# Second Report on a Cooperative Investigation of the Composition of Two Silicate Rocks

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GEOLOGICAL SURVEY BULLETIN 1113

U.S. DEPARTMENT OF THE INTERIOR

March 3, 1849

# Second Report on a Cooperative Investigation of the Composition of Two Silicate Rocks

*By* ROLLIN E. STEVENS *and others*

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*An investigation by staff members of University of Cape Town, South Africa; California Institute of Technology, Pasadena; Indiana Geological Survey, Bloomington; and U.S. Geological Survey*

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# SECOND REPORT ON A COOPERATIVE INVESTIGATION OF THE COMPOSITION OF TWO SILICATE ROCKS

## INTRODUCTION

By Michael Fleischer

U.S. Geological Survey Bulletin 980, "A Cooperative Investigation of Precision and Accuracy and Chemical, Spectrochemical, and Modal Analysis of Silicate Rocks," appeared in 1951. In the first section, H. W. Fairbairn wrote,

> Despite the dependence of petrologists and geochemists on such analyses, there has been little attempt at critical evaluation of the procedures used. We are presenting in this bulletin some facts and ideas which may stimulate interest in this aspect of quantitative measurement. * * * No part of the project under discussion in the following chapters is in any sense complete. * * * Since problems dealing with precision and accuracy literally have no final solution one must be content with reports of progress. This bulletin is such a report of progress, published at this time because we believe the topics under discussion are of surpassing interest to petrologists and geochemists.

And he added in the final summary,

> It is the hope of the authors that readers of this bulletin will be both disturbed and encouraged by its contents. It is notorious that the twin themes of precision and accuracy have not been accorded their proper rank in many branches of quantitative geological work, partly through lack of data but in part also through disregard of the significance of these problems.

The response to Bulletin 980 has been gratifying; the excellent critical review of it published by E. A. Vincent in Geochimica et Cosmochimica Acta (1952, v. 2, p. 304–306) doubtless contributed to its dissemination. Many laboratories throughout the world have requested and have been supplied with samples of the two rocks by the U.S. Geological Survey; subsequently there has been much research on the improvement of methods of analysis. The results have been reported in part in the many papers referred to in this bulletin, but many analysts have sent their data to the Geological Survey in private communications. Interest has been sufficient to justify assembling the new data in the present volume, to make the scattered published analyses and those previously unpublished more easily accessible.

The work here reported seems to show that real progress has been made and that a great deal more is now known about the compositions of these two rocks than in 1951. Improvements in previous methods and the use of new methods have given better data on major and minor elements, and new data on elements that could not be determined previously.

Nevertheless, the present volume does not, any more than its predecessor, complete the subject. Limited amounts of the two rocks are available to those seriously interested; requests should be addressed to the U.S. Geological Survey, Washington 25, D.C. It is the hope of the Survey that all analysts who make analyses of any kind will send in their results and information concerning any published data that have been overlooked.

Among the authors of the papers in this volume are L. H. Ahrens, University of Cape Town, South Africa, A. A. Chodos, California Institute of Technology, Pasadena, and R. H. Filby and R. K. Leininger of the Indiana Geological Survey, and F. J. Flanagan, Michael Fleischer, W. W. Niles, and Rollin E. Stevens of the U.S. Geological Survey. The U.S. Geological Survey wishes to express deep appreciation to the authors from other institutions for their cooperation in this project. We thank the many analysts quoted for supplying their results, W. J. Youden of the National Bureau of Standards for helpful criticism and advice on statistical matters, and William G. Schlecht, who has distributed samples of the two rocks, collected many of the analyses, and contributed much valuable advice.

# SECOND REPORT ON A COOPERATIVE INVESTIGATION OF THE COMPOSITION OF TWO SILICATE ROCKS

## PART 1. CHEMICAL ANALYSES OF THE GRANITE AND THE DIABASE

By Rollin E. Stevens and William W. Niles[1]

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### ABSTRACT

Results are compiled of more than 30 partial and complete new analyses of G–1 and W–1 from laboratories throughout the world. The new analyses are compared with each other and with previous analyses published in U.S. Geological Survey Bulletin 980. Conventional methods of rock analysis are examined for sources of error to account for the wide divergence of results. Although the range of results for each constituent is large, arithmetic means and medians of all and of preferred values, for both the new and the old analyses, show general agreement with published results by competent analysts and with results by methods other than conventional. Further evidence is given that low results for $SiO_2$ are obtained in most laboratories with techniques and procedures in present use. There is lack of precision and apparent positive bias in results for $Al_2O_3$ and $Fe_2O_3$. Results for $K_2O$ tend to be low. Results for other constituents are in better agreement and seem to be more reliable. The need for improvement in the field of rock analysis is again shown.

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[1] U.S. Geological Survey.

## INTRODUCTION

The publication of results of chemical analyses of the carefully prepared samples of granite (G-1) and diabase (W-1) made by rock analysts in 35 laboratories throughout the world (Fairbairn and others, 1951) has created considerable interest among geologists, petrologists, and geochemists, particularly chemists making or concerned with rock analyses. As a result of this publication, investigators in the earth sciences have been amazed and concerned to find that rock analyses from different laboratories and by different analysts may not agree even to whole percentages for predominant constituents. The concern of petrologists is well expressed by Chayes (Fairbairn and others, 1951, p. 67):

> Viewed in this light the scatter of tbe chemical results, whether as direct oxide percentages or as norms, must profoundly disturb every petrologist. * * * Normative variation is so extreme that in the absence of direct evidence to that effect there would be little reason to suppose all these analyses were of the same two rocks.

A number of papers deal with conclusions to be drawn from the first published analyses of G-1 and W-1. First conclusions are given by Schlecht, Stevens, Dennen, Ahrens, Chayes, and Fairbairn with the publication of the analyses in Geological Survey Bulletin 980 (Fairbairn and others, 1951). Schlecht (1951) has summarized the results of the work to chemists. A test of the accuracy of rock analyses, in which a glass of known composition simulating the composition of granite was analyzed by a number of laboratories, is described by Fairbairn and Schairer (1952). Results of this test of accuracy and conclusions drawn from analyses of G-1 and W-1 are further discussed by Fairbairn (1953). He presents a statistical study of precision of the analyses of G-1 and W-1, with regard to precision of a single analyst, precision of all analysts in a laboratory, and interlaboratory precision. He concludes that relative precision increases with increase in concentration of the constituent measured; this is obvious to the analyst, as pointed out by Fairbairn, since the analyst reports every constituent to the nearest 0.01 percent and hence the silica content is represented by a four digit number in contrast to one or two digits for manganese. Reports of rock analyses would be improved if each constituent were reported to the limit of accuracy of the determination. As a result of publication of analyses of G-1 and W-1, Chalmers and Page (1957) have discussed the reporting of chemical analyses of silicate rocks.

Fairbairn (1953) in apparent disagreement with Schlecht (1949) says "Since the correct analyses can never be known, the arithmetic mean for each constituent is the best estimate available and affords a basis for estimating precision." He accepts the arithmetic mean as his "preferred estimate" for all constituents of the chemical analyses except $SiO_2$ and $Al_2O_3$. Recognizing the apparent bias in analyses for $SiO_2$, shown by the analysis of the synthetic granite glass (Fairbairn and Schairer, 1952), Fairbairn adds 0.5 percent to the mean for $SiO_2$ in G–1 (preferred estimate 72.86 percent) and 0.35 percent to the mean for $SiO_2$ in W–1 (preferred estimate 52.69 percent). Because values for $SiO_2+R_2O_3$ in the analyses show normal distribution, in contrast to values for $SiO_2$ alone, and also from the supporting evidence of analyses of the synthetic granite glass, Fairbairn considers that this silica is being reported as $Al_2O_3$, and therefore subtracts these percentages from the arithmetic means for $Al_2O_3$ to obtain the preferred estimates of 13.94 percent $Al_2O_3$ for G–1 and 14.72 percent $Al_2O_3$ for W–1.

Schlecht (1951) says, with regard to the first published analyses of G–1 and W–1: "What has been accomplished, then, is a reconnaissance survey of the present state of rock analysis." New analyses here published do not markedly change the result of the reconnaissance. The present state of rock analysis should profoundly disturb every petrologist; it should also profoundly disturb chemists making rock analyses, in that grave doubt has arisen of the value of their product. A thorough review of techniques and closer supervision in laboratories making rock analyses seem to be needed. The fact that there were many divergent analyses of G–1 and W–1 has shown the need for improvement.

Whether the blame for divergence in results of rock analysis can be laid to methods or to personnel is arguable. Schlecht (1951) contends that, "It is not possible on the basis of present evidence to decide how much of the error in rock analysis is caused by lack of skill in the analyst and how much is inherent in the procedures themselves." Furthermore, it seems evident that more elaborate studies would not yield a quantitative evaluation of these two general causes of errors that would be fixed for all time and all places. Methods change and analysts differ in conscientiousness, knowledge, and skill. A few statements can be made, however, which serve to show that differences in these personal qualifications contribute a major part to the errors in rock analysis, and that the methods, if properly and skillfully applied, are quite dependable.

Methods are continuously being evaluated. Principles contained in books on rock analysis by Hillebrand (1919), Washington (1930), Hillebrand and others (1953), Groves (1951), and others have been so thoroughly tested and are so well established as to leave little doubt as to their validity if properly applied. When tested by analysts of adequate knowledge and skill, methods of analysis can be and have been shown to have definite characteristics of dependability, precision, and accuracy. Used by skilled analysts these methods give reliable values, as evidenced by the certified values for standard samples distributed by the National Bureau of Standards.

Dependability of results obtained by different analysts, however, will differ with the extent of knowledge of the individual analyst, his skill in carrying out the procedure, and the care he takes in performing each of many steps involved. Procedures used in different laboratories can be wrong in misapplying principles, and methods can be used for materials for which they are not applicable.

In the treatment of the new and old analyses, to follow, arithmetic means and medians are regarded as preferred estimates, and gross deviations from these preferred estimates are noted. This is in part merely a descriptive device to show how the results vary. From the data so far assembled the true value for each constituent cannot be definitely proven, and conclusions are limited to the extent of agreement in the values reported. Convictions as to whether or not preferred estimates based on arithmetic means closely approach true values depend on the extent of agreement of the values reported, on faith in the principles of rock analysis in present use, and on faith in the ability of most analysts to perform the analyses properly. That these most popular values can be wrong is evidenced by the apparent widespread errors in determining silica in G–1 and W–1.

## OUTLINE OF A CONVENTIONAL ROCK ANALYSIS

Most of the constituents determined in the conventional procedure of rock analysis depend upon prior removal of other constituents from the sample solution without removal of the constituent sought; other constituents are not determined but are calculated and depend upon correct values for constituents involved in the calculation. A knowledge of the procedures used in the conventional rock analysis is needed in order to understand the interdependence of the various determinations. In conventional rock analyses the following outline, or a modification thereof, is used.

*Outline of a conventional rock analysis*

Main portion

Decompose sample by fusing with $Na_2CO_3$. Dissolve in dilute HCl. Evaporate to dryness. Redissolve in dilute HCl. Filter. Evaporate filtrate to dryness. Redissolve in dilute HCl. Filter.

Combined filtrates

Neutralize with $NH_4OH$ to precipitate $R_2O_3$. Filter. Redissolve precipitate in dilute HCl. Reprecipitate with $NH_4OH$. Filter.

Combined precipitates

$SiO_2$+residue ($R_2O_3$+undissolved sample): Ignite and weigh. Add an excess of HF and a little $H_2SO_4$. Again ignite and weigh. Difference in weights is $SiO_2$. Add $SiO_2$ from $R_2O_3$ precipitate to get total $SiO_2$. Combine residue from $SiO_2$ with $R_2O_3$ precipitate.

Combined filtrates

Precipitate Ca as oxalate by adding excess of ammonium oxalate, $(NH_4)_2C_2O_4$. Filter. Redissolve $CaC_2O_4$ in dilute HCl. Neutralize with $NH_4OH$ and reprecipitate $CaC_2O_4$. Filter.

Precipitate

$R_2O_3$ ($Al_2O_3$, $Fe_2O_3$, $TiO_2$, $P_2O_5$, and others), residual $SiO_2$, traces of MnO, undissolved residue: Determine all constituents other than $Al_2O_3$ and calculate $Al_2O_3$ by difference. See analysis of $R_2O_3$ below.

Combined filtrates

Add an excess of $(NH_4)_2HPO_4$ and $NH_4OH$. Redissolve precipitate in dilute HCl and reprecipitate.

Precipitate

$CaC_2O_4$. Ignite and weigh as CaO.

Filtrates

Discard. Contain alkali metals and elements not completely separated in foregoing precipitations.

Precipitate

Mg as magnesium ammonium phosphate with most of the MnO, BaO, and other constituents not completely removed by preceding precipitations: Ignite and weigh as $Mg_2P_2O_7$. Determine Mn and subtract as $Mn_2P_2O_7$. Calculate MgO.

### *Analysis of* $R_2O_3$ *precipitate*

*Residual silica* ($SiO_2$).—Dissolve $R_2O_3$, from above, by fusion with pyrosulfate and solution in dilute $H_2SO_4$, evaporate to fumes of $SO_3$, dilute with water, and digest to coagulate $SiO_2$. Filter, and ignite the precipitate and weigh. The ignited precipitate is $SiO_2$+residue. Add HF, evaporate, ignite, and weigh residue. Difference in weights is residual $SiO_2$. Dissolve residue by fusion with a little pyrosulfate and combine with filtrate from residual $SiO_2$.

*Total iron as* $Fe_2O_3$.—May be determined on filtrate from $SiO_2$ in $R_2O_3$ or in a separate sample, by reduction to $Fe^{+2}$ and measurement of the quantity of oxidant needed to oxidize to $Fe^{+3}$. Ti, V, Cr and others may interfere in some procedures. Reductants used: For sulfuric acid solution, zinc amalgam, $H_2S$, or $SO_2$; for hydrochloric acid solutions, $SnCl_2$, silver metal, or $SO_2$. Standard oxidant solutions used: For sulfuric acid solutions, $KMnO_4$, or $Ce(SO_4)_2$; for hydrochloric acid solutions, $KMnO_4$ (in the presence of excess $Mn^{+2}$ and $H_3PO_4$), $K_2Cr_2O_7$, or $Ce(SO_4)_2$.

*Titanium dioxide* ($TiO_2$).—Usually determined either in filtrate from residual $SiO_2$ in $R_2O_3$ or in a separate sample by measuring the yellow color of peroxidized titanium in a sulfuric acid solution of the sample. Vanadium and iron may interfere.

*Phosphorus pentoxide* ($P_2O_5$).—Determined on a separate sample, dissolved in dilute $HNO_3$, by precipitating as the ammonium phosphomolybdate, and weighing as $Mg_2P_2O_7$ or determining colorimetrically.

*Alumina* ($Al_2O_3$).—Taken as $R_2O_3-$(Fe as $Fe_2O_3+TiO_2+SiO_2$ in $R_2O_3+P_2O_5$). Other constituents in the $R_2O_3$ ($Cr_2O_3$, $V_2O_5$ and others) are usually counted as $Al_2O_3$. Errors in determining other constituents in the $R_2O_3$ are reflected in errors in the figure for $Al_2O_3$.

### *Determinations made on separate samples*

**Ferrous and Ferric Oxides**

*Ferrous oxide* (FeO).—Determined on a separate sample by dissolving in $HF+H_2SO_4$, diluting with dilute $H_2SO_4$ containing boric acid (to complex the fluoride ion), and titrating with a standard oxidant. Air-oxidation and failure to dissolve all FeO cause low results. Air-oxidation while sample is being dissolved is prevented by steam (simple method), or nonoxidizing gas (usually $CO_2$).

Valid figures for FeO cannot be obtained in the presence of appreciable organic matter, sulfides, or other materials that are easily oxidized.

*Ferric oxide* ($Fe_2O_3$).—Total iron as $Fe_2O_3-1.1114$ FeO.

**Alkalies**

*Collection of mixed chlorides of sodium and potassium.*—Sample usually is decomposed by sintering with $CaCO_3$ and $NH_4Cl$ (J. Lawrence Smith method), alkalies leached from the sintered product with water, purified, and weighed as (Na,K)Cl.

*Potassium oxide* ($K_2O$).—Usually is separated and weighed as $K_2PtCl_6$ and calculated to KCl. Sometimes it is separated and weighed as $KClO_4$.

*Sodium oxide* ($Na_2O$).—(Na,K)Cl$-$KCl, calculated to $Na_2O$.

**Total Water**

Usually volatilized by strong ignition with a flux, water collected and weighed in a cold glass tube (Penfield method) or collected on an absorbant and weighed. Sometimes taken as loss on ignition, which includes loss of $CO_2$ and gain by oxidation of FeO to $Fe_2O_3$. Valid figures for total water cannot be obtained in the presence of organic matter.

*Uncombined water* ($H_2O^-$).—This is usually taken as the loss in weight at 105° to 110° C. Varies with humidity and temperature of the atmosphere and exposure thereto.

*Combined water* ($H_2O^+$).—Total $H_2O-H_2O^-$. In order for the figure for $H_2O^+$ to be valid the figures for total $H_2O$ and for $H_2O^-$ must be correct.

**Manganous Oxide (MnO)**

Determined on a separate sample, dissolved in $H_2SO_4$ or $HNO_3$, by oxidation with bismuthate or periodate to the purple permanganate.

## POSSIBLE ERRORS IN A CONVENTIONAL ROCK ANALYSIS AND THEIR INTERRELATIONS

From the foregoing outline the reader can see that the normal course of the analysis involves systems of separations; most or all separations must be properly carried out in order that a particular determination will be acceptable. Rock analysis is a demanding discipline in which all steps must be done meticulously. The value for a single determination may give no evidence as to whether the steps involved in the procedure were properly done.

Following the course of the conventional rock analysis just outlined, errors frequently made and their interrelation are as follows:

*Silica* ($SiO_2$).—A common fault is failure to collect all the $SiO_2$. This is due to failure to evaporate to complete dryness, to make all or most of the $SiO_2$ insoluble. Some analysts merely evaporate the solution on the steam bath to apparent dryness; others use an oven at somewhat less than 110° C to assure complete dryness (Hillebrand and others, 1953, p. 678). The apparently low results for G–1 and W–1 reported by most analysts indicate that an oven or some other means of achieving complete dryness is necessary as a routine. The fluorine content of G–1 and W–1 is not sufficiently large to cause material loss of silicon by volatilization as silicon tetrafluoride during the acid evaporations for collecting the silica.

Uncollected silica may contaminate each of the precipitates that follow in the main portion of the conventional procedure, the $R_2O_3$, the CaO, and the MgO, and some may be left in the discarded filtrate at the end of the procedure. Because $SiO_2$ is the first constituent separated in the main portion, its value is essentially independent of the other determinations.

*Alumina* ($Al_2O_3$).—Because $Al_2O_3$ is calculated by subtracting all other constituents from the $R_2O_3$ group (more properly called mixed oxides, see Hillebrand and others, 1953, p. 494), a gross error in determining any constituent in the $R_2O_3$ group or failure to determine a constituent therein makes the figure for $Al_2O_3$ invalid. Fluoride ion interferes in the precipitation by forming a complex ion with aluminum or others of the group and thus preventing their complete precipitation. Because residual $SiO_2$ is almost always separated from the $R_2O_3$, the figure for $Al_2O_3$ is not affected by the presence of $SiO_2$ in the $R_2O_3$ if this separation is properly done.

If it is assumed that there were no gross errors and that all other constituents of the $R_2O_3$ group were determined, then the subtraction of all other constituents from the $R_2O_3$ group yields an alumina content whose error is the square root of the sum of the squares of the errors of all other constituents including $R_2O_3$. Obviously the alumina content is known less precisely than any of the mixed oxide group.

In most analyses, the $R_2O_3$ group is regarded as consisting only of $Al_2O_3$, $Fe_2O_3$, $TiO_2$, and $P_2O_5$. Other constituents present would be counted as $Al_2O_3$. In part 2 of this report residues that would have been left from treatment of the $SiO_2$ with HF, generally added to the precipitated $R_2O_3$ group, are shown to contain a number of unusual constituents of G–1 and W–1 that would have been reported as $Al_2O_3$.

*Magnesium oxide* (MgO).—High results for MgO indicate incomplete precipitation of calcium and its inclusion as phosphate in the $Mg_2P_2O_7$. Manganese is almost always determined in the $Mg_2P_2O_7$ and so its effect is eliminated. Small quantities of BaO in analyses of G–1 and W–1 would probably be counted as MgO.

*Potassium oxide* ($K_2O$).—The determination of $K_2O$ is essentially independent of other constituents, depending on complete extraction of alkalies and proper separation of potassium, usually as $K_2PtCl_6$.

*Sodium oxide* ($Na_2O$).—The reported figure for $Na_2O$ will be invalid if either the figure for total alkalies or for $K_2O$ is incorrect.

*Uncombined water* ($H_2O^-$).—Uncombined water is independent of other constituents. The moisture content ($H_2O^-$) will vary with weather conditions, which makes reporting of most rock analyses on a moisture-free sample desirable.

*Combined water* ($H_2O^+$).—Combined water, $H_2O^+$, is obtained by subtracting $H_2O^-$ from total water, so that obvious errors in either of these determinations make the figure for $H_2O^+$ unacceptable. Loss on ignition, unless corrected for $CO_2$ and for oxidation of FeO to $Fe_2O_3$, cannot be accepted as a measure of total water or of $H_2O^+$.

## NEW ANALYSES OF G–1 AND W–1

New analyses of G–1 are given in table 1, and those of W–1 in table 2. The analyses are listed and given numbers in table 1 in the order of increasing values of $SiO_2$ so that the individual analyst can find his analysis more quickly and any relationship of the value for $SiO_2$ with other results can be observed. In table 2 the analyses are also listed in the order of increasing $SiO_2$, but are given numbers corresponding to those in table 1 if the same chemist analyzed both samples. An alphabetical list of contributing chemists is included on pages 42-43.

Five analyses of each rock in tables 1 and 2 may be identified, as they have been published elsewhere. Analyses 49 are those reported by Mercy (1956) by a modification of the rapid procedure of Shapiro and Brannock (1952). Analyses 46 are those of Waters and Coombs, of the Geological Survey of Great Britain, reported by Guppy and Sabine (1956). Analyses 47 and 50 are the carefully made and cross-checked analyses of Goldich and Oslund (1956). Analyses 57 are those of C. G. Engel; they differ slightly from those reported later by this analyst in Engel and Engel (1958). All other analyses are not identified as to analyst.

TABLE 1.—*Results of analyses of granite (G–1) not reported in U.S. Geological Survey Bulletin 980*

[Values in parentheses ( ) are outside adopted limits of acceptability, $\bar{x}\pm S$, calculated from all analyses of G–1. Values in quotation marks " " are questionable because values from which they are calculated are outside adopted limits of acceptability, $\bar{x}\pm S$, calculated from all analyses of G–$1_2$]

| | Adopted limits of acceptability $\bar{x}-S$—$\bar{x}+S$ | Analysis No. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 35 [1] | 36 | 37 | 38 | 39 | 40 [2] | 41 | 42 | 43 |
| $SiO_2$ | 71.87–72.83 | (70.92) | 72.04 | 72.21 | 72.22 | 72.33 | 72.36 | 72.37 | 72.38 | 72.42 |
| $Al_2O_3$ | 13.95–14.69 | "14.44" | 14.64 | (14.74) | "14.24" | (13.79) | 14.06 | 14.29 | "14.24" | "14.49" |
| $Fe_2O_3$ | .65– 1.25 | (1.56) | 1.86 | (.62) | (1.30) | "1.14" | .96 | .85 | (1.94) | (1.44) |
| FeO | .89– 1.10 | 1.02 | ------ | (1.12) | .97 | 1.07 | .98 | .94 | 1.00 | 1.02 |
| MgO | .27– .53 | (2.55) | .32 | .51 | .41 | .44 | .36 | .35 | .28 | (.58) |
| CaO | 1.28– 1.52 | (2.04) | (1.25) | (1.26) | 1.44 | 1.45 | 1.33 | 1.31 | (1.14) | (1.60) |
| $Na_2O$ | 3.08– 3.54 | (2.62) | (3.59) | 3.26 | 3.32 | 3.26 | 3.27 | 3.32 | 3.41 | (2.84) |
| $K_2O$ | 5.03– 5.81 | (3.97) | 5.26 | 5.31 | 5.48 | 5.55 | 5.54 | 5.56 | 5.23 | (4.48) |
| $H_2O^-$ | ------ | .04 | ------ | .06 | .07 | .05 | .04 | .04 | .22 | .11 |
| $H_2O^+$ | .18– .54 | .36 | ------ | .37 | .31 | .35 | .43 | .27 | .20 | .47 |
| $TiO_2$ | .22– .30 | (.13) | .25 | .27 | .25 | (.20) | .24 | .25 | (.17) | (.18) |
| $P_2O_5$ | .04– .16 | .14 | ------ | .07 | .08 | .11 | .086 | .09 | .12 | .15 |
| MnO | .02– .04 | (.06) | ------ | .03 | .02 | .04 | .025 | .03 | (.01) | .02 |
| $CO_2$ | ------ | ------ | ------ | ------ | ------ | ------ | .08 | .07 | ------ | ------ |
| Loss on ignition | ------ | ------ | .43 | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| BaO | ------ | ------ | ------ | ------ | ------ | .24 | [2].11 | ------ | ------ | ------ |
| SrO | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | .08 |
| S | ------ | ------ | ------ | ------ | ------ | ------ | .014 | ------ | ------ | ------ |
| F | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| Cl | ------ | ------ | ------ | ------ | ------ | ------ | $<$.01 | ------ | ------ | ------ |
| $Cr_2O_3$ | ------ | ------ | ------ | ------ | ------ | ------ | $<$.01 | ------ | ------ | ------ |
| $V_2O_3$ | ------ | ------ | ------ | ------ | ------ | ------ | $<$.01 | ------ | ------ | ------ |
| $(Ce, Y)_2O_3$ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| $ZrO_2$ | ------ | ------ | ------ | ------ | ------ | ------ | .02 | ------ | ------ | ------ |
| $Ga_2O_3$ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| $Li_2O$ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| $Rb_2O$ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| CuO | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| NiO | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| PbO | ------ | ------ | ------ | ------ | ------ | ------ | .03 | ------ | ------ | ------ |
| Total | ------ | 99.85 | 99.64 | 99.83 | 100.11 | 100.02 | 99.93 | 99.74 | 100.34 | 99.88 |
| Less O=F+Cl +S | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| Total | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| Total $H_2O$ | ------ | .40 | ------ | .43 | .38 | .40 | .47 | .31 | .42 | .58 |
| Total Fe as $Fe_2O_3$ | 1.76– 2.32 | (2.69) | 1.86 | 1.87 | (2.38) | (2.33) | 2.05 | 1.89 | (3.05) | (2.57) |
| $R_2O_3$ | 16.32–17.12 | (17.40) | 16.75 | 16.95 | 16.95 | 16.43 | 16.46 | 16.52 | (17.58) | (17.39) |
| $Na_2O+K_2O$ | 8.26– 9.22 | (6.59) | 8.85 | 8.57 | 8.80 | 8.81 | 8.81 | 8.88 | 8.64 | (7.32) |
| $Al_2O_3$ corrected for 0.09 percent $P_2O_5$ ($\bar{x}$ of all $P_2O_5$ determinations) | ------ | ------ | 14.55 | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| $Al_2O_3$+minor $R_2O_3$ constituents listed | ------ | ------ | ------ | ------ | ------ | ------ | 14.08 | ------ | ------ | ------ |
| CaO+SrO listed | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | 1.68 |
| MgO+BaO weighed as phosphate | ------ | ------ | ------ | ------ | ------ | (.59) | .43 | ------ | ------ | ------ |
| $K_2O+Rb_2O$ weighed as $Rb_2PtCl_6$ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |

See footnotes at end of table.

