in terms of relative deviation (table 21). All other methods have so far given precision inferior to both of these methods. Only the reproducibility of analyses given in Bureau of Standards certificate for Albite Feldspar No. 99 compares with that obtained in this work.

In table 22 the X-ray spectrographic data on Na_2O are compared with gravimetric data, giving good to satisfactory agreement.

In this table two sets of X-ray data are given. The 1962 data were obtained after dedrifting, the 1963 data were obtained by the intensity ratio method. In both cases calibration curves were drawn through points representing rocks G-1 and W-1. Figures 15a, b give two calibration curves for sodium; the upper is based on counting time directly and includes corrections; the lower is based on intensity ratios measured in 1963. Similarity of the iron-ground and the ceramic-ground sample splits is remarkable here, as in all other cases.

To check the accuracy of this X-ray method for sodium and potassium, a correction

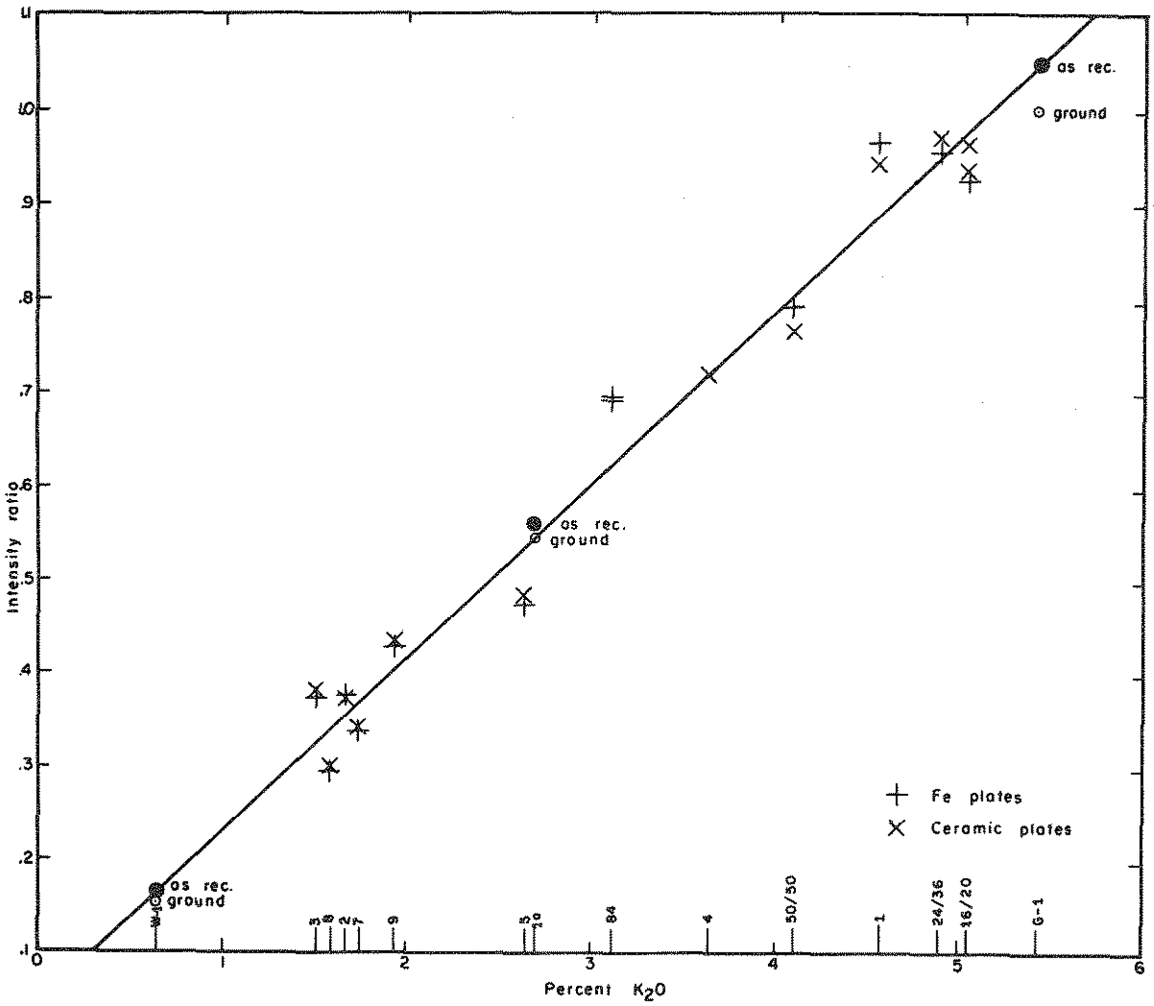


FIGURE A14. Calibration curve for X-ray spectrographic determination of K_2O. Slight decrease in intensity upon further grinding is noticeable in standards W-1, Syenite 1^a, and G-1.

of gravimetric data for sodium was made, assuming the X-ray data for potassium to be correct. This assumption is possible because the sodium is determined indirectly by difference on the basis of the amount of potassium detected in the chemical procedure, and therefore depends mostly on the quality of the potassium determination. In seven cases out of eight, the points corrected moved closer to the calibration curve, as indicated by the arrows, figure 15a; the eighth point was displaced by 0.25 percent away from this line. This is an indication of the accuracy of the X-ray method.

Two methodical gravimetric errors by this author were discovered after larger than acceptable deviations had been checked and recalculated. These rather large corrections are indicated by dotted horizontal lines in figure 15a. Embarrassing as this is, it shows how, with X-ray checks, one can detect errors. In this case, the incident served to increase the author's confidence in this method's accuracy.

Only the two rhyolitic tuffs, numbers 1 and 4, and the weathered adamellite 50/50, fall short of satisfactory agreement with the gravimetric data if the same calibration curve is used, despite checks of original analysis and correction for X-ray spectrographic potas-

TABLE A19. Comparison of X-ray Spectrographic and Gravimetric Data for K_2O

Rock Fe–iron ground Cer–cer. ground	K_2O Content (percent)		Deviation	Analyst, Chemical
	Chemical	X-ray		
G-1, as rec.	5.43	5.43	0.00	Stevens and others (p. 78, 1960)
W-1, as rec.	0.64	0.64	0.00	Stevens and others (p. 78, 1960)
W-1, ground	0.64	0.60	-0.04	Stevens and others (p. 78, 1960)
Basalt 3, Fe	1.52	1.77	+0.25	Volborth, $KClO_4$
Basalt 3, Cer.		1.81		
Andesite 8, Fe	1.60	1.35	-0.25	Volborth, $KClO_4$
Andesite 8, Cer.		1.35		
Andesite 2, Fe	1.67	1.78	+0.11	Volborth, $KClO_4$
Andesite 2, Cer.		1.77		
Basalt 7, Fe	1.75	1.57	-0.18	Volborth, $KClO_4$
Basalt 7, Cer.		1.58		
Andesite 6, Fe	1.94	2.08	+0.14	Volborth, $KClO_4$
Andesite 6, Cer.		2.11		
Andesite 5, Fe	2.65	2.30	-0.35	Volborth, $KClO_4$
Andesite 5, Cer.		2.37		
Syenite 1^a, as rec.	2.71	2.78	+0.07	Nonmetall. Std. Comm. report, (1961)
Syenite 1^a, ground	2.71	2.71	0.00	Nonmetall. Std. Comm. report, (1961)
Granite 84, Pica	3.12 X-ray	3.50	(+0.38)	(Baird, X-ray)
Granite 84, 1 hr.	3.12 X-ray	3.48	(+0.36)	(Baird, X-ray)
Rhyolite 4, Cer.	3.64	3.64	0.00	Volborth, $KClO_4$
Rhyolite 1, Fe	4.57	5.00	+0.43	Volborth, $KClO_4$
Rhyolite 1, Cer.		4.85		
Adamellite 50, Fe	4.11	4.03	-0.08	Vincent, flame
Adamellite 50, Cer.		3.88		
Granite 24/36, Fe	4.90	4.93	+0.03	Vincent, flame
Granite 24/36, Cer.		5.00		
Granite 16/20, Fe	5.05	4.76	-0.29	Vincent, flame
Granite 16/20, Cer.		4.81		
Granite 16/10, Cer.		4.97		
Basalt 7, Fe	1.71	1.57	-0.14	Vincent, flame
Andesite 8, Fe	1.47	1.35	-0.12	Vincent, flame

ium. Here obviously one has to consider the elasticity and shielding effects of the biotite micas and clay minerals, and also the different porosities of these rocks. Tuffaceous volcanic rocks, unlike other volcanic rocks, were the hardest to press, and most of the pellets cracked upon removal from the die. Experiments should be conducted with tuffs of different composition but similar physical properties, to show whether a parallel calibration curve could be established, as indicated on figure 15a. Results given for these rocks were obtained from a separate calibration curve not displayed here.

In figure 16 it is shown that G-1 could be used as an additional standard for plagioclase in the range of albite to andesine. For this purpose, points representing BS-99 and G-1 were connected, and the sodium of the two plagioclase powders of Emmons (1953, p. 18, Nos. 1 and 9) determined:

1 Albite	10.40% X-ray,	11.38% Na_2O chem.
9 Andesine	5.28% X-ray,	5.48% Na_2O chem.

Although additional analyzed feldspar powders were not available, the complete X-ray analysis of feldspars is definitely possible. It would have the advantage of permitting X-ray diffraction work to be done on the same pellet surfaces as those being spectrograph-

TABLE A20

Statistical Interpretation of Deviations of X-ray Results from Gravimetric and Flame Photometric Data

Statistical term	Gravimetric ($KClO_4$ and $K_2 Pt Cl_6$) $n = 12$	Flame Photometric $n = 5$
S	0.21	0.18
$s_{\bar{x}}$	0.06	0.08
$C_{1\% K_2O}$	21	8.0
$C_{3\% K_2O}$	7	2.7
$C_{5\% K_2O}$	4	1.6
$E_{1\% K_2O}$	6	3.6
$E_{5\% K_2O}$	1.2	0.7

ically analyzed. As shown in the chapter on silica, 300 milligrams of fine powder should be sufficient for the analysis of all elements with low atomic numbers.

MANGANESE AS MnO

Instrumental settings for the determination of manganese are listed in table 3. Because of the considerable background due to the iron K_α radiation, two background readings were taken on both sides of the manganese peak at a distance of $1° 2\theta$, and in each case the mean background was calculated separately and subtracted from the total count.

Precision of this method was tested on rocks W-1, G-1, Granite 84, and Andesite 5, and statistical data compiled in table 23. Comparison of the X-ray spectrographic precision with the precision achieved by direct reading spectrometric, colorimetric, and emission spectrographic methods, described by Stevens and others (1960), shows that the X-ray spectrographic method is much superior. For rock W-1, in terms of relative deviation, the precision is twice as good as the direct reading spectrometric precision, and for rock G-1 it can be called absolute. One should also note the perfect reproducibility within 10 parts per million, of MnO of pellets 78, 79, 80, 81, 82, and 114 of the rock W-1, indicating the superiority of this pelletizing method. This degree of reproducibility was also occasionally achieved with all other constituents during this work, but only during perfectly stable net current at night (see silica). It is this writer's opinion that reproducibility of the pellets is at present as good as the counting statistics chosen.

In figure 17 the correlation of Mn intensity ratios with colorimetric results on standards G-1, W-1, and 1^a is perfect. The accuracy of the X-ray method is here demonstrated by the fact that MnO value is the only "recommended" value for Syenite 1^a given in the report (1961) of the Nonmetallic Standards Committee of the Canadian Association of Applied Spectroscopy.

X-ray spectrographic results for MnO are compared with colorimetric data in table 24. In general, a satisfactory agreement of both data can be seen, taking into account the fact that the chemical data are based on single determinations. In all cases the X-ray results are apparently to be preferred to the chemical.

TABLE A21. Precision of X-ray Spectrographic Determination of Na_2O

Mineral	Pellet No.	Percent Na_2O	P/B	X-ray Statistical Data (64,000 total cts)	Comparative Statistical Data
BS-99, Albite, glass					Bureau of Standards
disc, 300 mg	23	10.77	16	$n = 8$	No. 99, albite, $n = 6$
"	24	10.70		$\bar{x} = 10.733$	$\bar{x} = 10.73$
"	25	10.71	G-1	$S = 0.014$	$S = 0.06$
500 mg	31	10.79	16	$s_{\bar{x}} = 0.005$	$s_{\bar{x}} = 0.02$
"	32	10.76		$C = 0.13$	$C = 0.56$
"	33	10.69	W-1	$E = 0.05$	$E = 0.23$
1000 mg	26	10.73	6		
"	28	10.72			
BS-99, Albite, plastic disc, 300 mg	22	10.82		$n = 10$	G-1, 3.32% Na_2O, direct reading spectrometric, $n = 32$
500 mg	20	10.73		$\bar{x} = 10.746$	$\bar{x} = 3.42$
"	21	10.73		$S = 0.059$	$S = 0.114$ (Stevens and others 1960)
564 mg	13	10.73		$s_{\bar{x}} = 0.019$	$s_{\bar{x}} = 0.020$
670 mg	9	10.66		$C = 0.55$	$C = 3.32$
"	10	10.73		$E = 0.17$	$E = 0.59$
643 mg	11	10.80			
743 mg	12	10.66			
623 mg	14	10.78			
680 mg	15	10.82			
Andesite 5,					G-1, 3.32% Na_2O
ground 1 hr.	68	4.12		$n = 6$	Stevens and others (1960)
	69	4.12		$\bar{x} = 4.113$	$C = 7.06$ all anal., $n = 60$
	70	4.11		$S = 0.004$	$C = 3.3$ pref. values
	71	4.11		$s_{\bar{x}} = 0.002$	$C = 8.6$ spectr.
	72	4.11		$C = 0.10$	
	73	4.11		$E = 0.04$	

One rock, Andesite 2, with unacceptable colorimetric value for Mn has been placed last in table 24. Deviations in table 24 show a negative bias of colorimetric results. This is possibly due to incomplete oxidation of manganese and reduction of permanganate, and partly to the "biotite effect". In six cases out of eight, the iron-ground samples show slightly higher intensity for manganese than the ceramic-ground samples. This amounts to about 0.01 percent MnO, and is probably caused partly by the enhancement of manganese radiation by iron, and partly by the introduction of traces of manganese from the iron plates.

TABLE A22. Comparison of X-ray Spectrographic and Gravimetric Data for Na_2O

	Na_2O Content (percent)			Na_2O%	Na_2O%	
Rock, Fe, Cer-ground	Chemical (K_2O corr)	X-ray 1962	Deviation	X-ray 1963	Original Report	Analyst, Chemical
W-1		2.07	0.00	2.07	2.07	Stevens and others (1960)
Andesite 6, Fe	3.16	3.27	+0.11	2.99	3.27	Volborth
Andesite 6, Cer.		3.28		3.03		
G-1		3.32	0.00	3.32	3.32	Stevens and others (1960)
Basalt 3, Fe	3.73	3.75	+0.02	3.46	4.67	Volborth
Basalt 3, Cer.		3.75		3.43		
Basalt 7, Fe	3.87	3.86	-0.01	3.42	3.72	Volborth
Basalt 7, Fe	3.60	3.86	+0.26			Vincent, flame
Basalt 7, Cer.		3.79		3.44		
Andesite 2, Fe	3.90	3.48	-0.42	3.19	3.98	Volborth
Andesite 2, Cer.		3.47		3.15		
Andesite 8, Fe	4.12	4.00	-0.12	3.68	3.91	Volborth
Andesite 8, Fe	3.87	4.00	+0.13			Vincent, flame
Andesite 8, Cer.		4.00		3.73		
Andesite 5, Fe	4.26	4.12	-0.14	3.81	3.98	Volborth
Andesite 5, Cer.		4.16		3.84		
				3.89		
Syenite 1[a]			+0.37	3.36	2.99	Nonmetall. Std. Comm. Report (1961)
Adamellite 50/50, Fe			0.00	4.11	4.11	Vincent
Adamellite 50/50, Cer.				4.03		
Rhyolite 1, Fe	2.67	1.30	0.00	3.03	3.03	Volborth
Rhyolite 1, Cer.		1.38		2.90		
Rhyolite 4, Cer.	4.83	3.96		4.89	4.89	Volborth
Granite 16/20, Fe			-0.28	2.66	2.94	Vincent
				2.66	2.94	
Granite 16/20, Cer.				2.63		
				2.60		
Granite 24/36, Fe			-0.22	2.66	2.88	Vincent
				2.70	2.88	
Granite 24/36, Cer.				2.73		
				2.76		
Granite 84			-0.02	4.10	4.12 (X-ray, Baird)	
			+0.03	4.15	4.12 (X-ray, Baird)	

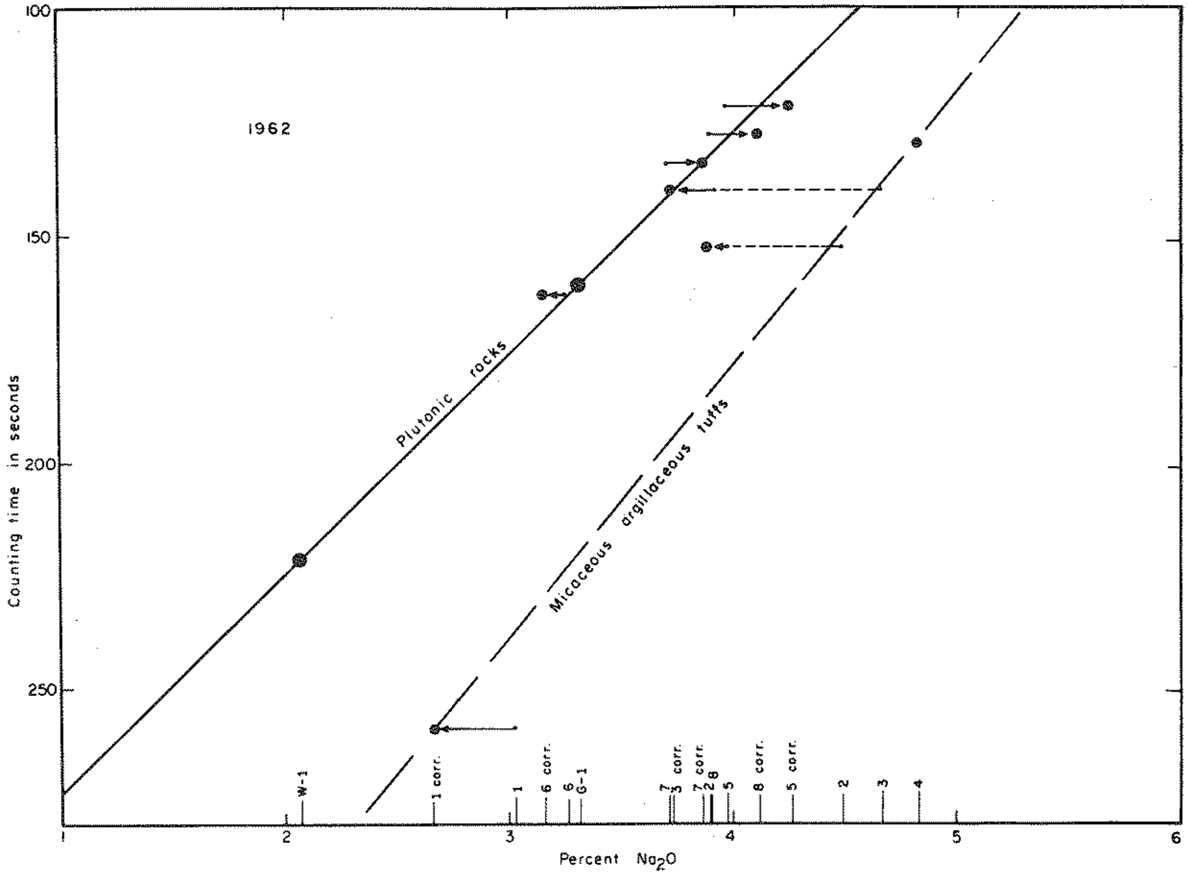
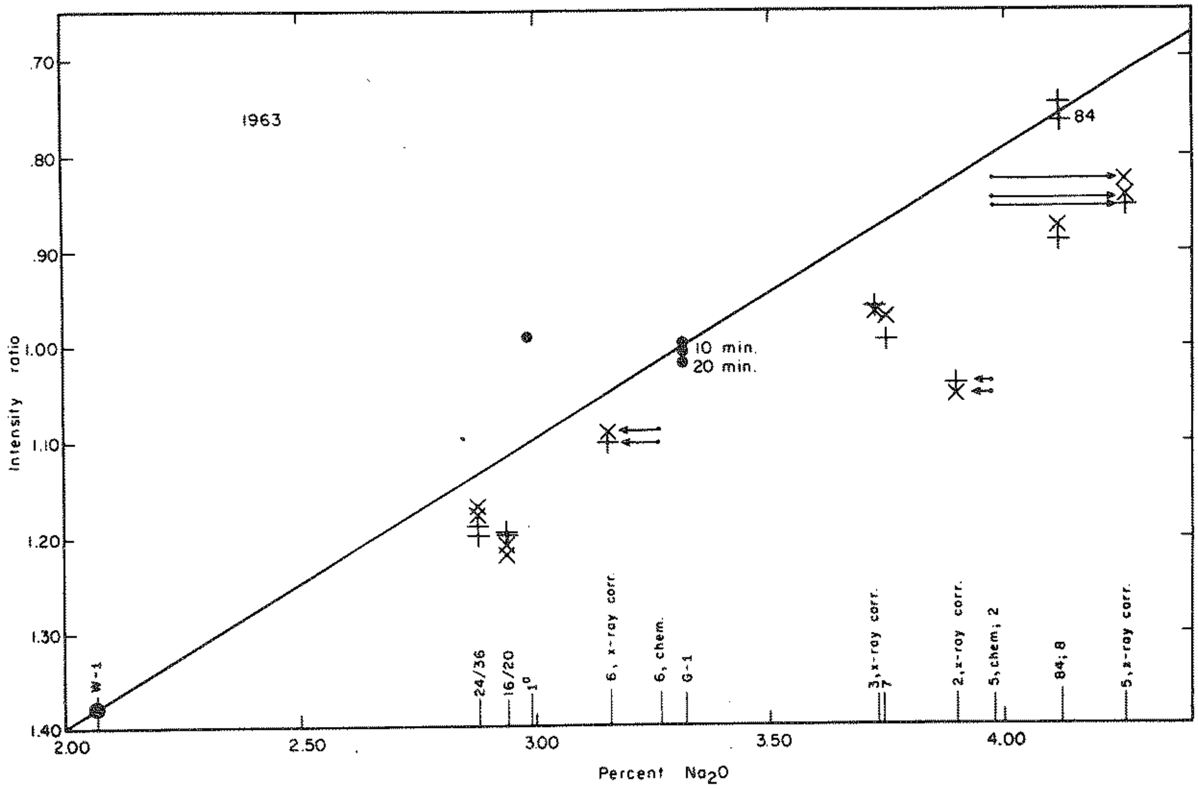


FIGURE A15. Calibration curves for X-ray spectrographic determination of Na_2O. In the upper curve, done in 1962, the solid line represents the plutonic rocks, the dashed line is a suggestion for approximate relative position for tuffaceous argillized rocks. Dashed horizontal lines represent errors discovered in gravimetric Na_2O determination, and the solid horizontal line with arrows represent the displacement of points upon correction for K_2O, determined X-ray spectrographically. In the lower (1963) curve intensity ratios are used. It represents an entirely different set of determinations.



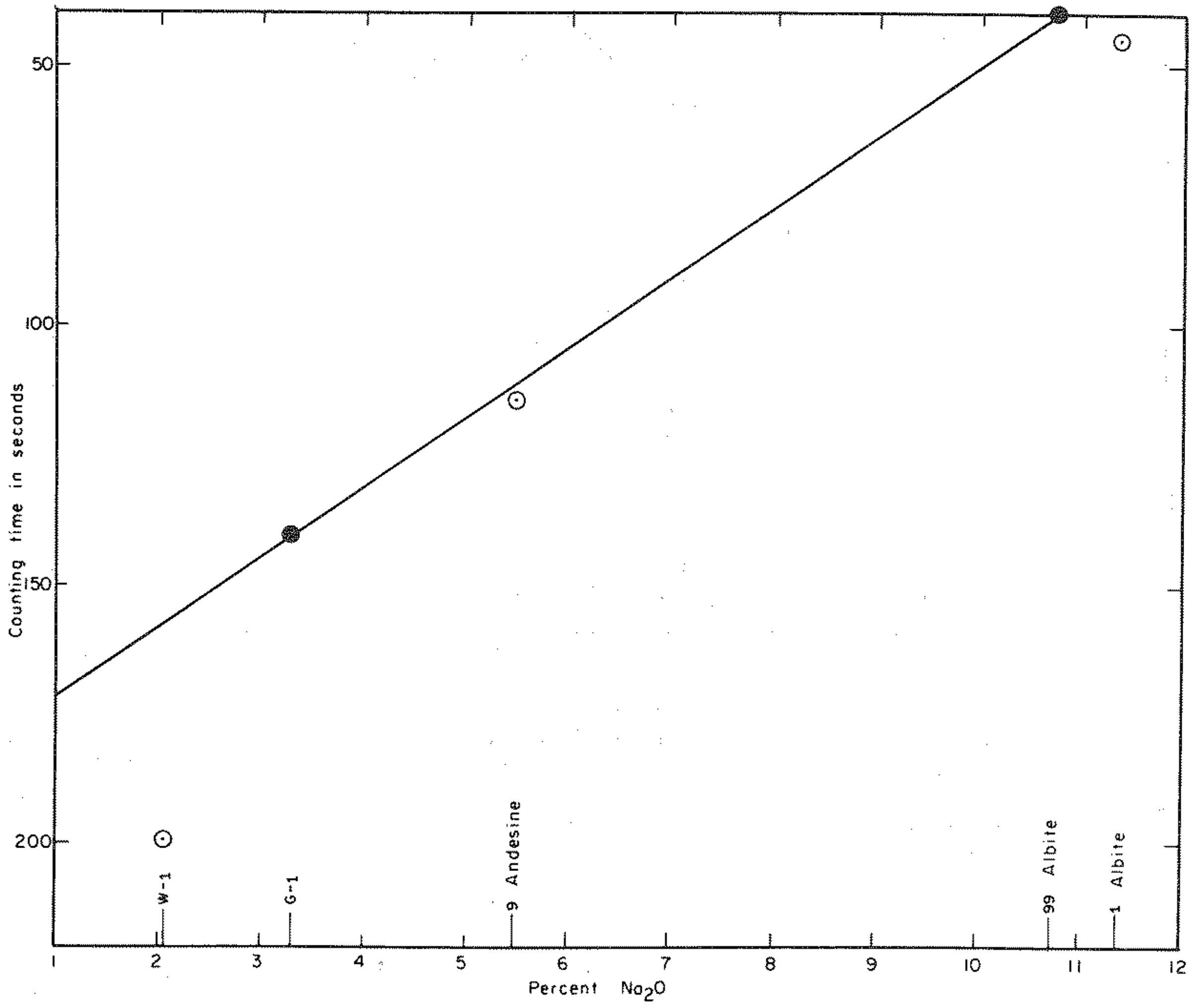


FIGURE A16. Calibration curve for X-ray spectrographic determination of Na_2O in feldspars in the range albite to andesine, using G-1, and U. S. Bureau of Standards standard No. 99, Albite.

TABLE A23

Precision of X-ray Spectrographic Determination of MnO

			Statistical Data			
Rock	Pellet	MnO%	X-ray	Direct Reading Spectrometric	Colorimetric	Spectrographic
			n = 10	n = 32		
W-1, as rec.	75	0.182	$\bar{x} = 0.178$			
W-1, as rec.	76	0.187		$\bar{x} = 0.17$		
W-1, as rec.	77	0.179	S = 0.004	S = 0.008		
W-1, as rec.	78	0.176				
W-1, as rec.	79	0.176	$s_{\bar{x}} = 0.001$	$s_{\bar{x}} = 0.001$	Stevens and others, (1960)	Stevens and others (1960)
W-1, as rec.	80	0.176			all anal.:	
W-1, as rec.	81	0.176	C = 2.15	C = 4.70	C = 32.33	C = 10.9
W-1, as rec.	82	0.176			C = 12.5, pref.	
W-1, as rec.	83	0.175	E = 0.68	E = 0.83		
W-1, 20 min.	114	0.176				
			n = 4	n = 32		
G-1, as rec.	87	0.027	S = 0.000	S = 0.0016		
G-1, as rec.	88	0.027	$s_{\bar{x}} = 0.000$	$s_{\bar{x}} = 0003$		
G-1, as rec.	89	0.027	C = 0.00	C = 5.57	C = 33.62	C = 33.1
G-1, as rec.	85	0.027	E = 0.00	E = 0.98	C = 20.0, pref.	
			n = 4			
Granite 84	68	0.122	S = 0.000			
Granite 84	69	0.122	$s_{\bar{x}} = 0.000$			
Granite 84	70	0.122	C = 0.00			
Granite 84	71	0.122	E = 0.00			
			n = 4			
Andesite 5,	96	0.127	S = 0.0012			
cer. plates	97	0.129	$s_{\bar{x}} = 0.0006$			
cer. plates	98	0.128	C = 0.90			
cer. plates	95	0.129	E = 0.45			

TABLE A24

Comparison of X-ray Spectrographic and Gravimetric Data for MnO

Rock Fe-plates Cer.-plates	MnO Content (percent)			
	Chemical	X-ray	Deviation	Analyst, Chemical
Rhyolite 1, Cer.	Trace	0.000	(0.000)	Volborth
Rhyolite 1, Fe		0.007		
Rhyolite 4, Cer.	Trace	0.033	+0.033	Volborth
G-1	0.027	0.027	0.000	Stevens and others (1960)
Granite 24/36, Cer.	0.04	0.070	+0.030	Vincent
Granite 24/36, Fe		0.070		
Granite 16/20, Cer.	0.05	0.078	+0.028	Vincent
Granite 16/20, Fe		0.078		
Adamellite 50/50, Cer.	0.06	0.087	+0.027	Vincent
Adamellite 50/50, Fe		0.087		
Basalt 3, Cer.	0.07	0.112	+0.042	Volborth
Basalt 3, Fe		0.101		
Andesite 5, Cer.	0.10	0.119	+0.019	Volborth
Andesite 5, Fe		0.128		
Granite 84, Fe		0.122		
Andesite 8, Cer.	0.11	0.131	+0.021	Volborth
Andesite 8, Fe		0.128		
Andesite 6, Cer.	0.13	0.106	-0.026	Volborth
Andesite 6, Fe		0.116		
Basalt 7, Cer.	0.18	0.162	-0.018	Volborth
Basalt 7, Fe		0.175		
W-1	0.18	0.180	0.000	Stevens and others (1960)
Syenite 1[a]	0.42	0.420	0.000	Nonmetall. Std. Comm. report, (1961)
Andesite 2, Cer.	0.02	0.122		Volborth,
Andesite 2, Fe		0.135		colorimetric error?

PRECISION OF THE METHOD

In table 25, the ranges of the relative deviations of all X-ray spectrographic determinations of all major and some minor components of all the rocks here analyzed, are compared with relative deviations achieved by different laboratories analyzing rocks G-1 and W-1. The "one laboratory" data are grouped first because of the absence of the dichotomy factor. The A. R. L. Emission Quantometer data by Matocha and Tingle (Stevens and others, 1960), which had the highest precision for most of the elements so determined, show less precision than those obtained with this X-ray method. In many cases this is by a factor of ten to twenty. Silicon is the only element where comparable but nevertheless clearly inferior precision has been achieved by the double HCl precipitation method. The range of oxides analyzed in this work is much wider than the range represented by rocks G-1 and W-1, indicating the applicability of the X-ray spectrographic method to a wide variety of rocks. Comparison of flame photometric data in column four of table 25 with X-ray spectrographic data on potassium and sodium, also shows the high precision of the X-ray method.

TABLE A25

Precision of X-ray Spectrographic Determination of All Major Components in Plutonic Rocks as Compared with Other Methods

C = Relative Deviation = Standard Deviation / Mean x 100.

Oxide	X-ray One Lab.	Emission Quantometer One Lab.	Gravimetric One Lab.[1]	Flame One Lab.[1]	Gravimetric, preferred.[2]	Emission Intralab.[2]	Gravimetric Intralab.[2]	Range of Oxide (weight percent)
SiO_2	0.07 - 0.4	1.4 - 1.7	0.3 - 0.6		0.2 - 0.4	2.5 - 2.7	0.66	50 - 80
Al_2O_3	0.2 - 0.9	2.0 - 2.5	1.2 - 3.2		1.2	2.5 - 3.6	2.6 - 4.2	10 - 20
Fe_2O_3	0.1 - 1.6	2.3 - 3.0	(19.3-33.4)			2.5 - 5.9	2.5-13.9	0.4 - 12
CaO	0.1 - 0.4	2.2 - 5.9	0.8 - 6.5		0.7 - 5.1	6.3-13.0	1.4 - 9.0	0.3 - 11
MgO	0.1 - 1.2	2.0 - 2.3	6.0 - 9.9		1.5-14.6	3.0 - 6.6	5.3-32.2	0.2 - 6.6
K_2O	0.6 - 1.6			3.8 - 7.1	2.7 - 4.7		7.3-19.0	0.6 - 5.5
Na_2O	0.1 - 0.6	3.3		5.7 - 6.2	3.3 - 5.3	4.3 - 8.6	7.1 - 9.8	2.0-11.0
TiO_2	0.5 - 5.0	4.3 - 9.2	4.2-11.2		5.7 - 6.5	12.9-15.0	16.6-18.3	0.2 - 1.6
MnO	0.0 - 2.2	4.7 - 5.6	15.6-30.5		12.5-20.0	10.9-33.1	32.3-33.6	0.00-0.42

1. Fairbairn and others (1961)
2. Stevens and others (1960)

Because the highest counts accumulated were of the order of 600,000 total counts for Si, Ca, and Fe, and because the lowest peak to background ratios recorded were still in the order of 6, one can, by simply increasing the counting time, improve the precision achieved for most elements listed. This has been done in the case of silica, where relative deviation improved to 0.07 in one case, and to 0.09 in another (table 4). This means that the method is nearly absolute in terms of relative deviation, and that the pellets are perfectly reproducible, since silica is the major component and possible inhomogeneity of samples should affect it most.

Analyses given in all tables include data for both ceramic- and iron-ground material. The closeness of these results in all cases demonstrates the high precision of the different splits as well as specific contamination influence by the different grinding media.

ACCURACY OF THE METHOD

It is nearly impossible to determine the absolute accuracy of rock analyses, even when known amounts of oxides are mixed or fluxed. So many factors influence the final composition that only a close approximation of the true composition of the mixture can be expected. There are, however, simple means by which the accuracy of a certain procedure can be indicated, and a fairly satisfactory picture obtained. These methods are, however, based on the assumption that no bias is involved in the absolute methods with which the results are compared.

The following points serve as indications of the accuracy of the X-ray method described in this report:

1. The points based on gravimetric data are symmetrically distributed on both sides of the weight percent to intensity ratio calibration curves.

2. These points are close to, or coincide with, calibration curves which in all instances are based on the assumption that the values of rocks G-1 and W-1 recommended by Stevens and others (1960), are correct.

3. Values for Na_2O, corrected on the basis of the X-ray spectrographic determination of K_2O (fig. 12), conform more closely to the calibration curve than do the uncorrected values.

4. The only value recommended in the report of the Nonmetallic Standards Committee (1961), namely that for MnO, falls exactly on the projection of the manganese calibration line drawn between rocks G-1 and W-1 (fig. 17).

5. The accuracy test performed on 56 rock powders, assuming the gravimetric data to be correct, gives relative deviation at 95 percent confidence in the order of 1.0 percent for granitic rocks (fig. 18).

6. X-ray spectrographic data on 9 of 12 rock analyses fall about 1 percent short of 100 percent (tables 26 and 27), when recalculated on the basis of chemical data (substitution made where no X-ray analyses were possible), indicating that the minor elements known to exist in most rocks have not been determined.

In connection with the last point, it is definitely known that such trace elements as Li, Be, B, F, S, C, Ar, Sc, V, Ga, Fe, As, Rb, Sr, Y, Zr, Nb, Mo, Sn, Cs, Ba, La, Ce, Hf, Ta, Pb, Ra, Th, and U are almost always present in these types of rocks in detectable amounts, amounting in many instances to a total of 1 - 1.5 percent in oxide form. An example of this would be the Syenite 1^a (Nonmetall. Std. Comm. Report, 1961).

Where these elements co-precipitate at different stages and are reported within other

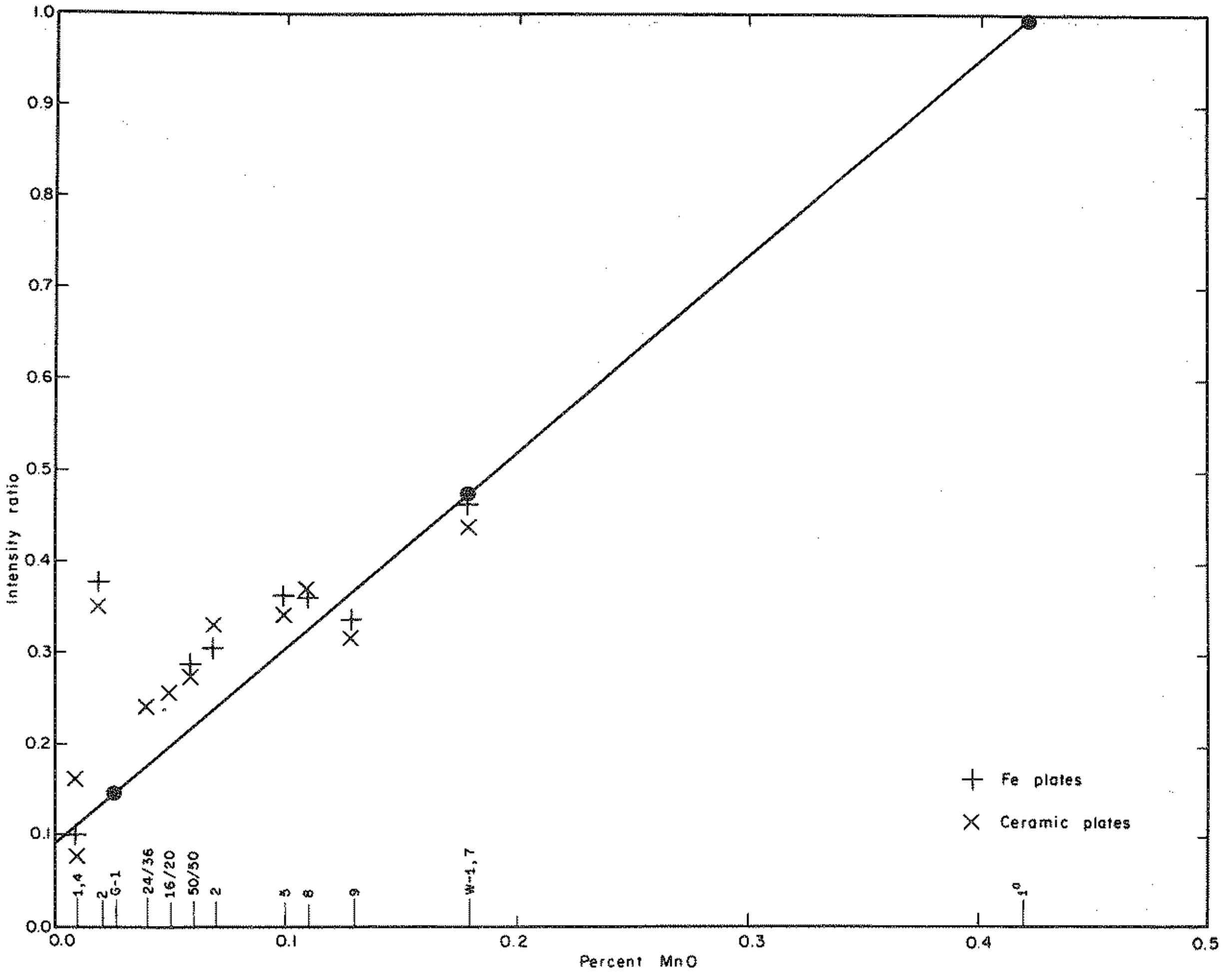


FIGURE A17. Calibration curve for X-ray spectrographic determination of MnO using G-1, W-1, and Syenite 1[a] powders as standards. A slight but definite intensity increase is shown in powders ground by iron plates.

constituents, lower total percentages should be expected from X-ray work when these elements are not determined, because the X-ray method discriminates against these elements, whereas the gravimetric methods do not. The present work indicates that this difference in rocks is surprisingly large, amounting to about one percent of the total. It is apparently the magnitude of this effect that is responsible for the trend toward the low totals seen in tables 26 and 27, despite some remaining accuracy problems, especially in the X-ray analysis of aluminum and magnesium, and in rocks with biotite, and tuffs.

In tables 26 and 27, the X-ray analyses are compared with gravimetric data. Where no X-ray determination was possible, or for some reason was not done, the gravimetric data are substituted in parentheses in the X-ray columns. In all cases the totals are first given, then corrected for the FeO factor on the basis of titrimetric work, and, where applicable, subsequently corrected for F in the same manner. This was done to show the expected lower total percentages. In granites, apparently due to the biotite effect on overall accuracy, this trace element effect cannot be observed. One must also consider that the chemical results for G-1 and W-1 have in most instances not been

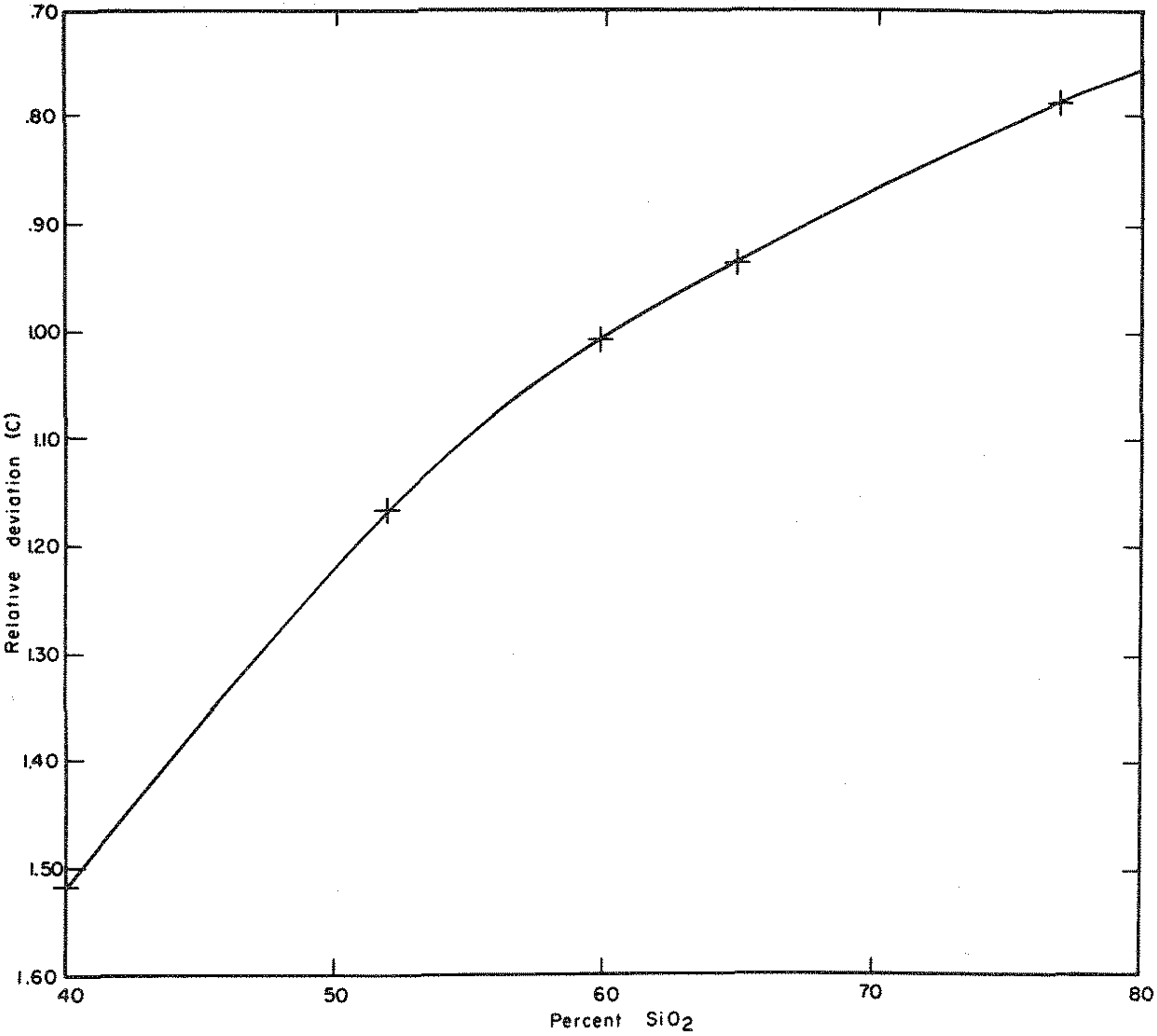


FIGURE A18. Relative deviation of X-ray spectrographic determinations, assuming that the gravimetric silica determinations are accurate. It is based on analyses of eight volcanic and four granitic rocks using G-1 and W-1 as standards, and assuming a linear calibration curve. It covers the region of 40-80 percent SiO_2, and is intended only as an indication of this methods' accuracy at the present time.

corrected for all co-precipitating elements, which introduces a slight positive bias in all X-ray spectrographic determinations based on them.

Considering the amount of data accumulated in this work, it may be stated that the overall accuracy of the X-ray method in rock analysis, if based on good standards, is as good, if not better, than that of other conventional methods.

BIOTITE EFFECT

Biotite and muscovite or sericite micas, because of their platy nature and considerably different composition as compared to the bulk composition of the rocks, cause more inter-

TABLE A26

Comparison of X-ray Spectrographic and Chemical Analyses of Volcanic Rocks

All Results are Given in Weight Percent of Oxides

Oxide	Rhyolite 1		Rhyolite 4		Andesite 2		Andesite 6		Andesite 8		Andesite 5		Basalt 3		Basalt 7	
	X-ray	Chemical	X-ray	Chemical	X-ray	Chemical	X-ray	Chemical	X-ray	Chemical	X-ray	Chemical	X-ray	Chemical	X-ray	Chemical
SiO_2	76.45	76.77	75.85 cer.	75.66	58.20	59.05	57.45	57.60	57.05	57.83	55.60	54.79	52.75	53.24	52.45	52.12
TiO_2	0.13*	0.19	0.11*	0.24	0.72*	0.75	0.62*	0.80	0.75	0.76	1.04	1.08	1.32	0.86	1.58	1.63
Al_2O_3	13.05	12.23	12.90	12.62	16.00	16.78	15.15	17.58	17.48	18.11	17.70	17.02	16.70	17.66	16.00	16.08
Fe_2O_3, total	0.84*	(1.07)	1.84*	(1.76)	6.42	(6.47)	6.79	(6.95)	7.51	(7.52)	6.96	(8.51)	9.16	(9.18)	9.46	(10.50)
FeO + Fe_2O_3	(0.76)	0.97	(1.68)	1.61	(5.84)	5.29	(6.14)	6.28	(7.19)	7.20	(6.76)	8.27	(8.53)	7.77	(8.81)	9.78
MgO	0.38	0.42	0.22	0.22	4.08	3.01	4.05	2.99	3.00	2.97	2.66	2.66	4.30	4.08	4.03	4.24
CaO	0.42	0.27	(0.64)	0.64	5.47	5.76	5.75	6.04	6.34	6.36	7.06	7.65	6.71	6.82	7.29	7.51
K_2O	5.00	4.57	3.64	3.64	1.78	1.67	2.08	1.94	1.35	1.60	2.30	2.65	1.77	1.52	1.57	1.75
Na_2O	3.03	2.67	4.89	4.83	3.48	3.90	3.27	3.16	4.00	4.12	4.12	4.26	3.75	3.73	3.86	3.87
MnO	0.000	Trace	0.033	Trace	0.122	0.02	0.106	0.13	0.131	0.11	0.119	0.10	0.112	0.07	0.162	0.18
H_2O+	(1.30)	1.30	(0.58)	0.58	(2.16)	2.16	(2.23)	2.23	(1.15)	1.15	(0.44)	0.44	(1.29)	1.29	(1.77)	1.77
H_2O-	(0.21)	0.21	(0.23)	0.23	(0.51)	0.51	(0.17)	0.17	(0.26)	0.26	(0.20)	0.20	(0.75)	0.75	(0.43)	0.43
P_2O_5	(0.06)	0.06	(0.05)	0.05	(0.27)	0.27	(0.27)	0.27	(0.21)	0.21	(0.51)	0.51	(0.51)	0.51	(0.79)	0.79
Total	100.87	99.66	100.98	100.32	99.21	99.17	97.94	99.19	99.23	100.68	98.71	99.63	99.12	98.30	99.39	100.15
O**	0.08		0.16		0.58		0.65		0.32		0.20		0.63		0.65	
Total, corrected for FeO	100.79		100.82		98.63		97.29		98.91		98.51		98.49		98.74	

* Loose Powder

** Line 4 minus Line 5

TABLE A27. Comparison of X-ray Spectrographic and Chemical Analyses of Granitic Rocks*

All Results are Given in Weight Percent of Oxides

Oxide	Granite 24/36		Granite 16/20		Q. Monzonite 84		Adamellite 50/50		Syenite 1^a	
	X-ray (Volborth)	Chem. (Vincent)	X-ray (Volborth)	Chem. (Vincent)	X-ray (Baird)	X-ray (Volborth)	X-ray (Volborth)	Chem. (Vincent)	X-ray (Volborth)	Chem.**
SiO_2	69.30	68.23	67.85	68.06	66.77	66.60	64.90	64.63	60.65	59.29
TiO_2	0.78	1.26	0.84	1.74	0.59	0.55	1.14	1.78	0.40	0.52
Al_2O_3	13.47	13.99	14.95	13.79	15.06	15.37	13.40	13.71	9.30	9.32
Fe_2O_3, Total	4.68	(4.66)	5.08	(4.20)	2.69	3.46	6.70	(6.26)	8.10	(8.94)
$FeO+Fe_2O_3$	(4.36)	4.34	(4.71)	3.89	-	-	(6.26)	5.85	(7.48)	8.26
MgO	1.08	1.02	1.15	1.11	0.70	1.23	1.29	1.31	4.02	4.02
CaO	2.40	2.36	2.45	2.32	2.92	2.00	2.94	2.98	9.37	10.24
K_2O	4.93	4.90	4.76	5.05	3.12	3.48	4.03	4.11	2.71	2.71
Na_2O	2.68	2.88	2.66	2.94	4.12	4.13	4.11	4.11	3.36	2.99
MnO	0.070	0.04	0.078	0.05	-	0.122	0.087	0.06	0.420	0.42
H_2O +	(0.47)	0.47	(0.57)	0.57	-	-	(0.94)	0.94	(0.46)	0.46
H_2O -	(0.06)	0.06	(0.00)	0.00	-	-	(0.30)	0.30	(0.21)	0.21
P_2O_5	(0.27)	0.27	(0.29)	0.29	-	-	(0.49)	0.49	(0.19)	0.19
F	(0.15)	0.15	(0.16)	0.16	-	-	(0.30)	0.30	-	-
BaO	(0.09)	0.09	(0.04)	0.04	-	-	-	-	(0.03)	0.03
SrO	(0.02)	0.02	(0.02)	0.02	-	-	(0.02)	0.02	(0.04)	0.04
Total	100.45		100.90		95.97	96.94	100.65		99.26	
$-[Fe_2O_3 -(FeO + Fe_2O_3)]$	0.32		0.37				0.44		0.62	
Total, corr. FeO	100.13	100.08	100.53	100.03			100.21	100.59	98.64	98.70
-F = O	0.06	0.06	0.07	0.07			0.13	0.13		
Total	100.07	100.02	100.46	99.96	95.97	96.94	100.08	100.46	98.64	98.70

* In this table, data borrowed from preceeding or following column appear in parentheses. In the case of iron, data not used in the calculation of totals also appear in parentheses.

** Chemical analysis from report of the Nonmetallic Standard Committee of the Canadian Association of Applied Spectroscopy (1961).

TABLE A28. Demonstration of Biotite Effect

Rock	Pellet No.	Percent Oxide	Grinding Time per 1.5 g	Intensity
G-1, SiO_2	10 pellets	72.65	as received	
"	110	72.62	10 min.	decreasing
"	111	72.61	10 min.	decreasing
"	112	72.00	20 min.	decreasing
"	113	72.00	40 min.	decreasing
W-1, SiO_2	10 pellets	52.63	as received	
"	114	52.50	20 min.	decreasing
G-1, CaO	4 pellets	1.46	as received	
"	110	1.40	10 min.	decreasing
"	112	1.39	20 min.	decreasing
"	113	1.36	40 min.	decreasing
W-1, Ca	10 pellets	10.94	as received	
"	114	10.94	20 min.	no effect
G-1, Fe_2O_3	9 pellets	1.46	as received	
"	110	1.70	10 min.	increase
"	111	1.72	10 min.	increase
"	112	1.86	20 min.	increase
"	113	1.96	40 min.	increase
W-1, Fe_2O_3	10 pellets	10.64	as received	
"	114	11.10	20 min.	increase
G-1, MnO	7 pellets	0.027	as is, P/B = 4	
"	110	0.032	10 min.	increase
"	112	0.039	20 min.	increase
"	113	0.043	40 min. P/B = 4.5	increase
W-1, MnO	9 pellets	0.178	as received	
"	114	0.176	20 min.	no effect

ference problems than any other minerals. In addition, the elastic properties of micas cause difficulties in the pressing of the pellets. Unless great care is exercised in increasing and releasing the pressure, the pellets crumble upon removal from the die. This difficulty was encountered with all biotite rich rocks in this group (No. 1, Biotite rhyolite tuff with sericite; No. 4, Biotite-anorthoclase rhyolite, and to a minor degree with all the granites).

Chodos and Engel (1961) mention the difficulty of reducing the grain size of biotite in rocks, and suggest that biotite is one major source of error in X-ray spectrographic determinations. With the high precision of the present method, it was possible to detect definite trends in the variation of intensities of the elements determined in biotite-rich rocks. It was observed, for example, that the intensities of iron, manganese, magnesium, aluminum, and titanium increase considerably when a relatively coarse granite powder is reground, but that the intensities of silicon and calcium definitely decrease, and that the intensity of potassium increases only slightly sporadically, or not at all (table 28). Theoretically the intensities of all elements should increase when the powder is reduced in particle size (Claisse, 1956; Claisse and Samson, 1961). When this abnormal decrease was first noticed during the work on silica, the first thought was that biotite by its relatively larger surface acts like a filter, and is apparently the cause of this effect. In calcium this effect was even more puzzling and an explanation was sought by investigating the general composition of biotite mica in this type of granitic rocks. The approximate composition of biotite mica in potassium-rich granitic rock is: SiO_2 - 35; Al_2O_3 - 14;

Fe_2O_3 - 40; MgO - 2; K_2O - 9; TiO_2 - 2; and MnO - 0.8 percent, and only traces of calcium oxide. This is about half the amount of silica present in the rock and ten to twentyfold the amount of iron oxide. In magnesium oxide and potassium oxide, this is about two to tenfold, in titanium oxide - five to tenfold, and in manganese oxide - twenty to forty times that of the granite.