TABLE 1.—*Results of analyses of granite (G–1) not reported in U.S. Geological Survey Bulletin 980*—Continued

| | Adopted limits of acceptability $\bar{x}-S$—$\bar{x}+S$ | Analysis No. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 44 [3] | 45 | 46 | 47 [2] | 48 | 49 | 50 [2] | 51 | 52 |
| $SiO_2$ | 71.87–72.83 | [2] 72.42 | 72.42 | 72.45 | 72.45 | 72.5 | 72.5 | 72.50 | 72.52 | 72.53 |
| $Al_2O_3$ | 13.95–14.69 | 14.41 | 14.26 | 14.13 | 14.18 | 14.1 | 14.0 | 14.22 | 14.49 | 14.29 |
| $Fe_2O_3$ | .65– 1.25 | .83 | .92 | .80 | .75 | 1.8 | .76 | .83 | 1.09 | .82 |
| $FeO$ | .89– 1.10 | 1.02 | .97 | .93 | .98 | ------ | .94 | .95 | 1.01 | .95 |
| $MgO$ | .27– .53 | .49 | .45 | .38 | .35 | (.15) | .46 | .38 | (.24) | .37 |
| $CaO$ | 1.28– 1.52 | 1.46 | 1.39 | 1.34 | 1.36 | 1.5 | 1.5 | 1.34 | (1.60) | 1.36 |
| $Na_2O$ | 3.08– 3.54 | “3.40” | (3.57) | 3.50 | 3.28 | 3.4 | (3.8) | 3.35 | (3.00) | 3.26 |
| $K_2O$ | 5.03– 5.81 | (4.99) | 5.43 | 5.71 | 5.54 | 5.7 | 5.4 | 5.49 | 5.06 | 5.62 |
| $H_2O^-$ | ------ | .19 | .08 | .02 | .03 | ------ | ------ | .04 | .25 | .03 |
| $H_2O^+$ | .18– .54 | .35 | .39 | .33 | .26 | ------ | .40 | .24 | .47 | .31 |
| $TiO_2$ | .22– .30 | .27 | .25 | .26 | .26 | .25 | .26 | .26 | (.20) | .26 |
| $P_2O_5$ | .04– .16 | .08 | .07 | .12 | .09 | .08 | .08 | .08 | .07 | .11 |
| $MnO$ | .02– .04 | .026 | .03 | .03 | .02 | .04 | .02 | .02 | .02 | .03 |
| $CO_2$ | ------ | .086 | ------ | ------ | .08 | ------ | ------ | .08 | ------ | .07 |
| Loss on ignition | ------ | ------ | ------ | ------ | ------ | .42 | ------ | ------ | ------ | ------ |
| $BaO$ | ------ | .12 | ------ | .10 | .10 | ------ | ------ | .10 | ------ | ------ |
| $SrO$ | ------ | .05 | ------ | ------ | .02 | ------ | ------ | .02 | ------ | ------ |
| $S$ | ------ | .01 | ------ | .02 | .01 | ------ | ------ | ------ | ------ | ------ |
| $F$ | ------ | .045 | ------ | ------ | ------ | ------ | ------ | .07 | .007 | ------ |
| $Cl$ | ------ | .16 | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| $Cr_2O_3$ | ------ | .004 | ------ | .01 | ------ | ------ | ------ | ------ | ------ | ------ |
| $V_2O_3$ | ------ | .003 | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| $(Ce, Y)_2O_3$ | ------ | .035 | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| $ZrO_2$ | ------ | .027 | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| $Ga_2O_3$ | ------ | .003 | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| $Li_2O$ | ------ | tr | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| $Rb_2O$ | ------ | ------ | ------ | ------ | .02 | ------ | ------ | .02 | ------ | ------ |
| $CuO$ | ------ | tr | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| $NiO$ | ------ | tr | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| $PbO$ | ------ | .003 | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| Total | ------ | 100.48 | 100.23 | 100.13 | 99.78 | 99.9 | 100.1 | 99.99 | 100.03 | 100.01 |
| Less $O=F+Cl+S$ | ------ | .06 | ------ | .01 | ------ | ------ | ------ | .03 | ------ | ------ |
| Total | ------ | 100.42 | ------ | 100.12 | ------ | ------ | ------ | 99.96 | ------ | ------ |
| Total $H_2O$ | ------ | .54 | .47 | .35 | .29 | ------ | .40 | .28 | .72 | .34 |
| Total Fe as $Fe_2O_3$ | 1.76– 2.32 | 1.96 | 2.00 | 1.84 | 1.84 | 1.8 | 1.81 | 1.89 | 2.21 | 1.88 |
| $R_2O_3$ | 16.32–17.12 | 16.76 | 16.58 | 16.36 | 16.37 | (16.2) | (16.15) | 16.45 | 16.97 | 16.54 |
| $Na_2O+K_2O$ | 8.26– 9.22 | 8.39 | 9.00 | 9.21 | 8.82 | 9.1 | 9.2 | 8.84 | (8.06) | 8.88 |
| $Al_2O_3$ corrected for 0.09 percent $P_2O_5$ ($\bar{x}$ of all $P_2O_5$ determinations) | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| $Al_2O_3$+minor $R_2O_3$ constituents listed | ------ | 14.48 | ------ | 14.14 | ------ | ------ | ------ | ------ | ------ | ------ |
| $CaO+SrO$ listed | ------ | 1.51 | ------ | ------ | 1.38 | ------ | ------ | 1.36 | ------ | ------ |
| $MgO+BaO$ weighed as phosphate | ------ | (.57) | ------ | .44 | .41 | ------ | ------ | .44 | ------ | ------ |
| $K_2O+Rb_2O$ weighed as $Rb_2PtCl_6$ | ------ | ------ | ------ | ------ | (5.56) | ------ | ------ | 5.51 | ------ | ------ |

See footnotes at end of table.

TABLE 1.—*Results of analyses of granite (G–1) not reported in U.S. Geological Survey Bulletin 980*—Continued

| | Adopted limits of acceptability $\bar{x}-S$—$\bar{x}+S$ | Analysis No. | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | | 53 | 54 | 55 | 56 | 57 [3] | 58 [3] [4] | 59 [5] | 60 [2] | 61 |
| $SiO_2$ | 71.87–72.83 | 72.54 | 72.55 | 72.55 | 72.60 | 72.65 | 72.68 | 72.70 | 72.76 | (73.0) |
| $Al_2O_3$ | 13.95–14.69 | 14.32 | 14.16 | 14.39 | 14.27 | 14.54 | 14.61 | 14.62 | 14.12 | 14.1 |
| $Fe_2O_3$ | .65– 1.25 | .83 | .85 | 1.18 | .83 | .85 | .77 | (1.50) | .76 | [3] (1.88) |
| FeO | .89– 1.10 | .92 | .99 | .96 | .96 | .90 | .91 | .60 | 1.04 | -------- |
| MgO | .27– .53 | .36 | .35 | .28 | .36 | .37 | .47 | (.25) | .36 | -------- |
| CaO | 1.28– 1.52 | 1.33 | 1.34 | 1.39 | 1.33 | 1.36 | 1.46 | 1.40 | 1.38 | -------- |
| $Na_2O$ | 3.08– 3.54 | 3.23 | 3.28 | "3.30" | 3.23 | 3.34 | 3.24 | 3.10 | 3.50 | -------- |
| $K_2O$ | 5.03– 5.81 | 5.41 | 5.50 | (4.87) | 5.52 | 5.48 | 5.28 | 5.12 | 5.37 | -------- |
| $H_2O^-$ | ------------ | .03 | .00 | .03 | .04 | .00 | .07 | .09 | .33 | -------- |
| $H_2O^+$ | .18– .54 | .26 | .38 | .33 | .29 | | (.17) | .18 | | |
| $TiO_2$ | .22– .30 | .26 | .25 | .26 | .25 | .24 | .26 | .24 | .21 | [3] (.42) |
| $P_2O_5$ | .04– .16 | .09 | .09 | .08 | .09 | ------- | .04 | ------- | .09 | .10 |
| MnO | .02– .04 | .03 | .03 | .03 | .03 | ------- | .03 | ------- | .03 | (.05) |
| $CO_2$ | ------------ | .06 | .09 | -------- | .07 | ------- | ------- | ------- | ------- | -------- |
| Loss on ignition | ------------ | ------- | ------- | -------- | ------- | ------- | ------- | ------- | ------- | -------- |
| BaO | ------------ | ------- | ------- | -------- | ------- | ------- | .13 | ------- | .13 | -------- |
| SrO | ------------ | ------- | ------- | -------- | ------- | ------- | ------- | ------- | ------- | -------- |
| S | ------------ | ------- | ------- | -------- | ------- | ------- | ------- | ------- | ------- | -------- |
| F | ------------ | ------- | ------- | -------- | ------- | ------- | ------- | ------- | ------- | -------- |
| Cl | ------------ | ------- | ------- | -------- | ------- | ------- | ------- | ------- | ------- | -------- |
| $Cr_2O_3$ | ------------ | ------- | ------- | -------- | ------- | ------- | ------- | ------- | ------- | -------- |
| $V_2O_3$ | ------------ | ------- | ------- | -------- | ------- | ------- | ------- | ------- | ------- | -------- |
| $(Ce, Y)_2O_3$ | ------------ | ------- | ------- | -------- | ------- | ------- | ------- | ------- | ------- | -------- |
| $ZrO_2$ | ------------ | ------- | ------- | -------- | ------- | ------- | ------- | ------- | ------- | -------- |
| $Ga_2O_3$ | ------------ | ------- | ------- | -------- | ------- | ------- | ------- | ------- | ------- | -------- |
| $Li_2O$ | ------------ | ------- | ------- | -------- | ------- | ------- | ------- | ------- | ------- | -------- |
| $Rb_2O$ | ------------ | ------- | ------- | -------- | ------- | ------- | ------- | ------- | ------- | -------- |
| CuO | ------------ | ------- | ------- | -------- | ------- | ------- | ------- | ------- | ------- | -------- |
| NiO | ------------ | ------- | ------- | -------- | ------- | ------- | ------- | ------- | ------- | -------- |
| PbO | ------------ | ------- | ------- | -------- | ------- | ------- | ------- | ------- | ------- | -------- |
| Total | ------------ | 99.67 | 99.86 | 99.65 | 99.87 | 99.73 | 100.12 | 99.80 | 100.08 | -------- |
| Less O=F+Cl+S | ------------ | ------- | ------- | -------- | ------- | ------- | ------- | ------- | ------- | -------- |
| Total | ------------ | ------- | ------- | -------- | ------- | ------- | ------- | ------- | ------- | -------- |
| Total $H_2O$ | ------------ | .29 | .38 | .36 | .33 | .00 | .24 | .27 | .33 | -------- |
| Total Fe as $Fe_2O_3$ | 1.76– 2.32 | 1.85 | 1.95 | 2.25 | 1.90 | 1.85 | 1.78 | 2.17 | 1.92 | 1.88 |
| $R_2O_3$ | 16.32–17.12 | 16.52 | 16.45 | 16.98 | 16.51 | 16.79 | 16.69 | 17.03 | 16.34 | 16.50 |
| $Na_2O+K_2O$ | 8.26– 9.22 | 8.64 | 8.78 | (8.17) | 8.75 | 8.82 | 8.52 | (8.22) | 8.87 | -------- |
| $Al_2O_3$ corrected for 0.09 percent $P_2O_5$ ($\bar{x}$ of all $P_2O_5$ determinations) | ------------ | ------- | ------- | -------- | ------- | 14.45 | ------- | 14.53 | ------- | -------- |
| $Al_2O_3+$ minor $R_2O_3$ constituents listed | ------------ | ------- | ------- | -------- | ------- | ------- | ------- | ------- | ------- | -------- |
| CaO+SrO listed | ------------ | ------- | ------- | -------- | ------- | ------- | ------- | ------- | ------- | -------- |
| MgO+BaO weighed as phosphate | ------------ | ------- | ------- | -------- | ------- | ------- | (.55) | ------- | .44 | -------- |
| $K_2O+Rb_2O$ weighed as $Rb_2PtCl_6$ | ------------ | ------- | ------- | -------- | ------- | ------- | ------- | ------- | ------- | -------- |

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[1] Analysis omitted from all calculations.
[2] Mean of two or more analyses.
[3] Mean of two analyses.
[4] Recalculated to include total water.
[5] Report gave $Fe_2O_3$ 14.62 percent, $Al_2O_3$ not given, summation 99.80. Interpreted as shown.

TABLE 2.—*Results of analyses of diabase (W-1) not reported in U.S. Geological Survey Bulletin 980*

[Values in parentheses ( ) are outside adopted limits of acceptability, $\bar{x}\pm S$, calculated from all analyses of W-1. Values in quotation marks " " are questionable because values from which they are calculated are outside adopted limits of acceptability, $\bar{x}\pm S$, calculated from all analyses of W-1]

| | Adopted limits of acceptability $\bar{x}-S$ $\bar{x}+S$ | Analysis No. | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 62 | 35[1] | 43 | 63 | 64 | 37 | 38 | 51 | 65 | 55 | 44 | 46 | 61 | 39 | 57[2] |
| $SiO_2$ | 52.07–52.73 | (51.66) | (51.78) | (51.92) | (52.01) | 52.15 | 52.22 | 52.24 | 52.26 | 52.36 | 52.39 | [2] 52.41 | 52.43 | 52.5 | 52.51 | 52.51 |
| $Al_2O_3$ | 14.48–15.74 | "14.70" | (16.65) | 15.62 | "15.23" | 15.15 | 15.24 | 15.34 | "14.92" | 14.55 | 14.83 | 15.18 | 14.86 | 15.0 | 14.99 | 15.62 |
| $Fe_2O_3$ | .91– 2.33 | "2.03" | (2.84) | 1.32 | 1.58 | 1.22 | 1.22 | 1.47 | "1.95" | 1.23 | "2.26" | 1.42 | 1.57 | | 1.18 | "1.29" |
| FeO | 8.22– 9.04 | 8.84 | 8.93 | 8.86 | 8.83 | 8.83 | 8.85 | 8.91 | 8.82 | 9.01 | 8.50 | 8.68 | 8.67 | | 8.96 | 8.63 |
| MgO | 6.23– 6.93 | 6.79 | (2.57) | 6.77 | 6.61 | (6.96) | 6.58 | 6.30 | 6.49 | 6.50 | 6.61 | [2] 6.38 | 6.70 | | 6.72 | 6.54 |
| CaO | 10.81–11.13 | (11.34) | (11.79) | (11.16) | (11.19) | 10.88 | 11.03 | 10.96 | 10.81 | 11.10 | (10.52) | 10.91 | 10.91 | | 11.06 | 11.02 |
| $Na_2O$ | 1.87– 2.27 | (1.84) | (1.51) | 1.93 | (1.82) | 1.98 | 1.96 | 2.13 | "1.92" | 2.13 | 1.90 | [2] (1.73) | (2.41) | | 2.15 | |
| $K_2O$ | .54– .80 | .78 | (2.27) | .59 | .57 | .57 | .60 | .67 | .54 | .65 | .58 | .63 | .67 | | .71 | |
| $H_2O-$ | | .15 | .10 | .14 | .12 | .13 | .10 | .21 | .36 | .18 | .17 | .24 | .16 | | .16 | (0.9) |
| $H_2O+$ | .34– .74 | .42 | (.24) | (.27) | (.27) | .67 | .73 | .52 | (.27) | (.92) | .50 | .61 | .56 | | .38 | |
| $TiO_2$ | .87– 1.27 | (1.44) | (.13) | .90 | 1.11 | 1.26 | 1.15 | 1.11 | .91 | 1.06 | 1.00 | 1.02 | 1.13 | (1.68) | 1.11 | 1.10 |
| $P_2O_5$ | .09– .21 | .14 | .12 | (.32) | (.48) | .13 | .13 | .14 | .12 | .11 | .18 | .17 | .11 | .12 | .15 | |
| MnO | .12– .22 | .15 | (.24) | .16 | .18 | .14 | .16 | .14 | .15 | .17 | .16 | .16 | .17 | .13 | .17 | |
| $CO_2$ | .03– .09 | | | | | | | | | (.13) | | [2] .075 | | | | |
| Loss on ignition | | | | | | | | | | | | | | | | |
| BaO | | | | | | | | | | | | .03 | .02 | | | |
| SrO | | | | | | .015 | | | | | | [2] .05 | | | | |
| S | | | | | | .018 | | | | | | .007 | .03 | | | |
| F | | | | | | | | | | | | tr | | | | |
| Cl | | | | | | | | | | | | .09 | | | | |
| $Cr_2O_3$ | | | | | | | | | | | | .014 | .02 | | | |
| $V_2O_3$ | | | | | | | | | | | | .032 | | | | |
| $(Ce, Y)_2O_3$ | | | | | | | | | | | | .005 | | | | |
| $ZrO_2$ | | | | | | | | | | | | .009 | | | | |
| $Ga_2O_3$ | | | | | | | | | | | | [2] .002 | | | | |
| $Li_2O$ | | | | | | .004 | | | | | | tr | | | | |
| $Rb_2O$ | | | | | | | | | | | | | | | | |
| CuO | | | | | | .012 | | | | | | .012 | | | | |
| NiO | | | | | | | | | | | | .009 | | | | |
| PbO | | | | | | | | | | | | .001 | | | | |
| Total | | 100.28 | 99.26 | 99.96 | 100.00 | 100.12 | 99.97 | 100.14 | 99.52 | 100.10 | 99.60 | 99.88 | 100.42 | | 100.25 | |
| Less O=F+Cl+S | | | | | | .01 | | | | | | .03 | .01 | | | |
| Total | | | | | | 100.11 | | | | | | 99.85 | 100.41 | | | |
| Total $H_2O$ | | .57 | .34 | .41 | .39 | .80 | .83 | .73 | .63 | 1.10 | .67 | .85 | .72 | | .54 | .09 |
| Total Fe as $Fe_2O_3$ | 10.94–11.50 | (11.85) | (12.77) | 11.17 | 11.39 | 11.03 | 11.06 | 11.37 | (11.75) | 11.24 | (11.71) | 11.07 | 11.21 | 11.05 | 11.14 | (10.88) |
| $R_2O_3$ | 27.06–28.02 | (28.13) | (29.76) | 28.01 | (28.21) | 27.57 | 27.58 | 27.96 | 27.70 | (26.96) | 27.72 | 27.50 | 27.33 | 27.85 | 27.39 | 27.79 |
| $Na_2O+K_2O$ | 2.48– 3.00 | 2.62 | (3.78) | 2.52 | (2.39) | 2.55 | 2.56 | 2.80 | (2.46) | 2.78 | 2.48 | (2.36) | (3.08) | | 2.86 | |

| | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Al_2O_3$ corrected for 0.15 percent $P_2O_5$ ($\bar{x}$ of all $P_2O_5$ determinations) | ------- | ------- | ------- | ------- | ------- | ------- | ------- | ------- | ------- | ------- | ------- | ------- | ------- | ------- | ------- | 15.47 |
| $Al_2O_3$+minor $R_2O_3$ constituents listed | ------- | ------- | ------- | ------- | ------- | ------- | ------- | ------- | ------- | ------- | ------- | 15.24 | 14.88 | ------- | ------- | ------- |
| CaO+SrO listed | ------- | ------- | ------- | ------- | ------- | 10.90 | ------- | ------- | ------- | ------- | ------- | 10.96 | ------- | ------- | ------- | ------- |
| MgO+BaO weighed as phosphate | ------- | ------- | ------- | ------- | ------- | ------- | ------- | ------- | ------- | ------- | ------- | 6.40 | 6.71 | ------- | ------- | ------- |

See footnotes at end of table.

TABLE 2.—*Results of analyses of diabase (W–1) not reported in U.S. Geological Survey Bulletin 980*—Continued

| | Adopted limits of acceptability $\bar{x}-S$ $\bar{x}+S$ | Analysis No. | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | 40 [3] | 47 [3] | 45 | 41 | 50 [3] | 48 | 53 | 68 | 58 [2,4] | 56 | 54 | 66 | 52 | 60 | 67 [2] | 49 |
| $SiO_2$ | 52.07–52.73 | 52.51 | 52.51 | 52.53 | 52.58 | 52.59 | 52.6 | 52.60 | [2] 52.63 | 52.65 | 52.65 | 52.66 | 52.69 | 52.69 | 52.70 | 52.70 | (53.4) |
| $Al_2O_3$ | 14.48–15.74 | 14.87 | 14.97 | 15.01 | 15.10 | 14.99 | 14.7 | 15.17 | [2] 14.76 | 15.04 | 15.23 | 15.30 | 15.90 | 15.12 | 14.93 | 15.18 | 14.7 |
| $Fe_2O_3$ | .91– 2.33 | 1.35 | 1.41 | 1.73 | 1.36 | 1.44 | 11.0 | 1.37 | 1.81 | "1.19" | 1.29 | 1.43 | "2.02" | 1.37 | 1.18 | 1.67 | 1.3 |
| FeO | 8.22– 9.04 | 8.85 | 8.70 | [2] 8.40 | 8.73 | 8.69 | | 8.71 | 8.51 | 8.76 | 8.74 | 8.69 | (8.19) | 8.67 | [3] 8.95 | 8.51 | 8.8 |
| MgO | 6.23– 6.93 | 6.69 | 6.59 | 6.59 | 6.56 | 6.58 | 6.5 | 6.58 | [2] 6.64 | 6.76 | 6.57 | 6.50 | 6.76 | 6.57 | 6.78 | 6.58 | 6.7 |
| CaO | 10.81–11.13 | 10.86 | 10.98 | 10.98 | 10.90 | 10.97 | (11.2) | 10.93 | [2] 10.92 | 11.09 | 10.92 | 10.85 | 11.01 | 10.95 | 10.97 | 11.03 | (10.8) |
| $Na_2O$ | 1.87– 2.27 | 2.07 | 2.12 | (2.30) | 2.19 | 2.15 | 2.2 | 2.08 | [2] 2.10 | 2.05 | 2.08 | 2.10 | (1.66) | 2.08 | [3] 2.02 | (2.53) | (2.4) |
| $K_2O$ | .54– .80 | .64 | .63 | .68 | .64 | .61 | .66 | .66 | .63 | .64 | .63 | .68 | .71 | .69 | [3] .62 | .60 | .70 |
| $H_2O-$ | | .17 | .13 | .15 | .13 | .16 | | .12 | | .23 | .13 | .12 | .22 | .11 | .20 | .20 | |
| $H_2O+$ | .34– .74 | .55 | .46 | .58 | .46 | .43 | | .48 | [2] .60 | (.26) | .46 | .51 | .57 | .45 | .67 | | .6 |
| $TiO_2$ | .87– 1.27 | 1.07 | 1.10 | 1.08 | 1.08 | 1.07 | 1.1 | 1.06 | 1.10 | 1.10 | 1.07 | 1.09 | (.80) | 1.09 | 1.02 | 1.10 | 1.1 |
| $P_2O_5$ | .09– .21 | .13 | .13 | (.07) | .15 | .14 | .16 | .14 | [2] .14 | .13 | .15 | .14 | .13 | .15 | .14 | .14 | .15 |
| MnO | .12– .22 | .17 | .16 | .14 | .18 | .16 | .18 | .17 | [2] .15 | .17 | .17 | .17 | .12 | .13 | .18 | .16 | .14 |
| $CO_2$ | .03– .09 | .03 | .06 | | .06 | .07 | | .05 | | | .06 | .03 | | .05 | | | |
| Loss on ignition | | | | | | | .10 | | | | | | | | | .06 | |
| BaO | | .01 | | | | | | | | .02 | | | | | | | |
| SrO | | | .01 | | | | | | | | | | | | | | |
| S | | .024 | .02 | | | | | | | | | | | | | | |
| F | | | | | | .02 | | | | | | | | | | | |
| Cl | | | | | | | | | | | | | | | | | |
| $Cr_2O_3$ | | .026 | | | | | | | | | | | | | | | |
| $V_2O_3$ | | | | | | | | | | | | | | | | | |
| $(Ce, Y)_2O_3$ | | | | | | | | | | | | | | | | | |
| $ZrO_2$ | | .03 | | | | | | | | | | | | | | | |
| $Ga_2O_3$ | | | | | | | | | | | | | | | | | |
| $Li_2O$ | | | | | | | | | | | | | | | | | |
| $Rb_2O$ | | | | | | | | | | | | | | | | | |
| CuO | | | | | | | | | | | | | | | | | |
| NiO | | | | | | | | | | | | | | | | | |
| PbO | | | | | | | | | | | | | | | | | |
| Total | | 100.05 | 99.98 | 100.24 | 100.12 | 100.07 | 100.4 | 100.12 | 99.99 | 100.09 | 100.15 | 100.27 | 99.97 | 100.12 | 100.36 | 100.46 | 100.79 |
| Less O=F+Cl+S | | | .01 | | | .01 | | | | | | | | | | | |
| Total | | | 99.97 | | | 100.06 | | | | | | | | | | | |
| Total $H_2O$ | | .72 | .59 | .73 | .59 | .59 | | .60 | .60 | .49 | .59 | .63 | .79 | .56 | .87 | | |
| Total Fe as $Fe_2O_3$ | 10.94–11.50 | 11.19 | 11.08 | 11.07 | 11.06 | 11.10 | 11.0 | 11.05 | 11.26 | (10.93) | 11.00 | 11.08 | 11.12 | 11.01 | [3] 11.13 | 11.13 | 11.1 |
| $R_2O_3$ | 27.06–28.02 | 27.32 | 27.28 | 27.23 | 27.39 | 27.30 | (26.96) | 27.42 | 27.27 | 27.20 | 27.45 | 27.62 | 27.14 | 27.37 | 27.23 | 27.55 | (27.0) |
| $Na_2O+K_2O$ | 2.48– 3.00 | 2.71 | 2.75 | 2.98 | 2.83 | 2.76 | 2.86 | 2.74 | 2.73 | 2.69 | 2.71 | 2.78 | (2.37) | 2.77 | 2.64 | (3.13) | (3.1) |

| | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $Al_2O_3$ corrected for 0.15 percent $P_2O_5$ ($\bar{x}$ of all $P_2O_5$ determinations) | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- |
| $Al_2O_3$+minor $R_2O_3$ constituents listed | -------- | 14.93 | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- |
| CaO+SrO listed | -------- | -------- | 10.99 | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- |
| MgO+BaO weighed as phosphate | -------- | 6.70 | -------- | -------- | -------- | -------- | -------- | -------- | -------- | 6.77 | -------- | -------- | -------- | -------- | -------- | -------- | -------- |

[1] Analysis omitted from all calculations.
[2] Mean of two analyses.
[3] Mean of two or more analyses.
[4] Recalculated to include total water.

All analyses in tables 1 and 2 have been corrected for arithmetical errors; for example, analysis 59 of table 1 was apparently not correctly reported as noted in the footnote to the table. A few analyses were reported on a moisture-free sample and had to be recalculated to make them conform with the others. In some analyses (36 and 59 of table 1, and 57 of tables 1 and 2) no determination of $P_2O_5$ was made, and the figure for $Al_2O_3$ given would include $P_2O_5$; for these the value for $Al_2O_3$ corrected for $P_2O_5$ is given below in the tables. In analyses 40, 44, and 46, minor constituents of the $R_2O_3$ group, not determined in other analyses, are listed, and these have been added to the figure for $Al_2O_3$, below in tables 1 and 2, to make the figures comparable with the others. Similarly SrO has been added to CaO to make values comparable. If barium is not previously removed it accompanies magnesium and is weighed as a mixture of $Ba_2P_2O_7$ and $Ba_3(PO_4)_2$ in the $Mg_2P_2O_7$ (Hillebrand, and others 1953, p. 640). Consequently, in the few analyses in which BaO was determined the BaO is multiplied by 0.63 and this figure added to the figure for MgO, and the recalculated value for MgO is listed below in tables 1 and 2. Where $Rb_2O$ is determined a figure for $K_2O+Rb_2O$ is also shown. These corrected figures, given below in the tables, are used in the comparisons and statistical calculations. Analyses in U.S. Geological Survey Bulletin 980 were similarly recalculated.

To point out those values most in disagreement with the arithmetic means, $\bar{x}$, values differing from the arithmetic mean by the value for the standard deviation, $S$, are placed in brackets. Values which are within the limits $\bar{x}\pm S$ (which will be called the adopted limits of acceptability), but which are calculated from values outside these limits are placed in quotation marks. Support for the validity of average values is not merely in the extent of agreement of many analysts on a value but mainly in the faith that the many agreeing analysts are capable of properly selecting, testing, and carrying out a procedure for determining a constituent. These average values are further supported by general agreement with the published analyses of G-1 and W-1 by analysts of recognized competence. Average values are important in evaluating and correcting widespread errors in analytical procedures, which become known as the composition of G-1 and W-1 becomes more fully established.

Analyses 35 of tables 1 and 2 are so far in disagreement with the results of other analysts that they are omitted from all calculations. There is no proof here given that analyses 35 are not correct, but the burden of evidence is against their acceptance.

## STATISTICAL DATA FOR ANALYSES OF G-1 AND W-1

In U.S. Geological Survey Bulletin 980 results of the determinations are plotted in histograms to show the distribution of values of the various analyses. The shape of the histogram depends upon the interval used in grouping results.

In the present study, in order to show more precisely the values for individual results and also show the distribution of values, S curves of distribution are used to illustrate the variations in results for $SiO_2$, $Al_2O_3$, $Fe_2O_3$, and FeO (figs. 1, 2, 3, 4, 5, 6). In these S curves of distribution the values obtained are plotted against order of increasing content. The most popular range of values is shown by the nearly perpendicular central part of the resulting S, and a skewed distribution is shown by the shape of the upper or lower portion of the S. A long sloping bottom portion and a peaked or sharply set off upper portion shows that the results are negatively skewed, and may be evidence of a negative bias. An arithmetic mean appreciably below the median value may also be taken as evidence of a negative bias.

The median, or middle, value of the values arranged in order of increasing magnitude, is designated by the letter "M" on the curves. This is sometimes called the probable value, as a value selected at random is just as likely to be located above the median as below. It is affected by the number of extreme values, but is not affected by the magnitude of the extreme values as is the arithmetic mean. For moderately skewed distribution, the mode or most frequent value, not indicated on the S curves, would be three times as distant from the mean as is the median and in the same direction. When the distribution is normal (symmetrical) the value of the mean, median, and mode coincide. Distances between the mean and mode and between the mean and median may be taken as measures of skewness. A coefficient of skewness can be calculated, but it does not seem necessary for the present purposes.