It is obvious that a micaceous mineral increases its total surface relatively more than non-micaceous minerals upon further grinding. Assuming that this is so, and assuming that the 30,000 psi pelletizing pressure enhances this effect forcing the mica flakes into a parallel position, this increase of total relative surface of biotite in the surface film of the pellet should cause higher intensities for iron, titanium, manganese, potassium, and magnesium, and lower intensities for silicon and calcium, which last mentioned, is practically absent from biotite. The percentage of alumina in this type of biotite is about equal to that of the rock itself, and should be little affected in the whole rock analysis. However, in quartz-rich rocks the increase of biotite surface relative to quartz surface should cause a slight increase in intensity of aluminum upon further grinding, which in fact has been observed (see G-1, fig. 8). To be recorded the decrease of intensity for silicon and calcium due to the biotite effect must be of greater magnitude than the regular increase due to finer grain size. Similarly, in the case of iron, which should be affected most because of its high concentration in biotite, the increase in intensity includes also the regular increase due to finer grain size. This should produce a relatively higher increase in intensity for iron than for titanium, and a yet higher relative increase for manganese, which is also partially due to the enhancement of manganese radiation by iron. These suggestions appear to be supported by the data given in table 28. The apparent lack of any detectable effect on potassium can be explained by the fact that in this type of rock most of the potassium is concentrated in potassium feldspar, so that the relative increase due to further grinding of biotite is minimal. For titanium this effect also is less, because most of the titanium is found in sphene. Magnesium intensity also increases strongly upon grinding of biotite-rich granitic rocks (fig. 11).

With a suitable collection of modally analyzed granitic and other biotite-bearing rocks, it should be possible to establish quantitatively the effect of biotite in relation to the biotite mode in the different rocks. For highest accuracy, a correction factor could then be established, based on the modal composition of rocks. When fusion techniques are used this problem does not exist.

THEORETICAL CONSIDERATIONS

The amount of SiO_2 in igneous rocks varies from about 45 to 80 weight percent. In granitic rocks, oxygen alone comprises about 46, and silicon about 28 percent by weight (Barth, 1948). Barth emphasizes, however, that in percent by volume, oxygen in these rocks amounts to about 92 percent, whereas all the other seven major constituents represent by volume only about one percent each. This is due to the relatively large ionic radius of oxygen. In all silicates, which usually form more than 99 percent of silicate rocks, all silicon atoms are always surrounded by a group of four oxygens in tetrahedral position. All cations in silicates also form structural units in which their atoms are surrounded by oxygen atoms depending on the coordination number. Therefore, rocks or mixtures of silicates can be regarded as dispersions or dilutions of such cations as Al, Fe, Mg, Ca, K, Na, Mn, and Ti in a stable silica-oxygen framework, where the dilution ratios vary, in weight percent, approximately from 1 to 10 for major elements, and to as much as 1 to 1,000 and more for the minor elements. In volume percent, for large atomic size potassium, the ratio is 1 to 45, and rapidly increases for the other elements. These relatively large dilution ratios in the "oxygen-silica framework" make silicate mixtures in many cases directly suitable for X-ray analysis. Therefore the inhomogeneity effects in silicates are apparently much less than anticipated. This statement should apply also to carbonates, phosphates, sulfates, and even some oxide mixtures. Inter-element effects are of course a very serious problem in analysis of metals, alloys, and sulfides, and exclude the possibility of the direct approach used in this work.

The biotite effect, the effect of micaceous minerals, is perhaps the main contributor to inhomogeneity effects in rocks.

To achieve highest reproducibility in rock or cement analysis, one must: 1, equalize the grain size until no further grinding effect can be detected; 2, use a fully reproducible pelletizing method providing glass-like surfaces of pellets; 3, avoid all kinds of mixing, diluting, fluxing, or heavy media techniques, using as far as possible only the undiluted, pressed-rock, cement, or other oxide and silicate powders; 4, take into account the possible mica effects, if micas are present; and 5, apply, if possible, a dual grinding procedure, in both steel and mullite for example, which enables a closer approximation to the original composition of the uncontaminated rock.

The great advantages of this last mentioned dual-grinding method, applied to all samples in this work, are obvious when one compares the data on silica and iron. By establishing how much silica has been introduced by mullite plates, and how much iron by the steel plates, one can easily calculate the original composition of each rock, much closer than if any one of these grinding media had been used alone. In general, the principle should always be that of the least possible handling of the material to be analyzed.

Another advantage of this approach is the greatly increased sensitivity, especially for trace and light elements, as compared with the addition and dilution methods. The counting statistics of the plain pelletized rock powders are in all cases superior, because of higher counting rates. The only problems are caused by inhomogeneity and mass absorption effects, mainly affecting the accuracy in certain rocks, but not precision, if the rock is fine enough. This problem is, however, less serious in geochemical work because the geochemist is usually concerned with composition changes or gradients in similar rocks. There is little doubt of the usefulness of the newly introduced heavy absorber La_2O_3 technique of Rose and others (1962), when analyzing substances of widespread composition for major, heavier elements, starting with potassium. The direct rock powder pelletizing technique is, however, more precise and accurate when relatively narrow composition ranges are investigated using good standards, and it encompasses all the major constituents of silicate rocks. Recently it has been shown that the accuracy and precision of the direct pelletizing method is roughly comparable to that of the heavy absorber, addition, and fluxing methods when used in the same laboratory, this method being the more sensitive (Baird and others, 1963a). However, the precision reported by these authors is inferior to the precision achieved in this work, making direct comparison difficult at this stage.

ANALYSIS OF TiO_2 AND MnO ON LOOSE POWDERS

When the mylar window is used, the intensity loss for silicon K-alpha radiation is considerable. The increase of silicon intensity measured in turn on loosely packed powders, pressed powders with mylar window, and finally pressed powders without the window, is demonstrated by the increase in counts per second from about 70 cps for loose powder of rock G-1 packed over mylar, to about 400 cps for pelletized G-1 powder pellet with mylar, and about 1,000 cps for the same pellet without the mylar window. Because of this, no mylar window was used in X-ray analysis of pellets. High intensity is the main advantage of a direct pelletizing method. Relatively low intensity is the main reason for poor results obtained by analyzing alumina and silica on loosely-packed powders.

Elements with shorter wave length fluorescent radiations obviously can be analyzed very satisfactorily by using loosely packed powders, as demonstrated by Chodos and Engel (1961). To show the high quality of results possible, TiO_2 and MnO also were determined in the volcanic rocks on loose powders packed into the conventional aluminum boat with a mylar window. The packing was done by placing the mylar window against a glass or bakelite plate of equal dimensions and turning a 500 g weight, in the form of a piston, placed over the powder, without pressing, in order to get a uniform pack.

In tables 29 and 30, a comparison of a series of X-ray determinations of these oxides with the colorimetric results is presented. In these tables inconsistent colorimetric data are underlined. One can see that reproducibility even during different months is very good, and the accuracy as compared to the colorimetric results is satisfactory. Good agreement also exists between these data and the pressed pellet data on the same rocks presented in tables 11 and 24. Three sets of powders were used, those ground by ceramic plates, those ground by iron plates, and the original coarse analytical powders.

DISCUSSION AND CONCLUSIONS

From data presented, it may be concluded that X-ray spectrographic analysis of all major components and some minor components of rocks can be performed on pressed rock powders of a wide modal and chemical composition range. Excellent precision and high accuracy can be achieved with relatively few standards. Rocks G-1 and W-1 are shown to be sufficient as the only standards for igneous rocks, using the intensity ratio method. It can be assumed that similar results can be obtained for other suites of rocks if suitable standards are chosen for calibration purposes. A method is described for the direct pressing of finely-ground rock powders into pellets, without the addition of any binding material.

The main advantages of this direct pressing method are its simplicity, sensitivity, speed, precision, and accuracy; because no weighing, dilution, fluxing, or addition of any kind are necessary. Natural silicate mixtures do not seem to require further dilution for analysis of major components and some minor components in the fifteen rocks analyzed. It is yet to be shown whether most of the trace elements can directly be determined by this method, but using the Mn determination as an example this should be possible with equivalent precision and accuracy, because manganese represents an unusually difficult case due to the nearness of its peak to the iron K-alpha peak.

Plagioclase can be analyzed for silicon, sodium, potassium, aluminum, or calcium with high precision. Most of these determinations alone will give an accurate estimate of the anorthite content, and together these data should be sufficient for an accurate description of the feldspar. Also, the same pellet surfaces can be used for diffraction work.

The biotite and the elasticity effects described influence the intensities of most elements, but corrections can be established for very accurate work.

TABLE A29

Determinations of TiO_2 Content in Loose Powders of Volcanic Rocks

Rock No.	1	4	2	5	6	8	3	7
				Colorimetric				
	0.19	0.24	0.75	1.08	0.62	0.78	0.86	1.63
				X-ray				
Fe pl.	0.140	0.127	0.825	1.060	0.810	0.793	1.375	1.607
	0.135	0.137	0.893					
Anal. powd.	0.127	0.105	0.715	1.060	0.803	0.747	1.290	1.565
Cer. pl.	0.130	0.115	0.793	1.037	0.793	0.760	1.365	1.590
								1.630

TABLE A30

Determinations of MnO Content in Loose Powders of Volcanic Rocks

	Rock No.	1	4	2	5	6	8	3	7
				Colorimetric					
		tr	tr	0.02	0.10	0.13	0.11	0.07	0.18
				X-ray					
Dec. 61	Fe pl.	0.024	0.054	0.136	0.131	0.118	0.129	0.106	0.170
		0.019	0.053						
Jan. 62	Fe pl.	0.019	0.055	0.138	0.133	0.118	0.132	0.103	0.174
Dec. 61	Cer. pl.	0.005	0.042	0.118	0.126	0.113	0.123	0.100	0.158
Jan. 62	Cer. pl.	0.007	0.046	0.119	0.126	0.114	0.128	0.105	0.164
Dec. 61	Anal. powd.	0.015	0.057	0.119	0.126	0.119	0.129	0.101	0.165
Jan. 62	Anal. powd.	0.013	0.056	0.126	0.130	0.123	0.128	0.103	0.170

Geochemically, the ability to do complete fast rock analysis with the degree of precision achieved in this work, opens entirely new possibilities in studies of all major and some minor elements in rocks. Such petrographically well described but quantitatively little known phenomena as silicification, potassium metasomatism, propylitization, skarn formation, and all major composition changes in rocks, now can be quantitatively investigated quickly and efficiently.

In the past, in geochemistry the emphasis has been mostly on trace elements, and due to the difficulty of the task of the conventional analysis for all the major components, this particular aspect has been insufficiently explored. The X-ray methods make possible fast quantitative geochemical work on major components in rocks. In studies of mineralized areas, emphasis can now be placed on the compositional changes of major components, which should give a far better and more true picture of the migration characteristics and association of trace elements as well.

In general the amount and quality of analytical data, which can be obtained by the X-ray methods, make statistical studies of trace and main element distribution in plutons or any other kind of geological bodies feasible, by applying, for example, a computer program developed for trend surfaces of high order (Baird and others, 1963b).

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Mr. L. L. Knowles executed the grain-size distribution experiment and ground numerous samples. Mr. K. Uchida ground most of the samples. The use of glass discs was encouraged by Mr. Robert C. Horton. Mr. J. T. Ryan built the pressure die, and Mr. J. B. Murphy cut the glass discs used in this work.

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Prof. R. L. Rose, San Jose State College, has kindly provided a short petrographic description and location map of volcanic rocks analyzed.

The standard rock powders G-1 and W-1 were provided by the U. S. Geological Survey; the Syenite 1^a powder by Mr. G. R. Webber of McGill University, Montreal, and by Prof. A. K. Baird; the Albite standard No. 99 by the U. S. Bureau of Standards; and the andesine and albite powders of Emmons by Prof. D. B. Slemmons.

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APPENDIX

DESCRIPTION AND LOCATIONS OF ANALYZED ROCKS

Volcanic Rocks

The locations and short petrographic and geologic description of the volcanic rocks analyzed, has been kindly provided by Professor Robert L. Rose of San Jose State College (private communication, 1962). Detailed geology, modal analyses, and description of these rocks will appear in a future Nevada Bureau of Mines Bulletin to be entitled:

"Geology of the Southeastern Part of the Virginia Mountains, Nevada"

The locations from which these samples were taken, are shown in figure 19.

Rock 1. Devitrified biotite rhyolite welded tuff:

From the lower part of the Hartford Hill formation near Ramsay, Churchill Butte Quadrangle.

A light green felsophyric rock with abundant phenocrysts of quartz, sanidine, and oligoclase-albite and rare biotite crystals enclosed in a microcrystalline matrix of tridymite and alkali feldspar. Feldspar phenocrysts are partly sericitized. The groundmass has a relic vitroclastic texture with flattened devitrified glass shards with an axiolitic structure.

Rock 2. Hypersthene-augite andesite:

From the Alta formation south of Ramsay, Churchill Butte Quadrangle.

A greenish-gray porphyritic rock with phenocrysts of calcic andesine, augite, and hypersthene in an intersertal matrix of sodic andesine, cryptofelsite, magnetite, apatite, and calcite. Hypersthene phenocrysts have been largely replaced by antigorite with minor amounts of magnetite. Plagioclase phenocrysts have been slightly altered and partly replaced by calcite, albite and epidote.

Rock 3. Olivine trachybasalt:

From the upper part of the Chloropagus formation near Clark Station, Wadsworth Quadrangle.

A dark gray slightly porphyritic rock with small olivine and labradorite phenocrysts in an intersertal groundmass consisting of sodic labradorite, augite, ilmenite, apatite, and dark colored glass containing finely divided magnetite. Bowlingite partly replaces the olivine phenocrysts and groundmass.

Rock 4. Biotite-anorthoclase rhyolite:

Angular clasts from a vitric-lithic crystal tuff in the upper part of the Chloropagus formation near Clark Station, Wadsworth Quadrangle.

A light colored, conspicuously layered, sparsely porphyritic rock with small phenocrysts of quartz, sodic oligoclase, biotite, and anorthoclase enclosed in a microspherulitic groundmass consisting of anorthoclase, cristobalite, biotite, quartz, and magnetite. Tridymite lines some of the microvesicles.

Rock 5. Hornblende-augite trachyandesite:

From the Mustang formation south of Clark Station, Wadsworth Quadrangle.

A light gray porphyritic rock with abundant phenocrysts of hornblende and calcic andesine in an intergranular groundmass of andesine, augite, cristobalite, apatite, and opaque minerals. Hornblende phenocrysts are largely replaced by a granular mixture of augite and magnetite; anorthoclase occurs as thin rims on many of the plagioclase phenocrysts and microlites.

Rock 6. Hornblende-pyroxene andesite:

From the lower part of the Kate Peak formation near the Ramsay Comstock mine, Churchill Butte Quadrangle.

A gray porphyritic rock with phenocrysts of calcic andesine, hornblende and hypersthene enclosed in an intersertal matrix consisting of sodic andesine, augite, cryptofelsite, apatite, magnetite, calcite, and chlorite. Hypersthene phenocrysts are small, scarce and replaced by antigorite; hornblende phenocrysts have been replaced by a granular mixture of magnetite, augite, and chlorite. Plagioclase phenocrysts are partly replaced by calcite, albite, and epidote.

Rock 7. Olivine-augite trachyandesite:

From the lower part of the Chloropagus formation southwest of Wadsworth, Wadsworth Quadrangle.

A dense, black, vaguely porphyritic rock with small olivine phenocrysts in a pilotaxitic matrix of sodic labradorite, augite, ilmenite, apatite, and brown glass containing an abundance of finely divided magnetite. Olivine phenocrysts have been largely altered to bowlingite and iddingsite.

Rock 8. Hornblende-hypersthene-augite andesite:

From the lower part of the ?Desert Peak formation near Clark Station, Wadsworth Quadrangle.

A gray porphyritic felsophyric rock with phenocrysts of zoned-andesine-labradorite and hornblende enclosed in a pilotaxitic matrix of andesine, hypersthene, augite, cristobalite, apatite, magnetite with small patches of quartz-alkali-feldspar micropegmatite. Hornblende phenocrysts are largely replaced by a granular mixture of augite and magnetite. Xenocrysts of quartz with augite reaction rims are present in minor amounts.

Granitic Rocks

The three granitic rocks analyzed in this report were taken from areas of rapakivi granites within a complex of Precambrian metamorphic and intrusive rocks of the Gold Butte area in the extreme eastern part of Clark County, Nevada. General descriptions of the petrographic features, as well as chemical analyses of these rocks, are reported by Volborth (1962, p. 824-827). Figure 20 shows the general locations of the sampling areas; Plate 1 of Volborth's (1962) report shows the locations at much larger scale.

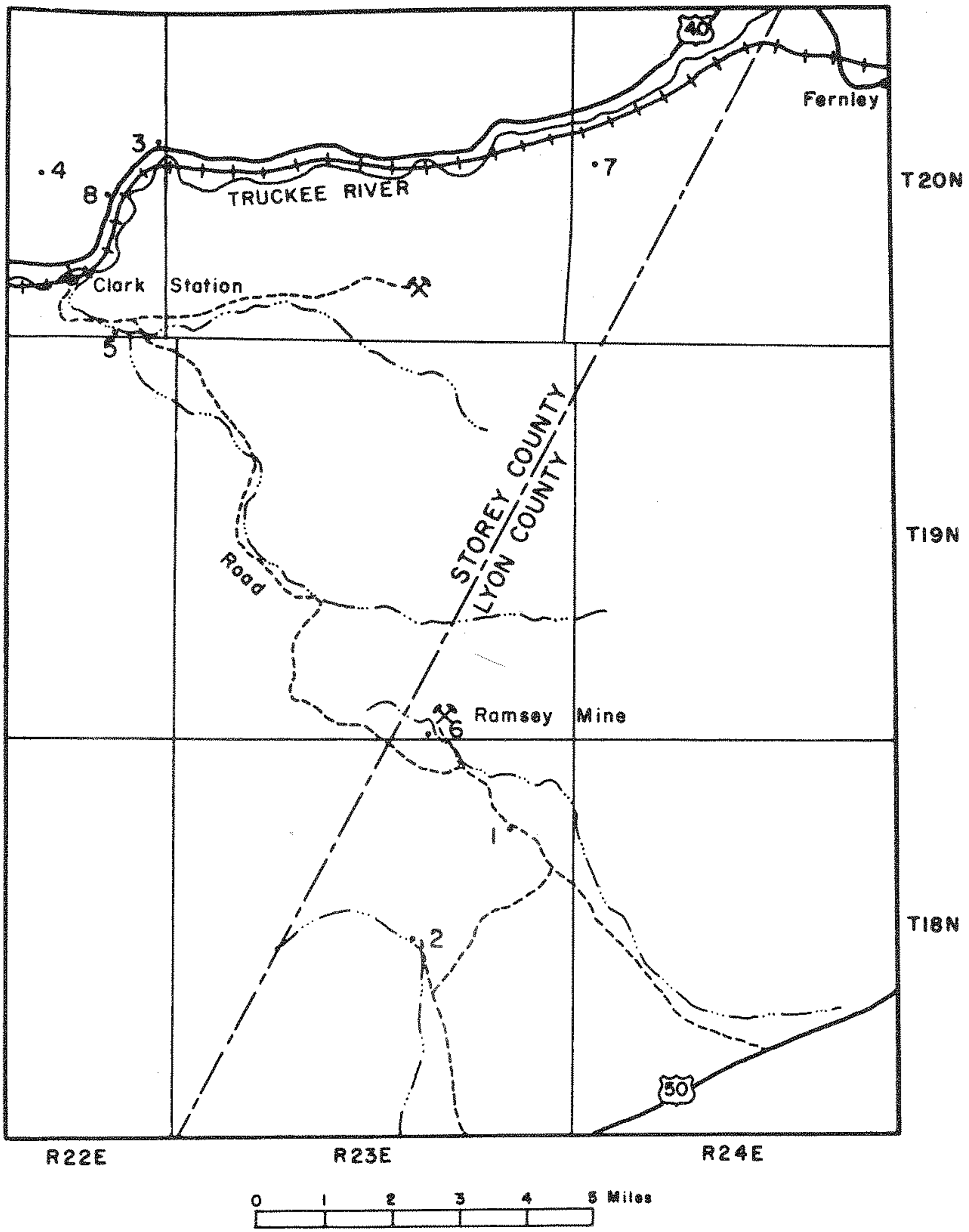

FIGURE A19. Location of volcanic rocks analyzed. Storey and Lyon Counties, Nevada.

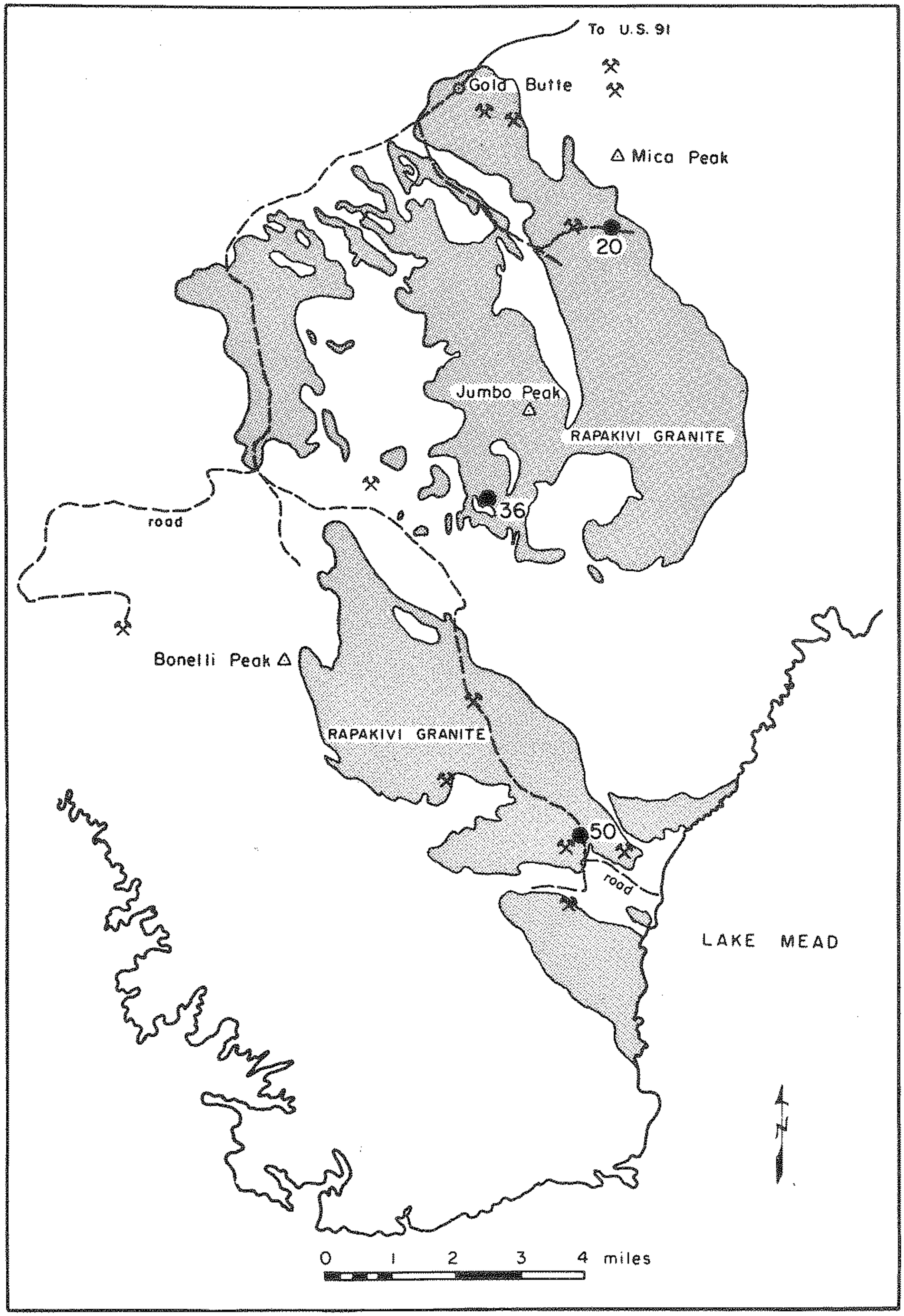

FIGURE A20. Location of granitic rocks analyzed. Clark County, Nevada.

TOTAL INSTRUMENTAL ANALYSIS OF ROCKS

PART B

OXYGEN DETERMINATION IN ROCKS BY NEUTRON ACTIVATION

By A. Volborth

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PART B

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OXYGEN DETERMINATION IN ROCKS BY NEUTRON ACTIVATION

By A. Volborth

ABSTRACT

Oxygen content of two basalts, four andesites, two rhyolites, Syenite 1^a and Diabase W-1 is determined using Granite G-1 and distilled water as standards. The reaction $O^{16}(n,p)N^{16}$ is induced by a 14 m.e.v. neutron flux produced by bombardment of a tritiated titanium target by deuteron beam of 500 microamperes accelerated at 150 kv. The gamma activity of the 7.5 second nitrogen is counted by a NaI(Tl) scintillation crystal and a 256 channel analyzer. The method is fast and nondestructive. The precision achieved is 2 to 3 percent in relative deviation. Accuracy, based on four independent determinations is about 1 percent of oxygen present, or 10 mg of oxygen in two-gram rock samples containing about 50 percent oxygen.

INTRODUCTION

BRIEF DESCRIPTION OF NEUTRON ACTIVATION ANALYSIS

Because this paper is directed not only to specialists in the field, but also to readers with different backgrounds in the earth sciences, it was deemed necessary to explain the basic principles utilized by this method.

When elements are irradiated by certain nuclear particles, such as neutrons, protons, deuterons, tritons, helions, or high energy gamma photons, some of the atoms interact with these particles and undergo nuclear transmutations. Thus, different isotopes of the same element, or isotopes of other elements, are formed. These new atoms are often radioactive. The subatomic particles used as projectiles in this process are produced in nuclear reactors and in different types of particle accelerators.

Specific nuclear reactions occur when given particles are accelerated to specific energy levels. The radioactivity of isotopes produced by these methods can be measured, and the elements identified, on the basis of their characteristic energy spectra. This radioactivity can be of a relatively short or long duration, which is expressed as the half life ($T_{\frac{1}{2}}$) of the isotope. During one half life, half of the atoms originally present decay. This half life is a constant for any specific radioactive species.

Analytical techniques employing different types of elemental particle interactions with matter are called nuclear activation analysis (Wainerdi and Du Beau, 1963). When only neutrons are used we speak of neutron activation analysis.

Neutrons are the most useful and effective subatomic particles for activation analysis. Neutrons of a broad energy spectrum are used for these purposes, and are commonly classified according to their energies into thermal (0.025 e.v.) and epithermal (0.1 to 100 e.v.) neutrons, collectively called "slow" neutrons; intermediate (10^2 to 10^5 e.v.) neutrons; and "fast" neutrons, with energies above 0.1 m.e.v. Being electrically neutral, neutrons penetrate the electron shell of the atom and are captured by the nucleus. Each isotope has a different capability of capturing neutrons of specific energy, this is called its neutron cross-section.

Neutron activation analysis was developed simultaneously with the development of atomic reactors. Neutron fluxes with broad spectral characteristics, covering mainly the 0. to 8 m.e.v. region, are typical for this type of neutron source. Samples to be irradiated are simply introduced into the reactor and exposed to radiation (activated) for different periods of time depending on the half lives of the element or elements analyzed. Nuclear reactors can provide thermal neutron fluxes of 10^{14} n/sec/cm^2, and at least 70 elements can be determined by thermal neutron activation. Analyses for all naturally occuring elements have been performed, using one or another of the different activation methods.

Because of the width of the neutron energy spectrum in nuclear reactors, and the presence of other active subatomic particles, a whole series of possible interactions and transmutations is possible. This somewhat complicates the process of spectrometric separation, and has prompted the use of different types of particle accelerators capable of generating high deuteron fluxes for production of fast neutrons, utilizing, for example, the reaction:

$$H^3(d,n)He^4 + 17.6 \text{ m.e.v.}$$

This equation means that tritium is bombarded by deuterons, producing neutrons and helium. The neutrons so produced have energies of 14.1 m.e.v., and induce specific reactions, for example those of the (n,p), (n,α) or the (n,2n) types. Cross-sections for these reactions can be relatively easily determined because of the monoenergetic nature of the neutrons utilized. Fast neutrons are exceptionally suitable for the activation of some light elements, for example N, O, F, Si, P, and S. Fite and others (1962) list 48 reactions for 48 isotopes irradiated by 14.1 m.e.v. neutrons.

In the present work the reaction $O^{16}(n,p)N^{16}$ is used. This equation means that when oxygen of atomic weight 16, the most common isotope, is bombarded by neutrons of 14.1 m.e.v. energy, nitrogen-16 isotope is produced and a proton is formed. Isotope N^{16} is radioactive, and emits gamma rays of 6.13 and 7.13 m.e.v. energy. It decays again to O^{16} with a half life of 7.3 seconds.