The explanation of why negative skewness in the analytical results indicates a negative bias lies in an understanding of the sources of error and their size and direction. Were negative errors alone possible in the analytical method, the values would be distributed in a curve with the number of values decreasing away from the true value and with the mean, median, and mode being close to or far from the true value depending upon whether or not the negative errors were easily avoided and upon whether or not the measurement was free from empirical corrections. Most analytical methods are designed and tested to measure constituents without addition or subtraction of an

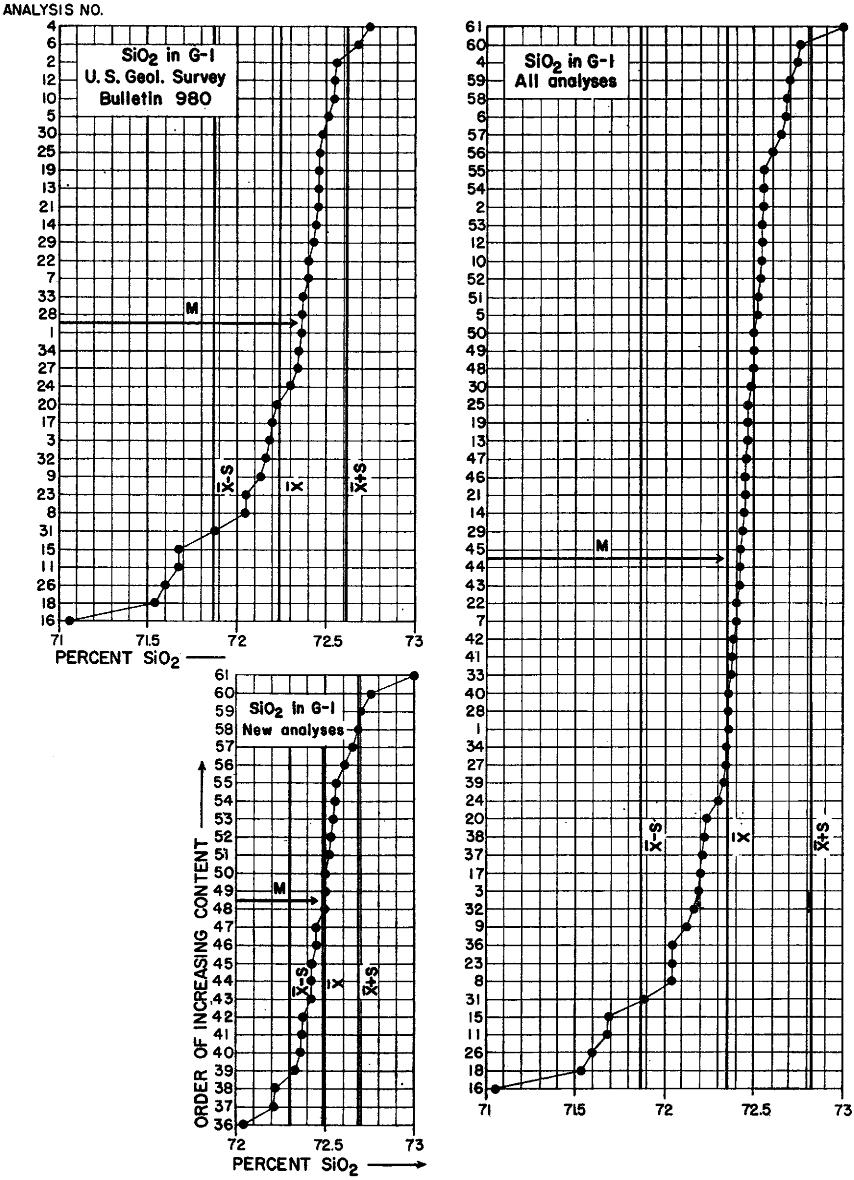


FIGURE 1.—S curves of distribution for determinations of $SiO_2$ in analyses of G–1.

empirical factor. The S curves for $SiO_2$ in figures 1 and 4 presumably illustrate negative errors predominating over positive errors, only a few analyses forming the top of the S. Similar reasoning correlates a positive skew with predominence of positive errors. Valid empirical corrections that are not used would throw the mean, median, and mode above or below the true value.

Results for $SiO_2$ from U.S. Geological Survey Bulletin 980 are negatively skewed, showing a wide sweeping bottom to the S curve of distribution and an arithmetic mean far below the median, indicating serious negative bias in the results. The new results show a partial elimination of the apparent bias. The arithmetic mean and median may also share this tendency toward low results, and it is expected that the actual content of $SiO_2$ is somewhat above the arithmetic means and medians obtained.

A positive skew, and presumably a positive bias, is shown by the S curves for $Al_2O_3$. Analytical causes of high results for $Al_2O_3$ may be due to failure to completely remove the alkalies in washing the voluminous $R_2O_3$ precipitate, to low recovery of the $SiO_2$ in the $R_2O_3$, and to contaminants. The positive bias indicated in the S curves for $Fe_2O_3$ compensates to some extent for the positive bias in figures for $Al_2O_3$ from the causes just mentioned. Results for total iron as $Fe_2O_3$, and consequently also for $Fe_2O_3$, would tend to be high through failure to eliminate or exclude from the solution materials, other than ferrous iron, that would consume the oxidizing titrant (for example titanous ion, residual $H_2S$ and $SO_2$, organic matter, chlorides, and reduced nitrogen compounds).

The S curves for FeO in G–1 of figure 3, on the other hand, show normal distribution and values for arithmetic means and medians are in close agreement within and between new analyses, old analyses, and all analyses reported. This, together with other strong supporting evidence later given, permits some confidence in the arithmetic mean and median values for FeO in G–1. Four low results for FeO in W–1, analyses 22, 10, 27 and 11, cause a negative skew in the S curve that would otherwise show a normal distribution.

Other constituents of the two rocks show essentially normal distribution with no indication of bias, and so are not illustrated by S curves. An exception is that of $K_2O$ in G–1. Values for these other constituents are adequately covered in the statistical tables.

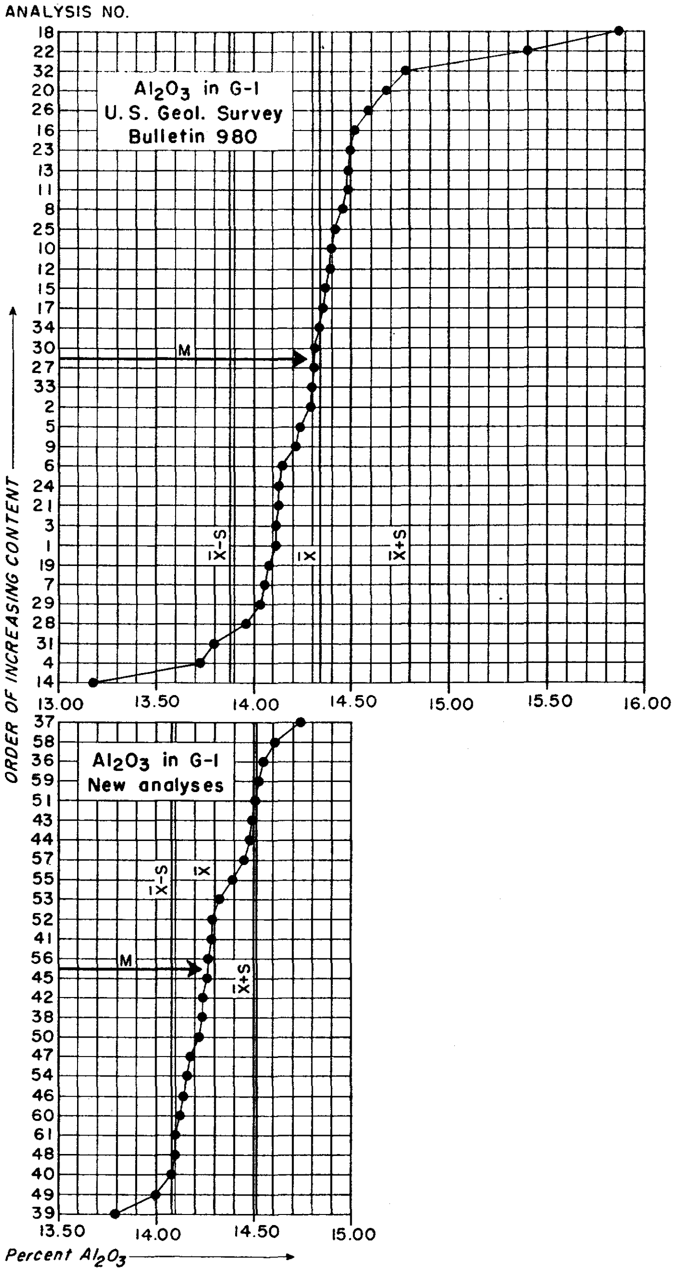
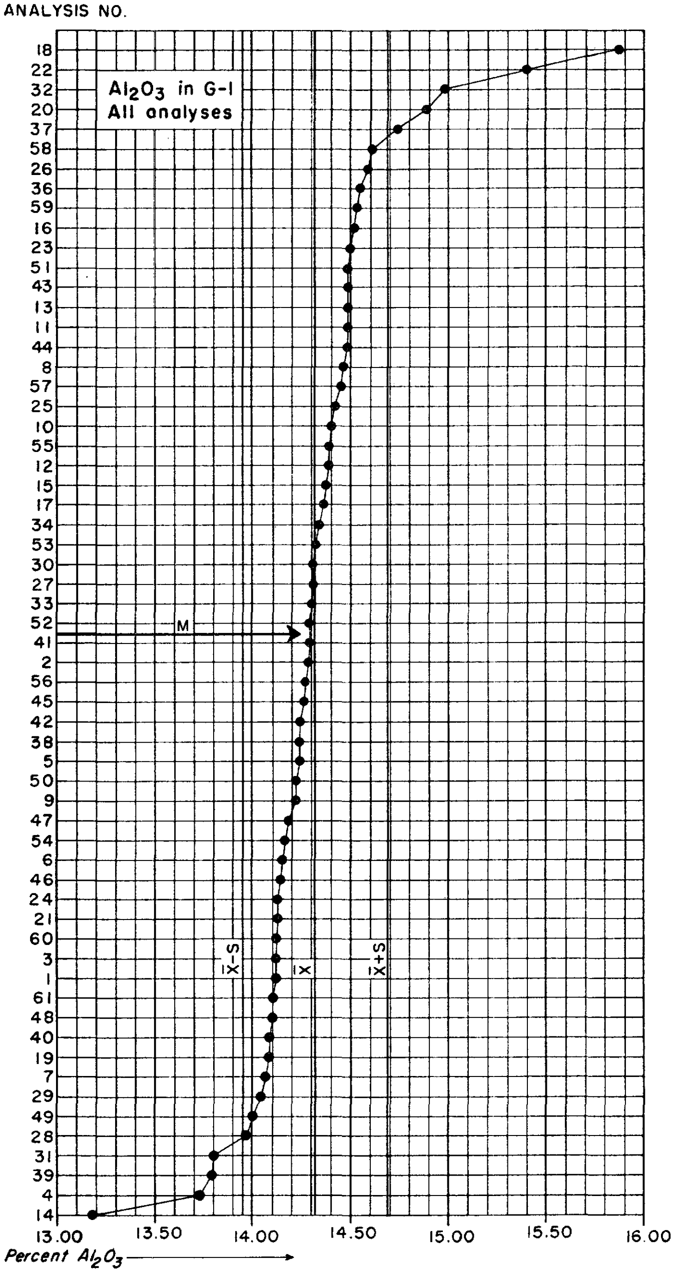


FIGURE 2.—S curves of distribution for



determinations of $Al_2O_3$ in analyses of G-1.

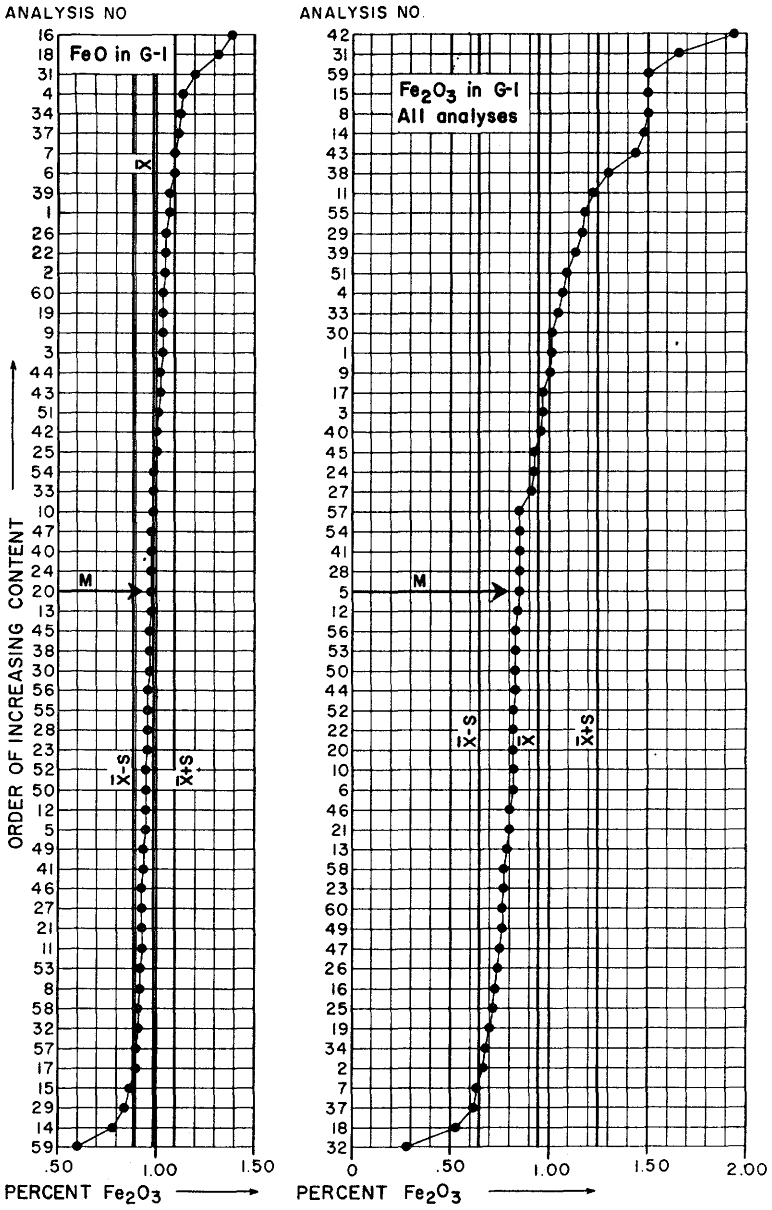


FIGURE 3.—S curves of distribution for determinations of FeO and $Fe_2O_3$ in analyses of G-1.

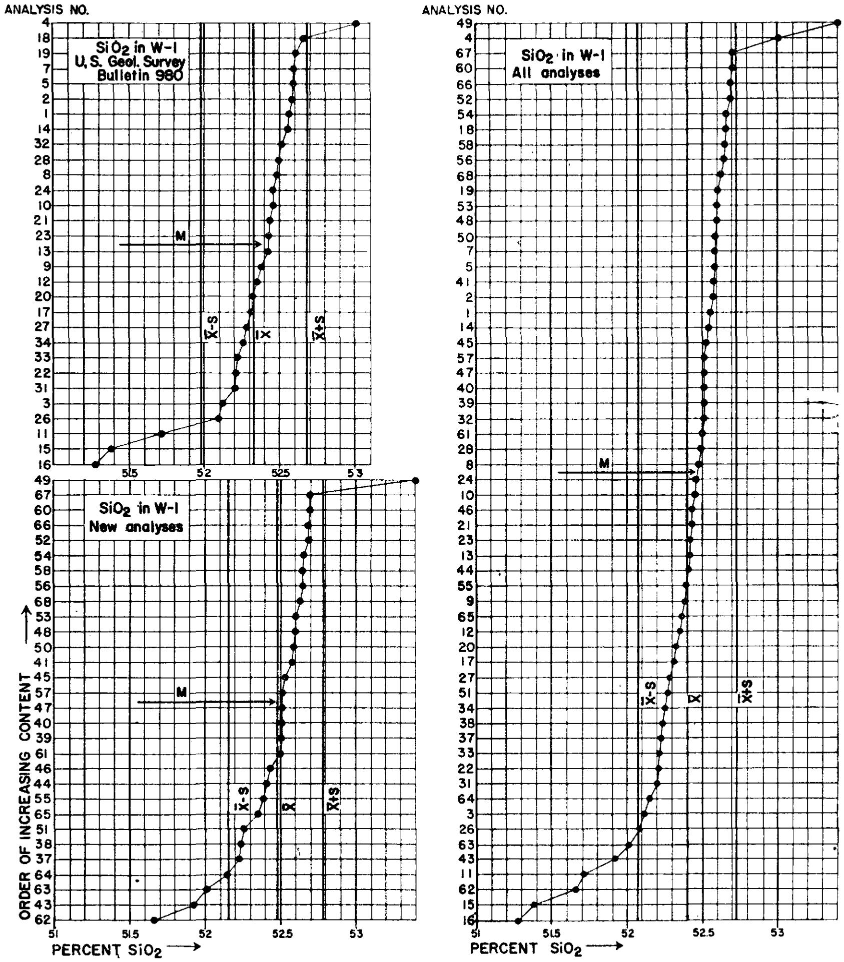


FIGURE 4.—S curves of distribution for determinations of $SiO_2$ in analyses of W-1.

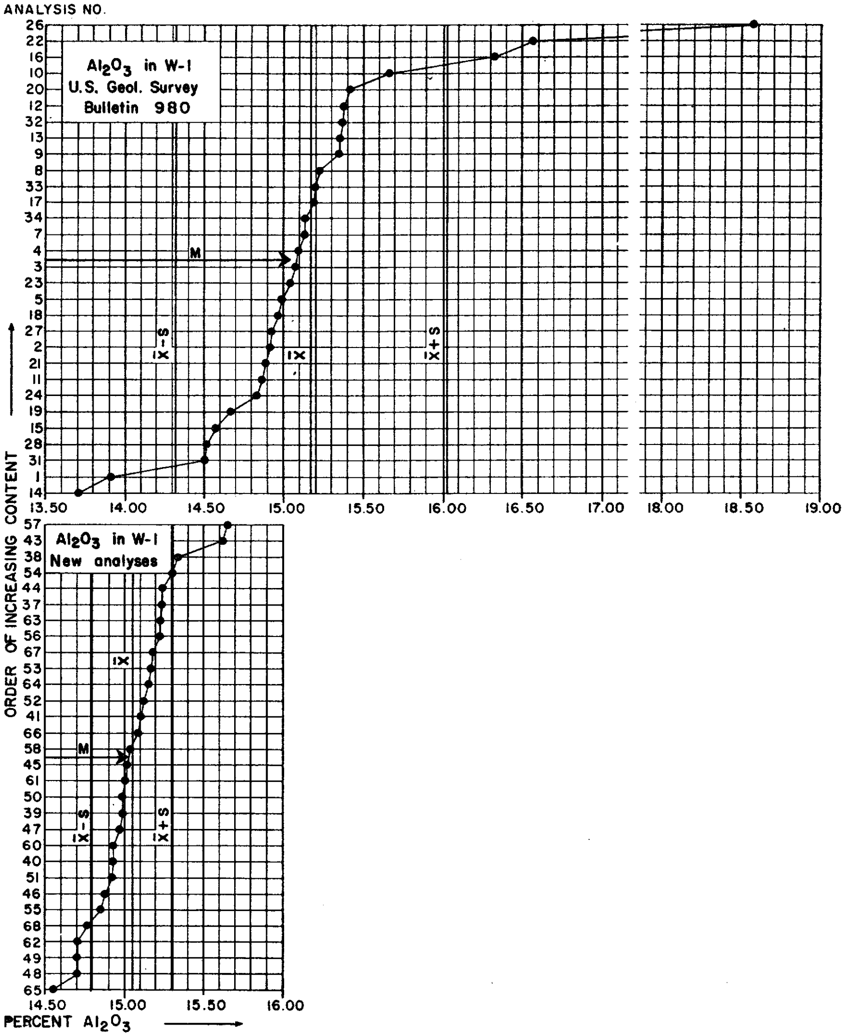
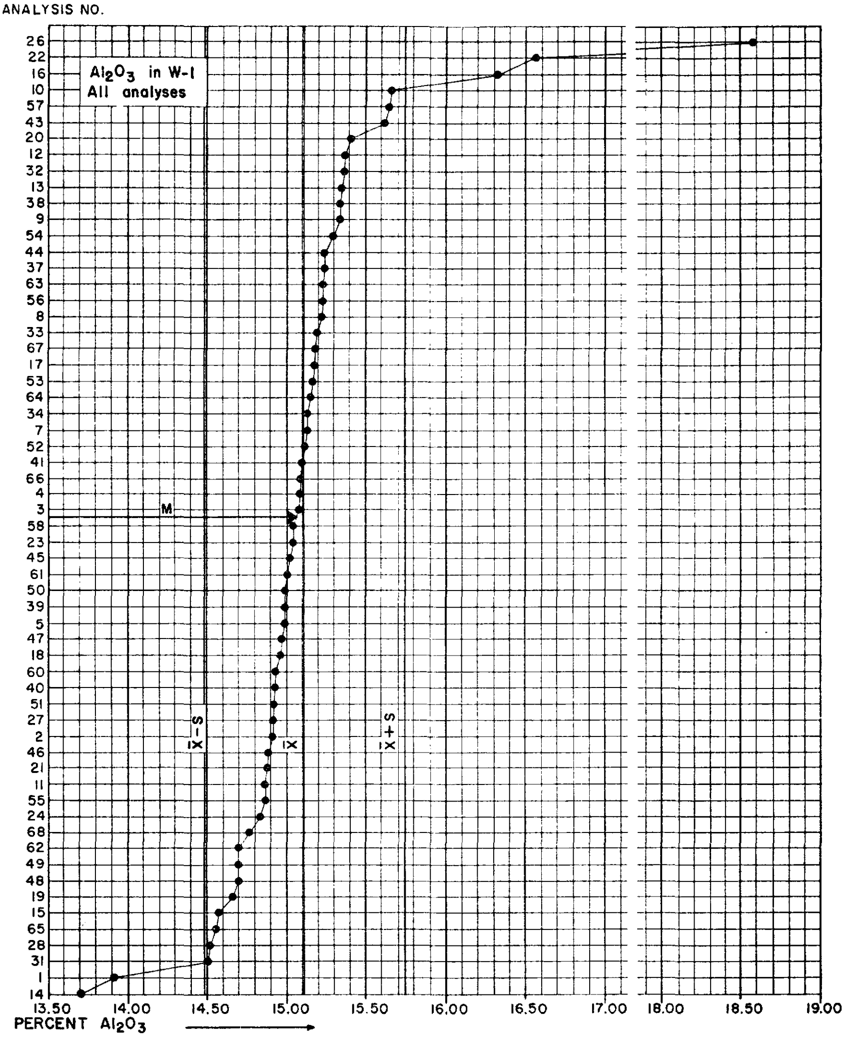


FIGURE 5.—S curves of distribution for



determinations of $Al_2O_3$ in analyses of W-1.

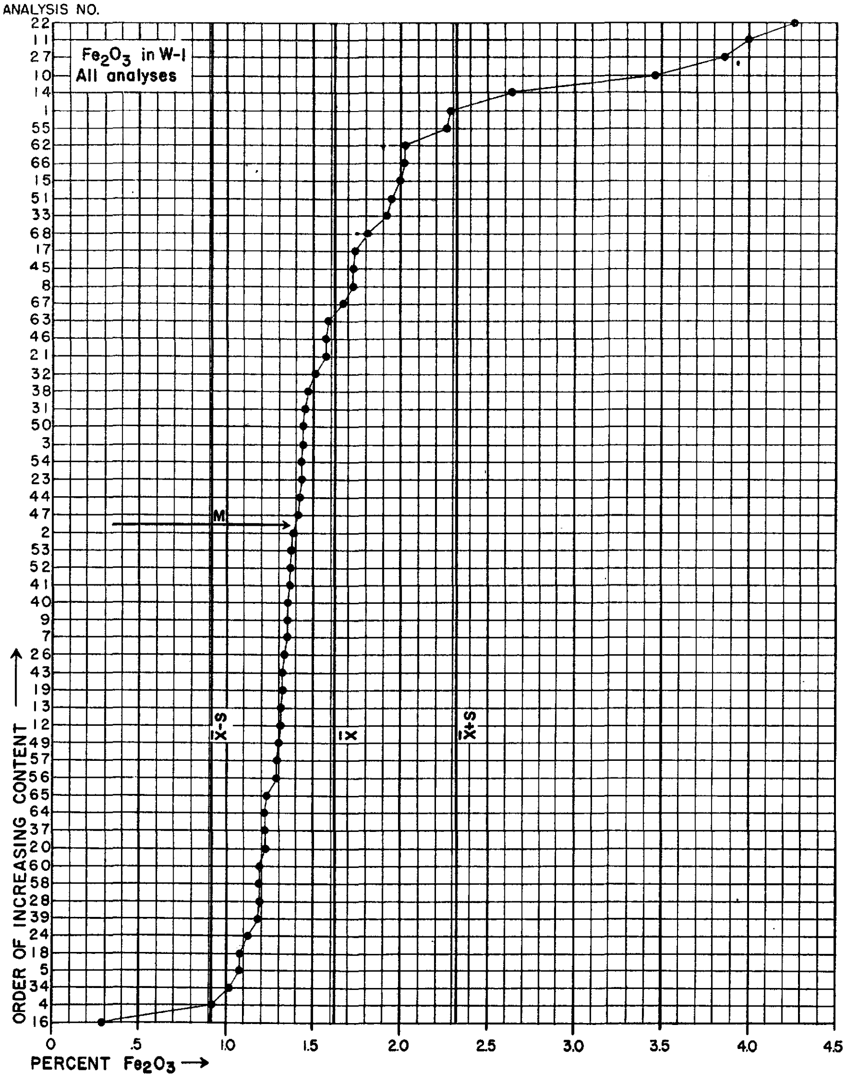
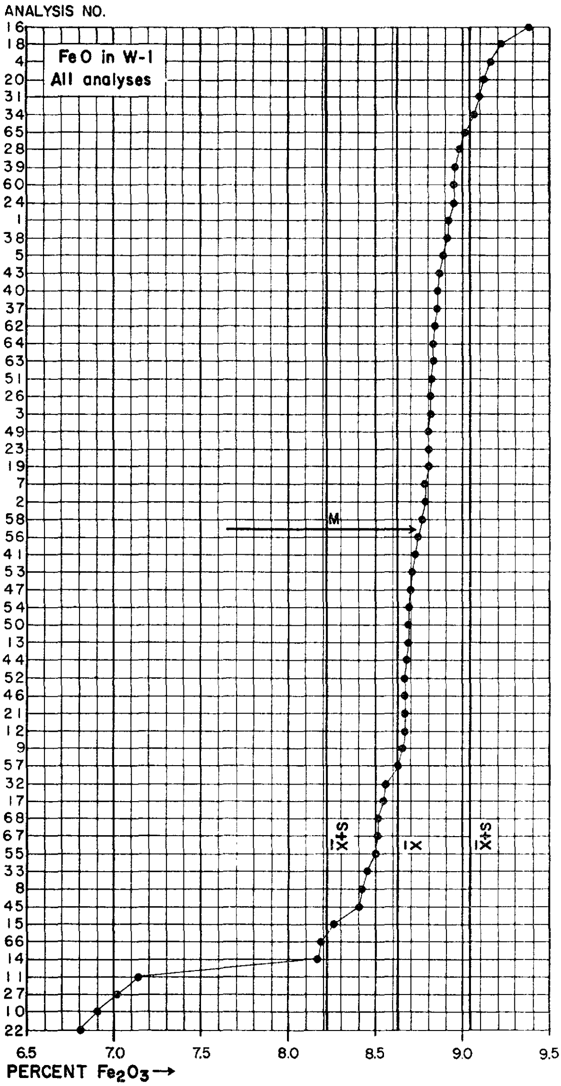


FIGURE 6.—S curves of distribution for determinations



of $Fe_2O_3$ and of FeO in analyses of W-1.

Statistical data calculated from the analyses are given in table 3 for G–1 and in table 4 for W–1. The following symbols and formulas were used:

$n$ is the number of determinations.
$\bar{x}$ is the arithmetic mean or average.
$d$ is the deviation of an analytical result from $\bar{x}$.
$M$ is the median.

$S$, the standard deviation $=\sqrt{\dfrac{d^2}{n-1}}$

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

Statistical data for the analyses in U.S. Geological Survey Bulletin 980 have been recalculated for purposes of comparison. Fairbairn's statistical data (Fairbairn, 1953) differ somewhat from those in tables 3 and 4 representing analyses in Bulletin 980, because in Fairbairn's calculations several analyses were omitted.

Although the precision of the analyses as a whole is low, as evidenced by values for standard and relative deviations, the arithmetic means and medians are in fair agreement for new analyses compared to old ones and for new and old analyses compared with all analyses. These agreements seem to indicate that the analyses as a whole, although varying widely, are valid measurements of composition.