In general, we can write for the rate of formation of product nuclei

$$NF\sigma \qquad (1)$$

per second, where N is the amount of stable isotope in a sample, F is the neutron flux per second per cm^2, and σ is the cross-section for the capture of these neutrons by the target nucleus. Since the product nuclei are radioactive, and disintegrate at a certain rate, we will finally approach a point at which the disintegrations per second will equal the rate of formation of new nuclei. This point is called the saturation point. At this point we can write

$$A_o = NF\sigma \qquad (2)$$

where A_o is disintegrations per second. In activation analysis it is important to remember that saturation has values of 1/2, 3/4, 7/8, and 15/16 with irradiation times corresponding to 1, 2, 3, and 4 half lives respectively. This means that with short half lives one gains little by irradiating for more than four half lives, and that with longer half lives it is seldom necessary to irradiate for more than one or two half lives.

From the equations given one can see that by simply increasing the neutron flux one would extend the detection limit by producing more product nuclei. This means that in neutron activation, detection limits are proportional to the fluxes used.

The technique by which the radioactive isotopes are identified is called gamma ray spectrometry. Gamma rays emitted by radioactive isotopes are used preferably for identification, because, unlike the beta rays, they are monoenergetic, and also relatively much more penetrating. The monoenergetic nature of gamma rays helps to identify specific isotopes by their so-called gamma ray spectra, and the high penetration of gammas minimizes the problem of self absorption in the sample.

A thallium-activated sodium-iodide [NaI(Tl)] scintillation crystal with a photomultiplier tube, pre-amplifier, and a multichannel pulse height analyzer, preferably with an oscilloscope screen, are used for the detection and identification of the gamma ray energy spectra. Pulses of different energy are accumulated and stored in different channels, and the multichannel analyzer is calibrated to cover a specific energy region or spectrum. This spectrum can be viewed on the oscilloscope screen and recorded by typewriter or tape. The advances in these techniques have been recently described (Guinn, 1962).

The origins of activation can be traced as far back as the year 1936, when Hevesy and Levy first applied this principle in thermal neutron activation to determine dysprosium in yttrium metal. However, only during the last few years has nuclear activation analysis become a widely used and generally accepted technique. This is due to the increase in the number of atomic reactors, and the development of new, relatively low-cost deuteron accelerators, and also to the advances in transistorized electronics, resulting in highly precise and versatile multichannel pulse height analyzers, also of reasonable cost. Complete systems for entirely instrumental neutron activation analysis based on gamma ray spectrometry (Guinn, 1962; Guinn and Johnson, 1960) have recently been designed, and considerable experience in operation of low-cost neutron generators has been accumulated (Guinn, 1961; Guinn and Wagner, 1960; Meinke, 1960; Meinke and Shideler, 1962; Stallwood, Mott, and Fanale, 1963; Steele and Meinke, 1961, 1962; and Veal and Cook, 1962).

The main advantages of nuclear activation methods are: 1, independence from the matrix; 2, speed, permitting analyses in a few minutes; 3, extreme sensitivity, permitting the detection of some elements down to parts per billion; 4, nondestructiveness in the absence of specific interferences; and 5, selectivity, when the multitude of possible reactions is considered.

The main disadvantages at present are the relatively high cost of tritiated targets used in the low-cost accelerators. In thermal neutron activation one also often is faced with the necessity of preliminary chemical separations, which have to be performed quickly. In all instances one has to be aware of the dangers in handling of radioactive materials when working with activated samples. Shielding of a neutron source of high yield may present difficulties, if equipment is to be installed in laboratory buildings not designed specifically for this purpose. Fast transfer and timing systems have to be used if shortlived isotopes such as N^{16} are determined.

The great advantages of this method by far outweigh the disadvantages in a general evaluation of its usefulness. Activation analysis is without doubt already one of the most useful of all analytical techniques. It may, if properly applied, help solve many as yet unsolved problems in geochemistry, mineralogy, crystallography, and geology.

PREVIOUS AND PRESENT INVESTIGATIONS

This paper is based on a method developed and work done with Dr. H. E. Banta at the Oak Ridge Institute of Nuclear Studies (Volborth and Banta, 1963a, b).

In standard gravimetric analyses of rocks and minerals the main constituents are conventionally reported as oxides, despite the fact that total oxygen is not determined independently. Nevertheless, when sulphur, fluorine, chlorine, and some other elements which structurally occupy similar positions as oxygen, are determined, even relatively minor corrections for equivalent oxygen are introduced. It is shown in Part A of this report that rapid, sensitive, and highly precise and accurate X-ray emission analysis of all major constituents of rocks, excluding only oxygen, can now be performed. Independent determination of the major constituent of rocks - oxygen, comprising for example about 46 percent of granitic rocks, is therefore highly desirable if not mandatory. One can say that such analysis will permit us to balance out a rock or mineral analysis and will make it more "complete". In the present state of X-ray analysis we seem to be able to detect the effect of the non-determination of trace elements (see Accuracy of the Method, Part A). Independent oxygen determination is therefore of great significance, and the accuracy of the total analysis is apparently approaching the necessary limit for indirect ferrous-ferric iron determination based on total oxygen.

To be of practical value for geochemical research, an oxygen determination procedure has to be compatible in speed, precision, and accuracy with the X-ray method. Two such methods adaptable to rocks have been recently developed. These are: 1, the soft X-ray technique as developed by Henke (1963) and applied to rock powders by Baird and others (1963); and 2, the neutron activation method applied to rocks by Volborth and Banta (1963a, b).

Neutron activation techniques developed for oxygen are relatively recent (Stallwood and others, 1963; Steele and Meinke, 1962; Veal and Cook, 1962). These methods were developed for determination of oxygen as a minor constituent in organic materials, and the precision achieved is 10 to 25 percent in relative standard deviation. For rocks, much higher precision is necessary to achieve meaningful results. Precision of 0.39 percent in relative standard deviation was achieved on water (88.89 percent oxygen) used as a standard for oxygen analysis in rocks (Volborth and Banta, 1963a, b).

All of the neutron activation methods mentioned above use the reaction:

$$O^{16}(n,p)N^{16}$$

The high energy 7.1 and 6.1 m.e.v. gamma rays, emitted by the 7.3 second isotope nitrogen-16, are counted in large flat or well-type NaI(Tl)-crystal scintillation counters after fast pneumatic transfer of samples.

Three major difficulties are encountered: 1, the interference of the primary reaction $F^{19}(n, \alpha)N^{16}$; 2, the interference of the reaction $B^{11}(n,p)Be^{11}$ with 6.8 m.e.v. gammas; and 3, the short half life of 7.3 seconds of the gamma radiation of nitrogen-16 which affects the precision and requires fast transfer of sample. Fortunately points 1 and 2 are usually of minor importance, because in most igneous rocks the amounts of fluorine and boron are small, and knowing the concentration of these elements, corrections for oxygen can be made. The use of a dual transfer and counting system has been proposed to improve the precision (Volborth and Banta, 1963b).

This work has been partially supported by both the National Science Foundation (grant number GP-864), and by the United States Atomic Energy Commission.

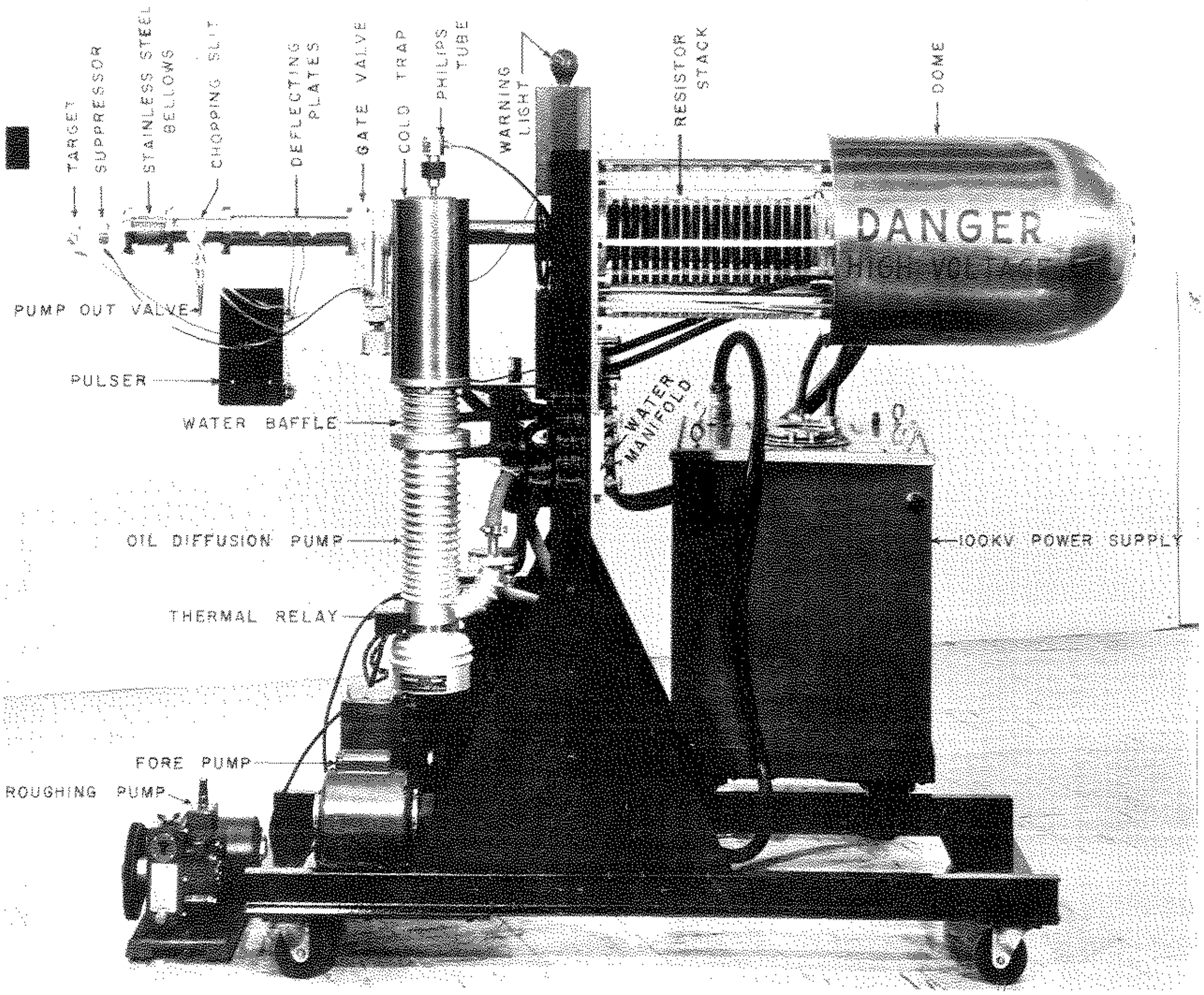

FIGURE B1. Texas Nuclear Corporation neutron generator. A similar generator, but with a 150 KV power supply, was used for the oxygen analysis described in this report.

EXPERIMENTAL

APPARATUS

Apparatus consists of the Texas Nuclear neutron generator (fig. 1) and control (fig. 2). This generator was equipped with the Oak Ridge ion source (Moak and others, 1951). A Radiation Counter Laboratories 256 channel analyzer and a 3 X 3 inch Harshaw Integraline NaI(Tl) crystal were used for the detection. The spectra are printed out by an IBM computer typewriter. The spectra are cut off at channel 55, corresponding to the 4 m.e.v. energy level of the gamma radiation. A fast transfer system, similar to that described by Meinke (1960-1961) and built in Oak Ridge Institute of Nuclear Studies, is used. Estimated sample transfer time is 0.6 seconds. The reaction $H^3(d,n)He^4$ is induced by bombarding an extra thick 10 curie, 1.3 c/cm^2, tritiated titanium target by deuteron beam of 500 microamperes accelerated at 150 kilovolts. The extra thick tritium targets were obtained from the U. S.

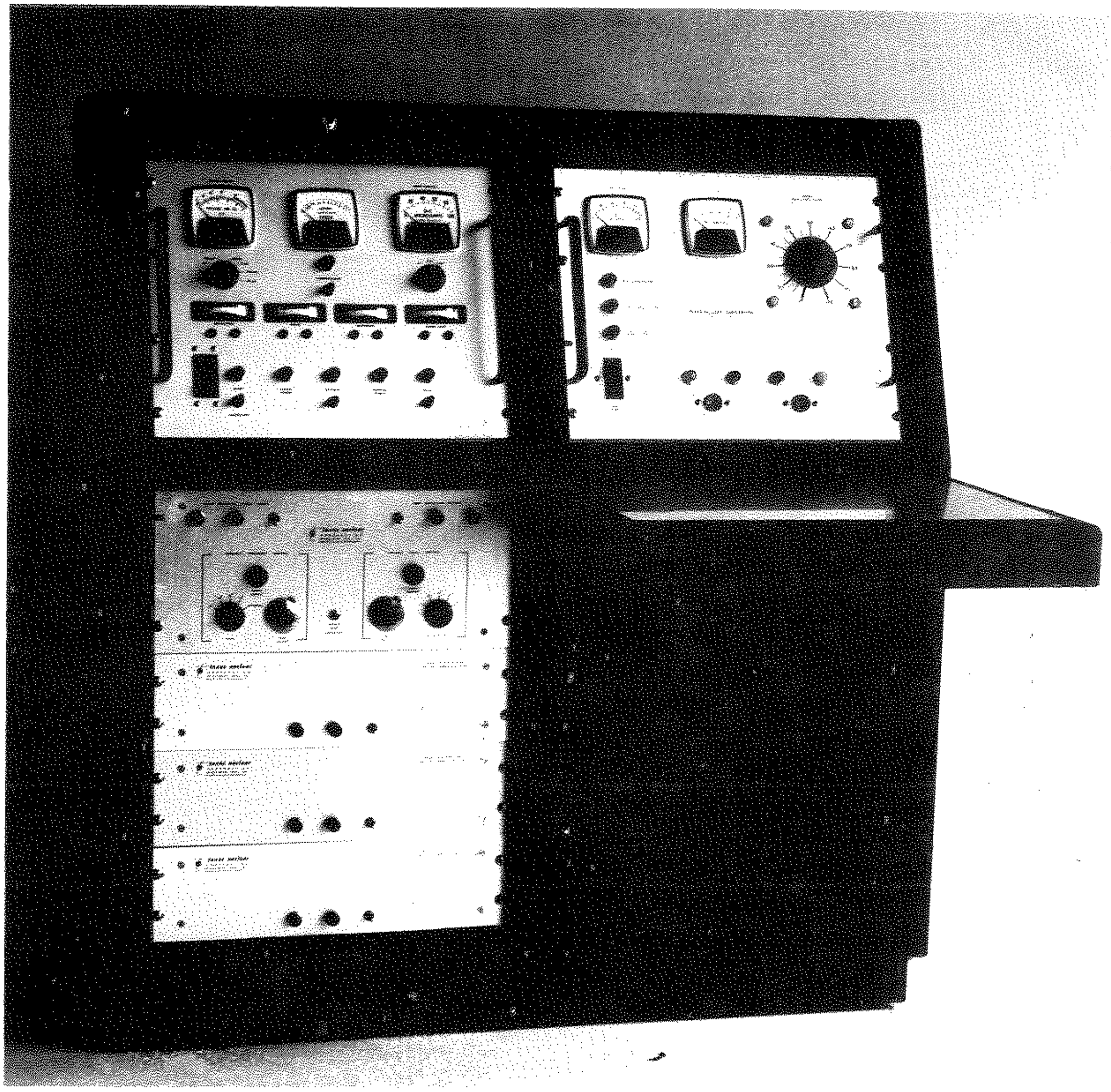

FIGURE B2. Control panel for the neutron generator and the sample transfer system.

Radium Corporation, Morristown, New York. The initially generated flux of 14 m.e.v. neutrons was approximately 7 X 10^8 n/cm^2/sec. Associated alpha particle counting system used, was described earlier (Volborth and Banta, 1963).

SAMPLES

Samples analyzed consisted of United States Geological Survey Standards Granite G-1, Diabase W-1 (Stevens and others, 1960), distilled water, Syenite 1^a (Nonmetall. Std. Comm. report, 1960), and four andesites, two basalts, and two rhyolites described in Part A of this report. All volcanic rocks analyzed were ground by ceramic plates. Screw-top cylindrical sample containers 2.8cm long and 1.5cm in diameter with circular flanges to reduce friction were used (fig. 3). Internal volume of these containers was 1000 mm^3 ± 10 mm^3 with the screw top in place. The material used in these machined

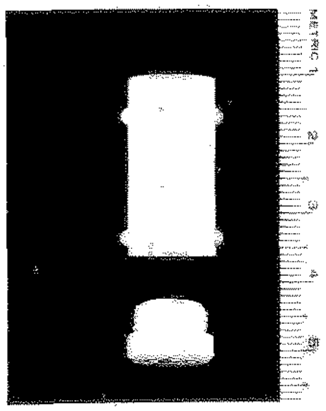

FIGURE B3. Exact-scale photograph of the Marlex container (rabbit) used for sample transfer.

"rabbits" was Marlex, manufactured by Phillips Petroleum Company of Bartlesville, Oklahoma. The oxygen content of similar material has been determined by Stallwood and others (1963, p. 8). Sample weight varied from 1.7 to 2.4 grams, with oxygen content of 0.8 to 1.1 gram (table 1). Contribution of atmospheric oxygen and the oxygen in the Marlex container could be ignored, because oxygen was the major constituent of the samples.

ACTIVATION

Activation and sample transfer consisted of 1 minute irradiation and punch button pneumatic transfer of the rock powder in the container, and accumulative counting for 30 seconds. Four irradiations were performed on each sample, alternating with the G-1 standard each time. This procedure permitted the spread of each activation over a relatively wide target decay period, insuring a greater degree of random distribution in the intensity. The intensity ratios of each unknown sample to the two neighboring samples of G-1 were computed, and the mean values of four determinations so obtained plotted versus equivalent oxygen on a linear coordinate net.

RESULTS

Residual spectra were taken from rocks Syenite 1[a] and Andesite 5 to further ascertain that no interference from other elements exists in this spectral region when whole rock powders are irradiated. Each spectrum was projected on the oscilloscope screen and superimposed on logarithmic scale to detect possible irregularities. These data are demonstrated in figure 4, showing remarkable absence of interference by long lived high-energy gamma rays, and practically identical spectra. Half lives of N^{16} in water, and in rocks G-1 and W-1, have been determined earlier to show absence of interference (Volborth and Banta, 1963a, b). The only interference detected is that of primary reaction $F^{19}(n, \alpha)N^{16}$, and reaction $B^{11}(n,p)Be^{11}$ with 6.8 m.e.v. gammas. Precision of this method was determined on twelve rock samples. In terms of relative standard deviation it varies between 2 and 3 percent in nine cases out of ten. This is inferior to the precision obtained with the water sample (Volborth and Banta, 1963b), but it is probably more typical for

TABLE B1

Comparison of Oxygen Analyses by Neutron Activation with Equivalent Oxygen

Sample	Sample Weight (grams)	Equivalent Oxygen Percent	Equivalent Oxygen Weight (grams)	Intensity Ratio Sample: G-1	Oxygen 1) Weight determined (grams)	Percent Error	Oxygen 2) Weight determined (grams)	Percent Error
3a, Basalt	2.2423	45.50	1.020	0.974	1.019	0.1	1.000	2.0
G-1, Granite	2.1334	48.76	1.040	1.000	1.049	0.9	1.040	0.0
7a, Basalt	2.2965	45.56	1.046	1.003	1.052	0.6	1.045	0.1
8a, Andesite	2.2953	46.39	1.065	1.007	1.057	0.8	1.050	1.4
1^a, Syenite	2.3872	44.86	1.071	1.013	1.063	0.7	1.060	1.0
1a, Rhyolite	2.1639	49.88	1.079	1.027	1.079	0.0	1.081	0.2
2a, Andesite	2.3678	46.98	1.112	1.055	1.111	0.1	1.123	1.0
6a, Andesite	2.4013	46.82	1.124	1.067	1.124	0.0	1.142	1.6
H_2O	1.2504	88.89	1.112	1.048	1.103	0.8	1.112	0.0
4a, Rhyolite	1.7712	49.44	0.876	.878	(.909)	3.8	.854	2.5
5a, Andesite	1.9589	45.53	0.892	.926	(.965)	8.1	.927	3.9
W-1, Diabase	2.0404	44.85	0.915	.920	(.958)	4.7	.918	0.3

1) *Calibration line drawn only over composition range* 1020-1125 *mg*.
2) Calibration line drawn through G-1 and H_2O points.

this nonspecialized equipment when applied to rock powders using other rock powders as standards.

When the means of four independent determinations were plotted versus theoretical oxygen content of the samples based on cation determinations by X-rays in tables 26 and 27, Part A, a linear calibration curve was obtained, fig. 5. The data from this calibration are compiled in table 1. One can see from the analyses in this table, that the accuracy of the neutron activation method is high when very similar amounts of oxygen are analyzed. The relatively higher intensities of the three rocks Diabase W-1, Rhyolite 4, and Andesite 5, are apparently due to the effect of shorter dead time due to the smaller amount of counts accumulated by the multi-channel analyzer. This effect is relatively strong when working with very short half lives, because the analyzer corrects for dead time at the end of the counting period, when no more quanta are received.

In figure 5, the calibration curve is drawn according to the least square principle, using points in the 1020-1130 mg oxygen region, and also by simply connecting G-1 and H_2O points. If the curve is drawn through standard points H_2O and G-1, better results for rocks W-1, Andesite 5, and Rhyolite 4 are obtained (table 1). This was done to show that despite the dead time effect which flattens the slope, a linear calibration curve can be used. Only one acceptable analysis of W-1 was available, making this point less significant than others on this figure.

From these observations one can conclude that the matrix and absorption effects are relatively small for these high energy gammas. When water was used as the standard, and rock and mineral N^{16} intensity ratios were plotted to water, this effect was not detected (Volborth and Banta, 1963b, fig. 4). Nevertheless, the use of similar matrixes as standards, similar masses, volumes, and samples of similar oxygen content, is very important for high precision and accuracy.

The results in table 1 and figure 5 are not to be regarded as absolute values, but as a basis of, and an example for stoichiometric comparison of total cation determination in

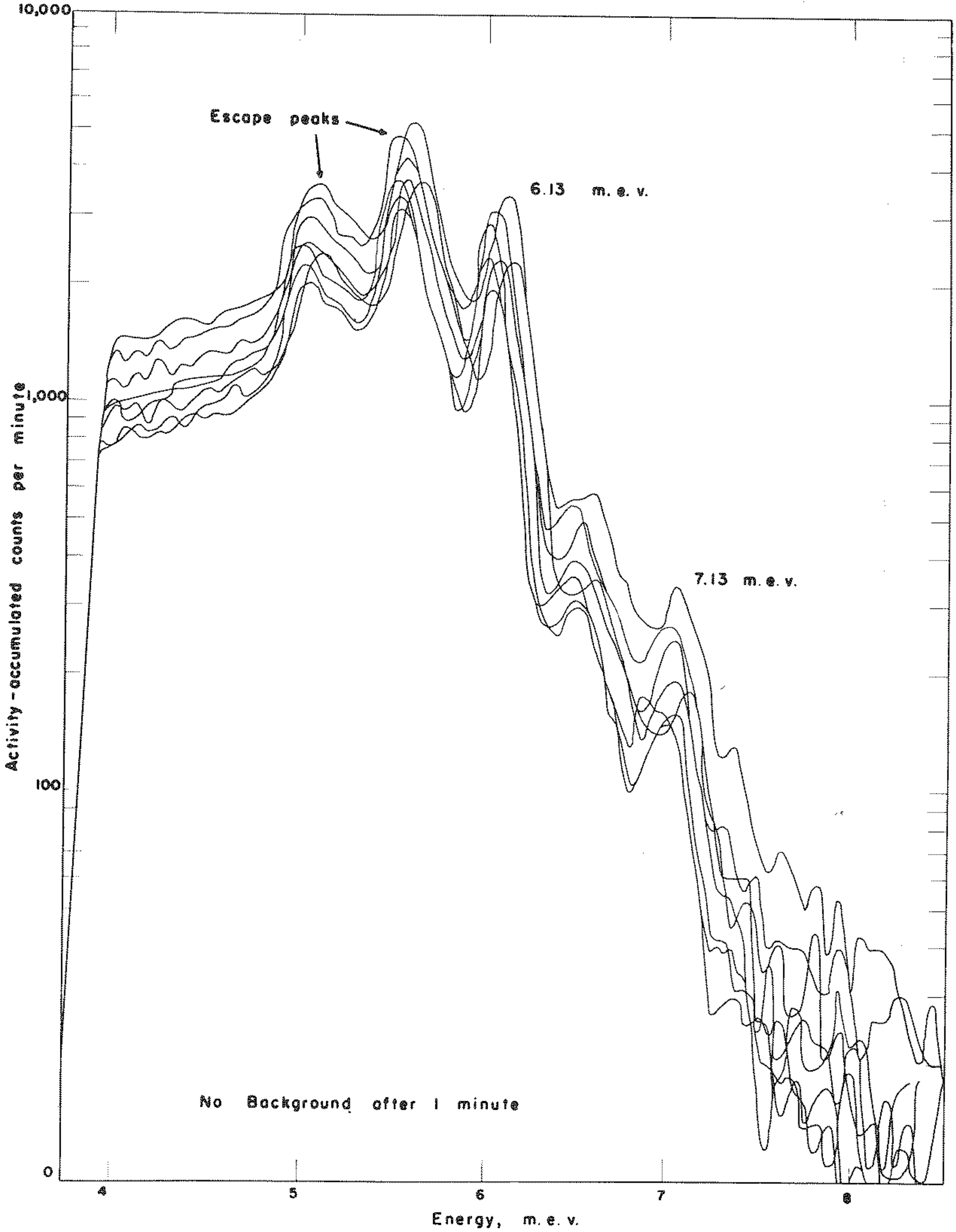

FIGURE B4. The N^{16} gamma spectra of two basalts, four andesites, and two rhyolites superimposed on logarithmic scale. Due to target decay, integrated intensities are consecutively decreasing. The discriminator was set at channel 55, corresponding with an energy level of approximately 4 m.e.v.