Arithmetic means, medians, and adopted limits of acceptability of tables 3 and 4 are the basis for selection of values on pages 38 and 39.

The limits of acceptability were arbitrarily selected as ±1 standard deviation from the arithmetic mean. Although this method sets fairly close limits on the values for the major constituents, a study of the methods used and of results of analyses submitted by a large number of competent rock analysts gives some confidence in the selection of these limits. Present studies of the compositions of G–1 and W–1 permit the prediction that the more accurate results expected in the future will still fall within these arbitrarily selected limits.

TABLE 3.—*Statistical data on granite, G-1*

| | Number of determinations $n$ | Arithmetic mean $\bar{x}$ | Standard deviation $S$ | Relative deviation $C$ | Median $M$ | Adopted limits of acceptability | |
|---|---|---|---|---|---|---|---|
| | | | | | | $\bar{x}-S$ | $\bar{x}+S$ |
| **Analyses in table 1** | | | | | | | |
| $SiO_2$ | 26 | 72.49 | 0.19 | 0.26 | 72.50 | 72.30 | 72.68 |
| $Al_2O_3$ | 26 | 14.30 | .22 | 1.53 | 14.26 | 14.08 | 14.52 |
| $Fe_2O_3$ | 23 | .98 | .32 | 32.04 | .85 | .66 | 1.30 |
| FeO | 23 | .96 | .09 | 9.82 | .97 | .87 | 1.05 |
| MgO+0.63 BaO | 25 | .40 | .11 | 28.09 | .41 | .29 | .51 |
| CaO+SrO | 25 | 1.39 | .11 | 8.06 | 1.38 | 1.28 | 1.50 |
| $Na_2O$ | 25 | 3.32 | .19 | 5.74 | 3.28 | 3.13 | 3.51 |
| $K_2O+Rb_2O$ | 25 | 5.35 | .29 | 5.36 | 5.43 | 5.06 | 5.64 |
| $H_2O-$ | 20 | .08 | .07 | 91.82 | .04 | .01 | .15 |
| $H_2O+$ | 21 | .32 | .09 | 26.91 | .33 | .23 | .41 |
| $TiO_2$ | 26 | .25 | .01 | 5.60 | .25 | .24 | .26 |
| $P_2O_5$ | 23 | .09 | .02 | 24.39 | .09 | .07 | .11 |
| MnO | 23 | .03 | .01 | 29.80 | .03 | .02 | .04 |
| $CO_2$ | 9 | .08 | .01 | 13.04 | .08 | .07 | .09 |
| Total | ---------- | 100.04 | ---------- | ---------- | 99.90 | ---------- | ---------- |
| Total Fe as $Fe_2O_3$ | 26 | 2.03 | 0.29 | 14.36 | 1.90 | 1.74 | 2.32 |
| $R_2O_3$ | 26 | 16.66 | .34 | 2.06 | 16.53 | 16.32 | 17.00 |
| $Na_2O+K_2O$ | 25 | 8.68 | .35 | 4.09 | 8.81 | 8.33 | 9.03 |
| **Analyses in Bulletin 980** | | | | | | | |
| $SiO_2$ | 34 | 72.24 | 0.37 | 0.51 | 72.36 | 71.87 | 72.61 |
| $Al_2O_3$ | 34 | 14.34 | .46 | 3.21 | 14.31 | 13.88 | 14.80 |
| $Fe_2O_3$ | 34 | .92 | .29 | 31.55 | .84 | .63 | 1.21 |
| FeO | 34 | 1.01 | .12 | 12.19 | .98 | .89 | 1.13 |
| MgO+0.63 BaO | 34 | .39 | .14 | 35.32 | .42 | .25 | .53 |
| CaO+SrO | 34 | 1.40 | .14 | 9.66 | 1.38 | 1.26 | 1.54 |
| $Na_2O$ | 34 | 3.30 | .26 | 7.99 | 3.30 | 3.04 | 3.56 |
| $K_2O$ | 34 | 5.48 | .46 | 8.41 | 5.50 | 5.02 | 5.94 |
| $H_2O-$ | 28 | .05 | .03 | 59.81 | .05 | .02 | .08 |
| $H_2O+$ | 30 | .39 | .22 | 5.65 | .36 | .17 | .61 |
| $TiO_2$ | 34 | .25 | .06 | 23.20 | .26 | .19 | .31 |
| $P_2O_5$ | 31 | .11 | .07 | 65.12 | .09 | .04 | .18 |
| MnO | 33 | .03 | .01 | 36.33 | .03 | .02 | .04 |
| $CO_2$ | 0 | (1) | ---------- | ---------- | ---------- | ---------- | ---------- |
| Total | ---------- | 99.91 | ---------- | ---------- | 99.88 | ---------- | ---------- |
| Total Fe as $Fe_2O_3$ | 34 | 2.05 | 0.28 | 13.76 | 1.98 | 1.77 | 2.33 |
| $R_2O_3$ | 34 | 16.76 | .45 | 2.68 | 16.64 | 16.31 | 17.21 |
| $Na_2O+K_2O$ | 34 | 8.78 | .53 | 6.08 | 8.82 | 8.25 | 9.31 |
| **All analyses** | | | | | | | |
| $SiO_2$ | 60 | 72.35 | 0.48 | 0.66 | 72.42 | 71.87 | 72.83 |
| $Al_2O_3$ | 60 | 14.32 | .37 | 2.60 | 14.29 | 13.95 | 14.69 |
| $Fe_2O_3$ | 57 | .95 | .30 | 31.49 | .85 | .65 | 1.25 |
| FeO | 57 | .99 | .11 | 11.26 | .98 | .89 | 1.10 |
| MgO+0.63 BaO | 59 | .40 | .13 | 32.15 | .41 | .27 | .53 |
| CaO+SrO | 59 | 1.40 | .12 | 8.95 | 1.38 | 1.28 | 1.52 |
| $Na_2O$ | 59 | 3.31 | .23 | 7.06 | 3.30 | 3.08 | 3.54 |
| $K_2O+Rb_2O$ | 59 | 5.42 | .39 | 7.26 | 5.48 | 5.03 | 5.81 |
| $H_2O-$ | 48 | .06 | .05 | 80.53 | .04 | .01 | .11 |
| $H_2O+$ | 51 | .36 | .18 | 48.70 | .35 | .18 | .54 |
| $TiO_2$ | 60 | .26 | .04 | 16.59 | .26 | .22 | .30 |
| $P_2O_5$ | 54 | .10 | .06 | 55.10 | .09 | .04 | .16 |
| MnO | 56 | .03 | .01 | 33.62 | .03 | .02 | .04 |
| $CO_2$ | 9 | .08 | .01 | 13.04 | .08 | .07 | .09 |
| Total | ---------- | 100.03 | ---------- | ---------- | 99.96 | ---------- | ---------- |
| Total Fe as $Fe_2O_3$ | 60 | 2.04 | 0.28 | 13.90 | 1.94 | 1.76 | 2.32 |
| $R_2O_3$ | 60 | 16.72 | .40 | 2.42 | 16.61 | 16.32 | 17.12 |
| $Na_2O+K_2O$ | 59 | 8.74 | .48 | 5.49 | 8.81 | 8.26 | 9.22 |

None reported.

TABLE 4.—*Statistical data on diabase, W-1*

| | Number of determinations $n$ | Arithmetic mean $\bar{x}$ | Standard deviation $S$ | Relative deviation $C$ | Median $M$ | Adopted limits of acceptability | |
|---|---|---|---|---|---|---|---|
| | | | | | | $\bar{x}-S$ | $\bar{x}+S$ |
| **Analyses in table 2** | | | | | | | |
| $SiO_2$ | 30 | 52.48 | 0.31 | 0.58 | 52.51 | 52.17 | 52.79 |
| $Al_2O_3$ | 30 | 15.05 | .26 | 1.73 | 15.02 | 14.79 | 15.31 |
| $Fe_2O_3$ | 28 | 1.49 | .29 | 19.64 | 1.39 | 1.20 | 1.78 |
| FeO | 28 | 8.72 | .18 | 2.07 | 8.74 | 8.54 | 8.90 |
| MgO+0.63 BaO | 29 | 6.62 | .13 | 2.03 | 6.59 | 6.49 | 6.75 |
| CaO+SrO | 29 | 10.98 | .15 | 1.37 | 10.97 | 10.83 | 11.13 |
| $Na_2O$ | 28 | 2.07 | .20 | 9.46 | 2.08 | 1.87 | 2.27 |
| $K_2O$ | 28 | .64 | .04 | 6.49 | .64 | .60 | .68 |
| $H_2O-$ | 26 | .17 | .06 | 34.42 | .16 | .11 | .23 |
| $H_2O+$ | 25 | .50 | .16 | 30.75 | .50 | .34 | .66 |
| $TiO_2$ | 30 | 1.10 | .15 | 13.88 | 1.10 | .95 | 1.25 |
| $P_2O_5$ | 29 | .16 | .07 | 47.71 | .14 | .09 | .23 |
| MnO | 29 | .16 | .02 | 10.44 | .16 | .14 | .18 |
| $CO_2$ | 10 | .06 | .03 | 46.12 | .06 | .03 | .09 |
| Total | ---------- | 100.20 | ---------- | ---------- | 100.06 | ---------- | ---------- |
| Total Fe as $Fe_2O_3$ | 30 | 11.18 | 0.23 | 2.07 | 11.10 | 10.95 | 11.41 |
| $R_2O_3$ | 30 | 27.48 | .34 | 1.23 | 27.40 | 27.14 | 27.82 |
| $Na_2O+K_2O$ | 28 | 2.72 | .21 | 7.69 | 2.73 | 2.50 | 2.90 |
| **Analyses in Bulletin 980** | | | | | | | |
| $SiO_2$ | 30 | 52.33 | 0.35 | 0.68 | 52.42 | 51.98 | 52.68 |
| $Al_2O_3$ | 30 | 15.17 | .85 | 5.61 | 15.08 | 14.32 | 16.02 |
| $Fe_2O_3$ | 30 | 1.75 | .95 | 54.21 | 1.40 | .80 | 2.70 |
| FeO | 30 | 8.55 | .69 | 8.07 | 8.78 | 7.86 | 9.24 |
| MgO+0.63 BaO | 30 | 6.53 | .47 | 7.26 | 6.66 | 6.07 | 7.01 |
| CaO+SrO | 30 | 10.96 | .17 | 1.58 | 10.94 | 10.78 | 11.12 |
| $Na_2O$ | 30 | 2.07 | .21 | 10.20 | 2.09 | 1.86 | 2.28 |
| $K_2O$ | 30 | .70 | .17 | 24.61 | .66 | .53 | .87 |
| $H_2O-$ | 28 | .15 | .07 | 47.37 | .16 | .08 | .22 |
| $H_2O+$ | 30 | .57 | .24 | 41.39 | .52 | .33 | .81 |
| $TiO_2$ | 30 | 1.04 | .23 | 22.56 | 1.06 | .81 | 1.27 |
| $P_2O_5$ | 29 | .14 | .04 | 29.48 | .13 | .10 | .18 |
| MnO | 30 | .18 | .07 | 40.77 | .17 | .11 | .25 |
| $CO_2$ | 0 | (1) | ---------- | ---------- | ---------- | ---------- | ---------- |
| Total | ---------- | 100.14 | ---------- | ---------- | 100.07 | ---------- | ---------- |
| Total Fe as $Fe_2O_3$ | 30 | 11.26 | 0.32 | 2.88 | 11.15 | 10.94 | 11.58 |
| $R_2O_3$ | 30 | 27.61 | .61 | 2.20 | 27.50 | 27.00 | 28.22 |
| $Na_2O+K_2O$ | 30 | 2.77 | .30 | 10.78 | 2.75 | 2.47 | 3.07 |
| **All analyses** | | | | | | | |
| $SiO_2$ | 60 | 52.40 | 0.33 | 0.63 | 52.45 | 52.07 | 52.73 |
| $Al_2O_3$ | 60 | 15.11 | .63 | 4.16 | 15.06 | 14.48 | 15.74 |
| $Fe_2O_3$ | 58 | 1.62 | .71 | 43.50 | 1.40 | .91 | 2.33 |
| FeO | 58 | 8.63 | .41 | 4.72 | 8.75 | 8.22 | 9.04 |
| MgO+0.63 BaO | 59 | 6.58 | .35 | 5.29 | 6.61 | 6.23 | 6.93 |
| CaO+SrO | 59 | 10.97 | .16 | 1.46 | 10.96 | 10.81 | 11.13 |
| $Na_2O$ | 58 | 2.07 | .20 | 9.76 | 2.08 | 1.87 | 2.27 |
| $K_2O$ | 58 | .67 | .13 | 19.00 | .64 | .54 | .80 |
| $H_2O-$ | 54 | .16 | .06 | 40.77 | .16 | .10 | .22 |
| $H_2O+$ | 55 | .54 | .20 | 37.32 | .50 | .34 | .74 |
| $TiO_2$ | 60 | 1.07 | .20 | 18.34 | 1.09 | .87 | 1.27 |
| $P_2O_5$ | 58 | .15 | .06 | 40.51 | .14 | .09 | .21 |
| MnO | 59 | .17 | .05 | 32.33 | .17 | .12 | .22 |
| $CO_2$ | 10 | .06 | .03 | 46.12 | .06 | .03 | .09 |
| Total | ---------- | 100.20 | ---------- | ---------- | 100.07 | ---------- | ---------- |
| Total Fe as $Fe_2O_3$ | 60 | 11.22 | 0.28 | 2.49 | 11.13 | 10.94 | 11.50 |
| $R_2O_3$ | 60 | 27.54 | .48 | 1.76 | 27.48 | 27.06 | 28.02 |
| $Na_2O+K_2O$ | 58 | 2.74 | .26 | 9.35 | 2.74 | 2.48 | 3.00 |

[1] None reported.

## VALUES BY METHODS OTHER THAN CONVENTIONAL

### RAPID METHODS

Results of analyses 48, 49, and 61 in tables 1 and 2 are those from three laboratories using various modifications of rapid methods. These are largely based upon photometric measurements, which have the advantages of speed and coverage of a large number of constituents in the same sample solution, without the elaborate separations needed for gravimetric procedures. These rapid analyses are valuable for obtaining cheaply the large mass of data of moderate accuracy needed in many geologic investigations. Although they are less accurate than are the conventional methods, they gain in dependability because most of the determinations are independent of one another and hence are not affected by the accuracy with which prior separations and determinations of other constituents have been made. They are also, in general, more simple and therefore less subject to gross error through improperly performed steps. Comparisons of accuracy by rapid and conventional methods have been published by Shapiro and Brannock (1952, 1956), Mercy (1956), and Riley (1958).

Rapid methods differ markedly from the conventional methods. Whereas the conventional procedure uses a 1 gram sample, the weight of sample in rapid methods may vary from only a few milligrams to 0.1 gram. For this reason sampling errors may be large if care is not taken to avoid them. $SiO_2$ and $Al_2O_3$ are usually determined photometrically on aliquots of one sample, and in aliquots from another sample, total iron as $Fe_2O_3$, $TiO_2$, MnO, and $P_2O_5$ are determined photometrically, and MgO and CaO by photometric titration using ethylenediaminetetraacetic acid (EDTA). $Na_2O$ and $K_2O$ are determined by flame photometry. Simple rapid procedures have also been developed for FeO, total $H_2O$, and $CO_2$. For various rapid methods see Hedin (1947), Shapiro and Brannock (1952 and 1956), Miller and Chalmers (1953), Corey and Jackson (1953), Bannerjee and Colliss (1955), Mercy (1956), and Riley (1958).

The rapid analyses, made by methods differing markedly from those of the conventional system, serve as a check on the validity of results on G-1 and W-1 by the conventional procedure. For the most part the results of rapid methods in tables 1 and 2 fall within the limits $\bar{x} \pm S$, here taken as criteria for selecting preferred values.

### DIRECT DETERMINATIONS OF ALUMINA

There are a number of direct methods for determining $Al_2O_3$ (photometric, gravimetric, and volumetric) that help to confirm the results obtained in the usual way. The photometric results are those in the rapid analyses 48 and 49 of tables 1 and 2. In analyses 58 the direct gravimetric method of Kassner and Ozier (1950) was used, in which aluminum is precipitated with 8-hydroxyquinoline in the presence of tartrate, cyanide, and peroxide to form complex ions of elements other than aluminum and prevent their precipitation. In analyses 60, of tables 1 and 2, iron and titanium were removed by precipitating them with cupferron before the 8-hydroxyquinoline precipitation of aluminum. $Al_2O_3$ in analyses 61 of tables 1 and 2 was determined by the method of Miller and Chalmers (1953), in which aluminum from a 5 mg sample is separated from iron, titanium, vanadium, and zirconium by extracting the cupferron precipitates of these metals with o-dichlorobenzene, the aluminum then being precipitated from the aqueous phase with 8-hydroxyquinoline and weighed. Milner and Woodhead (1955) determined $Al_2O_3$ by titration with ethylenediaminetetraacetic acid. Watts (1958) developed a new method for $Al_2O_3$ by acidimetric titration, and used it to determine $Al_2O_3$ in G–1 and W–1. Analysis 11 of U.S. Geological Survey Bulletin 980 was done by separating iron and titanium with cupferron and precipitating $Al_2O_3$ and $P_2O_5$ with ammonia. P. G. Jeffery (written communication, 1959), Geological Survey of Great Britain, obtained 14.02, 14.04, and 14.09 percent $Al_2O_3$ in G–1 and 14.99, 15.02, and 15.05 percent $Al_2O_3$ in W–1 by gravimetric determinations with 8-hydroxyquinoline.

Results of direct determinations of alumina are given in the following table.

*Direct determinations of alumina* ($Al_2O_3$)

| Analysis No. | Type of method | Percent $Al_2O_3$ | |
|---|---|---|---|
| | | G–1 | W–1 |
| 48 | Photometric | 14.1 | 14.7 |
| 49 | do | 14.0 | 14.7 |
| 58 | Gravimetric | 13.51 | 14.83 |
| 60 | do | 14.12 | 14.93 |
| 61 | do | 14.1 | 15.0 |
| 11 | do | 14.49 | 14.86 |
| Jeffery (1959) | do | 14.05 | 15.02 |
| Milner and Woodhead (1955) | Volumetric | 14.35 | 14.93 |
| Watts (1958) | do | 14.29 | 15.40 |
| Arithmetic mean | | 14.1 | 14.9 |

## TOTAL IRON

In addition to the volumetric methods conventionally used for iron, photometric and gravimetric procedures are sometimes used. In analyses 48 (rapid), of tables 1 and 2, iron was determined by the color of the ferric ion in hydrochloric acid (Pinsl, 1944), and in analyses 49 it was determined by the color developed with thioglycollic acid by the method of Milner and Groom (1951). Analyses 60 and determinations by R. B. Ellestad, reported by Goldich and Oslund (1956), were made photometrically by the o-phenanthroline method.

Additional photometric results, method not given, are reported in analyses 61 and 70 (70 not given in tables 1 and 2 because only total Fe, $P_2O_5$, and $TiO_2$ were determined). Analyses 40 were made gravimetrically by precipitating iron with $H_2S$ in ammoniacal tartrate solution (averages for these and volumetric results are shown in tables 1 and 2). Results of a method, well known but seldom used, in which ferric ion is titrated with titanous ion, are given in analyses 21 of Bulletin 980.

Results for total iron as $Fe_2O_3$ by methods differing from the conventional procedures are compiled in table 5.

TABLE 5.—*Results for total iron as* $Fe_2O_3$ *by methods differing from the conventional volumetric methods*

| Analysis | Type of method | Percent $Fe_2O_3$ | | | |
|---|---|---|---|---|---|
| | | G-1 | | W-1 | |
| | | Value | Average | Value | Average |
| 48 | Photometric | 1.8 | | 11.0 | |
| 49 | do | 1.81 | | 11.1 | |
| 60 | do | 1.91 | | 11.13<br>11.09<br>11.05<br>11.20<br>11.18 | 11.13 |
| R. B. Ellestad | do | 1.85<br>1.85 | 1.85 | | |
| 61 | do | 1.85<br>1.90 | 1.88 | 11.0<br>11.1 | 11.05 |
| 70 | do | | 1.77 | | 11.10 |
| Arithmetic mean | | | 1.84 | | 11.07 |
| 40 | Gravimetric | 2.01<br>2.10 | 2.05 | 11.18<br>11.18 | 11.18 |
| 21 | Volumetric | | 1.83 | | 11.21 |

## SODIUM AND POTASSIUM OXIDES

Independent checks on the conventional gravimetric procedure are given by numerous results by the flame photometer: 38, 42, 48, 49, 58, 60, and 67 of tables 1 and 2; analyses 71 and 72 (alkalies only determined); results by Goldich and Horstman reported by Goldich and Oslund (1956); and results of analyses 2, 3, 4, and 5 of Bulletin 980. In these analyses, the J. Lawrence Smith method or a modification was used for extracting the alkalies in analyses 58, 67, 3, and those by Goldich and Horstman; the method of decomposition was not specified for analyses 72 and the analyses by O'Leary (Geological Survey of Northern Nigeria, written communication, 1959); decomposition with HF and $H_2SO_4$ was used for all others.

Greenewalt, Herzog, and Pinson (1955) reported 0.62 percent of $K_2O$ in W-1, using a mass spectrometer and isotope dilution method. Goldich and Oslund (1956) reported results by Burwash and by

Oslund and Baadsgaard using the J. Lawrence Smith method of decomposition, separating the potassium as $K_2PtCl_6$, and testing the precipitate for sodium with the flame photometer.

Results for $Na_2O$ and $K_2O$ in analysis 36 of table 1 and analysis 73 (alkalies only) were obtained by the J. Lawrence Smith method of extraction, separation of sodium and potassium with an ion exchange column, and measurement of the separated sodium and potassium chlorides by volumetric determinations of chloride by Mohr's method.

Results of these diverse methods of determining $Na_2O$ and $K_2O$ are given in table 6.

TABLE 6.—*Determinations of* $Na_2O$ *and* $K_2O$ *in percent, by methods other than conventional*

| Analysis | Type of method | Results | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | | G-1 | | | | W-1 | | | |
| | | $Na_2O$ | | $K_2O$ | | $Na_2O$ | | $K_2O$ | |
| | | Value | Average | Value | Average | Value | Average | Value | Average |
| 58[1] | J. L. Smith, flame photometer. | 3.23<br>3.25 | 3.24 | 5.16<br>5.39 | 5.28 | 2.03<br>2.06 | 2.05 | 0.62<br>.66 | 0.64 |
| 67 | do | ------ | ------ | ------ | ------ | 2.50<br>2.56 | 2.53 | .59<br>.60 | .60 |
| Goldich and Horstman | do | 3.25 | ------ | 5.52 | ------ | ------ | ------ | ------ | ------ |
| 3 | do | 3.27 | ------ | 5.30 | ------ | 2.09 | ------ | .60 | ------ |
| 72 | Flame photometer | 3.45 | ------ | 5.53 | ------ | 2.23 | ------ | .66 | ------ |
| O'Leary (1959) | do | 3.39 | ------ | 5.54 | ------ | 2.30 | ------ | .64 | ------ |
| 48 | $HF+H_2SO_4$, flame photometer. | 3.4 | ------ | 5.7 | ------ | 2.2 | ------ | .66 | ------ |
| 49 | do | 3.8 | ------ | 5.4 | ------ | 2.4 | ------ | .70 | ------ |
| 60 | do | 3.38<br>3.64<br>3.58<br>3.42 | 3.50 | 4.95<br>5.05<br>5.04<br>5.08<br>5.28 | 5.08 | 1.97<br>2.06<br>2.03 | 2.02 | .60<br>.64<br>.63 | .62 |
| 71 | do | 3.32 | ------ | 5.66 | ------ | 2.05 | ------ | .64 | ------ |
| 38 | do | 3.32 | ------ | 5.48 | ------ | 2.13 | ------ | .67 | ------ |
| 42 | do | 3.41 | ------ | 5.23 | ------ | ------ | ------ | ------ | ------ |
| 2 | do | 3.35 | ------ | 5.51 | ------ | 2.14 | ------ | .68 | ------ |
| 4 | do | 3.78 | ------ | 5.44 | ------ | 2.40 | ------ | .66 | ------ |
| 5 | do | 3.50 | ------ | 5.64 | ------ | 2.28 | ------ | .69 | ------ |
| Arithmetic mean | | ------ | 3.43 | ------ | 5.44 | ------ | 2.21 | ------ | 0.65 |
| Greenewalt, Herzog, and Pinson (1955). | Mass spectrometer, isotope dilution. | ------ | ------ | ------ | ------ | ------ | ------ | 0.62 | ------ |
| Burwash | J. L. Smith, $K_2PtCl_6$ flame photometer. | 3.27 | ------ | 5.54 | ------ | ------ | ------ | ------ | ------ |
| Oslund and Baadsgaard | do | 3.32 | ------ | 5.52 | ------ | ------ | ------ | ------ | ------ |
| 36 | Ion exchange, volumetric. | 3.59 | ------ | 5.26 | ------ | ------ | ------ | ------ | ------ |
| 73 | do | 3.27<br>3.30 | 3.29 | 5.52<br>5.56 | 5.54 | 2.13 | ------ | .57 | ------ |

[1] Determinations recalculated to include $H_2O$ in sample.

## ANALYSES OF GOLDICH AND OSLUND

The analyses by Goldich and Oslund (1956), analyses 47 and 50 of tables 1 and 2, have been so thoroughly checked for major constituents by many coworkers at the University of Minnesota and by independent methods of analysis that they present convincing evidence of the composition of G–1 and W–1. The averages of these analyses calculated to moisture-free samples are given in the following table.

*Analyses of Goldich and Oslund (1956) calculated to moisture-free samples*

| | G–1 | W–1 | | G–1 | W–1 |
|---|---|---|---|---|---|
| $SiO_2$ | 72.51 | 52.62 | $TiO_2$ | 0.26 | 1.08 |
| $Al_2O_3$ | 14.21 | 15.00 | $P_2O_5$ | .08 | .12 |
| $Fe_2O_3$ | .78 | 1.41 | F | .07 | .02 |
| FeO | .97 | 8.72 | S | .01 | .02 |
| MnO | .025 | .161 | | | |
| MgO | .37 | 6.60 | | 99.92 | 100.04 |
| SrO | .02 | .01 | Less O=F and S | .03 | .02 |
| CaO | 1.35 | 11.00 | | | |
| BaO | .10 | ---- | Total | 99.89 | 100.02 |
| $Rb_2O$ | .022 | .00 | Total Fe as $Fe_2O_3$ | 1.86 | 11.11 |
| $K_2O$ | 5.52 | .62 | $R_2O_3$ | 16.41 | 27.31 |
| $Na_2O$ | 3.29 | 2.14 | $R_2O_3+SiO_2$ | 88.92 | 79.93 |
| $H_2O+$ | .25 | .45 | $Na_2O+K_2O+Rb_2O$ | 8.83 | 2.76 |
| $CO_2$ | .08 | .07 | | | |

The results for most determinations by nonconventional methods just presented and those by Goldich and Oslund agree with the statistical selection of values, in the following section, within a few hundredths of a percent. Values for $SiO_2$, $Al_2O_3$, and $Fe_2O_3$ in G–1 and W–1 and $K_2O$ in G–1 are most in question. Percentages of $SiO_2$ obtained by Stevens and Chodos (Part 2 of this bulletin) are 0.19 percent higher for G–1 and 0.15 percent higher for W–1 than those of Goldich and Oslund. The results of Stevens and Chodos lack the precision needed to prove convincingly a higher value for $SiO_2$. The tendency for values of $SiO_2$ in general to be low has been clearly shown here as well as by Fairbairn (1953) and by Fairbairn and Schairer (1952). Goldich and Oslund do not present evidence that all the $SiO_2$ in their samples was collected.

The following section shows that more rigorous elimination of results of analyses by statistical selection gives values for $Al_2O_3$ closely approaching those of Goldich and Oslund. The tendency toward high values for $Fe_2O_3$ in many of the analyses, and the lowering of the preferred estimate by more rigorous elimination, support the carefully determined values for $Fe_2O_3$ of Goldich and Oslund. High values for $Fe_2O_3$ in many analyses seem to be attributable to high values for total iron as $Fe_2O_3$, rather than to errors in FeO, as these are generally in close agreement.

## STATISTICAL SELECTION OF VALUES FOR G–1 AND W–1

Tables 7 and 8 give the statistical selection of values for G–1 and W–1 (recalculated to moisture-free samples), including the arithmetic means ($\bar{x}$ for all analyses, $\bar{x}'$ for preferred values for all analyses, $\bar{x}''$ for the new analyses, and $\bar{x}'''$ for preferred values of the new analyses), and the medians ($M$ for all analyses, $M'$ for preferred values for all analyses, $M''$ for new analyses, and $M'''$ for preferred values of the new analyses). Preferred values are those which are within the adopted limits of acceptability, $\bar{x} \pm S$ and $\bar{x}'' \pm S''$ ($\bar{x}''$ and $S''$ being the arithmetic mean and standard deviation respectively for all new analyses). The values under $\bar{x}$, $M$, $\bar{x}'$, and $M'$ and under $\bar{x}''$, $M''$, $\bar{x}'''$, and $M'''$ represent progressively increasing elimination of values which appear to be faulty; increasing or decreasing values progressing across these series are presumed to show progressive elimination of bias through dropping of discordant values.