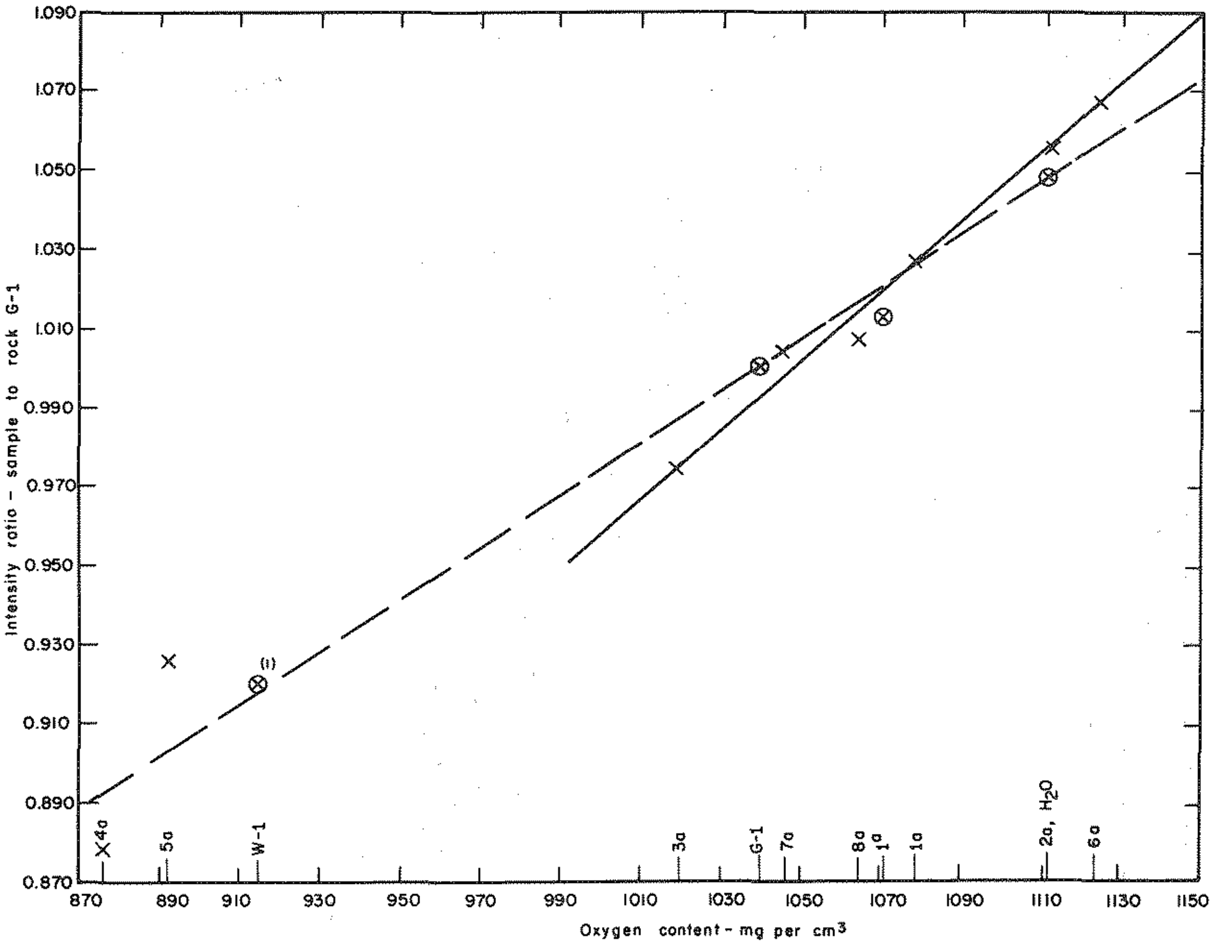

FIGURE B5. Calibration of oxygen analyses in 11 rocks. Two linear calibration curves are used. The solid line calibration curve is based on oxygen content in the region of 1020-1130 milligrams. The dashed line is based on connecting standard points G-1 and H_2O. *Results of both methods appear in two separate columns in table 1.*

rocks with equivalent oxygen. Only in Andesite-6a has the difference of the present total of 98.97 percent from 100 percent been recalculated to oxygen assuming 40 percent equivalent oxygen. In none of the other oxygen calculations have the trace elements been taken into account, and the X-ray data have not been recalculated to 100 percent. It can be estimated that if this were to be done the equivalent oxygen would change by not more than 0.4 percent, corresponding to not more than 10 mg oxygen in each two-gram sample. This would also require corresponding recalculations for rocks G-1 and W-1. Neither the present status of total rock analysis, nor the precision here achieved, yet warrant the amount of work that such recalculation would require. To emphasize this uncertainty, the oxygen percentages by neutron activation are not given in this table. They can, however, be easily calculated from data given.

DISCUSSION AND CONCLUSIONS

The ability to detect the effect of nondetermination of trace elements (see Accuracy of the Method, Part A, tables 26 and 27), and the ability to determine total oxygen independently, bring us closer to the goal of total rock analysis in the true meaning of this word. When precision and accuracy both of the cation determinations and the total oxygen determination are improved, we will have in the combined X-ray emission and neutron activation methods a tool for fast total analysis of rocks. This constitutes a nearly complete instrumental approach to the analysis of silicates, which can be extended to carbonates, sulfates, phosphates, oxides, and their mixtures, with the ability of independent check for equivalent oxygen.

Oxidation states and ratios can be estimated quickly by this method. For example, the ferrous-ferric iron ratio could be determined in rocks. A rock containing 10 percent Fe_2O_3 has nearly one percent more iron-bound oxygen than the same rock containing the same amount of iron in the bivalent state. Assuming an ideal case in which a rock has been analyzed for all constituents including oxygen, and was found to contain 10 percent total iron given as Fe_2O_3, but an excess of 0.50 percent oxygen, and assuming that iron is the only element present displaying multiple valence, one can estimate the ratio of $2FeO:Fe_2O_3$ to be 1:1. Therefore, should it become possible to determine oxygen in rocks with a precision and accuracy of 0.1 percent oxygen, the ferric ferrous ratio could be estimated to within 1 percent FeO or Fe_2O_3. Fortunately igneous rocks contain no other major elements displaying simultaneously multiple valence. In most cases it is also possible to detect petrographically whether the rock contains sulfides, and the valence of the transition elements in rocks is also mostly known.

It is hardly possible to achieve better precision than 2 to 3 percent in relative standard deviation with the equipment used here, mainly because of neutron flux variations, but since the distribution of the gamma-ray energy is strictly Gaussian, and practically no interference or background are observed, accuracy of nearly one percent can be achieved in most cases, when four independent activations accompanied by consecutive activation of standards are done, as shown in table 1. To achieve better precision and accuracy, a dual transfer and counting system is being planned in this laboratory.

The difference of the total oxygen content of rocks G-1 and W-1 is about four percent, and it appears to be possible to distinguish certain groups of rocks on the basis of their total oxygen content. Since oxygen is assumed to be "squeezed" out from the depths of the earth's crust, it may be possible, by studying the oxygen content of similar rocks, to get some indication as to their original position in depth. Total oxygen determination in connection with deep drilling projects and the studies of batholithic bodies, may yield important information on the oxygen gradient in the earth's crust. Some information relative to the original depth of emplacement of batholithic bodies could also be obtained by studying the oxygen gradient.

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NEVADA BUREAU OF MINES

VERNON E. SCHEID, DIRECTOR

REPORT 6

TOTAL INSTRUMENTAL ANALYSIS OF ROCKS

PART C

SECTION 1

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By ALEXIS VOLBORTH and BRENT FABBI

SECTION 2

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By BRENT FABBI and ALEXIS VOLBORTH

MACKAY SCHOOL OF MINES
UNIVERSITY OF NEVADA

1970

TOTAL INSTRUMENTAL ANALYSIS

NEVADA BUREAU OF MINES REPORT 6, PART C

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PART C

FOREWORD

Sections 1 and 2

In Parts A and B of this report, printed by this agency in 1963 (Volborth, 1963a; 1963b), a total nondestructive analysis for all major constituents in rocks was demonstrated. Absorption, enhancement, and matrix effects on X-ray fluorescence (XRF) determination of trace elements, as well as widely varying concentration of each of these elements in rocks analyzed, forced a more thorough investigation of each of the 38 trace elements of interest and thus delayed publication of this third part. An effort was made to acquire emission spectrographic data from other laboratories in order to have an unbiased basis for comparison of the accuracy of our X-ray spectrographic methods. These determinations were made by A. A. Chodos of the Geology Department of the California Institute of Technology, Pasadena, and A. T. Myers of the U. S. Geological Survey in Denver. The methods used by these laboratories were routine, as our purpose had been to develop a rapid routine X-ray procedure for trace element determination. As a result of our studies, it became apparent that in X-ray spectroscopy, as in arc-emission spectroscopy, one can roughly distinguish between *semiquantitative and quantitative techniques, in addition to purely* qualitative analysis.

Extensive inter- and intralaboratory comparative studies were made during the period of 1963-1968. As a result, we believe that describing any carefully obtained instrumental data on trace elements as "quantitative" is unjustified unless data from not less than two other independent laboratories indicate at least the same order of magnitude in concentration of the elements analyzed in the same sample, and, preferably, when two different analytical methods are employed to avoid possible bias. Further improvement of results within a certain laboratory seems merely to indicate improvement in precision, not accuracy.

This report is divided into two sections: one, reporting results of analyses by the XRF method in comparison to data obtained by other methods and laboratories; the other, presenting results without comparison to data obtained from other laboratories.

Unfortunately, some repetition was unavoidable in the sample preparation description. Correction procedures described also are partially repeated, but the structure of the reports is such that successive steps necessary to obtain better accuracy are described in the increasing order of complexity of the procedure or correction, so that the reader may proceed from one step to the next while advancing through the text. Basically, the sample preparation techniques described in Part A of this report (Volborth, 1963a) have remained unchanged through the years. The high precision achieved in counting trace element X-ray quanta is, in the opinion of the authors, due to sample homogeneity and pressing against *glass as described in part* A.

It is hoped that the procedures described may be useful in other laboratories analyzing rocks by X-ray fluorescence.

No claims of superiority to other methods are made in connection with the described techniques; however, the authors believe that equivalent qualitative and quantitative results can be obtained more rapidly by the methods presented. Inherently more precise, these X-ray methods may be of significance in geochemical work because small trace element concentration differences become distinguishable in similar rock samples.

This work was completed in 1968, but publication was delayed owing to the transfer of both authors. While much significant advance has occurred in the past two years, it is interesting to note that, since completion of this work, other analysts have used similar methods and arrived at identical conclusions, especially concerning the relative insignificance of mass absorption correction for major elements in rock analysis (Leake and others, 1969/1970, p. 7). Recently, it was also pointed out (Campbell and Gilfrich, 1970, p. 251) that direct comparison of XRF to other spectrographic methods is desirable.

The authors feel, therefore, that despite the delay in publication, Part C of this report may prove useful in part for XRF spectroscopists.

Alexis Volborth

Brent P. Fabbi

Nevada Bureau of Mines
University of Nevada, Reno
May, 1970

TOTAL INSTRUMENTAL ANALYSIS OF ROCKS

PART C

Section 1

SEMIQUANTITATIVE X-RAY SPECTROGRAPHIC DETERMINATION OF 38 ELEMENTS IN A NEVADA GRANITE AND IN STANDARD GRANITE G-1

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SEMIQUANTITATIVE X-RAY SPECTROGRAPHIC DETERMINATION OF 38 ELEMENTS IN A NEVADA GRANITE AND IN STANDARD GRANITE G-1*

By Alexis Volborth and Brent P. Fabbi**

ABSTRACT

Granite rock obtained in connection with the drilling for the Atomic Energy Commission Project Shoal in Nevada is analyzed for 38 trace elements by X-ray emission. Elements Ag, As, Ba, Cd, Ce, Co, Cr, Cs, Cu, Ga, Gd, Ge, Hf, Hg, In, La, Mo, Mn, Nb, Nd, Ni, Pb, Rb, Sb, Sc, Se, Sm, Sn, Sr, Ta, Th, Ti, U, V, Y, Yb, Zn, and Zr are determined in nonfused, pressed rock-powder pellets. Relative standard deviation varies from 1 to 10 percent over the composition range of 1 ppm to 7,000 ppm. Results are based on *linear calibration curves* obtained with synthetic standard powders made by homogenizing known amounts of the trace element compounds in a mixture containing 80 percent quartz and 20 percent Al_2O_3. To correct for the difference in total absorption and enhancement, standard G-1 is used. The accuracy of the method is demonstrated by comparison of our data with values for rock G-1 (and W-1). Results obtained fall near the recommended values for these standard rocks. Established detection limits vary mostly within the range of 1 to 50 ppm.

It is suggested that satisfactory semiquantitative trace element analysis can be performed by simple comparison of relative X-ray intensities in similar rocks. The high precision of this method makes it especially suitable for geochemical work where absolute accuracy is not necessarily required. This approach permits the detection of minute differences in composition of physically similar rocks. The analyzed granite powder is used as a secondary standard in the Nevada Mining Analytical Laboratory. Restricted amounts of the rock powder are available upon request.

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* This paper was presented at the XIII Colloquium Spectroscopicum Internationale in Ottawa, Canada, 1967; printed in abstract form (Volborth and Fabbi, 1967).

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INTRODUCTION

We intend to show that trace elements can be determined semiquantitatively in a granitic rock by X-ray emission using plain pressed powders and comparing the intensities with artificial standard samples of similar matrix. This approach should permit us to disregard in this particular case the absorption, enhancement, and mineralogical effects. If successful, this method may rival the semiquantitative optical emission spectrographic methods frequently used in practical geochemical investigations. No claim is made that this procedure may overcome the matrix and other well-known and established effects in X-ray emission, but we try to demonstrate that these effects may be mutually cancelling and are sufficiently minimized by using standards which have similar matrices. In geochemical and industrial types of analysis this method, if successful, may prove to be most adaptable and straightforward because of the nature of analytical problems in these fields.

In geochemistry one seldom compares analytical data of rocks greatly different in composition or mineralogical nature. It is the variation in composition of a rock type, a basalt, a granite, or a schist, for example, that we usually study. By selecting a typical secondary standard or making a composite sample one can often obtain relative results more rapidly than by attempting to get the absolute values on individual elements. It is usually easier to find out whether the concentration of an element is increasing or decreasing in physically similar samples than to search for the absolute value, which is never known in a strict sense. It is often not even necessary to analyze the secondary standard as long as all data reported are related to it. The question, therefore, is whether we can get meaningful results by analyzing a granite using a granite standard powder of similar grain size distribution, thus only partially compensating for the effects inherent in X-ray spectrographic methods.

It was shown previously (Volborth, 1963a; 1965), that major elements Al, Ca, Fe, Mg, Mn, Na, K, Si, and Ti can be determined satisfactorily in plain, nonfused, pressed rock powders by X-ray emission using similar granite powders as standards. The accuracy of this method was shown to be adequate by comparison with gravimetric data (Volborth, 1963a; 1965), by the detection of the effect of the "nondetermination" of trace elements (Volborth, 1963a; 1964b), through the demonstration of the biotite effect (Volborth, 1964c), and by independent stoichiometric accuracy checks by the fast-neutron activation analysis for total oxygen in the same rock powders (Volborth, 1963b; 1964a; Volborth and Banta, 1963). In the present paper this method is extended to cover a wide range of trace elements from atomic number 23 (Sc) to 92 (U).

It must be noted that at present most analysts in the field of X-ray emission analysis of minerals, rocks, and ores, prefer to flux their samples (Baird and others, 1962; Bertin and Longobucco, 1962; Claisse, 1965; Hooper, 1964; Longobucco, 1962; Rose and others, 1962; Welday and others, 1964). This is done mainly in order to homogenize the sample to avoid mineralogical effects or to achieve further dilution. In some cases a heavy absorber is added to minimize the matrix effect (Rose and others, 1962). Other workers recommend the use of fused glass discs to avoid grain-size effects (Norrish and Hutton, 1964). In all these cases one has to weigh the sample and the fluxing medium with the heavy absorber, and the fused sample has to be reground if pressed powders are used. When a flux is used, the counting rates suffer from the dilution effect and especially from the heavy absorber effect. which means longer counting, higher background, and relatively poor precision. When trace elements have to be determined, fluxing, heavy absorption, and all but moderate dilution techniques are at a disadvantage because of poor detection capabilities. In our system, using K_{α} lines, detection limits for trace elements in plain rock powders lie in range of 1 to 10 ppm. When using the L_{α} lines the detection limits are usually between 10 to 100 ppm.

Because rocks and minerals are water bearing and often carbonate bearing and contain other volatile substances, it is important also to be able to control the dilution effects of plus and minus water ($+H_2O$, $-H_2O$) on the X-ray intensities. If the rock is fused, weighed addition of flux, corresponding to the weight loss during the fusion, must be made (Welday and others, 1964, p. 901). This is cumbersome. In samples fused in graphite crucibles some elements may be partially reduced to metals (Cu, Bi, Ni, Co, Fe), and alkalies may be partially volatilized. Besides, the fluxing reagents are often water bearing, and may also be hygroscopic, making this type of control difficult when high accuracy is desired. It is cumbersome to control ignition losses during fluxing procedures because the losses depend on the temperature gradients, the varying humidity of the atmosphere, burner or oven temperature, time used for fluxing, cooling time and conditions during this period, and the time elapsed between the fluxing and the actual analysis. Factors influencing the X-ray intensities in a complex mixture are consequently numerous, and the multiple effects are so difficult to control experimentally that one solution seemed to be to ignore these interferences and see whether meaningful semiquantitative data could still be obtained.

The reasoning behind this decision is that rocks are mixtures of minerals composed mostly of light elements; oxygen, silicon, and aluminum form together 70 to 90 weight percent of a silicate rock; therefore, one can regard the other major or minor elements in silicate rocks as dilutions in a light matrix (Volborth, 1963a). Structurally, in silicate rocks, we can speak of silicon-oxygen and aluminum-oxygen tetrahedra in coordination with the much smaller cations surrounding these in an orderly manner, which means a certain similarity of basic structure despite the mineralogical differences. All this should indicate that silicate rock powders must, as such, possess some of the inherent built-in characteristics of artificially made dilutions and glasses.

Other work done in this field (Ball, 1965; Chodos and Engel, 1961; Hooper, 1964) seems partially to support nonfusion techniques within the limits governed by the multiple known interferences. Different rock types, or different minerals, naturally, cannot be analyzed by this method unless physically similar standards are available. Volborth (1963a, p. A61) has, for example, shown that a volcanic tuff cannot be compared directly with granites, andesites, or basalts of similar composition, and has emphasized the importance of the "biotite" effect due to the presence of a micaceous constituent in a rock (Volborth, 1964c; Baird and others, 1965). Fusion of rock powders (Claisse and Samson, 1962; Hooper, 1964; Longobucco, 1962; Welday and others, 1964) or heavy absorber addition (Rose and others, 1962), or specific corrections applied to unfused rocks (Alley and Myers, 1965; Baird and others, 1962; Kiss, 1966), coupled with computer programmed techniques (Hower and others, 1964), all add to the confidence in specific cases, but are generally more cumbersome than the undiluted plain powder techniques.

Thus it seems that the argument about the superiority of sample preparation methods is not whether the calibration curves are linear or nonlinear (Czamanske and others, 1966, p. 755-756), but should consist of an evaluation of the method's applicability to a particular problem within the limits shown or implied by the authors. For example, the effect of enhancement of Al by Si, detected, demonstrated, and empirically calculated for rocks G-1 and W-1 by Volborth (1963a, p. A24-A28), has been pinpointed more accurately recently by Czamanske and others, (1966, p. 748-753, Figs. 2 and 6, Tables 3 and 4). This effect has also been observed by A. K. Baird (personal communication, 1964). X-ray analysts working with rocks know that the calibration curves for these complex substances are, strictly speaking, nonproportional and nonlinear; so we must determine whether these combined effects will cause significantly erroneous results in our idealized systems. In the methods used here, the "measured" calibration curves (using Czamanske's terminology [1966, p. 750]), rather than "adjusted," are used, which automatically and, for our purposes, sufficiently corrects for the nonlinearities in the systems investigated. By using the term "sufficiently," we imply that our data would fall within the presently accepted limits for precision and accuracy in geochemistry.

Silicate rocks are mostly composed of low atomic number elements with characteristic X-radiations in the low energy range of 3 to 15 Å. Thus the critical depth diminishes to such a degree that the fluorescent radiation reaching the counter comes mainly from the surface. Enhancement effects and the efficiency of excitation decrease, resulting in relatively low counting rates, which would decrease even more in case any heavy absorber is introduced. However, fusion with a light flux naturally increases the depth of penetration of X-rays, partially offsetting the dilution effect. With the increase of the importance of the surface, the effect of micaceous minerals also increases (Baird and others, 1965; Volborth, 1964c); this may be critical in trace element work, as fusion is necessary when mica content of sample and standard is disproportional or when micas present are of different composition. The importance of surface reproducibility and equal grain size in low energy X-ray work cannot, therefore, be overemphasized, regardless of whether nonfusion or fusion is used. In our case, sample preparation has been solved satisfactorily by pressing moistened powders against glass (Volborth, 1963a, p. A9-A11). The principle of the least amount of handling of the sample, combined with the principle of a dual grinding and analysis (Volborth, 1965) should give us the best possible precision and, in most cases, sufficient accuracy in the determination of trace elements in rocks. The same pellets can be used in the determination of major elements as well.

The final goal is to show that accurate X-ray spectrographic analyses of trace elements can be done on igneous rocks using two sets of standards, one with a "pseudogranitic," another with a "pseudobasaltic" matrix. This paper deals with data obtained with the "pseudogranitic" synthetic standard. Very few corrections, based on combined measured enhancement, absorption, and line interferences, are necessary when using this system.

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Fleischer of the U. S. Geological Survey, Washington, D. C.; and Dr. H. A. Vincent, Nevada Mining Analytical Laboratory. While assuming full responsibility for the contents of this work, the authors express their gratitude for this help.

EXPERIMENTAL

APPARATUS

The apparatus consists of a Norelco vacuum X-ray spectrograph with scintillation and flow proportional counters, ethylene diamine d tartrate (EDDT) and lithium fluoride (LiF) crystals, constant potential power source, W-target Machlett X-ray spectrographic tube, goniometer, pulse height analyzer, ratemeter, and electronic counter. All these are standard Norelco-type equipment described earlier in more detail (Volborth, 1965).

SAMPLES

Two composite samples of granite, each 6 kg, were prepared by mixing 100 grams of ground powder taken at 50-foot intervals from a 3,000-foot long and 10-centimeter wide core obtained in connection with the deep drilling for the U. S. Atomic Energy Commission Project Shoal Event in Nevada. Petrographic description of this granite is given in the report listed (Shoal Event, 1963, p. 15-20). Two equivalent portions of this biotite granite (called here Shoal granite) were ground using ceramic and hardened steel plates as described previously (Volborth, 1965). Preparation of these samples is described in more detail in Final Report by the Nevada Bureau of Mines and Nevada Mining Analytical Laboratory on the Shoal Event (Weyler and Volborth, 1963). Approximately 1 gram (1,000 ± 10 mg) of the -325 mesh powder was pressed against a glass plate and backed by bakelite (Volborth, 1963a). Determination of the trace elements was performed on a series of pellets prepared from steel- and ceramic-ground rock. Results reported in this paper when different from those reported in the two Shoal Event reports (Volborth and others, 1963; Weyler and Volborth, 1963) supersede the earlier data.

STANDARDS

A comprehensive series of standards was prepared. Various amounts of oxides or other water-insoluble compounds of the trace elements in question were added to a well-homogenized ignited mixture, consisting of 80 percent purified quartz (99.89 percent SiO_2) and 20 percent c. p. grade Al_2O_3. It was found that soluble oxides "blossom" out from moistened pellets during pressing, and also while being stored, giving intensities which change in time. Therefore, only insoluble compounds were utilized as standards. In most cases three or four standards containing approximately 10, 100, 500, and 1,000 ppm of the trace element were prepared by homogenizing the mixture in v-shaped homogenizers. This powder may be called a "pseudogranite" standard, and presently we have prepared a standard which differs from the granite standard by containing 1 percent TiO_2, 10 percent

Fe_2O_3, 69 percent SiO_2, and 20 percent Al_2O_3 ("pseudobasalt"), to be used for semiquantitative analysis of basaltic rocks.

Most of the water-insoluble compounds used for standards were oxides; however, some carbonates, fluorides, phosphates, sulfates, and perchlorates were also used. To demonstrate the absorption effects of the different anions on X-ray intensities and the effect of dilution when these compounds are used in our "pseudogranitic" matrix, CaO, $CaCO_3$, $Ca_3(PO_4)_2$, CaF_2, $CaSO_4$, and $CaSO_4 \cdot 2H_2O$ were dispersed at concentrations of about 700 ppm in our matrix, and corresponding intensities recorded. Calcium was chosen because, being a light element, the effect of absorption by the surrounding elements of the anion would be more pronounced than in the case of trace elements of higher atomic number, assuming thus that this effect would be less for all other trace elements estimated in this paper. This experiment was performed by W. J. Tafuri, a graduate student at the Mackay School of Mines. Data so obtained are compared below:

Reagent	Cts/sec/713 ppm Ca
CaO	26.6
CaF_2	25.6
$CaCO_3$	31.2 (Relative standard
$CaSO_4$	31.5 deviation C = 8.4%)
$Ca_3(PO_4)_2$	27.8
($CaSO_4 \cdot 2H_2O$)	(21.2)

Considering that the concentration range of trace elements determined in this paper varies between about 1,200 and 1 ppm, one can, therefore, imply that a greater error than about ± 100 ppm is unlikely at higher concentration ranges if one considers only the overall precision and possible effect of different chemicals used for standards. At trace-element concentrations of about 200 ppm and lower, this effect can be ignored because it is unlikely that standard preparation methods and this X-ray fluorescence method as a whole can be regarded as more accurate than ± 10 percent in the 10-200 ppm range.

Of special interest to an X-ray spectroscopist are the data on anhydrite ($CaSO_4$) and gypsum ($CaSO_4 \cdot 2H_2O$). An effect apparently due to the micaceous nature of gypsum can be detected. First, our data on gypsum and anhydrite (which is not micaceous) were too far off to be accepted for this series of determinations. When an atomic absorption analysis of both powders was performed, it was discovered that both compounds were nonstoichiometric, the gypsum containing some anhydrite and vice versa. The analysis of anhydrite placed the cts/sec rate within the acceptable range (27.8 cts/sec/713 ppm Ca). Results in cts/sec/713 ppm Ca in gypsum (data in parentheses) improved but not sufficiently to be acceptable for our system. In view of the micaceous nature of this mineral, the discrepancy can be explained similarly to the biotite effect (Volborth, 1964c). It is apparently difficult to homogenize a micaceous substance at very low concentrations. Thus we do not advise using micaceous compounds for making trace-element standards which are powders.

Granite G-1 and Diabase W-1 (Fleischer, 1965; Stevens and others, 1960) were further ground to correspond in grain size to the Shoal granite (95 percent - 325 mesh) and pressed into pellets.

PROCEDURE

Plain rock powder pellets pressed at 30,000 psi against glass (Volborth, 1963a) and possessing glass-smooth surface were placed in the eight-position sample holder and exposed to X-rays four times in sequence with standard G-1 and at least two pseudogranitic standards chosen so as to bracket the G-1 and Shoal granite's composition (in terms of intensity recorded). The energy distribution in the specific two-theta region was studied, in order to choose best PHA settings. A predetermined count was taken and intensities plotted on a 5- to 3- point calibration curve, which was found to be linear for all trace elements studied over the composition ranges in question (10-7,000 ppm). The slope of the standard calibration curve was used for the unknowns after correction for specific background (if present as impurities). The corresponding intensity of G-1 was then used to fix the vertical position of the calibration curve. This empirical correction constituted an approximate normalization of the total absorption coefficients of the standard "pseudogranite" mixture with the G-1 granite powder. This curve was used for the estimation of trace elements in the Shoal granite, without further adjustments despite the fact that the total absorption coefficient of this granite was calculated to be about 5 percent (CuK_α) higher than that of G-1. Additional correction based on this figure was not considered objective since the accuracy of data reported for standards used could not be better than ± 10 percent of the trace element recorded.

Data reported for G-1 and W-1 are based on the "pseudogranite" calibration curves, taking into account determined interferences, and subtracting the background and the background due to the same element present in the standard as impurity. Thus, these data, when compared with recommended values, represent a good test of the usefulness of this method in rapid estimation of trace elements in granites.

The background was estimated on a "pseudogranite" standard blank at the same two-theta setting and at the same window width and voltage of the detector. In addition, the pulse height energy distribution was determined separately over the same area, as shown in figure C1. This was done with possible interfering neighboring elements present in different known concentrations in order to allow for possible enhancement and interfering line effects in the quantitative determination of the trace element in question. Specific cases of interference are listed in table C1.

The criteria for detection limits reported are based on blank "pseudogranite" pellets of which energy distribution curves were run and compared with similar curves run on the same material with known added trace elements of the element (see fig. C2). If no peak was detected, or if no distinction could be made between the background and the background plus an added known amount of the trace, the element was considered undetectable at that concentration. Only a definite effect of the addition of a known amount of a trace element over the background was regarded as evidence that this amount can be detected. Blank "pseudogranite" pellets frequently showed a background in the form of a distinct peak apparently due to the presence of the element sought in the standard matrix or to the line interference from other impurities in the X-ray tube or the X-ray spectrograph. This resulted in insufficient detection capability for some trace elements in our system (Rb, Sr, La, for example).

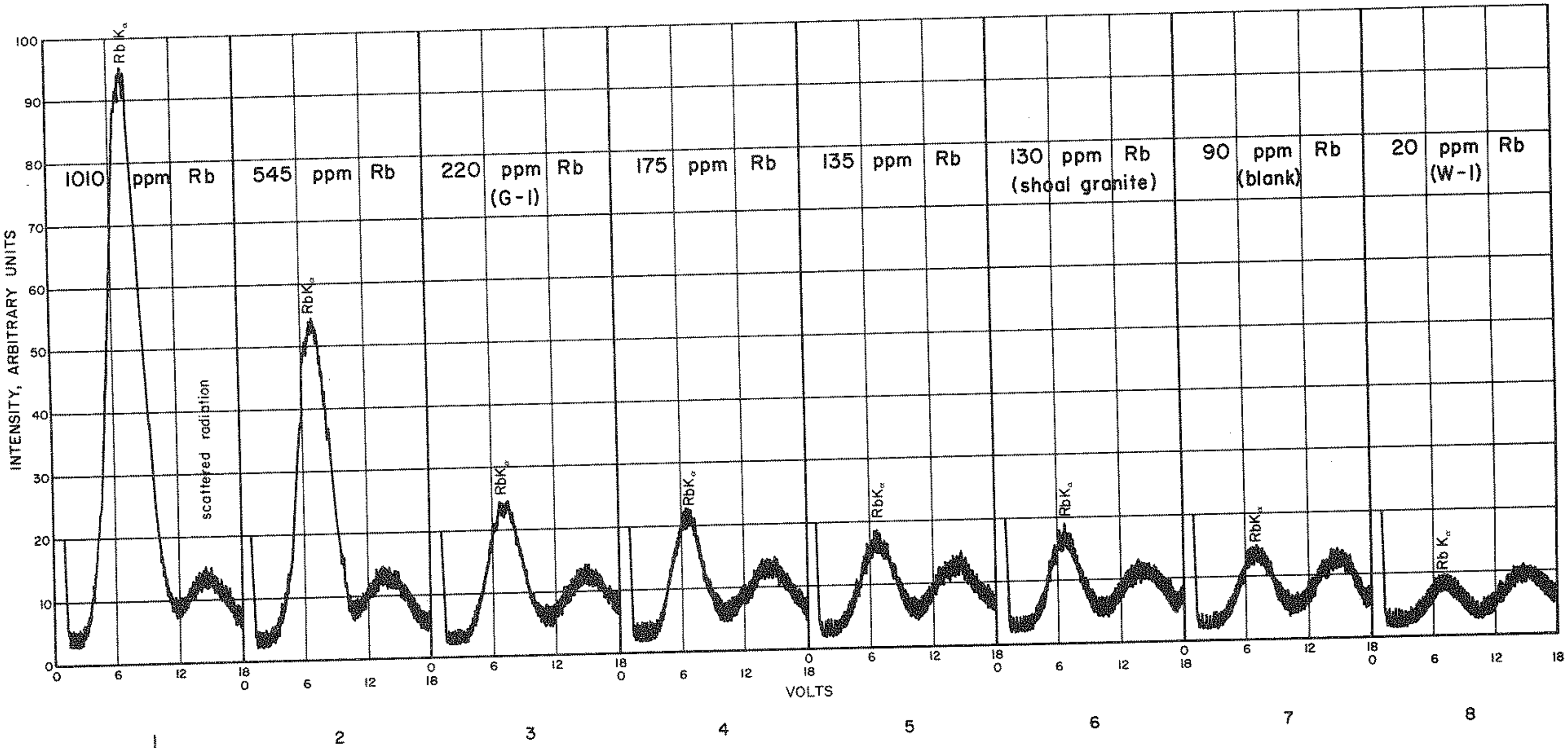


Figure C1. Eight energy distribution curves for Rb in different samples, using slow scanning with a 1-volt window. This figure demonstrates our ability to detect about 20 ppm of Rb in standard W-1. Detection limits and trace elements in the "blanks" were determined or estimated by this method. The figure also shows interference of some other radiation in the form of a peak of constant intensity on the right side of the Rb-energy distribution curves.

Table C1

Instrumental Conditions for Trace Element Analysis in Rocks by X-ray Spectrometry

Element	Base Volts PHA	Window Volts PHA	Amplifier Voltage	Collimator Crystal	Analytical Line, 20	Interference
Ag	2.4	8.4	600	5 mil, LiF	$K_\alpha = 15.95°$	Ag in system?
As	3.0	8.4	1400	5 mil, LiF	$K_\alpha = 33.92°$	Pb L_{α_1} 33.92° in system
Ba	3.0	9.0	1430	20 mil, EDDT	$L_\alpha = 36.74°$	Ti K_{α_1} 36.37°
Ba	2.4	7.2	1420	5 mil, EDDT	$L_\alpha = 36.74°$	Ti K_{α_1} 36.37°
Ba	3.6	7.2	1415	5 mil, LiF	$L_\alpha = 87.13°$	Rb K_{α_1} 87.21°, 3rd order
Cd	3.0	22.5	710	5 mil, LiF	$K_\alpha = 15.27°$	
Ce	4.8	7.8	1430	5 mil, EDDT	$L_\alpha = 33.81°$	Ti K_β 33.17°, > 0.5% TiO_2, Ba L_β 33.89°
Ce	4.8	6.0	1415	5 mil, LiF	$L_\alpha = 78.96°$	Ba L_{β_1} 79.18°
Co	2.1	14.4	785	5 mil, LiF	$K_\alpha = 52.74°$	Fe K_{β_1} 51.72° and Fe in system
Cr	3.0	12.0	770	5 mil, LiF	$K_\alpha = 69.29°$	Cr in system
Cs	1.8	7.2	1400	5 mil, EDDT	$L_\alpha = 38.34°$	W L_{α_1}, 2nd order
Cu	2.1	10.2	720	5 mil, LiF	$K_\alpha = 44.96°$	Cu in system
Ga	1.8	16.2	1425	5 mil, LiF	$K_\alpha = 38.86°$	Zn K_{β_1} 37.54° in system
Gd	1.8	9.0	1400	5 mil, EDDT	$L_\alpha = 26.86°$	Mn $K_{\alpha_{1,2}}$, Fe $K_{\alpha_{1,2}}$
Gd	8.2	9.6	1430	5 mil, LiF	$L_\alpha = 61.05°$	
Ge	1.5	16.5	1400	5 mil, LiF	$K_\beta = 32.55°$	
Hf	2.4	9.0	1360	5 mil, EDDT	$L_\alpha = 20.52°$	W L_{α_1} 19.29°
Hf	13.8	12.0	1450	5 mil, LiF	$L_\alpha = 45.85°$	Zr K_{α_1} 45.94°, 2nd order;
						Ba K_{α_1} 44.96°, 4th order
Hg	3.0	5.4	1320	5 mil, EDDT	$L_\alpha = 16.21°$	W $L_{\beta_{1,2}}$ 16.74°, 16.25°
In	4.2	21.0	700	5 mil, LiF	$K_\alpha = 14.61°$	Gd $K_{\beta_{1,3}}$
La	3.0	7.8	1420	20 mil, EDDT	$L_\alpha = 35.22°$	Ti K_{α_1} 36.37°
La	4.2	3.0	1390	5 mil, EDDT	$L_\alpha = 35.22°$	Ti K_{α_1} 36.37°, >1% TiO_2
La	7.8	13.2	1460	5 mil, LiF	$L_\alpha = 82.85°$	Ga K_{α_1} 83.43°, 2nd order
Mo	2.4	7.2	620	5 mil, LiF	$K_\alpha = 20.28°$	Mo radiation in system
Mn	2.1	12.9	745	5 mil, LiF	$K_\alpha = 62.91°$	Enhanced by Fe
Nb	6.0	12.6	725	5 mil, LiF	$K_\alpha = 21.37°$	
Nd	1.6	4.8	1360	5 mil, EDDT	$L_\alpha = 31.22°$	
Nd	5.4	8.4	1430	5 mil, LiF	$L_\alpha = 72.08°$	Zr K_{α_2} 72.19°
Ni	4.2	18.0	1650	5 mil, LiF	$K_\alpha = 48.61°$	Ni in system
Pb	3.0	10.2	720	5 mil, LiF	$L_{\beta_1} = 29.19°$	Pb in system
Rb	2.1	9.9	670	5 mil, LiF	$K_\alpha = 26.58°$	
Sb	2.4	7.8	580	5 mil, LiF	$K_\alpha = 13.40°$	Sb in system
Sc	2.1	5.7	1410	5 mil, EDDT	$K_\alpha = 40.26°$	Ca K_{β_1} 41.06°
Sc	1.2	9.6	1500	5 mil, LiF	$K_\alpha = 97.61°$	
Se	6.0	18.6	800	5 mil, LiF	$K_\beta = 28.51°$	
Sm	1.2	5.4	1370	5 mil, EDDT	$L_\alpha = 28.91°$	
Sm	6.6	10.2	1450	5 mil, LiF	$L_\alpha = 66.18°$	
Sn	3.0	18.0	675	5 mil, LiF	$K_\alpha = 14.00°$	
Sr	2.4	7.8	650	5 mil, LiF	$K_\alpha = 25.09°$	
Ta	3.0	12.6	775	5 mil, LiF	$L_{\alpha_1} = 44.40°$	Cu K_α and Ni K_β in system
Th	4.2	15.0	700	5 mil, LiF	$L_{\alpha_1} = 27.46°$	
Ti	6.0	12.2	870	5 mil, LiF	$K_\alpha = 86.07°$	Ba L_{α_1} 87.13°
Ti	10.2	12.6	1575	20 mil, EDDT	$K = 36.37°$	
U	6.0	16.2	700	5 mil, LiF	$L_{\alpha_1} = 26.14°$	Rb K_{α_1} 26.58° strong Sr K_{α_1} 25.09°
V	3.0	3.6	1370	5 mil, EDDT	$K_\alpha = 33.02°$	Ti K_{β_1} 33.17°
V	2.4	9.6	1420	20 mil, EDDT	$K_\alpha = 33.02°$	Ti K_{β_1} 33.17°
V	3.0	12.0	790	20 mil, LiF	$K_\alpha = 76.84°$	Ti K_{β_1} 77.24°, minimal
Y	2.4	6.6	630	5 mil, LiF	$K_\alpha = 23.75°$	
Yb	3.0	12.0	785	5 mil, LiF	$L_{\alpha_1} = 49.05°$	Ni in system
Zn	2.7	12.0	710	5 mil, LiF	$K_\alpha = 41.74°$	Zn in system
Zr	2.4	6.6	620	5 mil, LiF	$K_\alpha = 22.51°$	Sr K_{β_1} 22.42°

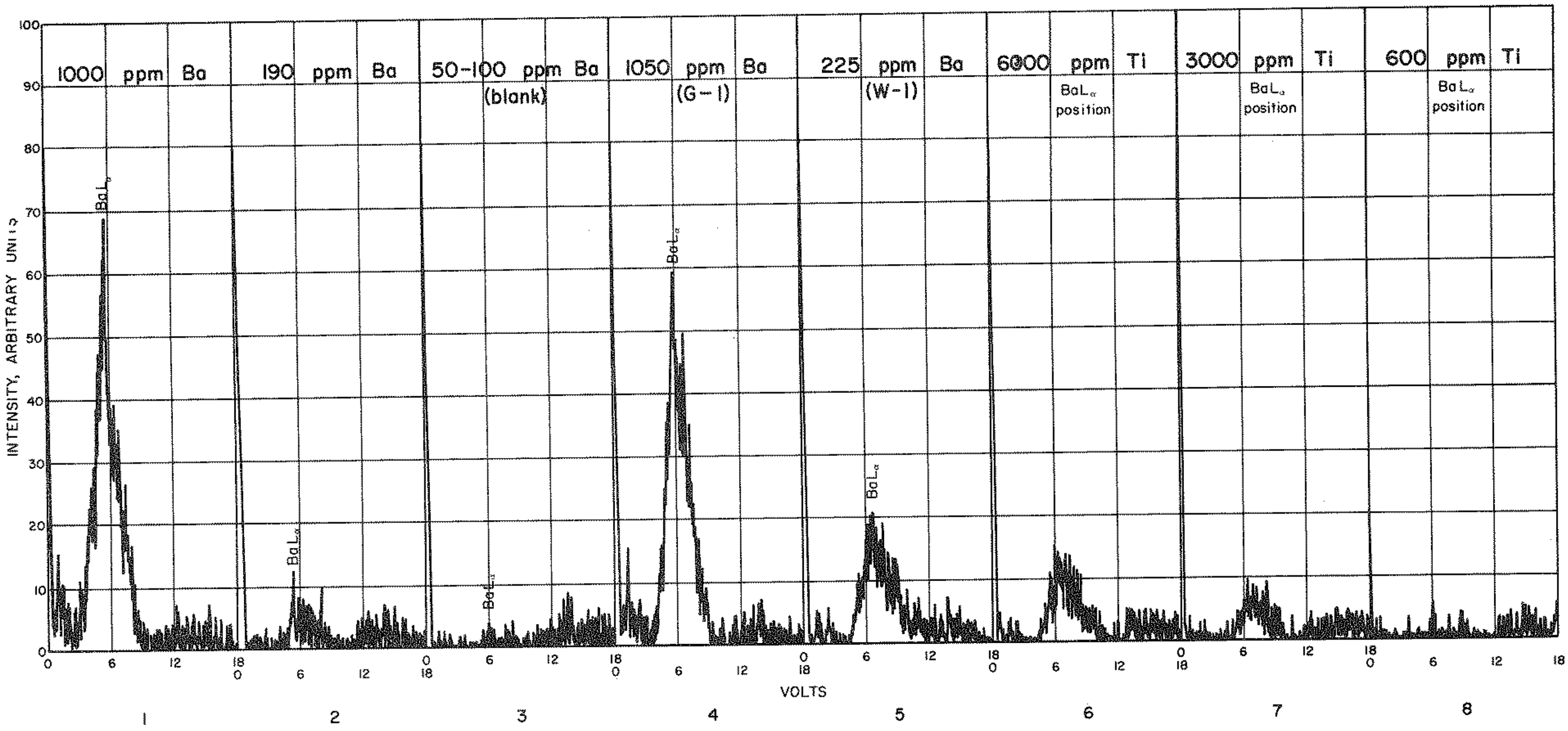


Figure C2. Eight energy distribution curves for Ba in different samples, and Ti in Ba two-theta position, demonstrate that the detection limit for Ba in these samples, using the Ba L_a radiation, lies at about 50 ppm and that titanium interference has to be taken into account in rocks carrying more than 600 ppm Ti. This figure shows how detection limits were determined and how corrections for known amounts of interfering elements were performed.

RESULTS

In table C1, instrumental conditions are given which were found experimentally to be optimum for the determination of trace elements Ag, As, Ba, Cd, Ce, Co, Cr, Cs, Cu, Ga, Gd, Ge, Hf, Hg, In, La, Mo, Mn, Nb, Nd, Ni, Pb, Rb, Sb, Sc, Se, Sm, Sn, Sr, Ta, Th, Ti, U, V, Y, Yb, Zn, and Zr in granitic matrix, with tungsten excitation at 35 mA and 50 kV. In many cases comparison is made between results obtained with LiF and EDDT crystals.

In general the trace elements determined vary from amounts not detectable by the present method and equipment, for example Mo<50 ppm, up to concentrations of about 7,000 ppm, as in the case of Ti. Table C2 gives the variations in relative standard deviation for all the elements determined in the composition ranges applicable to this type of granite. Theoretical counting precision can be obtained based on this table directly from the total counts taken and the signal to background ratio. Where these values do not coincide with the values given in the first column (which are based on actual results obtained), it is obviously due to the fact that the analysis is being performed near the detection limit and the energy distribution curve may show actually a "background peak" above which the specific radiation due to the trace element in sample can barely be detected (see Scandium, p. C22). Under these conditions the data reported can be considered only as an order of magnitude (see Chromium, p. C15).

It was observed that the overall background of the "pseudogranite" standard was higher than that of the standard rock G-1 near the detection limits of some trace elements (Cu, La, Nd, Sc, Yb, and Zn). This can be explained by the generally more highly scattered Compton radiation from light matrices. This effect is detectable only when careful high-precision work on trace elements is performed, but it can lead to serious errors, especially when the determination of an element is attempted near detection limits in the system described here. Whenever detectable, this effect has been accounted for in this work, even in the estimation of the major trace elements (Rb, Sr, and Zr).

Results of the single determination in ceramic- and iron-plate ground Shoal granite and also in rocks G-1 and W-1, based on at least three-point calibration curves for the standard mixtures, are given under individual elements below.

ANTIMONY

Antimony could not be detected in Shoal granite using K_α radiation. The detection limit was established at about 50 ppm for our standard samples. Our inability to detect antimony at lower concentrations is due to a high background in this region. The intensity in the antimony region in Shoal granite was barely less than that for G-1, for which 0.6 ppm Sb has been reported (Stevens and others, 1960). This must be second order and scattered radiation.

ARSENIC

The detection limit in our system is below 1 ppm (< 1). Our results are compared with data by others below:

Table C2

Precision of X-ray Spectrometric Determination of Trace Elements in Rocks

Elements	Collimator, Crystal	Rel. Std. Dev. 3C% - Range	Total Counts Range	Signal to Background Ratio Range	Composition Range ppm
Ag	5 mil, LiF	~20	Not counted	~1.5	100 - 1000
As	5 mil, LiF	1 - 7	2,800 - 32,000	1.5 - 7.0	10 - 750
Ba	5 mil, LiF	2 - 5	1,600 - 15,000	3.3 - 38	50 - 1400
Ba	20 mil, EDDT	1 - 4	7,000 - 45,000	3.4 - 23	50 - 1400
Ba	5 mil, LiF	2 - 7	550 - 3,392	3.0 - 16.0	50 - 1400
Cd	5 mil, LiF	1 - 10	180,000 - 270,000	1.0 - 1.5	10 - 875
Ce	5 mil, EDDT	2 - 8	600 - 6,000	1.2 - 5.5	50 - 1300
Ce	5 mil, LiF	2 - 4	1,400 - 7,600	3.0 - 9.0	50 - 1300
Co	5 mil, LiF	1 - 5	6,500 - 96,000	1.5 - 15.0	20 - 900
Cr	5 mil, LiF	3 - 50	14,000 - 21,000	1.1 - 2	10 - 700
Cs	5 mil, EDDT	~10	9,000 - 17,000	1.2 - 2.3	100 - 1000
Cu	5 mil, LiF	1 - 3	46,000 - 100,000	1.1 - 5	10 - 900
Ga	5 mil, LiF	1 - 2	59,000 - 460,000	1.5 - 4.3	5 - 750
Gd	5 mil, EDDT	2 - 6	4,600 - 21,000	1.2 - 5.5	10 - 900
Gd	5 mil, LiF	2 - 10	1,000 - 9,100	1.2 - 8.0	10 - 900
Ge	5 mil, LiF	4 - 5	4,500 - 13,400	1.5 - 2.5	1 - 765
Hf	5 mil, LiF	-	Not counted	~1.2	10 - 900
Hf	5 mil, EDDT	2 - 10	12,300 - 26,000	1.2 - 2.5	10 - 900
Hg	5 mil, EDDT	~25	Not counted	~1.2	150 - 1000
In	5 mil, LiF	1 - 10	190,000 - 300,000	1.0 - 1.5	30 - 840
La	5 mil, EDDT	1 - 5	1,000 - 5,000	6 - 36	10 - 900
La	20 mil, EDDT	1 - 6	7,000 - 28,000	1.1 - 4.7	10 - 900
La	5 mil, LiF	2 - 15	450 - 5,300	1.2 - 12.0	10 - 900
Mn	5 mil, LiF	1 - 3	16,000 - 198,000	1.6 - 13	50 - 1300
Mo	5 mil, LiF	~10	Not counted	1.1 - 3.0	100 - 1000
Nb	5 mil, LiF	1 - 1	130,000 - 500,000	1.5 - 2.9	10 - 700
Nd	5 mil, LiF	2 - 10	800 - 4,700	1.5 - 8.0	40 - 900
Nd	5 mil, EDDT	2 - 20	4,600 - 23,000	1.2 - 6.0	40 - 900
Ni	5 mil, LiF	1 - 2	5,000 - 78,000	1.5 - 13	1 - 290
Pb	5 mil, LiF	1 - 3	26,000 - 90,000	1.5 - 3.0	25 - 940
Rb	5 mil, LiF	1 - 3	160,000 - 370,000	1.4 - 12	10 - 1000
Sb	5 mil, LiF	~20	Not counted	~1.2	50 - 1000
Sc	5 mil, EDDT	2 - 10	2,000 - 16,000	1.5 - 16	5 - 700
Sc	5 mil, LiF	2 - 15	250 - 6,900	1.2 - 30.1	5 - 700
Se	5 mil, LiF	-	Not counted	1.2 - 2.0	50 - 700
Sm	5 mil, EDDT	2 - 8	2,200 - 10,000	1.2 - 5.2	10 - 900
Sm	5 mil, LiF	1 - 15	1,200 - 14,300	1.1 - 10.0	10 - 900
Sn	5 mil, LiF	1 - 10	210,000 - 310,000	1.0 - 1.5	55 - 850
Sr	5 mil, LiF	1 - 5	94,000 - 326,000	1.8 - 8	50 - 900
Ta	5 mil, LiF	-	Not counted	1.0 - 2.0	80 - 800
Th	5 mil, LiF	1 - 3	25,500 - 98,000	1.5 - 3.0	35 - 880
Ti	20 mil, EDDT	1 - 2	10,500 - 30,000	2.0 - 46.0	100 - 7000
Ti	5 mil, EDDT	1 - 8	5,000 - 95,000	1.5 - 27	100 - 7000
U	5 mil, LiF	-	Not counted	1.0 - 2.0	80 - 850
V	5 mil, EDDT	1 - 4	7,000 - 17,000	3 - 24	20 - 600
V	20 mil, EDDT	1 - 4	20,000 - 100,000	1.5 - 8	20 - 600
V	20 mil, LiF	1 - 3	40,000 - 186,000	1.5 - 7	20 - 600
Y	5 mil, LiF	1 - 3	86,000 - 345,000	1.1 - 4.5	5 - 900
Yb	5 mil, LiF	2 - 5	7,000 - 22,500	1.5 - 2.0	1 - 880
Zn	5 mil, LiF	1 - 3	27,000 - 120,000	1.2 - 11	10 - 900
Zr	5 mil, LiF	2 - 4	88,000 - 480,000	1.6 - 5.2	50 - 1000

Sample	ppm	Remarks
Shoal granite, ceramic plates	< 1	
Shoal granite, iron plates	< 1	
G-1	~1	
G-1	0.7-3.0	Fleischer (1965)
W-1	not detected	
W-1	2.2-3.0	Fleischer (1965)

Different matrix effects prevent the detection of this element at this low concentration in rock W-1.

BARIUM

Barium is determined in Shoal granite by using a least-square calibration curve drawn through the three "pseudogranite" standards and G-1 and W-1 points, after correcting for the effect of titanium, which is due to the vicinity of the Ti K_α line at 36.37° two theta to the Ba L_α line at 36.74° two theta. The effect of titanium was determined experimentally by determining the counts in Ba L_α position at different titanium concentrations introduced into the "pseudogranite" pellets (fig. C2). Data given for G-1 and W-1 are based on "pseudogranite" calibration curve alone, as in all cases in this work. Precision, given here and for other elements in this work at 99 percent confidence (± 3C), does not warrant mentioning the introduction of barium by the ceramic plates, but we want to emphasize that there appears to be an indication of this. Detection limit for barium, when using the L_α line, is about 5 ppm. However, our blank sample has been determined to have a background corresponding to approximately 100 ppm of barium. Our results are compared below with recommended values for G-1 and W-1.

Sample	Ba, ppm, ± 3C	Remarks
Shoal granite, ceramic plates	1245 ± 80	EDDT crystal
Shoal granite, iron plates	1235 ± 80	EDDT crystal
Shoal granite, ceramic plates	1380 ± 85	LiF crystal
Shoal granite, iron plates	1375 ± 85	LiF crystal
G-1	1050 ± 65	EDDT crystal
G-1	1010 ± 50	LiF crystal
G-1	1220	Stevens and others (1960); Fleischer (1965)
W-1	230 ± 25	EDDT crystal
W-1	240 ± 25	LiF crystal
W-1	225	Av. of 14, Stevens and others (1960)
W-1	180	Fleischer (1965)

Except for the interference of titanium, the barium curve seems to be linear over a wide composition range. This is due to the linear relationship of the concentration of Ba to the concentration of major elements Si, K, Fe, and Ca in the igneous rock series granite-basalt.

CADMIUM

Cadmium detection limit in our system was found to be about 10 ppm. There is definite contamination by cadmium introduced by the ceramic plates as can be seen from the following compilation:

Sample	Cd, ppm, ± 3C	Remarks
Shoal granite, ceramic plates	250 ± 30	LiF crystal
Shoal granite, iron plates	30 ± 5	LiF crystal
G-1	not detected	LiF crystal
W-1	not detected	LiF crystal
G-1	5	Stevens and others (1960)
G-1	0.06-< 0.3	Fleischer (1965)
W-1	6	Stevens and others (1960)
W-1	<0.2-<0.3	Fleischer (1965)

The 30 ± 5 ppm Cd indicated in the iron-ground Shoal granite appears also too high for a granite when compared with G-1, but can be tentatively suggested for this rock unless later work proves general contamination by Cd in our laboratory. A further geochemical study of Cd in the Shoal rock is, therefore, suggested.

CERIUM

Cerium determination by X-ray emission using the Ce L_α line is complicated mainly by the interferences of Ti K_α line and the enhancement by Fe K_α radiation which is balanced out at higher concentrations of Fe by the absorption effect of iron on Ce radiation. Thus it was necessary to prepare standards containing similar amounts of Fe and Ti. In addition to titanium, barium has been added to our standard to assure accurate results for Ce. Based on a standard containing 0.25 percent TiO_2, 1,200 ppm Ba, and 2.50 percent Fe_2O_3, we obtain the following results:

Sample	Ce, ppm, ± 3C	Remarks
Shoal granite, ceramic plates	280 ± 15	LiF crystal
Shoal granite, iron plates	285 ± 15	LiF crystal
Shoal granite, ceramic plates	(415 ± 40)	EDDT crystal
Shoal granite, iron plates	(420 ± 40)	EDDT crystal
G-1	385 ± 20	LiF crystal
G-1	435 ± 30	EDDT crystal
W-1	35 ± 5	LiF crystal
W-1	45 ± 10	EDDT crystal

G-1	600	Stevens and others (1960)
G-1	~200	Fleischer (1965)
W-1	70	Stevens and others (1960)
W-1	~25	Fleischer (1965)

The detection limit in our system is about 20 ppm Ce.

After evaluation of our data, which are based on several carefully prepared standards, we venture to propose that too much weight has been given by Fleischer (1965, p. 1268-1269) to recent neutron activation and mass spectrometric data on Ce.

We suggest that our 385 ± 20 ppm Ce for G-1 is closer to the probable value, which would give the old data reported by Ahrens and Fleischer in Stevens and others (1960) new significance. The W-1 results (35 ± 5 ppm and 45 ± 10 ppm Ce) have been obtained by plotting on a "pseudobasalt" curve and by taking the effect of 225 ppm Ba into consideration, thus based on our data the mean value of 40 ± 10 ppm Ce may be suggested.

In an accurate determination of Ce, LiF crystal is preferred because of the increasing interference of Ti and Ba when the EDDT crystal is used.

It may be appropriate to raise the question of whether in recent years there has not been an excessive tendency by spectroscopists to give more weight to thermal neutron activation data than may be warranted by the precision and accuracy inherent to these methods. This may result in some cases in somewhat biased standards and the rejection of "old" carefully retrieved data.

CESIUM

Cesium detection limit, using L_α radiation in "pseudo granite," was about 100 ppm, and none was detected in the Shoal granite. Cesium was the first of the heavier elements where L_{α_1} radiation was used as an analytical line in this work. Unfortunately the second order L_α line of tungsten at 39.16° two theta interferes (Cs L_{α_1} = 38.34°) in trace element determination in granitic rocks. This seems to be the main reason for the relatively high detection limit.

CHROMIUM

Chromium content of the Shoal granite is in the vicinity of the detection limit of 10 ppm.