For values of FeO, MgO, CaO, $Na_2O$, $H_2O^+$, $TiO_2$, $P_2O_5$, and $CO_2$ in G–1 and W–1 and $K_2O$ in W–1 arithmetic means and medians of preferred values in tables 7 and 8 agree within a few hundredths of a percent, and show similar close agreement with values reported by Goldich and Oslund. In selecting final preferred values it makes little difference which of these values is taken.

TABLE 7.—*Statistical selection of values on G–1, moisture free*

| | All analyses | | | | New analyses | | | |
|---|---|---|---|---|---|---|---|---|
| | Arithmetic mean $\bar{x}$ | Median $M$ | Arithmetic mean of preferred values $\bar{x}'$ | Median of preferred values $M'$ | Arithmetic mean $\bar{x}''$ | Median $M''$ | Arithmetic mean of preferred values $\bar{x}'''$ | Median of preferred values $M'''$ |
| $SiO_2$ | 72.39 | 72.44 | 72.45 | 72.47 | 72.54 | 72.53 | 72.53 | 72.53 |
| $Al_2O_3$ | 14.33 | 14.29 | 14.29 | 14.30 | 14.31 | 14.27 | 14.25 | 14.25 |
| $Fe_2O_3$ | .95 | .85 | .87 | .83 | .98 | .85 | .86 | .83 |
| FeO | .99 | .98 | .98 | .98 | .96 | .97 | .97 | .97 |
| MgO | .40 | .41 | .41 | .42 | .40 | .41 | .40 | .41 |
| CaO | 1.40 | 1.38 | 1.39 | 1.38 | 1.39 | 1.38 | 1.39 | 1.38 |
| $Na_2O$ | 3.31 | 3.30 | 3.32 | 3.30 | 3.32 | 3.28 | 3.31 | 3.28 |
| $K_2O$ | 5.42 | 5.48 | 5.46 | 5.48 | 5.35 | 5.43 | 5.40 | 5.45 |
| $H_2O^+$ | .36 | .35 | .34 | .35 | .32 | .33 | .32 | .33 |
| $TiO_2$ | .26 | .26 | .26 | .26 | .25 | .25 | .25 | .25 |
| $P_2O_5$ | .10 | .09 | .09 | .09 | .09 | .09 | .09 | .09 |
| MnO | .03 | .03 | .03 | .03 | .03 | .03 | .03 | .03 |
| $CO_2$[1] | .08 | .08 | .08 | .08 | .08 | .08 | .08 | .08 |
| Total | 100.02 | 99.94 | 99.97 | 99.97 | 100.02 | 99.90 | 99.88 | 99.88 |

[1] No values given in U.S. Geological Survey Bulletin 980.

Values for $SiO_2$ can be seen to increase progressively across tables 7 and 8, and it seems questionable if the optimum value is ever attained. Higher values (72.70 percent for G–1 and 52.77 for W–1) are shown by Stevens and Chodos (part 2 of this report) by methods designed to eliminate bias. $Al_2O_3$ shows a somewhat less pronounced decrease across tables 7 and 8, and slightly higher values than those of Goldich and Oslund (1956), which agree closely with the direct determinations of $Al_2O_3$ previously given. This evidence suggests the acceptance of the values of Goldich and Oslund for $Al_2O_3$. Analysis of materials retained by the $SiO_2$ and usually counted as $Al_2O_3$, as reported in part 2 by Stevens and Chodos, suggests that the true value for $Al_2O_3$ may be slightly lower still.

TABLE 8.—*Statistical selection of values on W–1, moisture free*

| | All analyses | | | | New analyses | | | |
|---|---|---|---|---|---|---|---|---|
| | Arithmetic mean $\bar{x}$ | Median $M$ | Arithmetic mean of preferred values $\bar{x}'$ | Median of preferred values $M'$ | Arithmetic mean $\bar{x}''$ | Median $M''$ | Arithmetic mean of preferred values $\bar{x}'''$ | Median of preferred values $M'''$ |
| $SiO_2$ | 52.48 | 52.53 | 52.54 | 52.58 | 52.54 | 52.59 | 52.60 | 52.61 |
| $Al_2O_3$ | 15.11 | 15.06 | 15.05 | 15.02 | 15.05 | 15.02 | 15.07 | 15.06 |
| $Fe_2O_3$ | 1.62 | 1.40 | 1.41 | 1.36 | 1.49 | 1.39 | 1.38 | 1.37 |
| FeO | 8.65 | 8.77 | 8.75 | 8.77 | 8.74 | 8.76 | 8.78 | 8.76 |
| MgO | 6.59 | 6.62 | 6.64 | 6.62 | 6.63 | 6.60 | 6.60 | 6.59 |
| CaO | 10.99 | 10.98 | 10.98 | 10.97 | 11.00 | 10.99 | 10.99 | 10.98 |
| $Na_2O$ | 2.07 | 2.08 | 2.07 | 2.09 | 2.07 | 2.08 | 2.10 | 2.10 |
| $K_2O$ | .67 | .64 | .64 | .64 | .64 | .64 | .64 | .64 |
| $H_2O^+$ | .54 | .50 | .53 | .52 | .50 | .50 | .50 | .50 |
| $TiO_2$ | 1.07 | 1.09 | 1.07 | 1.08 | 1.10 | 1.10 | 1.08 | 1.10 |
| $P_2O_5$ | .15 | .14 | .14 | .14 | .16 | .14 | .14 | .14 |
| MnO | .17 | .17 | .16 | .17 | .16 | .16 | .16 | .16 |
| $CO_2$[1] | .06 | .06 | .05 | .06 | .06 | .06 | .05 | .06 |
| Total | 100.17 | 100.04 | 100.03 | 100.02 | 100.14 | 100.03 | 100.09 | 100.07 |

[1] No values given in U.S. Geological Survey Bulletin 980.

A rather pronounced positive bias in values for $Fe_2O_3$ is indicated by the decrease of these values for all analyses and for new analyses across tables 7 and 8, as well as by the S curves of distribution in figures 3 and 4. The arithmetic means and medians of preferred values for $Fe_2O_3$ approach the values of Goldich and Oslund, which agree closely with values obtained by methods other than conventional. Values for FeO, on the other hand, are in close agreement. Finally the statistical data in tables 3, 4, 7, and 8 seem to indicate a negative bias in determinations of $K_2O$ in G–1, and suggest the acceptance of the values of Goldich and Oslund, which agree well with determinations by the flame photometer. $K_2O$ would tend to be low in routine analyses where insufficient care was taken to grind the sample to an impalpable powder with ammonium chloride, to heat properly, and to extract all of the alkalies from the product with water.

The statistical data here assembled, the special study of the $SiO_2$ content of the rocks elsewhere in this report, and the analyses of Goldich and Oslund seem to establish the composition of the rocks within narrow limits. In selecting final preferred values, minor elements known to be present in percentages above 0.01 should be included and corrections made for their effect on major constituents. Fluorine, sulfur, and carbon dioxide are no doubt present in both rocks in percentages above 0.01. The minor-element studies in

Part 4 of this report show several minor elements in amounts of more than 0.01 percent. The values for CaO need to be corrected for SrO; MgO needs correction for BaO; $K_2O$ in G–1 needs correction for $Rb_2O$; and finally $Al_2O_3$ in G–1 and W–1 needs correction for $ZrO_2$, $Ce_2O_3$, $La_2O_3$, $Nd_2O_3$, $Sc_2O_3$, $ThO_2$, and $V_2O_5$ found in the minor-element studies.

## ADDITIONAL ANALYSES

After the assembly of the foregoing analyses and the preparation of the manuscript, Riley (1958) published new analyses of G–1 and W–1 by a rapid procedure somewhat more elaborate than that of Shapiro and Brannock (1952, 1956), and Riley and Williams (1959b) published new analyses by microchemical procedures. These analyses are reproduced for comparison in the following table. They show generally good agreement with the statistical selection of values in tables 9 and 10, and the percentages of $SiO_2$ reported approach closely those of Stevens and Chodos (in part 2) of this report.

*Recent analyses of G–1 and W–1*

| | Rapid analyses [1] | | Microchemical analyses [2] | |
|---|---|---|---|---|
| | G–1 | W–1 | G–1 | W–1 |
| $SiO_2$ | 72.6 | 52.7 | 72.7 | 52.6 |
| $Al_2O_3$ | 14.1 | 15.1 | 14.00 | 14.95 |
| $Fe_2O_3$ | .87 | 1.56 | .86 | 1.48 |
| FeO | .93 | 8.65 | .93 | 8.74 |
| MgO | .40 | 6.7 | .43 | 6.42 |
| CaO | 1.4 | 10.8 | 1.35 | 10.75 |
| $Na_2O$ | 3.4 | 2.2 | 3.30 | 2.20 |
| $K_2O$ | 5.5 | .67 | 5.50 | .69 |
| $H_2O^+$ | .34 | .60 | .30 | .50 |
| $TiO_2$ | .24 | 1.05 | .23 | 1.10 |
| $P_2O_5$ | .08 | .13 | .069 | .125 |
| MnO | .029 | .17 | .025 | .16 |
| Total | 99.89 | 100.33 | 99.70 | 99.72 |

[1] By Riley (1958). Mean of 6 analyses.
[2] By Riley and Williams (1959b). Mean of 3 complete and 2 partial analyses.

Additional determinations received include the following:

P. G. Jeffery and A. D. Wilson, Geological Survey of Great Britain (written communication, 1959)[2] obtained 72.60 and 72.66 percent $SiO_2$ in G–1 and 52.63 and 52.67 percent $SiO_2$ in W–1 by a gravimetric procedure and photometric determination (molybdenum blue method) of the silica lost into the filtrate.

J. P. Riley and H. P. Williams (Riley and Williams, 1959a) reported 0.93 percent FeO in G–1 (average of 4 determinations) and 8.74

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[2] To be published in Geochimica at Cosmochimica Acta.

percent FeO in W–1 (average of 6 determinations) by a photometric method using 2, 2′ dipyridyl. They also reported 0.27 percent $H_2O$ and 0.1 percent $CO_2$ in G–1 and 0.50 percent $H_2O$ and 0.1 percent $CO_2$ in W–1.

Shapiro (1959), U.S. Geological Survey, Washington, D. C. reported 0.33, 0.36, and 0.38 percent MgO in G–1 by a photometric method using thiazole yellow.

D. J. O'Leary, Geological Survey Division, Northern Nigeria (written communication, 1959) obtained $Na_2O$ 3.39, $K_2O$ 5.54 percent in G–1; $Na_2O$ 2.30, $K_2O$ 0.64 percent in W–1, by a flame photometer procedure.[3]

## CONCLUDING REMARKS

It seems obvious that conclusions to be drawn from the many analyses of G–1 and W–1 must still be considered tentative. Fairbairn (1953) is no doubt right in saying that "* * * the correct analysis can never be known * * *." However, acceptance of values for the composition of G–1 and W–1, as for essentially all scientific data, is not on absolute knowledge but merely on convincing evidence. This convincing evidence will be the further assembling of data on G–1 and W–1 from chemists whose competence is unquestioned. In adopting arbitrary limits of acceptability, the only correct value may have been discarded. Acceptance of the most popular values is justified only on the faith that most rock analysts properly use well proven principles and methods[3].

This study of analyses of G–1 and W–1 has indicated that results by many rock analysts are dependable and that methods of rock analysis are reliable if they are carefully and properly applied. As a consequence, the studies serve as a warning to students of earth science that results of rock analysis must always be regarded as measurements whose reliability depends upon the abilities of the chemist making the analysis. Major accomplishments of the investigations of G–1 and W–1 have been in showing the individual analyst how his results compare with those of other analysts, in which determinations he may be making errors repeatedly through misapplication of procedures or through carelessness, and in what respects the procedures he is following may be defective. The studies may also serve to make some rock analysts more aware of many new techniques which make rock analyses rapid and reliable.

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[3] Collins, Diehl, and Smith (1959, Anal. Chemistry, v. 31, p. 1862) found total iron as $Fe_2O_3$ by a colorimetric method with 2, 4, 6-tripyridyl-s-triazine to be 1.85, 1.85, 1.84, 1.85, average 1.85 percent in G–1; 10.91, 10.94, 10.87, average 10.91 percent in W–1.

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# SECOND REPORT ON A COOPERATIVE INVESTIGATION OF THE COMPOSITION OF TWO SILICATE ROCKS

## PART 2. SPECIAL STUDY OF THE SILICA CONTENT OF G–1 AND W–1 BY COMBINED WET CHEMICAL AND SPECTROGRAPHIC METHODS

By ROLLIN E. STEVENS [4] and ARTHUR A. CHODOS [5]

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### ABSTRACT

Values of 72.70 and 52.77 percent $SiO_2$ for G–1 and W–1 (moisture free), respectively, were obtained by collecting and weighing the silica and by determining spectrographically and with wet chemical methods the corrections that were needed, owing to impurities in the separated silica, losses of silica in the chemical processes, and gains of silica from reagents and filter paper. Possible errors in the determinations were thus measured and tallied. These results are two- to three-tenths percent higher than the consensus mean of analyses made in the usual way and add to the evidence that complete recovery of silica is not usually attained in routine analytical procedures for silica in general use.

### INTRODUCTION

The many analyses of G–1 and W–1 have left the content of silica in the two rocks particularly in doubt, with results varying from less

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[4] U.S. Geological Survey.

[5] California Institute of Technology and U.S. Geological Survey.

than 71 percent to more than 73 percent $SiO_2$ for G–1 and with similar wide divergence of results for W–1.

Fairbairn and Schairer (1952) demonstrated that routine results for silica are generally low by submitting a synthetic granite glass (haplogranite), of known composition, to a number of cooperating laboratories. Because of the low results on this test, Fairbairn (1953) adds 0.5 percent to the mean of results for silica in G–1 to obtain his preferred estimate of 72.86 percent and 0.35 to the mean for silica in W–1 to obtain his preferred estimate of 52.69 percent, both estimates on a moisture free sample.

Recognition of this tendency toward low results for silica should cause re-examination of the routine methods for determining silica in many laboratories and changes in the procedures to assure that all the silica is collected in the analysis. This is an important step in the improvement of rock analysis in general as it affects not only the results for silica but also those for other constituents, especially alumina.

Two previously published analyses of G–1 and W–1, which may be assumed to have been done with particular care, also indicate that results for silica are usually low, although these analyses show a lower content of silica than the calculated preferred estimates of Fairbairn (1953). Goldich and Oslund (1956) give an average of 72.48 percent $SiO_2$ for G–1 (72.51 calculated to a moisture free sample) and 52.55 percent for W–1 (52.62 for moisture free sample). Waters and Coombs (see Guppy and Sabine, 1956), of the Geological Survey of Great Britain, give corresponding values of 72.45 (72.47 for a moisture free sample) and 52.43 (52.51 for a moisture free sample).

It seems apparent that in many routine analyses all the silica is not being collected. This is probably due to failure to evaporate the hydrochloric acid solution of the sample to complete dryness in order to make all or most of the silica insoluble. A part of this uncollected silica may be found in the ammonia group to follow, and it may contaminate the calcium and magnesium precipitates or be lost in the filtrate discarded at the end of the analysis.

New determinations of silica in G–1 and W–1 were undertaken, in which corrections needed owing to impurities in the weighed silica were made, and gains and losses of silica were measured. Most of these corrections were determined spectrographically, but when the corrections were appreciable photometric methods were used.

## GENERAL DESCRIPTION OF THE METHOD

The plan of the analyses for silica was to make two evaporations of the acid sample solution in the usual manner, to bake the salt residue from the second evaporation at 105° C, to determine the impurities in the weighed silica spectrographically and chemically and to correct for them, to determine spectrographically and to correct for the silica that was not separated but was left in the filtrate, and to determine spectrographically and to correct for silica added in distilled water, reagents, and filter paper (a blank determination run at the same time in the same way). All silica in the samples, losses of silica in the chemical separations, and additions of silica were thus measured and tallied. It was felt that in this way the bias in the determination of silica was removed and the results measured its true content, variations in results being caused by unbiased limitations in accuracy of measurements or nonuniformity of the samples.

Vessels and other equipment free of silica (such as those of platinum or polyethylene) were used throughout the chemical separations, as noted in the detailed description of the procedure below, in order to avoid contamination by silica.

The separates submitted for spectrographic and chemical analysis were given random numbers to hide their identity in order to remove any possible subjectivity in their analysis.

Determinations in duplicate were begun on the contents of four bottles of each rock, G–1 and W–1. One of the portions taken for each rock, portion 1B of G–1 and portion 3A of W–1, were abandoned because losses were known to have occurred in the chemical separations. The portions taken for G–1, together with the blank and quartz control, were run at one time, followed by a similar run on W–1. The blanks precisely duplicated the analysis of the rocks in treatment and in quantities of distilled water, other reagents, and filter papers used. Quartz controls (the quartz was a spectrographic standard, purity 99.99 percent, obtained from A. T. Myers) were run at the same time to indicate the accuracy of the work and to give assurance that water and other volatiles had been removed by the ignition of the silica obtained from the different portions.

The moisture content was first carefully determined on each portion by drying at 105° C so the effect of variations in moisture on values for $SiO_2$ could be taken into account.

## PROCEDURE

### CHEMICAL SEPARATIONS

The contents of each bottle of G–1 and W–1 were first made homogeneous by pouring the rock powder onto a large piece of glazed paper and rolling back and forth in opposite directions alternately 50 times. The rock powder was then scraped into a pile with a spatula and small portions from opposite quarters returned to the bottle until all the sample was returned. The bottles were tightly stoppered, and portions later removed for analyses in small increments with a spatula.

Portions weighing about 1 gram were placed in small weighing bottles, which had previously been heated to 105° C overnight, cooled in a desiccator, and weighed. Each weighing bottle with its contents was accurately weighed. The weighing bottle and contents were then heated repeatedly at 105° C for periods of not less than 2 hours and cooled in a desiccator, until constant in weight. $H_2O^-$ was calculated. The contents of the weighing bottle were transferred carefully to a platinum crucible, and the empty weighing bottle was again heated to 105° C for 2 hours, cooled in a desiccator, and weighed. The weight of the portion for $SiO_2$, in the platinum crucible, was calculated.

To the portion of rock powder in the platinum crucible was added 5 grams of powdered sodium carbonate, previously made essentially homogeneous by rolling a large batch of it on a glazed paper as was done for the rock powders. The sodium carbonate was stored in a polyethylene bottle. The contents of the platinum crucible were mixed by stirring with a platinum rod. The crucible and contents were heated over a low Bunsen burner flame until a quiescent melt was obtained, and the fusion continued at full heat of the burner for half an hour.

The contents of the crucible were left overnight in contact with 60 ml of distilled water (a supply for the entire series of analyses was kept in a polyethylene bottle) in a platinum dish with a polyethylene cover. In the morning 15 ml of concentrated hydrochloric acid (supply kept in polyethylene) was cautiously added. The contents of the dish were evaporated to dryness on the steam bath, with the polyethylene cover held up slightly with a small strip of polyethylene to promote evaporation yet prevent entry of dust. To the dry salts 10 ml of concentrated HCl was added, then 50 ml of distilled water; the dish was left covered on the steam bath until solution of the soluble salts was complete. The solution was then filtered through fine filter paper in a polyethylene funnel, and the filtrate was collected in a polyethylene beaker. The $SiO_2$ on the filter paper was washed 20 times with hot (1 percent) HCl.

The $SiO_2$ and paper were transferred to the platinum crucible, which had been thoroughly cleaned by repeated ignitions and fusions with sodium bisulfate. The filtrate from the first evaporation for silica was transferred to the platinum dish, again evaporated to dryness on the steam bath with the polyethylene cover over the dish, and finally baked (covered with a clean glass cover) at 105°C in an oven for 2 hours. The small quantity of $SiO_2$ obtained in the second evaporation was freed of soluble salts as before, and filtered onto a small filter paper in a polyethylene funnel, washing first with cold (1 percent) HCl and finally with distilled water. The collected silica was ignited in the platinum crucible, at first slowly over a low Bunsen flame and finally increasing the flame until the silica was white. It was then repeatedly ignited in a muffle at 1,000° C until constant in weight. The silica was then transferred to a clean agate mortar, any remaining in the crucible volatilized with HF, the crucible ignited briefly at 1,000° C, and weighed.

The silica in the mortar was then ground thoroughly to make it homogeneous and transferred to a polystyrene vial with a tight fitting cover. The vial was given a random number to hide its identity and submitted for spectrographic analysis of its contents.

The filtrate from the silica was evaporated to dryness and baked as before, the platinum dish and contents weighed on a rough balance, the residue ground in the dish with a boron carbide pestle to make it homogeneous, the powder transferred to a polystyrene vial, remaining residue in the platinum dish washed out with water and discarded, and the dish dried and weighed. The weight of the residue was calculated by difference. The residues in the polystyrene vials were given random numbers to hide their identity, and submitted for spectrographic determination of $SiO_2$. Residues (blanks), obtained by carrying out all steps in the procedure on reagents and filter papers, were similarly collected and submitted for spectrographic determination of $SiO_2$.

## ANALYSES OF THE SEPARATES

The spectrographic analysis of the silica precipitates and residues involved several different techniques. For the quantitative analysis for impurities in the silica precipitates, a standard was prepared which contained Al, Ca, Fe, K, Mg, Na, Nb, Pt, Ti, and Zr in a base of pure quartz. For other elements in trace quantities, existing standards for rock analysis were used. All standards were made of materials known to be pure by extensive spectrographic examinations. A separate exposure was made for phosphorus, using conditions of maximum sensitivity (0.02 percent). For the analysis of the residues for silica, a standard was prepared which contained quartz in a base of pure sodium chloride, approximating the composition of the residues. Standards and samples were always exposed on the same spectrographic plates to minimize variations from plate to plate.

Equipment and conditions of the spectrographic examinations are as follows:

Spectrograph: Jarrell-Ash 3.4-meter grating instrument, Wadsworth mount, with a dispersion of 5.2 A per mm in the first order.

Excitation: 13-ampere d-c arc (short circuit) from Jaco Varisource. Sample as the anode. Central 2 mm of a 4-mm analytical gap were magnified and focussed on the slit.

Slit width: 25 microns.

Sample: sample was diluted with 4 times its weight of spectrographic graphite. 20-mg portions were arced to completion.

Electrodes: high-purity ¼-inch graphite rod as anode. Shape described by Myers (1951). Pointed ⅛-inch cathode.

Wavelength range: 2,300–4,800 A in the first order for all elements but the alkalies, with 5,700–8,200 A for the alkalies.

Plates: Eastman Kodak III–O for all elements but the alkalies, with 1 L for the alkalies.

Processing: 4 minutes in DK–50 developer at 20°C, 20 seconds short stop, 10 minutes acid fix, and 20 minutes wash.

Plate calibration: selected iron lines by method of Dieke and Crosswhite (1943). Each plate calibrated.

Densitometer: ARL model 2250 and Jaco model 2100.

## VALUES FOR IMPURITIES IN THE SILICA AND FOR SILICA IN FILTRATES AND BLANKS

Table 9 shows the impurities found in the weighed silica, which would have been left in the residue after the treatment with hydrofluoric acid and a little sulfuric acid in the usual course of a rock analysis. The elements found and determined are considered to be present as the compounds listed.

The composition of the residue from silica in rock analysis is discussed by Hillebrand and others (1953) and Washington (1930), and has been investigated by Rankama (1939), who cites a number of such investigations.

The results for impurities in the silica in table 9 apply specifically to the rocks G–1 and W–1 and to the heat treatment used to render the silica insoluble. They apply only indirectly to the composition of the residue in the silica for rock analysis in general. Elements retained by the silica would depend not only on the composition of the rock being analyzed but also on the temperature used to dehydrate the silica. In the experiments of Rankama (1939) the temperature of the steam bath was used. Higher temperature results in more titania being retained in the silica; possibly other elements may also remain undissolved.

TABLE 9.—*Determinations of impurities in the weighed silica and of silica in filtrates and blanks*

[Looked for but not found in weighed $SiO_2$: As, Au, Be, Bi, Cd, Co, Ga, Ge, In, La, Mo, Pb, Sb, Sr, Ta, Tb, Tl, U, V, W, Y, Yb, Zn. $SiO_2$ for G-1 and W-1 was not corrected for $P_2O_5$. Less than 0.02 percent P was found making for an uncertainty in the $SiO_2$ values of no greater than 0.03 percent from this source]

| | G-1 | | | | | | | Quartz control | Blank | W-1 | | | | | | | Quartz control | Blank |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1A | 2A | 2B | 3A | 3B | 4A | 4B | | | 1A | 1B | 2A | 2B | 3B | 4A | 4B | | |
| Ag | 0.0001 | 0.0003 | 0.0001 | 0.0003 | 0.0003 | 0.0001 | 0.0003 | -------- | -------- | 0.0006 | 0.0003 | 0.0006 | 0.0006 | 0.0006 | 0.0006 | 0.0003 | -------- | -------- |
| $Al_2O_3$ | .011 | .017 | .015 | .015 | .016 | .017 | .038 | 0.0094 | -------- | .019 | .017 | .013 | .013 | .019 | .028 | .017 | 0.0038 | -------- |
| $BaSO_4$ | .0003 | .0008 | .0003 | .0003 | .0003 | .0003 | .0008 | .0003 | -------- | .0006 | .0003 | .0003 | .0003 | .0003 | .0003 | .0003 | .0003 | -------- |
| $B_2O_3$ | .0032 | .0032 | .0032 | .0032 | .0032 | .0032 | .0032 | .0032 | -------- | .010 | .010 | .0064 | .0032 | .0097 | .0032 | .0032 | .0032 | -------- |
| CaO | -------- | .014 | -------- | .028 | .048 | .028 | -------- | -------- | -------- | .070 | .028 | .042 | -------- | -------- | -------- | .112 | -------- | -------- |
| $Cr_2O_3$ | .0001 | .0001 | -------- | -------- | -------- | -------- | .0001 | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- |
| CuO | .0003 | .0001 | .0004 | .0001 | .0004 | .0001 | .0003 | .0006 | -------- | .0010 | .0010 | .0010 | .0010 | .0013 | .0013 | .0013 | .0004 | -------- |
| $Fe_2O_3$ | -------- | -------- | -------- | -------- | .028 | -------- | -------- | -------- | -------- | .021 | .014 | .028 | .0057 | .0071 | .014 | .0114 | -------- | -------- |
| KCl | -------- | -------- | -------- | -------- | -------- | -------- | .029 | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- |
| MgO | .0083 | .0083 | .0083 | .013 | .015 | .0099 | .0083 | -------- | -------- | .100 | .083 | .066 | .0099 | .0116 | .017 | .050 | -------- | -------- |
| MnO | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | .0006 | -------- | .0006 | -------- | -------- | -------- | .0007 | -------- | -------- |
| NaCl | .056 | .018 | .046 | .022 | .018 | .028 | .092 | .079 | -------- | .038 | .041 | .018 | .021 | .018 | .028 | .014 | .014 | -------- |
| $Nb_2O_5$ | .0071 | .0100 | .0086 | .0057 | .0071 | .0071 | .0071 | -------- | -------- | .0029 | .0029 | .0029 | .0014 | .0043 | .0129 | .0029 | -------- | -------- |
| NiO | .0003 | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | .0001 | .0001 | .0003 | .0003 | .0003 | .0003 | .0003 | .0001 | -------- |
| Pt | .0100 | .0100 | .0100 | .0020 | .0050 | .0050 | .020 | .0050 | -------- | .015 | .020 | .0078 | .020 | .015 | .020 | .0080 | .0020 | -------- |
| $SnO_2$ | -------- | -------- | -------- | .0090 | .0115 | -------- | -------- | -------- | -------- | -------- | .0013 | -------- | -------- | -------- | .0025 | -------- | -------- | -------- |
| $ZrO_2$ | .027 | .027 | .034 | .034 | .034 | .034 | .034 | -------- | -------- | .027 | .020 | .020 | .020 | .020 | .020 | .020 | -------- | -------- |
| $TiO_2$ | .050 | .050 | .067 | .058 | .100 | .100 | .067 | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | (.0003) | -------- |
| $TiO_2$, photometric | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | .97 | 1.08 | 1.52 | 1.02 | .74 | 1.25 | 1.11 | .080 | -------- |
| Total impurities percent | 0.17 | 0.16 | 0.19 | 0.19 | 0.29 | 0.23 | 0.30 | 0.093 | -------- | 1.28 | 1.32 | 1.73 | 1.12 | 0.85 | 1.40 | 1.35 | 0.10 | -------- |
| Weight of $SiO_2$+impurities | .7389 | .7494 | .7321 | .7289 | .7296 | .7327 | .7297 | 1.0006 | -------- | .5362 | .5376 | .5429 | .5495 | .5338 | .5349 | .5389 | 1.0081 | -------- |
| Weight of impurities | .0013 | .0012 | .0014 | .0014 | .0021 | .0017 | .0022 | .0009 | -------- | .0068 | .0071 | .0094 | .0061 | .0045 | .0075 | .0073 | .0010 | -------- |
| Weight of residue in filtrate | 6.4 | 6.4 | 6.35 | 6.65 | 6.8 | 6.35 | 6.4 | 5.8 | 5.7 | 6.9 | 6.9 | 7.0 | 6.9 | 6.8 | 6.8 | 6.9 | 5.6 | 5.6 |
| $SiO_2$ in residue in filtrate ---- percent | .0016 | .0016 | .0022 | .0024 | .0014 | .0014 | .0018 | .0024 | .0012 | .0018 | .0024 | .0022 | .0021 | .0018 | .0040 | .0027 | .0040 | .0018 |
| Weight $SiO_2$ in residue in filtrate | .0001 | .0001 | .0001 | .0002 | .0001 | .0001 | .0001 | .0001 | .00007 | .0001 | .0002 | .0002 | .0001 | .0001 | .0003 | .0002 | .0002 | .0001 |
| Weight $SiO_2$ in blank | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | .0001 | -------- | -------- | -------- | -------- | -------- | -------- | -------- | -------- | .0001 |

It seems apparent from table 9 that errors in the value for $Al_2O_3$ would be made by assuming that only elements normally in the ammonia group are present in the residue left after treatment of the silica with hydrofluoric acid, and by simply adding this residue to the precipitate obtained with ammonium hydroxide. It is a safer but somewhat lengthier procedure to fuse the residue with bisulfate, dissolve it, and add it to the solution before the precipitation with ammonium hydroxide. The silica contains not only elements of the ammonia group seldom if ever determined in a rock, but also others not considered part of that group. A weighable quantity of sodium chloride, too small to be readily measured by wet chemical methods, was retained by the silica in spite of thorough washing. In the silica of portion 4B there is a weighable quantity of potassium, apparently from incomplete decomposition of the sample. In these experiments unusual constituents in the silica would have caused errors of several tenths of a percent if added to the figure for $Al_2O_3$ as is usually done. In the usual procedure the residue is ignited after treatment with excess sulfuric acid; chlorides are thus converted to sulfates, and boron and phosphorus volatilize.