Sample	Cr, ppm, ± 1C	Remarks
Shoal granite, ceramic plates	10 ± 5	LiF crystal
Shoal granite, iron plates	20 ± 10	LiF crystal
G-1	20 ± 10	LiF crystal
G-1	22	Fleischer (1965)

The determination of chromium by X-ray spectrometry in these low concentration ranges is difficult because of apparent contamination of standard oxide mixtures and the Shoal granite samples by this element, and, therefore, the presence of high background in this region, as was shown by the pulse height analysis (PHA) distribution curves of all standards and rocks analyzed. This interference is equivalent to about 75 ppm Cr in the blank samples.

COBALT

Cobalt detection limit in our system is 1 ppm. Results are compiled below:

Sample	Co, ppm, ± 3C	Remarks
Shoal granite, ceramic plates	25 ± 6	LiF crystal
Shoal granite, iron plates	25 ± 1	LiF crystal
G-1	5 ± 1	LiF crystal
W-1	(145 ± 20)	LiF crystal
G-1	2.5	Stevens and others (1960)
G-1	2.4	Fleischer (1965)
W-1	50	Fleischer (1965)

It thus seems reasonable to suggest that the Shoal granite carries an unusual amount of cobalt. Our value for W-1 is too high, indicating interference of iron and the need of a "pseudobasalt" standard mixture, which is being prepared.

COPPER

Copper detection limit in our system is about 10 ppm, owing to the presence of higher order lines in the Cu K_α region, and about 30 ppm Cu in our blank sample.

Sample	Cu, ppm, ± 3C	Remarks
Shoal granite, ceramic plates	18 ± 2	LiF crystal
Shoal granite, iron plates	18 ± 2	LiF crystal
G-1	13 ± 2	LiF crystal
G-1	13	Stevens and others (1960); Fleischer (1965)

Because of absorption of copper K_α radiation by iron, a "pseudobasalt" standard is necessary to obtain meaningful data on W-1.

GADOLINIUM

Gadolinium detection limit is 10 ppm in our artificial standard. Because of interference of Mn $K_{\alpha_{1,2}}$ and Fe $K_{\alpha_{1,2}}$, the determination of Gd at L_{α_1}, 26.86° two theta, is difficult in rocks when the concentration of Gd is near the detection limit, and our system apparently gives results that are too high.

Shoal granite, ceramic plates	(45 ± 8 ppm Gd)
Shoal granite, iron plates	(35 ± 6 ppm Gd)
G-1	(45 ± 8 ppm Gd)
G-1	~5 ppm Gd, Fleischer (1965)

This interference becomes more pronounced in rock W-1, for which too high a value for Gd is also obtained.

GALLIUM

Gallium detection limit was found to be 5 ppm. The background radiation in our standard "pseudogranite" sample corresponds to about 20 ppm Ga. Results are compared below:

Sample	Ga, ppm, ± 3C	Remarks
Shoal granite, ceramic plates	21 ± 3	LiF crystal
Shoal granite, iron plates	21 ± 4	LiF crystal
G-1	18 ± 5	LiF crystal
W-1	not detected	LiF crystal
G-1	18	Stevens and others (1960); Fleischer (1965)
W-1	16	Stevens and others (1960); Fleischer (1965)

GERMANIUM

Germanium detection limit is below 1 ppm in our system. Data obtained are:

Sample	Ge, ppm	Remarks
Shoal granite, ceramic plates	2	LiF crystal
Shoal granite, iron plates	1	LiF crystal
G-1	1	LiF crystal
W-1	not detected	LiF crystal
G-1	1	Stevens and others (1960)
W-1	1.6	Stevens and others (1960)

HAFNIUM

Hafnium detection limit was found to be 5-10 ppm.

Sample	Hf, ppm	Remarks
Shoal granite, ceramic plates	<5	LiF crystal
Shoal granite, ceramic plates	<5	EDDT crystal
G-1	~5	EDDT crystal
W-1	<5	EDDT crystal
G-1	5-7	Fleischer (1965)
W-1	1.5-2.0	Fleischer (1965)

INDIUM

Indium detection limit of 30 ppm is indicated. Our data are:

Sample	In, ppm, ± 3C	Remarks
Shoal granite, ceramic plates	185 ± 20	LiF crystal
Shoal granite, iron plates	not detected	LiF crystal
G-1	not detected	LiF crystal
W-1	not detected	LiF crystal
G-1 and W-1	(< 0.2)	Fleischer (1965)

Apparently ceramic plates contaminate the granite sample with considerable indium. It is difficult to explain how this rare element could get into the plates in such quantities, and an investigation to answer this question has been started.

LANTHANUM

Lanthanum detection limit is 10 ppm. The blank standard showed a background equivalent to about 45 ppm La. The results are:

Sample	Pb, ppm, ± 3C	Remarks
Shoal granite, ceramic plates	75 ± 10	EDDT crystal, 5 mil collimator
Shoal granite, iron plates	75 ± 10	EDDT crystal, 5 mil collimator
Shoal granite, ceramic plates	85 ± 15	EDDT crystal, 20 mil collimator
Shoal granite, iron plates	75 ± 20	EDDT crystal, 20 mil collimator
Shoal granite, ceramic plates	70 ± 10	LiF crystal, 5 mil collimator
Shoal granite, iron plates	72 ± 10	LiF crystal, 5 mil collimator
G-1	130 ± 10	EDDT crystal, 5 mil collimator
G-1	105 ± 15	LiF crystal, 5 mil collimator
W-1	30 ± 10	EDDT crystal, 5 mil collimator

W-1	45 ± 10	LiF crystal, 5 mil collimator
G-1	150	Stevens and others (1960)
W-1	30	Stevens and others (1960)
W-1	20	Fleischer (1965)
G-1	120	Fleischer (1965)

Interference from Ti K_α in the region of La L_α has to be taken into account in accurate work. This effect was measured and accounted for in order to obtain data for W-1.

LEAD

Lead detection limit using L_α line has been determined as 15 ppm. Results are:

Sample	Pb, ppm, ± 3C	Remarks
Shoal granite, ceramic plates	36 ± 2	LiF crystal
Shoal granite, iron plates	35 ± 2	LiF crystal
G-1	50 ± 3	LiF crystal
W-1	<15	LiF crystal
G-1	49	Stevens and others (1960); Fleischer (1965)
W-1	8	Fleischer (1965)

MANGANESE

Manganese detection limit is near 10 ppm in our system. Good results are obtained:

Sample	Mn, ppm, ± 3C	Remarks
Shoal granite, ceramic plates	370 ± 35	LiF crystal
Shoal granite, iron plates	390 ± 35	LiF crystal
G-1	190 ± 20	LiF crystal
W-1	1,200 ± 40	LiF crystal
G-1	210	Stevens and others (1960), average
G-1	230	Fleischer (1965)
W-1	1,320	Fleischer (1965)

The analysis of four iron-ground and three ceramic-ground rock pellets shows a constant difference of 10 to 20 ppm between these two differently prepared samples, indicating introduction of manganese by iron-plate grinding. The calibration curve on which the Shoal granite data are based is drawn according to the least-squares principle through 3 of our standard points and also rock G-1 and W-1. Since the G-1 and W-1 points fall on the 3-

point "pseudogranite" calibration curve, the accuracy of this manganese determination leaves apparently little more to be desired if one overlooks the fact that, because of the enhancement effect on manganese by iron in the standard W-1 where there is more than 10 percent Fe_2O_3, the manganese intensity should be relatively higher. Apparently in this case the absorption effect equals nearly the enhancement effect, resulting in manganese intensity directly proportional to the composition, when compared with other samples. In rocks where total manganese increases linearly with total iron this method will work well; *in other cases corrections for total absorption and enhancement effects will be necessary.* Another reason for the seemingly perfect relative intensity plot for manganese is that manganese concentrations in igneous rocks of the "granite-basalt" series tend to vary linearly with Si, Mg, K, and Ca.

MERCURY

Mercury detection limit, using the Hg L_α at 16.21° two theta, is about 150 ppm. Reflected W $L_{\beta_{1,2}}$ at 16.74° and 16.25° two theta interferes, forming too high a background for trace determination. No mercury was detected in Shoal granite, the detection limit being far above the normal concentration for this element in a granite.

MOLYBDENUM

Molybdenum in granite in trace amounts is difficult to determine because of the interference of Zr K_{β_1}, at 20.04° two theta angle (Mo K_{α_1} = 20.28°). Based on PHA energy distribution curves and comparing with G-1, one can estimate that Shoal granite has less Mo than G-1, for which 7 ppm Mo has been recommended (Stevens and others, 1960, p. 94). Five ppm Mo would be a reasonable estimate for Shoal granite. The detection limit is at least 50 ppm, probably nearer to 5 ppm if based on similar granites, such as the G-1, for example. Interference from a high background in the system hinders the estimation.

An attempt to determine Mo by using the L_α radiation was unsuccessful, because even 1,000 ppm Mo could not be detected with our equipment.

NEODYMIUM

Neodymium detection limit in our system, using L_α line, is 30 ppm. The background of the blank sample corresponds to 40 ppm Nd. Results are:

Sample	Nd, ppm, ± 3C	Remarks
Shoal granite, ceramic plates	40 ± 6	EDDT crystal
Shoal granite, iron plates	40 + 6	EDDT crystal
Shoal granite, ceramic plates	45 ± 6	LiF crystal

Shoal granite, iron plates	40 ± 5	LiF crystal
G-1	80 ± 10	LiF crystal
W-1	(70 ± 10)	LiF crystal
G-1	110 ± 15	EDDT crystal
G-1	80	Stevens and others (1960)
G-1	~55	Fleischer (1965)
W-1	50	Stevens and others (1960)
W-1	~17	Fleischer (1965)

A different standard is necessary to determine Nd in W-1 more accurately, but an order of magnitude can be indicated based on granitic standards.

NICKEL

Nickel detection limit is less than 1 ppm with this system. Results are:

Sample	Ni, ppm, ± 3C	Remarks
Shoal granite, ceramic plates	10 ± 1	LiF crystal
Shoal granite, iron plates	10 ± 1	LiF crystal
G-1	2 ± 1	LiF crystal
W-1	(35 ± 1)	LiF crystal
G-1	1 - 2	Fleischer (1965)
W-1	78	Fleischer (1965)

A "pseudobasaltic" standard is necessary to determine Ni in W-1 because of strong absorption effect due to iron.

NIOBIUM

Niobium detection limit is determined as 5 ppm. Results are:

Sample	Nb, ppm, ± 3C	Remarks
Shoal granite, ceramic plates	25 ± 5	LiF crystal
Shoal granite, iron plates	5 ± 1	LiF crystal
G-1	20 ± 1	LiF crystal
W-1	not detected	LiF crystal
G-1	20	Stevens and others (1960); Fleischer (1965)
W-1	10	Fleischer (1965)

In iron-rich samples, Nb K_α radiation is strongly absorbed, necessitating another standard mixture.

RUBIDIUM

Rubidium detection limit is 10 ppm or lower. The background of our blank corresponds to 90 ppm Rb, not permitting accurate experimental estimation of detection limit in this case. Results are:

Sample	Rb, ppm, ± 3C	Remarks
Shoal granite, ceramic plates	130 ± 5	LiF crystal
Shoal granite, iron plates	120 ± 5	LiF crystal
G-1	220 ± 10	LiF crystal
W-1	30 ± 3	LiF crystal
G-1	220	Fleischer (1965)
W-1	22	Fleischer (1965)

It can be seen from the calibration curve (fig. C3) and the superimposed energy distribution curve for rubidium (fig. C1), that the accuracy in the determination of this element by X-ray spectrometry is high, and the calibration curve in the composition range of 10 to 1,000 ppm Rb is linear. As in the case of manganese, rubidium varies linearly with major elements Si, K, and Fe in the series granite-basalt, thus permitting construction of a linear working curve for rocks of this type over a wide composition range.

SAMARIUM

Samarium could not be detected in the Shoal granite based on our calibration curve, on which G-1 has a value of 20 ppm Sm. When the slight difference in background is considered, the value for G-1 is about 10 ppm Sm. The detection limit for samarium, when determined using the L_α radiation with this type of material is near 10 ppm.

SCANDIUM

Scandium detection limit is 5 ppm. Results group near the detection limit:

Sample	Sc, ppm, ± 3C	Remarks
Shoal granite, ceramic plates	~6	EDDT crystal
Shoal granite, iron plates	~6	EDDT crystal
Shoal granite, ceramic plates	~6	LiF crystal
Shoal granite, iron plates	~6	LiF crystal
G-1	not detected	LiF crystal
W-1	53 ± 6	LiF crystal
G-1	3	Fleischer (1965)
W-1	43	Stevens and others (1960)
W-1	34	Fleischer (1965)

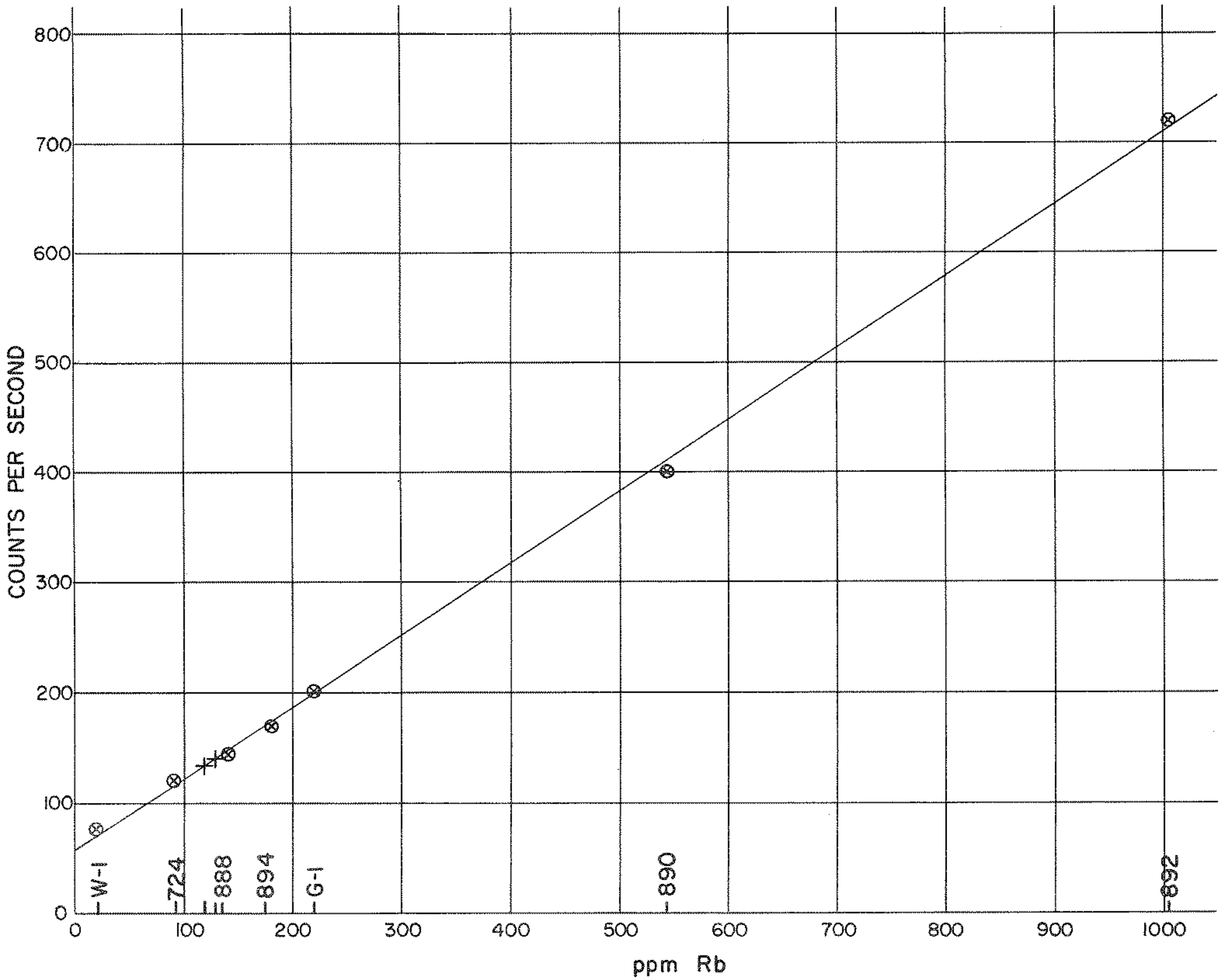


Figure C3. Calibration curve for Rb. Circles correspond to our standard samples and standards G-1 and W-1. Plus-marks correspond to the two Shoal granite samples ground by hardened steel and ceramic plates. Based on energy distribution curves (fig. C1) and relative intensities, it has been estimated that the "blank" (724) contains about 90 ppm Rb. The linearity of this curve is typical for other trace elements determined in this paper.

In rock W-1 (10.94 percent CaO) radiation, due to Ca K_{β_1} line at 41.06° two theta angle (Sc K_α - 40.26°), contributes to the total energy quanta counted. If this effect is not considered, the value for Sc in W-1 on our calibration curve would be about 78 ppm. The data above were obtained using a 5 mil collimator; a 20 mil collimator was also used but the effect of the Ca K_{β_1} radiation was too strong to obtain meaningful results. Working at the detection limit, the data given on Sc illustrate mainly the method's limitations and are only indications of the order of magnitude of this element in rocks analyzed.

SELENIUM

Selenium could be detected in our system only at the 1,000 ppm concentration level, using the K_α line. The reasons for poor sensitivity for this element (Z=34) as compared to Ge (Z=32) are being investigated.

SILVER

Silver is difficult to determine using the K_{α_1} line at 15.95° two theta because of the interference of scattered radiation in this region. Identical intensities for Shoal granite samples with the G-1 pellet were obtained. Under our conditions the detection limit was estimated at about 100 ppm.

STRONTIUM

Strontium detection limit is determined as 50 ppm. It actually appears to be nearer 10 ppm, but lack of proper Sr-free standards did not permit us to prove it. Our blank standard shows a background corresponding to 80 ppm Sr.

Sample	Sr, ppm, ± 3C	Remarks
Shoal granite, ceramic plates	880 ± 30	LiF crystal
Shoal granite, iron plates	875 ± 30	LiF crystal
G-1	250 ± 15	LiF crystal
G-1	250	Fleischer (1965)

Strontium was detected in W-1, but could not be estimated using the same granitic standard calibration curve due to absorption.

TANTALUM

Tantalum detection limit using the K_α is near 100 ppm. Ta was not detected in any samples analyzed.

THORIUM

Thorium detection limit, using L_α line, was determined at 35 ppm. Results are:

Sample	Th, ppm, ± 3C	Remarks
Shoal granite, ceramic plates	35	LiF crystal
Shoal granite, iron plates	35	LiF crystal
G-1	50 ± 5	LiF crystal
W-1	not detected	LiF crystal
G-1	52	Fleischer (1965)

TIN

Tin detection limit using the K_α line is about 50 ppm. The results are:

Sample	Sn, ppm, ± 3C	Remarks
Shoal granite, ceramic plates	(90 ± 5)	LiF crystal
Shoal granite, iron plates	not detected	LiF crystal
G-1	not detected	LiF crystal
W-1	not detected	LiF crystal

The high detection limit does not permit us to make any estimates of Sn in G-1 or W-1. Ceramic plates seem to contaminate the rock powder with Sn.

Titanium

Titanium detection limit is 5 ppm using the K_α line. Good agreement between data exists.

Sample	Ti, ppm, ± 3C	Remarks
Shoal granite, ceramic plates	1,680 ± 50	LiF crystal
Shoal granite, iron plates	1,680 ± 50	LiF crystal
Shoal granite, ceramic plates	1,920 ± 60	EDDT crystal
Shoal granite, iron plates	1,950 ± 60	EDDT crystal
G-1	1,270 ± 40	LiF crystal
G-1	1,440 ± 45	EDDT crystal
W-1	5,320 ± 160	LiF crystal
W-1	5,970 ± 180	LiF crystal, incl. G-1 point
W-1	6,475 ± 200	EDDT crystal
G-1	1,500	Fleischer (1965)
W-1	6,400	Fleischer (1965)
G-1	1,300	Maddock and Meinke *in* Fleischer, 1965, p. 1275 (neutron act.)
W-1	5,400	Maddock and Meinke *in* Fleischer, 1965, p. 1275 (neutron act.)

When titanium is determined with samples in vacuum, using the LiF crystal in rocks containing more than 0.1 percent BaO, the interference of Ba L_{α_1} at 87.13° two theta is detected (see fig. C3). As was noted in the case of Ba, Rb, and Mn, the good linearity of relative titanium intensities over a wide composition range in the series granite-basalt, is due to concurrent linearity in major element compositional changes (Si, K, Ca, Fe) in these rocks.

URANIUM

Uranium detection limit using L_{α} line was 40 ppm. No uranium was detected in any of the rocks here analyzed.

VANADIUM

Vanadium detection limit is 10 ppm using the K_{α} line. Results are:

Sample	V, ppm, ± 3C	Remarks
Shoal granite, ceramic plates	50 ± 2	LiF crystal, 20 mil collimator
Shoal granite, iron plates	50 ± 2	LiF crystal, 20 mil collimator
Shoal granite, ceramic plates	65 ± 15	EDDT crystal, 5 mil collimator
Shoal granite, iron plates	65 ± 6	EDDT crystal, 5 mil collimator
G-1	38 ± 3	EDDT crystal, 5 mil collimator
W-1	225 ± 15	EDDT crystal, 5 mil collimator
G-1	21	Stevens and others (1960)
G-1	16	Fleischer (1965)
W-1	240	Fleischer (1965)

The interference of Ti $K_{\beta_{1,3}}$ at 77.24° two theta (V K_{α_1} = 76.84°) is minimal. It is interesting to note that when a simple two-point G-1 to W-1 calibration curve is used, we obtain for vanadium in Shoal granite 40 ppm ± 3 ppm using the 20 mil collimator and EDDT crystal, and disregarding the effect of Ti K_{β} radiation. This indicates that reasonably good accuracy can be expected in the determination of vanadium if simply based on these two standard rocks. Our value for G-1 may be too high.

YTTERBIUM

Ytterbium detection limit is less than 1 ppm. Results are:

Sample	Yb, ppm	Remarks
Shoal granite, ceramic plates	1	LiF crystal
Shoal granite, iron plates	5	LiF crystal
G-1	1	LiF crystal
W-1	not detected	LiF crystal
G-1	1	Stevens and others (1960); Fleischer (1965)
W-1	3	Stevens and others (1960); Fleischer (1965)

YTTRIUM

Yttrium detection limit has been determined as 5 ppm. The results are:

Sample	Y, ppm, ± 3C	Remarks
Shoal granite, ceramic plates	~10	LiF crystal
Shoal granite, iron plates	~ 5	LiF crystal
G-1	20 ± 2	LiF crystal
G-1	21	Stevens and others (1960)
G-1	13	Fleischer (1965)

The intensity for Y in W-1 falls short of the established calibration curve, indicating the need of a different standard "pseudobasalt." Starting with Y, no vacuum was used in the crystal housing for elements of higher atomic number.

ZINC

Zinc detection limit was established at 10 ppm. Our blank contained about 20 ppm Zn.

Sample	Zn, ppm, ± 3C	Remarks
Shoal granite, ceramic plates	55 ± 3	LiF crystal
Shoal granite, iron plates	52 ± 3	LiF crystal
G-1	40 ± 3	LiF crystal
G-1	40	Stevens and others (1960)
G-1	45	Fleischer (1965)

The Zn value for W-1 falls below the calibration curve, due to strong absorption effect. There also seems to be some zinc contamination present in the system, possibly zinc from collimator blades.

ZIRCONIUM

Zirconium detection limit is 50 ppm. The background of our blank sample was equivalent to 200 ppm Zr. Results are:

Sample	Zr, ppm, ± 3C	Remarks
Shoal granite, ceramic plates	195 ± 15	LiF crystal
Shoal granite, iron plates	175 ± 20	LiF crystal
G-1	245 ± 15	LiF crystal
W-1	70 ± 6	LiF crystal
G-1	210	Stevens and others (1960); Fleischer (1965)
W-1	100	Stevens and others (1960); Fleischer (1965)

Our value for W-1 is probably low because of absorption effects; however, this composition lies within the acceptable values for W-1, indicating that in this type of rocks one could use for preliminary estimates of Zr the two-point calibration curve drawn through G-1 and W-1. Our data agree well with mass spectrometric data by Taylor and Kolbe (1964), who report 70 ppm Zr for W-1. The high background of our standard and scattered radiation affect the accuracy of our determination of Zr.

CONCLUSIONS

The plain-pressed rock powder method can be used for the semiquantitative determination of trace elements in the range of 1 to 7,000 ppm in granitic rocks. Calibration curves may be considered linear over this range for practical purposes, when main interferences are accounted for. It is important to have the synthetic standards of composition as close to that of the rock as is practically possible. Approximation of a granite composition by simply mixing 80 percent SiO_2 and 20 percent Al_2O_3 is sufficiently close for semiquantitative determination of most traces in granitic rocks, when the relatively high background of this mixture is taken into account and the total absorption effect corrected or based on standard G-1.

Data for G-1 obtained from "pseudogranite" calibration curves without the correction of the total absorption effect are within acceptable limits for these standards. This is often due to linear concentration changes in major elements in igneous rocks of granite-basalt composition and to partial mutual cancellation of enhancement, absorption, and mineralogical effect in complex mixtures. For basaltic composition a mixture of 69 percent SiO_2, 20 percent Al_2O_3, 10 percent Fe_2O_3, and 1 percent TiO_2 seems to be sufficient to take care of most absorption, enhancement, and background problems in this trace element range as demonstrated in the case of Ca. Due to interference of Ti with Ba, Ce, and La, it is advantageous to add 1 percent TiO_2 to this mixture.

Precision of this nondestructive technique compares favorably with the precision of other spectrographic methods, and good accuracy is demonstrated by the fact that all values obtained from our synthetic granite calibration curves for the granite G-1 fall very close to, or coincide with, the recommended or average values reported by Ahrens and Fleischer in Stevens and others (1960) and Fleischer (1965). In many cases approximate values for the diabase W-1 can also be obtained with this type of standards. Especially when a two-point calibration curve between G-1 and W-1 is used, acceptable values may be received for similar rocks because the differences in total absorption effects are thus partially corrected for. The close agreement of uncorrected data on G-1 and in some cases W-1 in our system seems to be due to a partial cancellation of enhancement, absorption, and mineralogical effects in such complex mixtures.

It appears that this plain rock powder method is most straightforward in accurate determination of traces by X-ray emission. Sufficient counting rates can be obtained for trace elements starting with Sc and up to U using the standard vacuum X-ray spectrograph. Specific application in geochemistry is suggested for trace element distribution investigations in similar rocks. Lowest detection limits and shortest sample preparation time theoretically possible for a direct, truly nondestructive X-ray spectrographic semiquantitative determination are indicated.

To extend the detection limits in X-ray spectrometry under our present instrumental conditions would require chemical pretreatment or destruction of the sample. Work on other trace elements in granites and other rocks is in progress (see section 2 of this report).

It is proposed that the method may find its application also as a preparatory or first step in a total nondestructive X-ray spectrographic analysis of major and trace elements in rocks. It appears that this approach will rapidly provide preliminary data to form a basis for absorption and enhancement corrections when ultimate accuracy is desired.

Since the empirical nature of this method seems to make it uniquely suitable for a computer programmed procedure, we are planning to adapt it to the Siemens Automatic Sequential X-ray Spectrometer SRS-1, which is interfaced to the Digital Equipment Corp.'s computer PDP-8. This equipment has been acquired by the Mackay School of Mines under a National Aeronautics and Space Administration contract.

The dual system of sample preparation and grinding (Volborth, 1965) as employed in this experiment permits us to pinpoint specific interferences or contamination due to, or introduced by, the grinding media. Thus there is no reason to speculate on the unusual concentration of Cd, In, and Sn in the Shoal granite, despite results obtained on samples ground with ceramic plates. Yet, if only the ceramic-ground powders were analyzed, the data doubtlessly would have caused speculation as to the significance of the unusual concentrations of these geochemically related trace elements in the granite studied.

TOTAL INSTRUMENTAL ANALYSIS OF ROCKS

PART C

Section 2

QUANTITATIVE X-RAY FLUORESCENT TRACE ANALYSIS FOR 20 ELEMENTS IN IGNEOUS ROCKS

By

Brent Fabbi

and

Alexis Volborth

CONTENTS

Section 2

ILLUSTRATIONS

QUANTITATIVE X-RAY FLUORESCENT TRACE ANALYSIS FOR 20 ELEMENTS IN IGNEOUS ROCKS

By Brent Fabbi and Alexis Volborth

ABSTRACT

Elements As, Ba, Ce, Co, Cr, Cu, Ga, Gd, Ge, La, Nd, Ni, Pb, Rb, Sc, Sr, V, Y, Yb, Zn, and Zr are analyzed in dual samples of eight igneous rocks. Two different grinding media are used. Hardened steel and ceramic plate comminution is applied to the same rock, resulting in two samples contaminated by different elements. Comparison is made between our XRF and arc-excited spectrographic results obtained by two different laboratories. X-ray intensities are corrected for iron absorption empirically, based on standard rocks G-1 and W-1. The correction procedure is graphically shown. Data obtained by this XRF method are shown to be comparable in accuracy to the routine quantitative arc-emission spectrographic data by two other laboratories. The XRF method has a higher degree of precision than the arc methods, thus permitting the detection of minor trace element differences in similar rock types.

INTRODUCTION

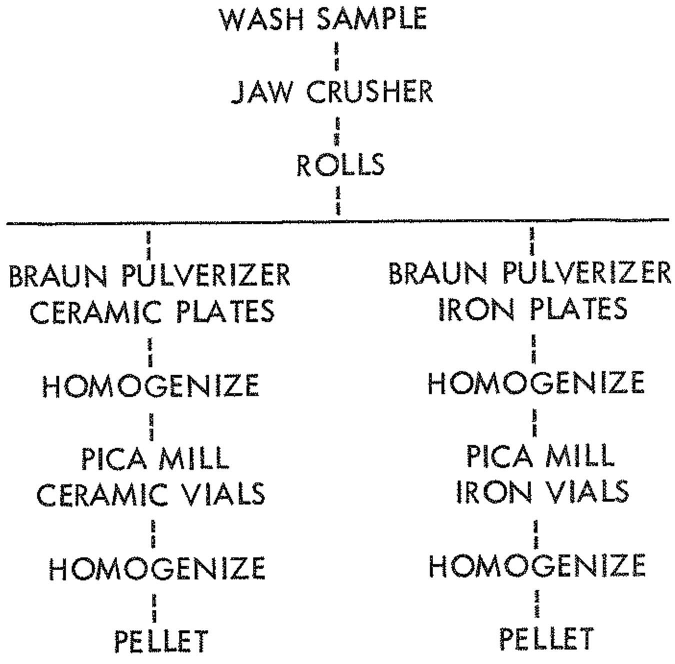
Earlier XRF work in this laboratory is referred to in the references. Recently an attempt has been made (Volborth, Fabbi, and Vincent, 1968) to demonstrate that total analysis of a rock for major as well as trace elements can be performed nondestructively. Precision in XRF analysis of silicates has been studied by Baird and Welday (1968). Analyses of major and trace constituents in rocks and other materials are now routinely performed (Campbell and Thatcher, 1962; Campbell and others, 1966; Carmichael and others, 1968; Kaye, 1965; Kodama and others, 1967; Rose and others, 1965; Stone and Rayburn, 1967). Many authors use preconcentration techniques (Bertin, 1968; Cowgill, 1968; Cutitta and Rose, 1968a, b; Davis and others, 1968; Rose and Cutitta, 1968; Rudolph and others, 1965; Spano and Green, 1966) to better the detection limits and avoid interference. Such procedures were considered long and tedious. Thus the method described in Section 1 of this paper was used for 21 elements with the additional procedure of empirical correction for absorption due to iron, which is the major heavy element in rocks analyzed.

This work was originally performed in order to calibrate the X-ray methods used in the Nevada Mining Analytical Laboratory and to compare the accuracy of these methods with that of optical emission spectrographic techniques, as used by the U. S. Geological Survey laboratories in Denver and the Geochemical Laboratory at the California Institute of Technology in Pasadena. For this purpose, identical dual samples of the same eight rocks, ground by different means, were submitted to the laboratories for routine analyses; the results are compared in this paper. For their kindness and effort in analyzing our samples, the authors are greatly indebted to A. T. Meyers, U. S. Geological Survey, Denver, and A. A. Chodos of the California Institute of Technology, Pasadena.

SAMPLE PREPARATION

All rock samples were washed, dried, and passed through a jaw crusher, which crushed the rocks to approximately a 1/4-inch size. The sample was then passed twice through rolls and reduced to 20 mesh. At this point it was split, one half to be ground by iron-grinding media and the other half by ceramic-grinding media. Splitting enabled later determination of contamination by the iron- and ceramic-grinding media. One split was ground to minus 100 mesh in an iron-plate Braun pulverizer and homogenized by tumbling in a V-blender. A 10-gram sample was split out and ground to 95 percent minus 400 mesh in a Pica mill using a tool steel vial. The 10 grams of minus 400 mesh material were rehomogenized and a 1-gram split taken to press into a pellet. The pellet was pressed at 30,000 psi for one minute against a glass disc to provide smooth plane surface (see part A, p. A9-A11). A backing and rim of amber bakelite provided extra strenght and durability to the pellet.

The other half of the split from the rolls was ground by ceramic media in the same manner. The sample preparation scheme is shown below.



INSTRUMENTATION

A Norelco Universal eight-sample holder vacuum spectrograph, with a tungsten target X-ray tube, LiF crystal, flow and scintillation counters, and a 5-mil collimator, was used in this work. A constant potential source and pulse height analyzer were employed. Each sample was counted four times for 64 seconds.

ABSORPTION CORRECTION

In our procedure, artificial standards containing from 100 ppm to 1,000 ppm of the oxide of interest in an 80 percent SiO_2 + 20 percent Al_2O_3 mixture establish a linear curve and its slope. G-1 and W-1 are displaced from the curve owing to absorption of the X-ray quanta of interest by the matrix, mainly because of the difference in the total iron (G-1 $\cong$ 2% Fe_2O_3 W-1 $\cong$ 11% Fe_2O_3). The 100 ppm to 1,000 ppm concentration is above the level in some rocks. However, the concentration of the elements in G-1 and W-1 is within the range being investigated. The artificial standards are used to establish a working curve and as such are used indirectly.

After plotting the counts-per-second values versus ppm in the artificial standards of the oxide of interest, parallel curves are drawn through points on the graph established by plotting X-ray counting rates versus the known concentrations of the elements in rocks G-1 and W-1 (fig. C4). A line perpendicular to the abscissa is drawn between the G-1 and W-1 curves and divided into eight equally spaced points. Eight parallel lines to the artificial standard curves are then drawn through these points. By so doing, a graphic representation of curves corresponding to rocks which would contain, hypothetically, from 2% Fe_2O_3 (as in G-1) to 11% Fe_2O_3 (as in W-1) is obtained. Assuming that the variation of concentration of iron is the main cause for different relative X-ray intensities, one needs only to plot counts per second versus percent Fe_2O_3 concentration versus ppm, depending on the Fe_2O_3 content of the rock analyzed. This is an empirical assumption made only in order to simplify trace element analysis by X-rays.

For example, iron-ground Andesite-2 yields 70.3 counts per second for strontium; the Fe_2O_3 concentration is known to be 5.8 percent. The concentration of Sr, 545 ppm, is therefore read from the 6 percent Fe_2O_3 line.

A mathematical, instead of graphic, method may, of course, be used. For Sr, the equation of the approximate calibration line is:

$$\text{ppm Sr} = 10.0528 \times \text{c/s} - 260 + 16.4\ (\%Fe_2O_{3\,(\text{unk})} - 2\%\ Fe_2O_{3\,(\text{G-1})}).$$

The b factor, -260, is a function derived from the equation, $y = mx + b$, of the parallel line passing through the point established by G-1 on the graph. The factor 16.4 is the absorption correction for b under the conditions of the analysis.

Again using Andesite-2 as an example:

ppm Sr $= 10.0528 \times 70.3 - 260 + 16.4\ (5.8 - 2.0) + 481 + 62 = 543$ ppm Sr, which is the calculated value.

Note that the Fe_2O_3 in G-1 is subtracted from the Fe_2O_3 in the unknown since the equation of the line is based on the parallel line passing through G-1. Samples having less

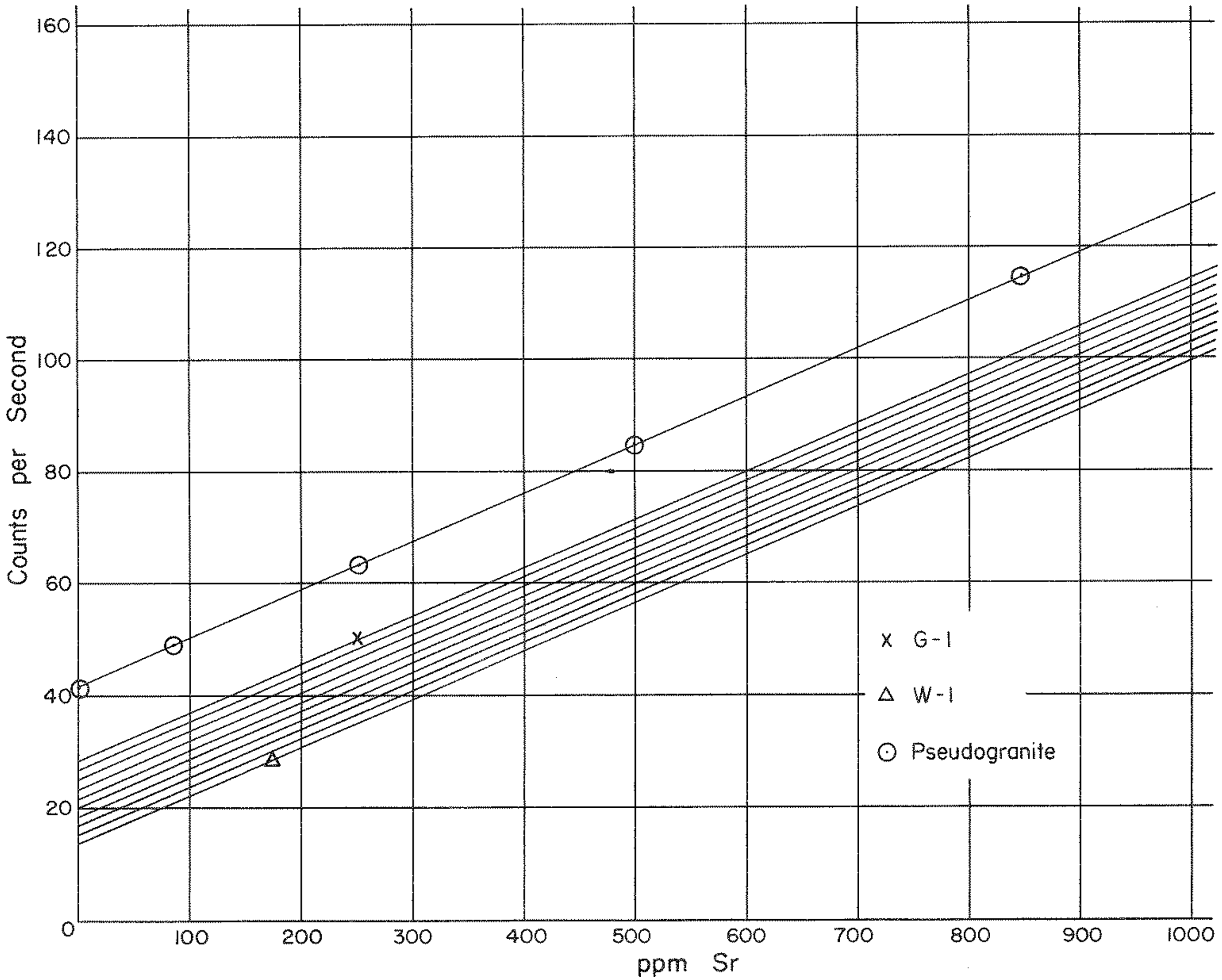


Figure C4. Empirical Fe absorption correction for Sr. The upper curve (circles) is a plot of counts per second versus parts per million of Sr in a SiO_2-Al_2O_3 matrix. The lines drawn parallel to the upper curve through the plotted points of G-1 (X) and W-1 (triangle), as well as those lines between G-1 and W-1, permit correction for the absorption of Sr radiation by Fe in silicate rocks.

than 2 percent Fe_2O_3 require a positive rather than a negative correction to correct for Fe_2O_3 absorption. An opposite correction applies for enhancement effects. Elements corrected for iron absorption include Co, Cr, Cu, Ga, Ni, Pb, Sr, Y, and Zn.

RESULTS

ARSENIC

Arsenic detection limit is <1ppm. Only tuffaceous rocks could be shown to contain arsenic. This element was not determined by the Cal. Tech. and U. S. G. S. laboratories.

As-Arsenic in ppm

		XRF	
No.	Sample	Fe	Cer
1	Rhyolite tuff	8	6
4	Rhyolite tuff	15	12

BARIUM

Detection limit is 5 ppm Ba.

Ba-Barium
in ppm

		XRF		Cal Tech		USGS	
No.	Sample	Fe, LiF	Cer, LiF	Fe	Cer	Fe	Cer
1	Rhyolite tuff	625	625	320	310	300	300
2	Andesite	1185	1190	1600	1300	1000	1000
3	Basalt	1250	1285	1600	1900	1250	1250
4	Rhyolite tuff	1490	1515	1600	1100	1500	1500
5	Andesite	1280	1290	2300	1700	1250	1250
6	Andesite	1290	1300	1600	1700	1250	1500
7	Basalt	1365	1360	1500	2400	1500	1250
8	Andesite	1120	1100	1800	1700	1000	1000

CERIUM

Detection limit is 20 ppm Ce.

Ce-Cerium
in ppm
LiF crystal

		XRF		Cal Tech		USGS	
No.	Sample	Fe	Cer	Fe	Cer	Fe	Cer
1	Rhyolite tuff	260	250	not detected		not detected	
2	Andesite	67	70				
3	Basalt	<20	<20				
4	Rhyolite tuff	350	342				
5	Andesite	110	107				
6	Andesite	70	75				
7	Basalt	<20	<20				
8	Andesite	<20	<20				

CHROMIUM

There is satisfactory agreement between X-ray fluorescent and spectrochemical analyses. The XRF values fall between the spectrochemical values of the other laboratories. Chromium contamination is apparent in samples ground by the iron media. The average increase is 60 ppm Cr. The XRF detection limit for Cr is 1 ppm.

Cr-Chromium
in ppm

		XRF		Cal Tech		USGS	
No.	Sample	Fe	Cer	Fe	Cer	Fe	Cer
1	Rhyolite tuff	95	3	78	4	100	5
2	Andesite	117	62	94	55	125	50
3	Basalt	118	69	70	59	125	60
4	Rhyolite tuff	95	1	59	~2	100	3
5	Andesite	98	44	77	43	125	30
6	Andesite	116	64	120	56	125	60
7	Basalt	155	112	180	110	250	125
8	Andesite	97	63	63	51	85	50

COBALT

There is reasonable agreement between the X-ray and the two spectrochemical analyses for cobalt. Some cobalt may have been introduced by the iron-grinding media. However, the differences between the Co determinations on the iron-ground material and on the ceramic-ground material by XRF tend to be greater than similar differences between values by emission spectrography. The detection limit by XRF for Co is 1 ppm.

Co-Cobalt
in ppm

No.	Sample	XRF Fe	XRF Cer	Cal Tech Fe	Cal Tech Cer	USGS Fe	USGS Cer
1	Rhyolite tuff	3	0	4	-	1	0
2	Andesite	37	22	15	15	17	15
3	Basalt	39	31	22	22	20	20
4	Rhyolite tuff	9	0	14	0	0	0
5	Andesite	15	12	19	18	20	17
6	Andesite	30	17	17	16	17	15
7	Basalt	21	14	23	22	25	17
8	Andesite	29	20	23	18	17	17

COPPER

The X-ray fluorescent analyses fall generally between the spectrochemical values. Four of the samples appear to have been considerably contaminated by the iron-grinding media. This may have been caused by a longer grinding time necessary because of the hardness and fine-grain size of the rock. Detection limit is 10 ppm by this method.

Cu-Copper
in ppm

No.	Sample	XRF Fe	XRF Cer	Cal Tech Fe	Cal Tech Cer	USGS Fe	USGS Cer
1	Rhyolite tuff	70	29	68	6	125	100
2	Andesite	108	49	120	43	150	60
3	Basalt	56	87	77	72	85	110
4	Rhyolite tuff	21	30	38	6	50	40
5	Andesite	245	128	200	120	175	100
6	Andesite	130	134	150	120	150	150
7	Basalt	116	70	130	59	150	70
8	Andesite	43	72	77	70	70	70

GADOLINIUM

Ten ppm is the detection limit for Gd. The data given appears too high, and unfortunately no comparison can be made with other laboratories.

Gd-Gadolinium
in ppm

No.	Sample	XRF Fe, LiF	XRF Cer, LiF	Cal Tech Fe	Cal Tech Cer	USGS Fe	USGS Cer
1	Rhyolite tuff	37	37	not determined		not determined	
2	Andesite	87	60				
3	Basalt	102	87				
4	Rhyolite tuff	35	30				
5	Andesite	90	65				
6	Andesite	90	60				
7	Basalt	117	90				
8	Andesite	90	75				

GALLIUM

Agreement between the two methods of analysis is satisfactory. X-ray fluorescent data fall between the spectrochemical values of the two other laboratories. No grinding effect is indicated. The XRF detection limit for Ga is 5 ppm.

Ga-Gallium
in ppm

No.	Sample	XRF Fe	XRF Cer	Cal Tech Fe	Cal Tech Cer	USGS Fe	USGS Cer
1	Rhyolite tuff	11	15	10	18	20	25
2	Andesite	19	18	13	13	30	30
3	Basalt	20	19	17	20	30	30
4	Rhyolite tuff	12	32	10	15	25	25
5	Andesite	23	23	18	13	40	30
6	Andesite	18	15	11	15	30	30
7	Basalt	22	24	10	18	40	30
8	Andesite	20	13	18	13	30	30

GERMANIUM

Germanium could be detected only in tuffaceous rocks. Detection limit is about 1-5 ppm. The data appear too high.

Ge-Germanium
in ppm

No.	Sample	XRF Fe	XRF Cer	Cal Tech Fe	Cal Tech Cer	USGS Fe	USGS Cer
1	Rhyolite tuff	(50	68)	not detected		not detected	
4	Rhyolite tuff	(27	74)				

LANTHANUM

Detection limit by this method is 10 ppm.

La-Lanthanum
in ppm

		XRF		Cal Tech		USGS
No.	Sample	Fe, LiF	Cer, LiF	Fe	Cer	
1	Rhyolite tuff	97	77	not determined		25
2	Andesite	97	95			0
3	Basalt	120	120			15
4	Rhyolite tuff	60	67			0
5	Andesite	110	110			40
6	Andesite	97	95			0
7	Basalt	125	125			30
8	Andesite	85	77			0

LEAD

X-ray fluorescent values are distributed more randomly in this instance because the X-ray determination is being performed close to the determination limit for this method. There is, nevertheless, close agreement between the two methods of analysis. There is apparently little effect from the grinding media on this determination. The detection limit by XRF for Pb is 15 ppm.

Pb-Lead
in ppm

		XRF		Cal Tech		USGS	
No.	Sample	Fe	Cer	Fe	Cer	Fe	Cer
1	Rhyolite tuff	51	60	33	24	30	25
2	Andesite	33	28	32	<20	40	17
3	Basalt	~15	24	30	<20	30	20
4	Rhyolite tuff	55	63	34	32	50	40
5	Andesite	45	40	43	20	60	30
6	Andesite	20	38	32	35	50	50
7	Basalt	30	28	29	<20	40	20
8	Andesite	~15	~15	-	-	17	17

NEODYMIUM

Detection limit is 30 ppm.

Nd-Neodymium
in ppm

No.	Sample	XRF Fe, LiF	XRF Cer, LiF	Cal Tech Fe	Cal Tech Cer	USGS Fe	USGS Cer
1	Rhyolite tuff	50	45	not determined		-	-
2	Andesite	75	57			-	-
3	Basalt	95	70			-	-
4	Rhyolite tuff	47	32			-	-
5	Andesite	90	70			70	70
6	Andesite	75	55			-	-
7	Basalt	110	80			-	-
8	Andesite	70	47			-	-

NICKEL

Agreement between the two methods is quite satisfactory. There is an indication of Ni contamination from the iron plates amounting to 5-10 ppm. The detection limit for Ni is <1 ppm.

Ni-Nickel
in ppm

No.	Sample	XRF Fe	XRF Cer	Cal Tech Fe	Cal Tech Cer	USGS Fe	USGS Cer
1	Rhyolite tuff	12	<1	17	-	15	3
2	Andesite	32	31	31	23	25	20
3	Basalt	45	52	47	43	30	30
4	Rhyolite tuff	12	~4	11	<4	10	0
5	Andesite	36	38	34	27	30	17
6	Andesite	37	40	39	28	30	20
7	Basalt	52	63	54	44	60	20
8	Andesite	40	41	33	31	30	25

RUBIDIUM

Detection limit is 10 ppm. Rubidium could not be determined by arc.

Rb-Rubidium
in ppm

No.	Sample	XRF Fe	 Cer
1	Rhyolite tuff	242	265
2	Andesite	71	47
3	Basalt	50	10
4	Rhyolite tuff	190	162
5	Andesite	50	20
6	Andesite	60	30
7	Basalt	45	10
8	Andesite	55	20

SCANDIUM

Detection limit is about 5 ppm. The XRF results tend to be higher than the spectrographic data, but are nevertheless of the same order of magnitude.

Sc-Scandium
in ppm

		XRF		Cal Tech		USGS	
No.	Sample	Fe	Cer	Fe	Cer	Fe	Cer
1	Rhyolite tuff	<5	<5	not detected		5	5
2	Andesite	18	18	14	15	10	10
3	Basalt	24	26	19	21	15	15
4	Rhyolite tuff	<5	<5	not detected		0	0
5	Andesite	20	22	17	17	12	12
6	Andesite	20	20	18	17	12	12
7	Basalt	28	28	24	23	20	17
8	Andesite	22	24	22	20	17	17

STRONTIUM

Detection limit is 10 ppm.

Sr-Strontium
in ppm

		XRF		Cal Tech		USGS	
No.	Sample	Fe	Cer	Fe	Cer	Fe	Cer
1	Rhyolite tuff	115	135	57	36	150	125
2	Andesite	545	565	560	400	1000	850
3	Basalt	500	505	680	800	1500	1250
4	Rhyolite tuff	110	110	40	29	150	125
5	Andesite	1075	1080	700	780	2500	2500
6	Andesite	500	535	350	740	1000	1000
7	Basalt	505	505	510	870	1250	1250
8	Andesite	525	515	630	610	1000	1000

VANADIUM

Detection limit is 10 ppm.

V-Vanadium
in ppm

		XRF		Cal Tech		USGS	
No.	Sample	Fe	Cer	Fe	Cer	Fe	Cer
1	Rhyolite tuff	~10	<10	17	12	20	15
2	Andesite	120	118	67	78	175	150
3	Basalt	185	184	130	166	225	175
4	Rhyolite	~10	~10	16	13	15	11
5	Andesite	150	150	140	130	200	175
6	Andesite	120	124	110	110	150	150
7	Basalt	240	215	150	170	250	175
8	Andesite	130	130	130	130	175	175

YTTERBIUM

Detection limit is<1 ppm.

Yb-Ytterbium
in ppm

		XRF		Cal Tech		USGS	
No.	Sample	Fe, LiF	Cer, LiF	Fe	Cer	Fe	Cer
1	Rhyolite tuff	1	1	2	2	2	2
2	Andesite	2	2	2	2	2	2
3	Basalt	3	3	3	3	3	3
4	Rhyolite tuff	1	1	2	<2	2	1.5
5	Andesite	2	3	3	3	2	2
6	Andesite	2	2	2	3	2	2
7	Basalt	3	3	5	4	3	3
8	Andesite	2	2	2	2	2	2

YTTRIUM

X-ray fluorescence data for yttrium may be considered acceptable in semiquantitative analysis. There is no concrete evidence of grinding media effects. Five ppm is the detection limit for Y by XRF.

Y-Yttrium
in ppm

		XRF		Cal Tech		USGS	
No.	Sample	Fe	Cer	Fe	Cer	Fe	Cer
1	Rhyolite tuff	17	44	37	25	25	15
2	Andesite	38	16	25	31	20	17
3	Basalt	25	30	37	42	30	30
4	Rhyolite tuff	8	22	~23	~20	12	12
5	Andesite	20	40	38	36	25	25
6	Andesite	~5	21	30	30	17	20
7	Basalt	65	57	53	51	30	25
8	Andesite	35	19	32	29	20	17

ZINC

Since the lower limit of determination for zinc by spectrochemical methods is 50-100 ppm, the X-ray fluorescence results could not be compared with optical spectrographic data. Some contamination of the samples by the ceramic plates is apparent. The detection limit by XRF for Zn is 10 ppm.

Zn-Zinc
in ppm

		XRF		Cal Tech		USGS	
No.	Sample	Fe	Cer	Fe	Cer	Fe	Cer
1	Rhyolite tuff	31	38	-	-	-	-
2	Andesite	65	79	-	-	-	-
3	Basalt	91	92	-	-	-	-
4	Rhyolite tuff	24	42	-	-	-	-
5	Andesite	77	88	looked	for	looked for	
6	Andesite	69	83	but not found		but not found	
7	Basalt	89	103	-	-	-	-
8	Andesite	87	84	-	-	-	-

ZIRCONIUM

Detection limit is 50 ppm.

Zr-Zirconium
in ppm

		XRF		Cal Tech		USGS	
No.	Sample	Fe	Cer	Fe	Cer	Fe	Cer
1	Rhyolite tuff	190	170	120	140	85	85
2	Andesite	177	145	120	130	85	110
3	Basalt	157	137	170	170	70	110
4	Rhyolite tuff	143	130	88	82	60	60
5	Andesite	185	183	160	160	70	85
6	Andesite	143	145	150	140	85	85
7	Basalt	155	153	190	200	120	150
8	Andesite	118	107	110	110	85	70

OTHERS

Antimony could not be detected in any of the rocks analyzed by any of the three laboratories.
Cesium was not detected; detection limit is about 50 ppm.
Hafnium was not detected; detection limit is about 10 ppm.
Mercury was not detected in any of the rocks; detection limit is about 150 ppm.
Molybdenum was not detected by XRF method; detection limit is about 50 ppm. USGS laboratory detected 3 ppm Mo in No. 4, ceramic ground; Cal Tech, <10 ppm in the same sample.

Selenium detection limit is about 5 ppm. None was detected in any of the samples.
Silver detection limit is about 50 ppm. None was detected in any of the samples.
Samarium detection limit is about 10 ppm. None was found in any of the samples.
Tantalum was not detected; detection limit is 100 ppm.
Thorium was not detected; detection limit is 35 ppm.
Uranium could not be detected owing to high detection limit of about 80 ppm by the XRF method.

CONCLUSIONS

Trace Elements As, Ba, Ce, Co, Cr, Cu, Ga, Gd, Ge, La, Nd, Ni, Pb, Rb, Sc, Sr, V, Y, Yb, Zn, and Zr can be analyzed accurately in igneous rocks using a straightforward comparative method and a correction technique based on standard rocks G-1 and W-1 and a series of carefully prepared standards composed of 80 percent SiO_2 and 20 percent Al_2O_3 with added trace element concentrations in the 50-1000 ppm region. Empirical correction for iron absorption seems to be the only requirement to obtain results equivalent to those routinely obtained by other laboratories using arc excitation spectrography. The advantage of X-ray spectrographic techniques is their high precision as shown in Parts A, B, and C of this report. In geochemical work, one is often faced with the necessity of selecting a precise technique to distinguish small variations of trace elements in rocks which are physically nearly identical, or samples from the same pluton, for example. The methods described in this report may sometimes give inaccurate results for single elements owing to the omission of specific corrections for all the absorption and enhancement effects, but this disadvantage may be counterbalanced by the simplicity, speed, and higher precision of the procedures described.

The proposed method may give preliminary quantitative and semiquantitative results in geochemical exploration more rapidly than optical spark and arc methods.

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