Phosphorus is mentioned by Hillebrand and others (1953) as being a frequent contaminant of the separated silica. However, special determinations of phosphorus by a spectrographic method sensitive to 0.02 percent did not reveal its presence, showing that the phosphorus content of the silica was less than this figure. The correction for $P_2O$, therefore, would be less than 0.03 percent in the value reported for $SiO_2$, as noted at the bottom of table 9. General agreement of the results for W–1 with those obtained by weighing the residue after hydrofluoric acid treatment also indicates that the phosphorus content of the silica is negligible.

To correct the weight of the silica for impurities found spectrographically and chemically, the impurities shown in table 9 are added and their total weight calculated. Table 9 also shows the spectrographic results for silica in filtrates and blanks and the calculation of their weights. The quantity of silica found in the filtrates was surprisingly low (generally 1 to 3 mg of $SiO_2$ is found in the $R_2O_3$), but these low values were confirmed by repeated examinations. Apparently the low values for silica in the filtrates are due to thorough dehydration of the acid evaporates.

Table 9 contains information on the content of $Nb_2O_5$ and $ZrO_2$ in G–1 and W–1, because these constituents would probably be almost completely retained in the separated $SiO_2$. If the percentages of $Nb_2O_5$ and of $ZrO_2$ found in the separated $SiO_2$ are recalculated to percentages of the original samples of the rocks, values of 0.005 percent $Nb_2O_5$ in G–1 and 0.002 percent $Nb_2O_5$ in W–1, 0.02 percent

$ZrO_2$ in G–1 and 0.01 percent $ZrO_2$ in W–1 are obtained, values in fair agreement with the minor-element studies elsewhere in this bulletin.

## RESULTS OF DETERMINATIONS OF SILICA IN G–1 AND W–1

The results of the determinations of $H_2O^-$ and of $SiO_2$ are assembled in table 10. The table also includes detailed data of sample weight, moisture content, and determined corrections for calculating the silica content. For G–1, results ranged from 0.06 to 0.07 percent $H_2O^-$, values which agree closely with the arithmetic means in table 3 of part 1 and which were precisely confirmed by other determinations on samples weighing as much as 3 grams. The values for $H_2O^-$ in W–1 in table 10 range from 0.22 to 0.26 percent. These were precisely confirmed by determinations on samples with a maximum weight of 5 grams. They are appreciably higher than the arithmetic means reported in table 3 of part 1 and indicate the desirability of reporting most rock analyses on an oven-dried sample as a general practice, as moisture content would vary with the weather.

The percentages of $SiO_2$ in table 10 were calculated by adding the weight of the unrecovered silica in the filtrate to the weight of collected silica and subtracting the weights of impurities in the silica and of the silica added as reagents, water, and filter papers (blanks).

For G–1, the values ranged from 72.58 to 72.82 percent $SiO_2$, calculated to a moisture-free sample, averaging 72.70; those for W–1 ranged from 52.70 to 52.82 percent $SiO_2$, averaging 52.77 percent. For G–1, the corrections on the weight of the silica were small, affecting the value for percentage of silica by only 0.1 to 0.2 percent, so that confidence could be placed in the sum of the corrections found spectrographically (the error in the value for $SiO_2$ would be the square root of the sum of the squares of errors in all determinations). For W–1, the corrections were as much as nearly 1 percent of the sample, because of retention of titania in the separated silica. For these the titania in the silica was determined photometrically, and the results for silica were confirmed by weighing the residue after treatment of the silica with HF and a little $H_2SO_4$ in the usual way. Checking the results by weighing the residue after HF also confirms the spectrographic results that show no appreciable percentage of $P_2O_5$ in the silica, as some phosphorus would be lost in the final ignition of the residue in the presence of sulfuric acid. The usual procedure of determining the residue in the silica by treating the silica with hydrofluoric acid is more precise but less informative (precision was lost because only 0.2 gram of the silica, reignited to constant weight, was used). Finally, the essentially theoretical values on the quartz controls of

TABLE 10.—*Determinations of* $SiO_2$ *in G–1 and W–1*

| | G–1 in bottle No. and portion as indicated | | | | | | | Quartz control | Blank | W–1, in bottle No. and portion as indicated | | | | | | | Quartz control | Blank |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | | 3 | | 4 | | | | 1 | | 2 | | 3 | 4 | | | |
| | A | A | B | A | B | A | B | | | A | B | A | B | B | A | B | | |
| Weight portion at room temperature | 1.0170 | 1.0282 | 1.0074 | 1.0008 | 1.0007 | 1.0058 | 1.0016 | 1.0009 | -------- | 1.0070 | 1.0087 | 1.0118 | 1.0328 | 1.0048 | 1.0030 | 1.0092 | 1.0074 | -------- |
| Weight after drying at 105° C | 1.0163 | 1.0275 | 1.0068 | 1.0002 | 1.0000 | 1.0052 | 1.0009 | 1.0008 | -------- | 1.0045 | 1.0061 | 1.0094 | 1.0306 | 1.0025 | 1.0006 | 1.0068 | 1.0073 | -------- |
| $H_2O$ (percent) 105° C | .07 | .07 | .06 | .06 | .07 | .06 | .07 | .01 | -------- | .25 | .26 | .24 | .22 | .23 | .24 | .25 | .01 | -------- |
| Weight $SiO_2$: | | | | | | | | | | | | | | | | | | |
| Impure | .7389 | .7494 | .7321 | .7289 | .7296 | .7327 | .7297 | 1.0006 | -------- | .5362 | .5376 | .5429 | .5494 | .5338 | .5349 | .5389 | 1.0081 | -------- |
| Plus correction for $SiO_2$ filtrate | .0001 | .0001 | .0001 | .0002 | .0001 | .0001 | .0001 | .0001 | -------- | .0001 | .0002 | .0002 | .0001 | .0001 | .0003 | .0002 | .0002 | -------- |
| Minus corrections for impurities in $SiO_2$ | .0013 | .0012 | .0014 | .0014 | .0021 | .0017 | .0022 | .0009 | -------- | .0068 | .0071 | .0094 | .0061 | .0045 | .0075 | .0073 | .0010 | -------- |
| Minus correction for $SiO_2$ in blank | .0001 | .0001 | .0001 | .0001 | .0001 | .0001 | .0001 | .0001 | 0.0001 | .0001 | .0001 | .0001 | .0001 | .0001 | .0001 | .0001 | .0001 | 0.0001 |
| Corrected weight $SiO_2$ | .7376 | .7482 | .7307 | .7276 | .7275 | .7310 | .7275 | .9997 | -------- | .5294 | .5306 | .5336 | .5433 | .5293 | .5276 | .5317 | 1.0072 | -------- |
| $SiO_2$ percent as received | 72.53 | 72.77 | 72.53 | 72.70 | 72.70 | 72.68 | 72.63 | -------- | -------- | 52.57 | 52.60 | 52.74 | 52.60 | 52.68 | 52.60 | 52.69 | -------- | -------- |
| Average $SiO_2$ percent as received | -------- | -------- | -------- | 72.65 | | -------- | -------- | -------- | -------- | -------- | -------- | -------- | 52.64 | | -------- | -------- | -------- | |
| $SiO_2$ percent, dry basis | 72.58 | 72.82 | 72.58 | 72.75 | 72.75 | 72.72 | 72.68 | 99.89 | -------- | 52.70 | 52.74 | 52.86 | 52.72 | 52.80 | 52.73 | 52.81 | 99.99 | -------- |
| Average $SiO_2$ percent for each bottle, dry basis | 72.58 | 72.70 | | 72.75 | | 72.70 | | -------- | -------- | 52.72 | | 52.79 | | 52.80 | 52.77 | | -------- | |
| Average $SiO_2$ percent for each rock, dry basis | -------- | -------- | | 72.70 | | -------- | | -------- | -------- | -------- | -------- | -------- | 52.77 | | -------- | -------- | -------- | -------- |
| Standard deviation | -------- | -------- | | .090 | | -------- | | -------- | -------- | -------- | -------- | -------- | -------- | .058 | -------- | -------- | -------- | -------- |
| Check of results by residue after HF: | | | | | | | | | | | | | | | | | | |
| Weight $SiO_2$, corrected for $SiO_2$ in residue and blank | | | | | | | | | | 0.5362 | 0.5377 | 0.5430 | 0.5494 | 0.5338 | 0.5351 | 0.5390 | -------- | -------- |
| Weight residue after HF | | | | | | | | | | .0062 | .0065 | .0095 | .0054 | .0042 | .0071 | .0079 | -------- | -------- |
| Corrected weight $SiO_2$ | | | | | | | | | | .5300 | .5312 | .5335 | .5440 | .5296 | .5280 | .5311 | -------- | -------- |
| $SiO_2$ percent, as received | | | | | | | | | | 52.63 | 52.59 | 52.73 | 52.67 | 52.71 | 52.64 | 52.63 | -------- | -------- |
| $SiO_2$ percent, dry basis | | | | | | | | | | 52.76 | 52.72 | 52.85 | 52.79 | 52.83 | 52.77 | 52.75 | -------- | -------- |
| Average $SiO_2$ percent, dry basis | | | | | | | | | | | | | 52.78 | | -------- | -------- | -------- | -------- |

table 10 (99.89 and 99.99 percent $SiO_2$), made at the same time as determinations on G–1 and W–1, show that volatile constituents, such as water and carbon dioxide, were not weighed with the separated silica.

These determinations seem to be sufficient in number and precision to establish the value for silica in G–1 and W–1 within about a tenth of a percent. The results were disappointing because better precision was not shown. This lack of precision may be considered the result of the accumulation of errors in the measurements, although some variation is to be expected from bottle to bottle of the samples and from segregation within a bottle (for example, mica flakes tend to float to the top of ground samples). In order that the determinations be accurate, essentially all known errors in the determinations have been considered, measured individually for each determination, and corrections made. Proof is not given that errors consistently positive or negative, which would bias the results, have not been made, although these are believed to be of small magnitude.

## COMPARISON OF RESULTS WITH OTHER REPORTED VALUES

The arithmetic means of the values here reported for silica in G–1 and W–1 are compared with other determinations and calculated estimates in the following table. The arithmetic means of values for silica reported in U.S. Geological Survey Bulletin 980, by Fairbairn and others (1951) are low (72.28 percent for G–1 and 52.41 percent for W–1). The consensus means of Dennen, Ahrens, and Fairbairn, based upon selection of values in Bulletin 980 close to the mode, are about 0.2 percent higher (72.49 and 52.58). Fairbairn's (1953) preferred estimates, in which 0.5 percent is added to the mean of results for $SiO_2$ in G–1 and 0.35 percent for that in W–1, are 72.86 percent for G–1 and 52.69 percent for W–1. The use of a smaller correction for W–1 (lower silica content) is contrary to the chemical principles involved in the determination, as the correction is one for solubility of the silica and would be essentially the same over a wide range of silica content. Fairbairn's preferred estimates become 72.86 and 52.84 percent for G–1 and W–1, respectively, if the same correction of 0.5 percent is applied to both rocks. The new analyses reported in part 1 of this report indicate a silica content for G–1 near 72.5 percent and for W–1 near 52.6 percent, values in fair agreement with the published analyses of Goldich and Oslund (1956) and of Waters and Coombs (see Guppy and Sabine, 1956). The values of 72.70 and 52.77 percent, obtained in the present study, indicate that the new analyses in part 1 may still reflect, to a small extent, the tendency for routine determinations of silica to be low.

*Comparison of results with other reported values*

All previously reported values are recalculated to a moisture-free sample using the value for $H_2O^-$ in the report]

| | Percent $SiO_2$ | |
|---|---|---|
| | G-1 | W-1 |
| Stevens and Chodos, arithmetic mean, this report | 72.70 | 52.77 |
| Calculated from analyses in U.S. Geological Survey Bulletin 980: | | |
| Arithmetic mean | 72.28 | 52.41 |
| Consensus mean of Dennen, Ahrens, and Fairbairn | 72.49 | 52.58 |
| Fairbairn's (1953) preferred estimate | 72.86 | 52.69 |
| Calculated from new analyses in part 1 of this report (analyses 35 omitted): | | |
| Arithmetic mean | 72.54 | 52.54 |
| Arithmetic mean of preferred values | 72.53 | 52.60 |
| Calculated from all analyses (analyses 35 and values of Stevens and Chodos omitted): | | |
| Arithmetic mean | 72.39 | 52.48 |
| Arithmetic mean of preferred values | 72.45 | 52.54 |
| Goldich and Oslund (1956) | 72.51 | 52.62 |
| Waters and Coombs (see Guppy and Sabine, 1956) | 72.47 | 52.51 |

## CONCLUSIONS

This study is an addition to the evidence of incomplete recovery of silica in routine rock analysis. Failure to adequately dehydrate the silica seems to be the cause of the low recoveries.

The values for silica reported here illustrate the danger of accepting without question as true values estimates based on arithmetic means, consensus means, or on elimination of results differing widely from the arithmetic mean. The values obtained here would fall outside the limits, $\bar{x}\pm S$, adopted as limits of acceptability in part 1. Bias in results for $Al_2O_3$, $Fe_2O_3$, and $K_2O$ have also been indicated in Part 1. The arithmetic mean for these and other constituents must be accepted with caution and results further studied.

A major objective of these investigations on G–1 and W–1 has been the evaluation of present practices in the analysis of silicate rocks. This study has contributed to the evaluation of the silica procedures in present use and to an understanding of how improvements can be made.

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# SECOND REPORT ON A COOPERATIVE INVESTIGATION OF THE COMPOSITION OF TWO SILICATE ROCKS

## PART 3. SPECTROGRAPHIC DETERMINATIONS OF THE MAJOR CONSTITUENTS OF GRANITE G-1 AND DIABASE W-1 [6]

By ROYSTON H. FILBY and R. K. LEININGER [7]

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### ABSTRACT

The advantages of spectrochemical methods of silicate analysis include rapidity, reasonable precision, use of small sample, and determination of several elements in one operation. Although systematic errors exist, such as those due to matrix

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[7] Indiana Department of Conservation, Geological Survey.

and self-absorption effects and those caused by use of synthetic or otherwise known standard samples, the methods can provide determinations that are adequately accurate for many purposes.

All available spectrographic determinations of the major constituents of G–1 and W–1 were studied to permit a comparison of the precision of analytical chemical and spectrographic methods. Examination of the spectrographic methods used by contributors shows frequent use of the direct-current arc with an air jet, and of a sample buffered with $Li_2CO_3$ or $SrCO_3$. The comparison of measures of precision reveals that spectrographic methods are as precise (and therefore probably as accurate) as chemical methods for several constituents. Fairbairn's correction for the bias in the chemical results for $SiO_2$ and $Al_2O_3$ is concluded to be too large in magnitude for $SiO_2$ and $Al_2O_3$ in G–1 and for $Al_2O_3$ in W–1.

A table of recommended values for the major constituents of the two reference samples may be summarized as follows (in the order, G–1, W–1): $SiO_2$, 72.65, 52.64; $Al_2O_3$, 14.23, 15.00; total iron as $Fe_2O_3$, 1.96, 11.10; MgO, 0.39, 6.61; CaO, 1.36, 10.94; $Na_2O$, 3.32, 2.07; $K_2O$, 5.43, 0.64; $TiO_2$, 0.24, 1.08; MnO, 0.027, 0.18. The $Al_2O_3$, CaO, MgO, and $K_2O$ values were corrected for trace elements which interfere with normal chemical determinations, for example, $K_2O$ has been corrected for $Rb_2O$.

Examination of the available spectrometric determinations shows the high precision and accuracy that may be obtained by the use of synthetic standards and direct-reading methods.

## INTRODUCTION

Granite sample G–1 and diabase sample W–1 have provided analysts with natural igneous materials for which the chemical composition is known more accurately than for any previously available samples. Spectrochemists, who must use relative methods that involve calibration, need accurate standards as the basis of their quantitative methods. Because of matrix effects in spectrochemical methods, standards similar in composition to the unknown material are required. This statement appears to be true even for methods that utilize large dilutions of the sample. Refinements, such as use of the Stallwood air jet (Stallwood, 1954), also have failed to eliminate matrix effects completely. Of course, complete elimination of the effects is impossible, but more successful methods than those now available should be possible.

The advantages of spectrochemical methods are now well known. They include rapidity, low cost, reasonable precision (reproducibility) and accuracy (closeness of approach to true value), use of small sample, and permanent record. In view of the difficulty of obtaining representative samples of geologic materials, spectrochemical procedures can provide information on the variability of a material and data for the estimation of average composition for the same expenditure as a single chemical analysis of a composite sample.

Generally speaking, spectrochemical methods are at a disadvantage to chemical methods for the determination of major constituents of a material because chemical methods tend to give relatively constant absolute error as concentration varies. Thus, the relative error decreases with concentration. Conversely, spectrographic methods tend to give constant relative errors as concentration varies. For low concentrations, spectrochemical methods are usually superior to normal chemical procedures.

The availability and distribution of samples G–1 and W–1 have met in part the need for standards, with regard to both major and minor constituents. These two samples have been subjected to a great deal of analytical examination, but spectrographic data on the major constituents are still limited. This lack of data is due in part to the inadequate supply of primary standards, and thereby to the development of only a few spectrochemical methods for determining major constituents. As stated by Fairbairn and others (1951, p. 1–6), the original purpose of the replicate chemical analyses of G–1 and W–1 was to provide "accurate calibration for spectrochemical work on the major elements."

The purpose of this section is to collect and evaluate the available data obtained by spectrochemical methods and compare them with the chemical data. Flame-photometric data, although possibly construed as spectrochemical, are not considered because of their inclusion in this report with the chemical data. An attempt has been made to estimate the usefulness of spectrographic versus chemical procedures for each major constituent of the rocks.

All known spectrochemical determinations of the major constituents of G–1 and W–1 have been included in this compilation; for example, the data in U.S. Geological Survey Bulletin 980 are repeated and tabulated with the new data. Regrettably, some results may have escaped the authors. An effort has been made to include only those data that were obtained by reference to standards other than G–1 and W–1. Such standards are either chemically analyzed rocks (for example, National Bureau of Standards feldspar, limestone, clay, and miscellaneous rocks) or they are synthetic mixtures of the oxides or other compounds of the rock-forming elements. Any bias of the chemical results will be reflected in the spectrochemical results unless the spectrochemist has preferred synthetic calibration. Normally, synthetic calibration is used less generally for major constituents; for any given spectrochemical analytical problem, the solid phases present in the standards and samples should be the same and of similar abundance, particularly if excitation is to be by an arc discharge. Solution methods, including preparation of glasses from standards and samples, may eliminate the bias due to differences in states of combination of the elements in standards and samples. Because of the attention that samples G–1 and W–1 have received, the results included here are perhaps more accurate than if the samples had been truly unknowns. This supposition is not restricted to determinations of major constituents by spectrochemical means, but probably applies also to determinations, including trace element determinations, by other techniques.

For the purposes of this section of the report, the major constituents are considered to be $SiO_2$, $Al_2O_3$, total iron as $Fe_2O_3$, MnO, MgO, CaO, $Na_2O$, $K_2O$, and $TiO_2$. This arbitrary classification is justified by common usage. For example, BaO is more abundant in G–1 than is MnO, but MnO is generally determined chemically as a constituent, whereas BaO is not. Also, MnO and $TiO_2$ are readily determined spectrographically owing to availability of usable lines of Mn and Ti in the ultraviolet region of the spectrum. This is not so for BaO. If the terms major and trace should be defined, a division such as greater than 0.1 percent for a major constituent and less than 0.1 percent for a trace constituent appears satisfactory.

Precision data are unfortunately lacking for many of the determinations reported. Proper evaluation of precision cannot be made on the data reported here alone, because the precision data are generally based on less than 30 observations. The actual range of determinations for each constituent is not known because some average results are included. However, even with the limited data available, statistical estimates of dispersion can be obtained to indicate probable ranges.

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## SPECTROGRAPHIC METHODS AND THEIR LIMITATIONS

Spectrographic methods of determining minor elements in natural materials are widely employed, but the use of spectrographic techniques for the determination of major elements is still limited. Spectrographic methods have several defects which may reduce precision and accuracy, although for trace elements, loss of precision and accuracy is often unimportant as compared to the high sensitivity and speed of the methods. For major elements, however, the precision (and probably accuracy) of a spectrographic determination is usually lower than that of a chemical determination. Nevertheless, the convenience of spectrographic techniques has led to the development of several general methods for the determination of major elements in silicates. A typical method is that of Hawley and MacDonald (1956). Although the precision of a single chemical determination is higher than that of a single spectrograhic determination, the facility with which replicate spectrographic determinations can be made is a considerable advantage.

In order to understand the problems involved in the spectrographic analysis of a silicate rock, a brief outline of the procedure is presented.

The rock powder is usually mixed with a diluent (commonly carbon, graphite, or a buffer material); the mixture then is loaded into a carbon or graphite electrode and arced, usually by d-c excitation. The light emitted by the excited atoms and ions is dispersed and integrated on a photographic emulsion. Usually, in quantitative work, an internal standard is used which partially corrects for changes in the electrical and photographic parameters during arcing and photographic processing. The internal standard may be either a rare element added to the sample mixture or it may be the buffer element. The relative intensities of the analytical and internal standard lines are measured, and the ratio $I_a/I_s$ (relative intensity analytical line/relative intensity internal standard line) is calculated.

For a series of standards of known composition, the ratio $I_a/I_s$ is plotted against concentration of the element. A plot of the intensity ratio against concentration, on log-log coordinates, is generally a straight line; from the working curve, concentrations of the unknowns may be determined.

Alternatively, the mutual standard method (Dennen and Fowler, 1955; Coulliette, 1943) may be used in which $I_a/I_s$ is plotted against concentration ratio $C_a/C_s$ (concentration of element being determined/concentration of mutual standard element).

Errors which may affect the precision and accuracy of a determination can be grouped into five categories: procedural and instrumental errors, sample inhomogeneity, matrix and interelement effects, errors in standard composition, and self-absorption in analytical and internal standard lines.

Matrix effects are probably the most serious of these errors and the most difficult to assess. The intensity of the light emitted in the arc column is dependent on the temperature of the arc, which in turn is controlled partly by the composition of the arc gas. Generally, the temperature of a direct current arc is determined by the major element with the lowest ionization potential in the arc gas. Changes in the composition of the arc gas depend on the rates of distillation of the components from the sample and components synthesized in the sample and arc column. The matrix effect arises from the different rates of volatilization shown by an element distilling from materials of different chemical composition or crystal structure. These matrix effects can be of large magnitude if the difference between standards and unknowns is great.

Control of the arc temperature may be attained by flooding the arc column with an element of low-ionization potential (usually a group Ia or IIa element). Buffers commonly mixed with the sample are $SrCO_3$ and $Li_2CO_3$; these serve to reduce matrix effects. Matrix effects also can be reduced by use of special techniques; for example, the air jet helps to prevent selective volatilization of the elements from the sample. Often, synthetic standards, which are similar in chemical composition to the unknowns, are prepared. However, in a synthetic standard, an element probably will be in a different crystal structure and state of combination than in the unknown. Thus for analysis of a silicate rock, standards of naturally occurring similar materials of known composition are the most desirable.

Interelement effects are probably less serious than matrix effects, but they may be important under certain conditions. Excited atoms and ions in the arc column may lose part of their energy by collision with unexcited atoms or atoms of low energy. Changes in the composition of the arc gas may alter the number and nature of such collisions and thus cause a change in line intensity that will affect the accuracy of the determinations.

As U.S. Geological Survey Bulletin 980 shows, chemical analyses of rocks are less precise than they were thought to be, and the number of well-analyzed rocks is small. Fairbairn (1953) has shown that chemical determinations of $SiO_2$ and $Al_2O_3$ may be systematically biased, and this conclusion has been verified by Stevens and Chodos, in part 2 of this report. Normal chemical determinations of $SiO_2$ and $Al_2O_3$ are probably biased, and the spectrographer is faced with using standards that he strongly suspects to be in error or with using synthetic standards. The investigation of the composition of G–1 and W–1 was initially undertaken to provide spectrographers and geochemists with two well-analyzed standards; as considerable data have now accumulated, the compositions of G–1 and W–1 are now known within narrow limits. For the spectrographer working with rocks that are not granite or diabase, a problem still exists. No equally well-analyzed limestone exists, for example.

Another consideration is involved in the choice between synthetic and chemically analyzed standards. As stated by Stevens and Niles, part 1, the chemical determinations of $Al_2O_3$, CaO, MgO, and $K_2O$, include contributions by $ZrO_2$, SrO, BaO, and $Rb_2O$, respectively. The spectrographic determination is specific and therefore is "in error," with respect to the chemical determination, to the extent of the contribution to the chemical result for a major constituent.

Self-absorption in the analytical or internal standard lines is another factor that may influence precision and accuracy of a determination. During the burning of the sample, the high-temperature arc column is surrounded by a sheath of cooler gas. Light emitted by an atom or ion in the central portion of the arc passes through this cooler sheath of gas and may be absorbed by a like atom in a lower energy state. In effect, an absorption spectrum is produced, and a reduction of line intensity is noticed. The higher the concentration of the element in the sample, the higher the concentration in the outer layer of gas and the greater the reduction in line intensity. When self-absorption occurs in an analytical line, use of the line tends to give low results. Similarly, if self-absorption occurs in an internal standard line, high results probably will be obtained. Poor reproducibility is common when self-absorption occurs.

The spectrographic methods used by the contributors to this section of the report are listed in table 11. To reduce matrix and interelement effects, most of the methods include the use of a buffer. In six of the methods either $SrCO_3$ or $Li_2CO_3$ is used as a buffer, and in only two of the methods is the sample arced alone. The air jet was used by four of the participants, and most contributors used internal or mutual standard techniques.

No attempt was made to assess the relative accuracy or precision of the individual methods.

TABLE 11.—*Details of methods used to determine the major constituents of G-1 and W-1*

| No.[1] | Analyst | Excitation | Sample preparation | Internal standards | Elements determined |
|---|---|---|---|---|---|
| 6 | Dennen | d-c-arc | Sample +LiAl $(SiO_3)_2$ | Li for Na; Na variable for K | Na, K |
| 7 | do | do | Sample alone or with carbon | Mutual: Al for Si, Fe, Ti, Mg, Ca, (and Al). | Si, Al, Fe, Ti, Mg, Ca |
| | | | | : Fe for K | K |
| 8 | Filby | d-c arc, air jet | Sample $+SrCO_3$ (+1 percent $In_2O_3$) +graphite. | Sr for Si, Al, Mn, Ti, Ca, Mg; In for Na | Si, Al, Mn, Ti, Mg, Ca, Na. |
| 9 | Hall | d-c arc | Sample arced alone | Total energy method | Si, Al, Mn, Ti, Mg, Ca Na, K |
| 10 | Joensuu | d-c arc, air jet | Sample $+Li_2CO_3+H_3BO_3+Co_3O_4$ +graphite. | Co | Si, Al, Mn, Ti, Mg, Ca |
| 11 | Shaw, Filby, Siroonian, and Yip | do | Sample a$+Li_2CO_3$ (+1 percent $In_2O_3$) | In | Na, K |
| | | | Sample b+graphite (+0.5 percent $La_2O_3$). | La | Ca |
| | | | Sample c+graphite (+Pd) | Pd | Ti, Mg, Mn |
| 12 | Leininger and Taylor | d-c arc | Sample a$+SrCO_3$+graphite | Sr | Ca, Mg, Mn |
| | | | Sample b$+SrCO_3$+graphite | Mutual: Si for Al (and Si) | Al, Si |
| 13 | Hawley and MacDonald | d-c arc, air jet | Sample a$+SrCO_3$+graphite | Sr | Si, Al, Ti, Mn, Mg, Ca |
| | | | Sample b$+SrCO_3$+graphite | Sr | Na, K |
| 22 | Shilstone | | | Semiquantitative | Si, Al, Mn, Ca, Mg, Na, K |
| 23 | Hodge and Baer | | | do | Ti, Mn, Fe, Ca, Mg, Na, K |
| 24 | Smith-Emery | | | do | Si, Al, Mn, Ti, Ca, Mg, Na, K |

[1] Numbers refer to headings in tables 12–14 and to the list of analysts appended. Numbers 14 to 21 are trace element methods and not included in this table.

## SPECTROCHEMICAL DATA ON MAJOR CONSTITUENTS IN G-1 AND W-1

### ACCUMULATED DATA

Tables 12–14 show the accumulated data for G-1 and W-1. The numerical headings for each column refer to contributors listed in table 11. The semiquantitative data are presented separately in table 14. In the calculations of means and other statistical measures, the semiquantitative results were omitted as were results reported as biased.

Statistical terms used in this section are those adopted by Dennen, Ahrens, and Fairbairn (1951), and are reviewed here.

$\bar{x}$, arithmetic mean.
$M$, median.
$n$, number of observations.
$d$, deviation of an observation from the mean.

$s$, standard deviation$=\sqrt{\frac{\Sigma d^2}{n-1}}$ (of a single observation).

$s_{\bar{x}}$, standard error$=s/\sqrt{n}$ (of the mean).

$C$, relative deviation$=(s_{\bar{x}})100$.

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

For comparisons of precision, $C$ is the measure usually employed. For each constituent, the determinations given in tables 12 and 13 were averaged to give the mean value, $\bar{x}$, and the values of $s$ and $C$ were computed. The interlaboratory relative deviation, $C$, is distinct from the intralaboratory deviation, $C'$, reported for particular observations in tables 12 and 13.

It should be emphasized that the results for each constituent listed in tables 12 and 13 do not form homogeneous populations. Several of the results are means of a large number of determinations, whereas others are single, or are means of duplicate determinations. Statistical data for some of the results reported were not available. Standard deviations for most constituents were calculated from populations of less than 10. Consequently, proper evaluation of precision cannot be obtained using such small heterogeneous populations. Unfortunately, with the present data, a more rigorous statistical treatment cannot be applied and more data are needed to form a good estimate of the interlaboratory precision of spectrographic methods.

Dennen and others (1951) listed the statistical data for the chemical analyses from 24 laboratories, and Fairbairn (1953) revised these when additional analyses became available; some analyses were omitted, however, from these calculations. Stevens and Niles (part 1, this

TABLE 12.—*Chemical and spectrographic data for the major constituents of G–1 and W–1*

| | Chemical averages | | | | | Spectrographic determinations | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | 1 | 2 | 3 | 4 | [1]5 | 6 | 7 | 8 | 9 | 10 | 11 | 12 | 13a | 13b | $\bar{x}$ | $n$ | $s$ | $C$ | $\bar{x}-s$ | $\bar{x}+s$ | $\bar{x}'$ |
| **G-1** | | | | | | | | | | | | | | | | | | | | | |
| $SiO_2$ | 72.24 | 72.86 | 72.49 | 72.35 | 72.45 | | 74.0 | 74.5 | 70.0 | 73.0 | | 71.6 | 70.2 | | 72.2 | 6 | 1.92 | 2.7 | 70.28 | 74.12 | 73.2 |
| C′ | .51 | .5 | .26 | .66 | | | | 5.93 | | | | | 8.1 | | | | | | | | |
| n | 34 | 29 | 26 | 60 | | | | 12 | | 2 | | | | | | | | | | | |
| $Al_2O_3$ | 14.34 | 13.94 | 14.30 | 14.32 | 14.29 | | 13.7 | 14.8 | 14.5 | 15.0 | | 15.1 | 13.98 | 14.41 | 14.5 | 7 | .52 | 3.6 | 13.98 | 15.02 | 14.4 |
| C′ | 3.21 | 2.2 | 1.53 | 2.6 | | | | 11.9 | | | | | 4.5 | 7.58 | | | | | | | |
| n | 34 | 28 | 26 | 60 | | | | 24 | | 2 | | | 17 | 100 | | | | | | | |
| Fe as $Fe_2O_3$ | 2.05 | 2.03 | 2.03 | 2.04 | 1.96 | | 2.10 | 1.92 | 2.00 | 2.01 | | | 1.97 | 1.99 | 2.00 | 6 | .059 | 2.95 | 1.94 | 2.06 | 1.99 |
| C′ | 13.76 | | 14.36 | 13.90 | | | | 11.9 | | | | | 3.3 | 11.08 | | | | | | | |
| n | 34 | 28 | 26 | 60 | | | | 12 | | 2 | | | 11 | 100 | | | | | | | |
| MgO | .39 | .39 | .40 | .40 | .41 | | .34 | .36 | .40 | .40 | .35 | .39 | .38 | .40 | .38 | 8 | .025 | 6.6 | .355 | .405 | .39 |
| C′ | 35.32 | 27 | 28.09 | 32.15 | | | | 11.4 | | | 17.6 | | 1.4 | 15.0 | | | | | | | |
| n | 34 | 28 | 25 | 59 | | | | 12 | | 2 | 8 | | 14 | 100 | | | | | | | |
| CaO | 1.40 | 1.41 | 1.39 | 1.40 | 1.39 | | 1.10 | 1.74 | 1.4 | 1.36 | 1.26 | 1.40 | 1.40 | 1.38 | 1.38 | 8 | .18 | 13.0 | 1.20 | 1.56 | 1.37 |
| C′ | 9.66 | 8.2 | 8.06 | 8.95 | | | | 11.2 | | | 22.7 | | 4.1 | 10.13 | | | | | | | |
| n | 34 | 29 | 25 | 59 | | | | 12 | | 2 | 6 | | 8 | 100 | | | | | | | |
| $Na_2O$ | 3.30 | 3.25 | 3.32 | 3.31 | 3.32 | 3.34 | 4.0 | 3.26 | 3.10 | | 3.44 | | 3.26 | 3.29 | 3.38 | 7 | .29 | 8.6 | 3.09 | 3.67 | 3.27 |
| C′ | 7.99 | 5.2 | 5.74 | 7.06 | | 2.55 | | 9.5 | | | 4.94 | | 1.1 | 14.29 | | | | | | | |
| n | 34 | 28 | 25 | 59 | | 5 | | 11 | | | 18 | | 7 | 100 | | | | | | | |
| $K_2O$ | 5.48 | 5.42 | 5.35 | 5.42 | 5.46 | 5.46 | 4.5 | | 5.54 | | 5.66 | | 5.70 | 5.41 | 5.37 | 6 | .63 | 11.7 | 4.74 | 6.00 | 5.55 |
| C′ | 8.41 | 6.8 | 5.36 | 7.26 | | 2.95 | | | | | 10.5 | | 5.6 | 8.87 | | | | | | | |
| n | 34 | 28 | 25 | 59 | | 5 | | | | | 15 | | 9 | 100 | | | | | | | |

## W-1

| | | | | | | | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| $SiO_2$ | 52.33 | 52.69 | 52.48 | 52.40 | 52.54 | ------ | 54.7 | 52.3 | ------ | 51.5 | ------ | 52.0 | 53.76 | ------ | 52.9 | 5 | 1.34 | 2.5 | 51.56 | 54.24 | 52.7 |
| C′ | .68 | .6 | .58 | .63 | ------ | ------ | ------ | 7.3 | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| n | 30 | ------ | 30 | 60 | ------ | ------ | ------ | 11 | ------ | 6 | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| $Al_2O_3$ | 15.17 | 14.72 | 15.09 | 15.11 | 15.09 | ------ | 14.8 | 14.7 | ------ | 15.0 | ------ | 15.6 | 14.78 | ------ | 15.0 | 5 | .37 | 2.5 | 14.63 | 15.37 | 14.8 |
| C′ | 5.61 | 3.3 | 1.90 | 3.11 | ------ | ------ | ------ | 7.1 | ------ | ------ | ------ | ------ | 3.3 | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| n | 30 | 32 | 30 | 60 | ------ | ------ | ------ | 12 | ------ | 6 | ------ | ------ | 10 | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| Fe as $Fe_2O_3$ | 11.26 | 11.19 | 11.18 | 11.22 | 11.15 | ------ | 10.90 | 12.3 | ------ | 11.29 | ------ | ------ | 10.87 | ------ | 11.3 | 4 | .67 | 5.91 | 10.67 | 12.01 | 11.0 |
| C′ | 2.88 | ------ | 2.07 | 2.49 | ------ | ------ | ------ | 9.3 | ------ | ------ | ------ | ------ | 9.5 | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| n | 30 | 30 | 30 | 60 | ------ | ------ | ------ | 11 | ------ | 6 | | ------ | 9 | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| MgO | 6.53 | 6.63 | 6.62 | 6.58 | 6.64 | ------ | 6.5 | 6.15 | ------ | 6.6 | ------ | 6.43 | 6.20 | ------ | 6.38 | 5 | .19 | 3.0 | 6.19 | 6.57 | 6.38 |
| C′ | 7.26 | 4.2 | 2.03 | 5.29 | ------ | ------ | ------ | 9.4 | ------ | ------ | ------ | ------ | .3 | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| n | 30 | 32 | 29 | 59 | ------ | ------ | ------ | 11 | ------ | 6 | ------ | ------ | 12 | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| CaO | 10.96 | 10.96 | 10.98 | 10.97 | 10.98 | ------ | 9.5 | 11.5 | ------ | 10.6 | 10.46 | 10.9 | 10.9 | ------ | 10.6 | 6 | .67 | 6.3 | 9.93 | 11.27 | 10.7 |
| C′ | 1.58 | 1.8 | 1.37 | 1.46 | ------ | ------ | ------ | 9.3 | ------ | ------ | 6.2 | ------ | 5.8 | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| n | 30 | 33 | 29 | 59 | ------ | ------ | ------ | 11 | ------ | 6 | 6 | ------ | 10 | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| $Na_2O$ | 2.07 | 2.00 | 2.07 | 2.07 | 2.07 | ------ | 1.9 | 1.94 | ------ | ------ | 2.10 | ------ | 1.98 | ------ | 1.98 | 4 | .086 | 4.34 | 1.89 | 2.07 | 1.94 |
| C′ | 10.20 | 9.3 | 9.46 | 9.76 | ------ | ------ | ------ | 5.6 | ------ | ------ | 5.58 | ------ | 32.3 | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| n | 30 | 32 | 28 | 58 | ------ | ------ | ------ | 11 | ------ | ------ | 10 | ------ | 10 | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| $K_2O$ | .70 | .63 | .64 | .67 | .64 | ------ | .8 | ------ | ------ | ------ | ------ | ------ | ------ | ------ | .80 | ------ | ------ | ------ | ------ | ------ | ------ |
| C′ | 24.61 | 23 | 6.49 | 19.00 | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |
| n | 30 | 32 | 28 | 58 | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ | ------ |

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[1] Moisture free.

report) have collected all chemical analyses to date and have recalculated the data of U.S. Geological Survey Bulletin 980 to include all listed analyses. Data from the latter two sources are included in the following discussion. The preferred chemical values listed by Stevens and Niles in tables 7 and 8 are for moisture-free samples. For purposes of comparison, these values were converted to "as received" figures, which are used in the following discussion.

For each constituent in tables 12 and 13, the mean ($\bar{x}$) of the selected spectrographic values is shown. The selected values were those remaining after rejecting values outside the range, $\bar{x}+s$ to $\bar{x}-s$, from the computation. The means, $\bar{x}'$, were then recalculated. This procedure eliminated determinations that are most likely to be in error.

In the following discussions, the spectrographic data are compared to the various chemical data, and an attempt is made to recommend values for the major constituents of G–1 and W–1.

TABLE 13.—*Spectrographic determinations of* MnO *and* TiO *in G–1 and W–1*

[Values in parentheses were reported as systematically biased]

| No.[1] | G–1 | | W–1 | |
|---|---|---|---|---|
| | MnO | $TiO_2$ | MnO | $TiO_2$ |
| 7 | -------- | 0.19 | -------- | 0.74 |
| 8 | 0.027 | .23 | 0.21 | .83 |
| 9 | .014 | .23 | -------- | -------- |
| 10 | .03 | .24 | .175 | 1.08 |
| 11 | .034 | .242 | (.128) | (.852) |
| 12 | .027 | -------- | .187 | -------- |
| 13a | .03 | .25 | .15 | 1.10 |
| 13b | .03 | .26 | -------- | -------- |
| 14 | .044 | -------- | .17 | -------- |
| 15 | .013 | -------- | -------- | -------- |
| 16 | .016 | -------- | -------- | -------- |
| 17 | .025 | .234 | .16 | 1.12 |
| 18 | 0.021 | 0.20 | 0.16 | 1.00 |
| 19 | -------- | .30 | -------- | 1.10 |
| 20 | .019 | -------- | .18 | -------- |
| 21 | .031 | -------- | .20 | -------- |
| $\bar{x}$ | .026 | .24 | .18 | 1.00 |
| $n$ | 14 | 10 | 9 | 7 |
| $s$ | .0086 | .031 | .02 | .15 |
| $C$ | 33.1 | 12.9 | 10.9 | 15.0 |
| $\bar{x}-s$ | .017 | .21 | .16 | .85 |
| $\bar{x}+s$ | .035 | .27 | .20 | 1.15 |
| $\bar{x}'$ | .027 | .24 | .18 | 1.08 |

[1] Numbers refer to analysts in table 11 and to the list of analysts on page 82.

TABLE 14.—*Semiquantitative spectrographic analyses of G–1 and W–1 (in percent)*

| | G–1 | | | W–1 | | |
|---|---|---|---|---|---|---|
| | 22 | 24 | 23 | 22 | 24 | 23 |
| Si | 35 | (1) | >10 | 29 | (1) | >10 |
| Ti | .1 | 0.2 | .1 | .4 | 1 | 1 |
| Al | 6 | (1) | 10 | 8 | (1) | 10 |
| Fe | 1 | 1 | 1 | 5 | 7 | 3 |
| Mn | .04 | .01 | [2].003 | .2 | .3 | [2].01 |
| Mg | .2 | .3 | .1 | 3 | 7 | >3 |
| Ca | 4 | 5 | 1 | 5 | (1) | 3 |
| Na | 1 | 3 | 1 | .9 | 1 | 1 |
| K | 2 | 4 | [2]1 | (3) | .4 | -------- |

[1] Major.
[2] Analysis outside ⅓ to 3× range of chemical value.
[3] Not detected.

## SILICA, $SiO_2$

Table 15 shows the chemical and spectrographic $SiO_2$ data for G–1 and W–1. The first values for $SiO_2$ in G–1 and W–1 are those calculated from the analyses given in tables 1 and 2, Bulletin 980. The second set of values are those given by Fairbairn (1953) and were adjusted for bias in the chemical methods of determining $SiO_2$. The adjustment was based on data obtained for a synthetic haplogranite glass analyzed by 12 laboratories. These results were reported by Fairbairn and Schairer (1952). The known concentrations of $SiO_2$ and $Al_2O_3$ in this glass indicated that the determined $SiO_2$ concentration was too low, whereas the $Al_2O_3$ concentration was too high. After elimination of determinations differing more than $2s$ from the mean of 11 results, the $Al_2O_3$ and $SiO_2$ means were found to differ from the known values by $-0.5$ and $+0.5$ percent, respectively.

TABLE 15.—*Chemical and spectrographic data for* $SiO_2$ *in G–1 and W–1*

| | G-1 | | W-1 | |
|---|---|---|---|---|
| | $\bar{x}$ | $c$ | $\bar{x}$ | $c$ |
| Bulletin 980: all analyses | 72.24 | 0.51 | 52.33 | 0.68 |
| Fairbairn (1953): revised data | 72.86 | .5 | 52.69 | .6 |
| Stevens and Chodos (special determinations) | 72.65 | .81 | 52.64 | .91 |
| Stevens and Niles: | | | | |
| All analyses | 72.35 | .66 | 52.40 | .63 |
| Preferred values, from all analyses, recast to as received basis | 72.40 | .25 | 52.41 | .32 |
| Spectrographic determinations | 72.2 | 2.7 | 52.9 | 2.5 |
| Spectrographic determinations: selected values | 73.2 | ---------- | 52.7 | ---------- |

Fairbairn and Schairer (1952) explained the discrepancies on the basis of incomplete recovery of $SiO_2$ during analysis and the incorporation of undetermined $SiO_2$ in the $R_2O_3$ fraction, which thus increased the $Al_2O_3$ determination. As a result of this finding, G–1 and W–1 values for $SiO_2$ were adjusted accordingly: 0.5 percent was added to $SiO_2$ in G–1 and 0.35 percent added to $SiO_2$ in W–1. For $Al_2O_3$, 0.5 percent and 0.35 percent were subtracted from the chemical values for G–1 and W–1 respectively.

Results obtained by Stevens and Chodos on $SiO_2$ by very careful analysis are given in part 2 of this report. The $SiO_2$ was precipitated carefully, and the amount that remained in the $R_2O_3$ residue was determined spectrographically. The precipitated $SiO_2$ also was analyzed spectrographically to determine the amount of impurities contained. The results are shown in table 15, and confirm the direction of Fairbairn's adjustment. The value Fairbairn recommended for $SiO_2$ in G–1 (72.86) seems too high, but the value for W–1 agrees well with that obtained by Stevens and Chodos.

Although the precision of the spectrographic determinations of $SiO_2$ is good, nothing can be deduced about accuracy. The histograms presented in plate 1, Bulletin 980, and in figure 2 (Fairbairn, 1953) show distinct, negative skewness. This skewness shows the tendency of the chemical methods to give low results. The shape of the histograms, however, is dependent on the class interval chosen, but the S curves shown in figure 1 (part 1) definitely indicate the negative skewness. The arithmetic means are considerably lower than the medians, indicating that the mean chemical values, with the exception of those of Stevens and Chodos, shown in table 15, are lower than the actual values. Hawley and MacDonald (1956), dealing with National Bureau of Standards standard sample 1a, which is lower than G–1 or W–1 in $SiO_2$ and $Al_2O_3$, found that their $SiO_2$ determination was lower than the chemical value, but that the reverse was true for $Al_2O_3$. They stated that the bias is in the opposite direction to the systematic error reported by Fairbairn and Schairer (1952). However, standards used in the construction of the working curves were chemically analyzed; hence, results obtained should be equal to the chemical values, within the limits of experimental error. The bias observed by Hawley and MacDonald is more likely spectrographic (matrix effects or self-absorption) than a difference between the true value and the chemical result. These authors point out this fact; hence, their results cannot be used to support or deny Fairbairn's adjustment.

Of the chemical values shown in table 15, those of Stevens and Chodos are perhaps the most accurate, as the results were corrected for $SiO_2$ losses and impurities in the $SiO_2$ precipitates. For G–1, the mean spectrographic value and the mean of the selected spectrographic values are lower and higher, respectively, than the value of 72.65 obtained by Stevens and Chodos. For W–1, the mean spectrographic value of 52.9 is considerably higher than the chemical value of 52.64, but the mean of the selected values (52.7) is close to this chemical value. It must be remembered, however, that many of the spectrographic values were obtained by reference to chemically analyzed standards which may introduce negative bias into the results.

The precision of the spectrographic $SiO_2$ determinations is considerably poorer than the precision of the chemical determinations. For rock classification procedures, therefore, chemical methods of analysis will be preferred. On the other hand, the spectrographic determination of $SiO_2$ is easy and many replicates can be readily made. For many purposes then, spectrographic determination is completely adequate, and methods are capable of providing statistical information usually difficult to obtain chemically. If $n$ determinations are made, the relative deviation is reduced to $C/\sqrt{n}$, thus precision is improved by making replicate determinations.

One further point is pertinent. Whereas the normal number of significant figures for gravimetric determination is four, spectrochemical determinations are usually limited to three. The reliability of the fourth chemical figure is probably of the same order as the reliability of the third spectrographic figure.

### ALUMINA, $Al_2O_3$

Chemical and spectrographic data on $Al_2O_3$ in G–1 and W–1 are shown in table 16. The corrected, preferred chemical values for $Al_2O_3$ in G–1 and W–1 were obtained by subtracting the $ZrO_2$, $Cr_2O_3$, $V_2O_5$, and $La_2O_3$ contents of G–1 and W–1, respectively, from the $Al_2O_3$ values. The Zr, Cr, V, and La values used were those recommended by Ahrens (1954a). These minor constitutents will be incorporated in the $R_2O_3$ residue, and unless separately determined, will be included in the $Al_2O_3$ determinations.

Much of what has been said about accuracy and precision of the $SiO_2$ determinations also applies to the determinations of $Al_2O_3$.

TABLE 16.—*Chemical and spectrographic data on alumina,* $Al_2O_3$, *in G–1 and W–1*

| | G–1 | | W–1 | |
|---|---|---|---|---|
| | $\bar{x}$ | $C$ | $\bar{x}$ | $C$ |
| Bulletin 980: all analyses | 14.34 | 3.21 | 15.17 | 5.61 |
| Fairbairn (1953): revised figures | 13.94 | 2.21 | 14.72 | 3.3 |
| Stevens and Niles: | | | | |
| All analyses | 14.32 | 2.60 | 15.11 | 4.16 |
| Preferred values, all analyses, recast to as received basis | 14.28 | 1.19 | 15.05 | 1.19 |
| Mean of preferred values corrected for $ZrO_2$, $Cr_2O_3$, $V_2O_5$, and $La_2O_3$ contents | 14.23 | ------------ | 14.98 | ------------ |
| Direct determinations | 14.12 | ------------ | 14.92 | ------------ |
| Spectrographic determinations | 14.5 | 3.6 | 15.0 | 2.5 |
| Spectrographic determinations: selected values | 14.4 | ------------ | 14.8 | ------------ |

As was noted in the discussion of the $SiO_2$ results, the $Al_2O_3$ adjustment made by Fairbairn (1953) was based on chemical results obtained for a haplogranite glass and is believed by Fairbairn to provide more correct values than the mean of the chemical determinations. Examination of the histograms for $Al_2O_3$ in G–1, plate 1, Bulletin 980, reveals skewness; no skewness is shown by the histogram for $Al_2O_3$ in W–1. The reason given by Fairbairn for the lack of skewness is that as $Al_2O_3$ is determined by difference from the $R_2O_3$ residue, analytical errors in the other constituents (total Fe, $P_2O_5$, $TiO_2$) may mask the $Al_2O_3$ bias. The skewness may be masked also by the choice of class interval. The S curves for $Al_2O_3$ in G–1 and W–1 shown in figures 2 and 5, part 2, have pronounced positive skewness, which provides evidence for the belief that the chemical figures for $Al_2O_3$ are too high.

Examination of table 16 shows that good agreement exists between the preferred chemical figures, corrected for interfering elements, and the means of the selected spectrographic values. For G–1, the value given by Fairbairn (1953) is lower than the other chemical values, and as is true for $SiO_2$, the $Al_2O_3$ figure appears to have been overcorrected.

The figure given by Fairbairn for $Al_2O_3$ in W–1 is also lower than the other chemical values in table 16, and has probably been overcorrected also. The mean of the direct chemical determinations of $Al_2O_3$ in W–1 is close to the mean of the selected spectrographic values and to the corrected preferred chemical figure. Many of the working curves used for the spectrographic determination of $Al_2O_3$ may have been constructed using chemically analyzed standards; hence, some spectrographic values may be biased.

Differences among the chemical values presented in table 16, excluding Fairbairn's figures, are of the order of a few hundredths of a percent and are of little significance to the spectrographer. The $Al_2O_3$ figures for G–1 and W–1 now appear sufficiently well substantiated to recommend the use of these rocks as spectrographic standards.

The precision of the data in table 16 shows that for the determination of $Al_2O_3$ there is very good agreement among spectrographers. For many purposes, spectrographic methods appear adequately accurate and precise for the determination of $Al_2O_3$ in silicate materials.

## TOTAL IRON AS $Fe_2O_3$

Chemical and spectrographic data on total iron as $Fe_2O_3$ in G–1 and W–1 are shown in the following table. The mean of the selected spectrographic values agrees well with the preferred chemical figure for G–1. The photometric value, however, is lower than the other chemical values.

For W–1, the mean of the selected spectrographic values is close to the preferred chemical figure; the photometric value also agrees well with the preferred chemical figure.

The X-ray fluorescence data were obtained using synthetic standards for the construction of working curves in order to eliminate errors arising from uncertainties in standard composition. The value of 11.5 for $Fe_2O_3$ in W–1 but is higher than the chemical or photometric values. The very low value of 1.42 for $Fe_2O_3$ in G–1 can possibly be attributed to a matrix effect or to the large grain size of the iron-containing biotite, which resits grinding.

*Chemical and spectrographic data on total iron as* $Fe_2O_3$ *in G–1 and W–1*

[Chemical and photometric data taken from part 1]

| | G-1 | | W-1 | |
|---|---|---|---|---|
| | $\bar{x}$ | $C$ | $\bar{x}$ | $C$ |
| Bulletin 980: all analyses | 2.05 | 13.76 | 11.26 | 2.88 |
| Stevens and Niles: | | | | |
| All analyses | 2.04 | 13.90 | 11.22 | 2.49 |
| All analyses: preferred values, recast to as received basis | 1.96 | ---------- | 11.10 | ---------- |
| Photometric determinations | 1.84 | ---------- | 11.06 | ---------- |
| Spectrographic determinations | 2.00 | 2.5 | 11.34 | 5.91 |
| Spectrographic determinations: selected values | 1.99 | ---------- | 11.0 | ---------- |
| X-ray fluorescence determinations [1] | 1.42 | ---------- | 11.5 | ---------- |

[1] G. R. Gates, Indiana Geological Survey.

Fairbairn (1951) considers G–1 and W–1 to be homogeneous on the basis of low values for the relative deviation of the silica determinations in the two rocks. The authors decided to remove the magnetic fraction from G–1 and took two portions of G–1 of approximately 1 gram and 1.5 grams each from the same bottle. The amount of magnetic material (principally magnetite) removed by a hand magnet in the first portion was 0.68 percent and in the second, 0.69 percent, indicating that this bottle of G–1 is homogeneous, although nothing can be said about the other bottles in use. In view of the ease with which magnetic particles aggregate, however, it is conceivable that G–1 may become heterogeneous, especially if placed in a magnetic field. As the spectrographer takes only a few milligrams of sample for analysis, the problem is more serious than it is for the chemist, who may take several grams. The problem of possible inhomogeneity of the sample is further aggravated by the large grain size of G–1 (−80 mesh) compared to W–1 (−100 mesh). Further grinding of G–1 does not solve the problem completely because it is very difficult to grind the biotite. Examination of table 12 shows that the value of $C$ for a particular constituent, except for $Fe_2O_3$ and $TiO_2$, is lower for W–1 than for G–1. The larger value of $C$ for $Fe_2O_3$ in W–1 is almost certainly due to the tendency of iron lines to be self-absorbed at high concentrations, a factor that causes poor reproducibility.

## MAGNESIUM OXIDE, MgO

The preferred chemical figures (see following table 2) corrected for BaO content, which unless determined separately is included in the MgO determinations, were obtained by subtracting the BaO values, multiplied by 0.63 (see part 1), from the MgO figures for G–1 and W–1, respectively. The Ba values used were those recommended by Ahrens (1954a).

For G–1, agreement between the mean of the spectrographic determinations and the chemical figure, corrected for BaO content, is poor. The chemical figure is considerably lower than the spectrographic figure. It should be noted that the spectrographic precision for the determination of MgO in G–1 is considerably better than the chemical precision. For concentrations of about 0.5 percent or less, spectrographic methods of determination would probably be superior to the chemical methods.

For W–1, the spectrographic figures for MgO are low compared to the chemical figures. Stevens and Niles reported that the S curves for MgO in G–1 and W–1 show no signs of skewness. The lack of skewness suggests that the chemical methods of determining MgO are free of systematic bias. At present, then, the corrected chemical figure of 6.61 for MgO in W–1 seems to be the most satisfactory.

*Chemical and spectrographic data on* MgO *in G–1 and W–1*

[Chemical data taken from part 1]

| | G-1 | | W-1 | |
|---|---|---|---|---|
| | $\bar{x}$ | $C$ | $\bar{x}$ | $C$ |
| Bulletin 980: all analyses | 0.39 | 35.32 | 6.53 | 72.6 |
| Stevens and Niles: | | | | |
| All analyses | .40 | 32.15 | 6.58 | 5.29 |
| All analyses: preferred values, recast to as received basis | .41 | 14.6 | 6.62 | 1.51 |
| Mean of preferred values, corrected for BaO content | .32 | | 6.61 | |
| Spectrographic determinations | .38 | 6.6 | 6.38 | 3.0 |
| Spectrographic determinations: selected values | .39 | | 6.38 | |

## CALCIUM OXIDE, CaO

The chemical determinations of CaO will include SrO, unless the SrO is first removed and determined separately. The corrected preferred chemical figures shown in the following table were obtained by subtracting the SrO percentages from the CaO figures; the Sr values for G–1 and W–1 obtained spectrographically by Turekian, Gast, and Kulp (1957) were used.

*Chemical and spectrographic data on* CaO *in G–1 and W–1*

[Chemical data taken from part 1]

| | G-1 | | W-1 | |
|---|---|---|---|---|
| | $\bar{x}$ | $C$ | $\bar{x}$ | $C$ |
| Bulletin 980: all analyses | 1.40 | 9.66 | 10.96 | 1.58 |
| Stevens and Niles: | | | | |
| All analyses | 1.40 | 8.95 | 10.97 | 1.46 |
| All analyses: preferred values, recast to as received basis | 1.39 | 5.05 | 10.95 | .74 |
| Mean of preferred values, corrected for SrO content | 1.36 | | 10.94 | |
| Spectrographic determinations | 1.38 | 13.0 | 10.6 | 6.3 |
| Spectrographic determinations: selected values | 1.37 | | 10.7 | |

Agreement between the corrected chemical and spectrographic figures for CaO is good for G–1 and fairly good for W–1. For the determination of CaO in both G–1 and W–1, the precision of the chemical determinations is superior to that of the spectrographic determinations, and chemical determination of CaO as a major constituent appears desirable. Below 1 percent, however, spectrographic methods are probably more accurate and precise.

### SODIUM OXIDE, $Na_2O$

Agreement between the preferred chemical figures for $Na_2O$ and the mean of the selected spectrographic values is good for G–1 and fairly good for W–1 as shown in the following table. The flame-photometric results shown in this table are higher than either the chemical or spectrographic values for $Na_2O$ in both G–1 and W–1.

Because of the difficulty of determining $Na_2O$ chemically, spectrographic or flame-photometric methods will probably give more accurate and precise results. Spectrographic methods of determining Na have the disadvantage that the lines of Na in the commonly used region of the spectrum (ultraviolet region) are self-absorbed unless special precautions are taken (use of the air jet, for example). This disadvantage may be circumvented by employment of relatively weak Na lines of longer wavelength as discussed by Ahrens (1954a, chapt. 5).

*Chemical and spectrographic data on* $Na_2O$ *in G–1 and W–1*

[Chemical and flame-photometric data taken from part 1]

| | G–1 | | W–1 | |
|---|---|---|---|---|
| | $\bar{x}$ | *C* | $\bar{x}$ | *C* |
| Bulletin 980: all analyses | 3. 30 | 7. 99 | 2. 07 | 10. 20 |
| Stevens and Niles: | | | | |
| All analyses | 3. 31 | 7. 06 | 2. 07 | 9. 76 |
| All analyses: preferred values, recast to as received basis | 3. 32 | 3. 3 | 2. 07 | 5. 3 |
| Flame-photometric determinations | 3. 43 | ---------- | 2. 21 | ---------- |
| Spectrographic determinations | 3. 38 | 8. 6 | 1. 98 | 4. 3 |
| Spectrographic determinations: selected values | 3. 27 | ---------- | 1. 94 | ---------- |

### POTASSIUM OXIDE, $K_2O$

Chemical and spectrographic data on $K_2O$ in G–1 and W–1 are shown in the following table. The mean of the preferred chemical $K_2O$ values for G–1 has been corrected for $Rb_2O$, which unless determined separately is incorporated in the $K_2O$ determination. The Rb value recommended by Smales (1955) was used for the correction. Agreement among this corrected chemical figure, the mean of the selected spectrographic values, and the flame-photometric figure is good. The precision of the spectrographic determinations is poorer than that of the chemical determinations.

Only two quantitative spectrographic determinations of $K_2O$ in W–1 were reported. Therefore, no discussion of the relative accuracy of the spectrographic and chemical results can be made.

The spectrographic determination of potassium is made difficult by the lack of sensitive potassium lines in the ultravioletregion of the spectrum. The lines at 4044 A and 4047 A are in areas of high background and may be self-absorbed. Ahrens (1954a, chapt. 5) has utilized relatively weak lines in the longer wavelength region of the spectrum for determination of potassium at high concentrations. In the same wavelength region, very sensitive K lines are available by means of which a few parts per million of potassium may be determined. Potassium is also difficult to determine chemically; consequently, the most satisfactory method of determining $K_2O$ is by flame-photometer.

*Chemical and spectrographic data on* $K_2O$ *in G–1 and W–1*

[Chemical and flame-photometric data taken from part 1]

| | G–1 | | W–1 | |
|---|---|---|---|---|
| | $\bar{x}$ | *C* | $\bar{x}$ | *C* |
| Bulletin 980: all analyses | 5.48 | 8.41 | 0.70 | 24.61 |
| Stevens and Niles: | | | | |
| All analyses | 5.42 | 7.26 | .67 | 19.00 |
| All analyses: preferred values, recast to as received basis | 5.46 | 2.74 | .64 | 4.68 |
| Mean of preferred values, corrected for $Rb_2O$ content | 5.43 | ---------- | .64 | ---------- |
| Flame-photometric determinations | 5.44 | ---------- | .65 | ---------- |
| Spectrographic determinations | 5.37 | 11.7 | ---------- | ---------- |
| Spectrographic determinations: selected values | 5.55 | ---------- | ---------- | ---------- |

## MANGANESE OXIDE, MnO

In the following table, agreement between the means of the selected spectrographic values and the preferred chemical figure is good for both G–1 and W–1.

The precisions of the chemical and spectrographic determinations are poor; this fact indicates poor agreement among analysts. The precision of the spectrographic determinations of MnO in W–1 is better than that of the chemical determinations. The value of *C* for the spectrographic determinations of MnO in W–1 is much lower than that obtained for the determinations of MnO in G–1. This difference may be due either to the large grain size of G–1, as mentioned in the discussion of the results for the determination of iron, or to the possible occurrence of some of the manganese in the magnetite which, as mentioned before, may tend to aggregate.

The amount of MnO in most silicate materials probably is best determined by spectrographic methods, provided that satisfactory natural or synthetic standards can be obtained. G–1 and W–1 will, no doubt, be most useful natural standards for manganese.

In table 13, the MnO determinations listed under numbers 14 to 21 were obtained by trace-element methods, which are not described in table 11.

*Chemical and spectrographic data on* MnO *in G–1 and W–1*

[Chemical data taken from part 1]

| | G-1 | | W-1 | |
|---|---|---|---|---|
| | $\bar{x}$ | $C$ | $\bar{x}$ | $C$ |
| Bulletin 980: all analyses | 0.03 | 36.33 | 0.18 | 40.77 |
| Stevens and Niles: | | | | |
| All analyses | .03 | 33.62 | .17 | 32.33 |
| All analyses: preferred values, recast to as received basis | .03 | 20.0 | .16 | 12.5 |
| Spectrographic determinations | .026 | 33.1 | .18 | 10.9 |
| Spectrographic determinations: selected values | .027 | | .18 | |

## TITANIUM DIOXIDE, $TiO_2$

The means of the selected spectrographic $TiO_2$ values for G–1 and W–1 are in close agreement with the preferred chemical figures (see table following). Examination of tables 3 and 4 in part 1 of this report shows that the ranges of $TiO_2$ values for G–1 and W–1 are greater than the ranges of values shown in table 13 of this section. For W–1, the range of the chemical values, 0.13 to 1.68, is extremely large. When G–1 and W–1 were analyzed chemically their compositions were not known, but the spectrographic data presented here, with one exception, were obtained after the publication of Bulletin 980. In a spectrographic determination, extremely divergent values, if obtained, probably would be attributed to bias and therefore not reported.

The $TiO_2$ determinations listed in table 13 under numbers 14 to 21 were obtained by trace-element methods, which are not described in table 11.

*Chemical and spectrographic data on* $TiO_2$ *in G–1 and W–1*

[Chemical data taken from part 1]

| | G-1 | | W-1 | |
|---|---|---|---|---|
| | $\bar{x}$ | $C$ | $\bar{x}$ | $C$ |
| Bulletin 980: all analyses | 0.25 | 23.20 | 1.04 | 22.56 |
| Stevens and Niles: | | | | |
| All analyses | .26 | 16.59 | 1.07 | 18.34 |
| All analyses: preferred values, recast to as received basis | .26 | 5.76 | 1.07 | 6.54 |
| Spectrographic determinations | .24 | 12.9 | 1.00 | 15.0 |
| Spectrographic determinations: selected values | .24 | | 1.08 | |

## RECOMMENDED VALUES

The original purpose of the investigation of the chemical composition of G–1 and W–1 was to provide spectrographers and geochemists with two rock samples whose compositions were known to a high degree of certainty. U.S. Geological Survey Bulletin 980 showed that chemical analyses were less precise than they were thought to be. The precision of the data for many of the constituents, notably those present in small amounts, showed that a single chemical analysis is not likely to be accurate to within a few hundredths of a percent.

Because of the large amount of data that has been accumulated and studied with regard to the chemical composition of G–1 and W–1 and because of the need for these samples in the standardization of spectrographic techniques, a list of recommended values for the major constituents is presented in table 17.

TABLE 17.—*Recommended values for the major constituents of G–1 and W–1* [1]

| *Constituent* | *G-1* | *W-1* |
|---|---|---|
| $SiO_2$ | 72.65 | 52.64 |
| $Al_2O_3$ | 14.23 | 15.00 |
| Total iron as $Fe_2O_3$ | 1.96 | 11.10 |
| MgO | .39 | 6.61 |
| CaO | 1.36 | 10.94 |
| $Na_2O$ | 3.32 | 2.07 |
| $K_2O$ | 5.43 | .64 |
| $TiO_2$ | .24 | 1.08 |
| MnO | .027 | .18 |

[1] As received basis.

*Silica* ($SiO_2$).—Only in the determinations of $SiO_2$ made by Stevens and Chodos was any rigorous attempt made to correct for the factors that bias the $SiO_2$ determination. Consequently, the authors feel that the values obtained by Stevens and Chodos, although from the spectrographer's point of view not greatly different from the preferred chemical figures, should be recommended.

*Alumina* ($Al_2O_3$).—No special study of the determination of alumina has so far been undertaken; hence, the preferred chemical figures, after correction for $ZrO_2$, $Cr_2O_3$, $V_2O_5$, and $La_2O_3$ contents, are recommended. Agreement between these chemical figures and the values obtained by the direct chemical methods is very good.

*Total iron as ferric iron* ($Fe_2O_3$).—The preferred chemical figures are recommended.

*Magnesium oxide* (MgO).—For MgO in G–1, the mean of the selected spectrographic values is recommended because the interlaboratory precision of the spectrographic determination is better than the chemical precision. For W–1, the preferred chemical figure, after correction for BaO, is recommended.

*Calcium oxide* (CaO).—The preferred chemical figures, after correction for SrO content, are recommended.

*Sodium oxide* ($Na_2O$).—Recommended values for $Na_2O$ in G-1 and W-1 must still be regarded as tentative. Disagreement exists between the preferred chemical figures and the flame-photometric figures, the latter being higher. The preferred chemical values are recommended, as the interlaboratory precision is good, and no bias in the method of determining $Na_2O$ is indicated by the S curves for $Na_2O$ in G-1 and W-1.

*Potassium oxide* ($K_2O$).—Agreement between the chemical and flame-photometric figures for $K_2O$ in G-1 and W-1 is very good. The preferred chemical figures, after correction for $Rb_2O$ content, are recommended.

*Titanium dioxide* ($TiO_2$).—The means of the selected spectrographic values for $TiO_2$ in G-1 and W-1 are recommended. Agreement between the chemical and spectrographic figures is good, but the interlaboratory spectrographic precision is superior to the chemical precision.

*Manganese oxide* (MnO).—The means of the selected spectrographic values for MnO in G-1 and W-1 are recommended, although for G-1 the interlaboratory precision is no better than the chemical precision. For MnO in W-1, spectrographic precision is clearly superior.

## DETERMINATIONS OF THE MAJOR CONSTITUENTS OF G-1 AND W-1 WITH A DIRECT-READING SPECTROMETER

Because of the differences between photoelectric and photographic recording, the spectrochemical determinations of the major constituents of G-1 and W-1 made by C. K. Matocha and W. H. Tingle of the Aluminum Company of America are treated separately in this section. An A.R.L. Quantometer was used for this work. The determinations are, to our knowledge, the only available direct-reading results, and are significant because of their high precision.

The authors wish to acknowledge the contribution made by C. K. Matocha and W. H. Tingle and the kind cooperation of the Aluminum Company of America. Arrangements for this work were made with J. R. Churchill.

The following outline, describing the method used and explaining the statistical data, has been condensed from a report by the analysts.

Table 18 lists $\bar{x}$, the average of two independent determinations $x_1$ and $x_2$; $k$, the composition of the synthetic standard used to obtain the sample analysis; and the statistical data. To obtain $x_1$, four pellets from each sample were compared to four pellets of the corresponding synthetic standard; four exposures were taken with each pellet. Intensity ratios, in terms of recorder divisions, were obtained for each element listed as an oxide in table 18. The averages were calculated, and the difference in divisions between the synthetic standard and sample was multiplied by the slope, percent per division, of the analytical curve at the point of analysis to obtain the concentration difference for each constituent. This difference was then, as required, added to or subtracted from the concentration of the synthetic standard. The above procedure was repeated on a different day using the same synthetic standard as reference to obtain $x_2$.

The slope of each analytical curve was determined by sparking standards of a similar matrix and plotting on linear coordinates intensity ratios in division versus concentration. When the sample and standard have the same matrix and the concentration difference between the sample and standard is small for the determined element, the matrix used for determining the slope of the analytical curve is unimportant.

TABLE 18.—*Direct-reading spectrometric data on the major constituents of G–1 and W–1*

| | $\bar{x}$ | $x_1$ | $x_2$ | $k$ | $s$ | $C'$ | $DF$ | $n$ | $s_{\bar{x}}$ | $E$ | $s_a$ | $E_a$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | | | | **G–1** | | | | | | | |
| $SiO_2$ | 72.2 | 71.9 | 72.4 | 71.1 | 1.04 | 1.44 | 60 | 32 | 0.18 | 0.25 | 0.26 | 0.36 |
| $Al_2O_3$ | 13.9 | 14.1 | 13.7 | 14.1 | .28 | 2.04 | 60 | 32 | .05 | .36 | .07 | .51 |
| $Fe_2O_3$ [1] | 1.87 | 1.90 | 1.84 | 2.40 | .055 | 2.96 | 60 | 32 | .010 | .52 | .014 | .74 |
| MgO | .38 | .37 | .38 | .40 | .008 | 2.03 | 60 | 32 | .001 | .36 | .002 | .51 |
| CaO | 1.36 | 1.35 | 1.38 | 1.45 | .080 | 5.92 | 60 | 32 | .014 | 1.04 | .020 | 1.47 |
| $Na_2O$ | 3.42 | 3.32 | 3.53 | 3.30 | .114 | 3.32 | 60 | 32 | .020 | .59 | .028 | .83 |
| $TiO_2$ | .22 | .22 | .23 | .30 | .020 | 9.23 | 60 | 32 | .004 | 1.63 | .005 | 2.30 |
| MnO | .024 | .024 | .023 | .00 | .0016 | 5.57 | 30 | 32 | .0003 | .98 | .0004 | 1.38 |
| | | | | | **W–1** | | | | | | | |
| $SiO_2$ | 52.5 | 52.6 | 52.4 | 52.3 | 0.88 | 1.67 | 60 | 32 | 0.16 | 0.30 | 0.22 | 0.42 |
| $Al_2O_3$ | 14.7 | 14.8 | 14.6 | 14.5 | .36 | 2.45 | 60 | 32 | .06 | .43 | .09 | .61 |
| $Fe_2O_3$ [1] | 11.2 | 11.3 | 11.0 | 11.5 | .27 | 2.38 | 60 | 32 | .05 | .42 | .07 | .59 |
| MgO | 6.74 | 6.75 | 6.73 | 6.40 | .15 | 2.28 | 60 | 32 | .027 | .40 | .038 | .57 |
| CaO | 10.8 | 10.9 | 10.7 | 10.9 | .25 | 2.28 | 60 | 32 | .04 | .40 | .06 | .57 |
| $Na_2O$ | 2.18 | 2.15 | 2.22 | 2.10 | .072 | 3.29 | 60 | 32 | .012 | .58 | .017 | .82 |
| $TiO_2$ | 1.04 | 1.04 | 1.03 | 1.12 | .045 | 4.31 | 60 | 32 | .008 | .76 | .011 | 1.08 |
| MnO | .17 | .17 | .17 | .16 | .008 | 4.70 | 60 | 32 | .001 | .83 | .002 | 1.17 |

[1] Total Fe as $Fe_2O_3$.

The details of the analytical procedure follow closely those published by Tingle and Matocha (1958). However, since some modifications were made, the specific details follow.

A 0.2000-gram portion of the sample was fused with 1.6000 grams of lithium tetraborate. The resulting bead was ground to 80 percent −200 mesh on a Wig-L-Bug grinder and 0.25 gram of the ground sample was mixed for 3 minutes with 1.00 gram of SP1–C graphite; three plastic balls, ⅛-inch in diameter, were used for mixing. The resulting mixture was formed into a pellet, ½ inch in diameter, at a gauge pressure of 20,000 pounds. Excitation and exposure conditions are those listed in table 1 of the article on the method (Tingle and Matocha, 1958) with the exception that the determination of

MnO in W–1 and G–1 and $TiO_2$, $Fe_2O_3$, and MgO in G–1 were made using an inductance of 180 microhenrys and an exposure period of 10 seconds.

A statistical evaluation of the procedure of analysis is included in table 18. From an analysis of variance comparing the variation among pellet means to the variation within pellet means, only 5 cases out of 30 for G–1 and 10 cases out of 32 for W–1 were significant at the 95 percent confidence level. Each standard deviation, $s$, listed in table 18 is the total $s$, pooled over the sample and standard and over all tests. In every case except MnO in G–1, this gives 60 degrees of freedom. The repeatability on standard pellets is known to be the same as on sample pellets of the same matrix.

The statistical terms used in table 18 ($s$, $C'$, $n$, $s_{\bar{x}}$, and $E$) have been defined elsewhere in this section (p. 65). The degrees of freedom, *DF*, listed are those associated with $s$ and $C'$. As the reported analysis of the sample depends on the difference between the average intensity ratio for the sample and that for the standard, the precision obtained for both the sample and standard must be taken into account when calculating the standard error of analysis, *sa;* thus

$$s_a=\sqrt{2}\ s_{\bar{x}}$$

$E_a$, the relative error of analysis$=\sqrt{2}E$. Both $s_a$ and $E_a$ are shown in table 18.

## DISCUSSION OF RESULTS

The precision of the data ($C'$ values) listed in table 18 is generally much better than that of the data ($C'$ values) reported for determinations by individual methods listed in table 12. No data are given in this section on the relative precision of various chemical methods, so a comparison between direct-reading spectrometric and chemical methods cannot be made. However, it seems safe to say that, for most constituents, a spectrometric method may be as precise, or in some instances more precise, than a chemical method. Direct-reading methods are undoubtedly more precise than normal spectrographic methods because the precision of the former is only limited, essentially, by homogeneity of the sample and by constancy of excitation. The method used to obtain the values in table 18 utilized solid solution of the sample and a–c spark excitation, both of which are normally more reproducible than the powdered sample d–c arc methods.

Because synthetic standards were used to obtain the values in table 18, errors in the results due to uncertainties in the standard composition are eliminated. The direct-reading values for $SiO_2$ in G–1 and W–1 are lower than the values obtained by Stevens and Chodos. Also, the values that were obtained for $Al_2O_3$ in G–1 and

W–1 are lower than the preferred chemical values given in table 16. This fact lends support to Fairbairn's conclusion that the chemical $Al_2O_3$ determinations are too high.

For the other constituents of G–1 and W–1, the values determined with the Quantometer agree well with the recommended values given in table 17.

*Sources of data in tables 12–14 and list of analysts*

[Numbers refer to headings in tables]

1. Stevens and Niles, tables 3 and 4: analyses in Bulletin 980.
2. Fairbairn, 1953: revised data.
3. Stevens and Niles, tables 3 and 4: new analyses.
4. Stevens and Niles, tables 3 and 4: all analyses.
5. Stevens and Niles, tables 7 and 8: preferred values ($\bar{x}'$).
6. Dennen, W. H.: spectrographic data from Dennen, W. H., Ahrens, L. H., and Fairbairn, H. W., 1951.
7. Dennen, W. H., Massachusetts Institute of Technology: written communication.
8. Filby, R. H., Geological Survey, Indiana Department of Conservation, Bloomington, Ind.
9. Hall, W. L., Texas Company, Bellaire, Texas: written communication.
10. Joensuu, Oiva, Heavy Mineral Corporation, Chattanooga, Tenn.: written communication.
11. Shaw, D. M., Filby, R. H., Siroonian, H., and Yip, C., McMaster University, Hamilton, Ontario, Canada: written communication.
12. Leininger, R. K., and Taylor, S. R., Geological Survey, Indiana Department of Conservation, Bloomington, Ind. (S. R. Taylor is now at University of Cape Town, South Africa.)

13a. Hawley, J. E., and MacDonald, Graham, 1956.

13b. Hawley, J. E., and MacDonald, Graham, Queens University, Kingston, Ontario, Canada: written communication.

14. Harvey, C. O., Geological Survey of Great Britain, London, England: Ahrens, L. H., and Fleischer, M., part 4 this report.
15. Yamasaki, K., Iida, C., and Yokoi, H., University of Nagoya, Japan: Ahrens, L. H., and Fleischer, M., part 4 this report.
16. Barnett, Paul, U.S. Geological Survey, Denver, Colo.: Ahrens, L. H., and Fleischer, M., part 4 this report.
17. Myers, A. T., U.S. Geological Survey, Denver, Colo.: Ahrens, L. H., and Fleischer, M., part 4 this report.
18. Chodos, A. A., California Institute of Technology, Pasadena, Calif.: Ahrens, L. H., and Fleischer, M., part 4 this report.
19. Young, E. J., Massachusetts Institute of Technology: Ahrens, L. H., and Fleischer, M., part 4 this report.
20. Murata, K. J., U.S. Geological Survey, Washington, D.C.: Ahrens, L. H., and Fleischer, M., part 4 this report.
21. Gorfinkle, L. G., and Ahrens, L. H., Massachusetts Institute of Technology· Ahrens, L. H., and Fleischer, M., part 4 this report.
22. Shilstone Testing Laboratory, Houston, Texas.
23. Hodge, E. S., and Baer, W. K., 1956.
24. Smith-Emery Company, Los Angeles, Calif. Analyst, T. C. McBurney.

# SECOND REPORT ON A COOPERATIVE INVESTIGATION OF THE COMPOSITION OF TWO SILICATE ROCKS

## PART 4. REPORT ON TRACE CONSTITUENTS IN GRANITE G-1 AND DIABASE W-1

By L. H. AHRENS [8] and MICHAEL FLEISCHER [9]

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### ABSTRACT

Data on trace constituents of the rocks G-1 and W-1 given in U.S. Geological Survey Bulletin 980 consisted mainly of spectrographic analyses by three laboratories. Since then the rocks have been studied by many laboratories and by chemical-colorimetric, isotope-dilution, and neutron-activation methods as well as by the spectrographic procedures. All available data have been assembled in this paper. It is now possible to give preferred values, many of which seem to be well established, for many elements.

### INTRODUCTION

The usefulness of the two rocks, granite G-1 and diabase W-1, as reference samples for studies on trace elements has been emphasized (Ahrens, 1957a, for example). The analyst may test his procedure by analyzing these rocks and, equally important, G-1 and W-1 may serve for the purpose of comparing and calibrating data from different laboratories.

The trace elements are now being determined by a variety of analytical procedures, of which the spectrochemical methods have been

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most frequently used. These methods offer many advantages in geochemistry and cosmochemistry (Ahrens, 1957b, and Taylor and Ahrens, in press) but they have one serious weakness in that they rely on standards; as synthetic standards are often used, significant systematic error (bias) may be introduced. The data for rubidium (Taylor, Emeleus, and Exley, 1956) serve as one good example of possible systematic error. Such error may be reduced or even eliminated if appropriate standards of naturally occurring material (G–1 and W–1, for example) are used for preparing spectrochemical working curves; or if not, these rocks could be included with a group of unknowns, and corrections applied if necessary.

A few determinations of the trace constituents in G–1 and W–1 were given in the first publication on these two rocks (Fairbairn and others, 1951); some later information was given by Ahrens (1954a). A considerable amount of new quantitative data on the trace constituents has since accumulated, but they are widely scattered in the literature. The purposes of this paper are to set out in convenient form the available data on trace elements as they stand at the moment and to attempt to derive some preferred values.

The task of deriving a preferred value is not simple. The quality and quantity of the data vary greatly from element to element; several determinations are described as semi-quantitative, whereas others such as the neutron-activation and isotope-dilution procedures are generally highly accurate. Where possible, cognizance will be taken of such differences. An attempt will be made to distinguish two categories of preferred values—the recommended values, given in bold type and which refer to elements for which the analytical data are, generally speaking, satisfactory, and the magnitudes. It will become clear that there are grades of recommended values and magnitudes.

## THE DATA

The data for each element are listed in four vertical columns. Within a vertical column, data are arranged according to the general analytical method in the first place, and for each method the sequence is in order of date of publication; the sequence for a given year is alphabetical according to the code letters (p. 105-111). Unless stated otherwise, all values are in parts per million.

Many of the determinations listed are from previously unpublished data. We wish to express our appreciation to the many analysts who have cooperated by furnishing such data.

*Arsenic* (As), *in parts per million*

| G-1 | | W-1 | | Method | Reference |
|---|---|---|---|---|---|
| Average | Value | Average | Value | | |
| 1.0 | 1. 0 | 1. 8 | 1. 8 | Chemical--- | ON 55 |
| | 1. 0 | | 1. 8 | | |

Although only one set of data is available the analytical procedure seems to be reliable and the average values should serve as good magnitudes.

*Gold* (Au), *in parts per million*

| G-1 | | W-1 | Method | Reference |
|---|---|---|---|---|
| Average | Value | | | |
| 0.0095 | 0. 009 | 0. 018 | Neutron activation-- | SV 55 |
| | 0. 01 | | | |

J. Crocket (written communication to L. H. Ahrens, 1957) also used a neutron-activation procedure and points out that because of self-shielding the values for gold should be reduced by 37 percent, namely, to 0.007 and 0.011, respectively, for G–1 and W–1. These values should serve as good magnitudes.[10]

*Boron* (B), *in parts per million*

| G-1 | W-1 | Method | Reference |
|---|---|---|---|
| [1] 1. 5 | [1] 17 | Chemical colorimetric- | HW 59 |
| 1 | 2. 6 | Spectrochemical------ | EU 54 |
| 30 | 20 | ----do-------------- | MB 56 |
| 20 | 10 | ----do-------------- | CH 57 |
| -------- | 10 | ----do-------------- | MU 51 |
| 7 | -------- | ----do-------------- | HL 58 |
| -------- | <12 | ----do-------------- | SH 58 |
| 1. 2 | 12 | ----do-------------- | HD 59 |

[1] Average of 10 analyses.

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[10] Vincent and Crocket (1960, Geochim. et Cosmochim. Acta, v. 18, p. 130–142, 143–148) give new determinations by neutron activation: 0.0046, 0.0043, average 0.0045 for G–1; 0.0085, 0.0083, average 0.0084 for W–1.

The chemical results, 1.5 and 17 for boron in G–1 and W–1, respectively, may serve as magnitudes. Considerable uncertainty must be attached to the spectrographic results; one possible cause may be the presence of boron in the carbon electrodes used in the spectrographic analyses.

*Barium* (Ba), *in parts per million*

| G-1 | W-1 | | Method | Reference |
|---|---|---|---|---|
| | Average | Value | | |
| 1, 100 | -------- | 270 | Chemical | HE 51 |
| 1, 300 | -------- | 270 | Spectrochemical | GA 51 |
| 3, 000 | -------- | 250 | do | MI 51 |
| 1, 300 | -------- | 390 | do | MU 51 |
| 900 | -------- | 180 | do | HA 54 |
| 1, 300 | -------- | 150 | do | NO 54 |
| 1, 100 | -------- | -------- | do | BA 55 |
| 3, 000 | -------- | -------- | do | SI 55 |
| 1, 600 | -------- | -------- | do | YA 55 |
| 1, 000 | -------- | 300 | do | HB 56 |
| 1, 340 | -------- | 190 | do | HM 56 |
| 1, 300 | -------- | -------- | do | MB 56 |
| 1, 400 | -------- | 200 | do | CH 57 |
| 1, 400 | 180 | 220<br>140 | do | LT 57 |
| 1, 080 | -------- | 145 | do | GU 58 |
| 1, 000 | -------- | -------- | do | HL 58 |
| 1, 150 | 145 | 120<br>170 | do | SH 58 |

Fifteen of the seventeen determinations of barium in G–1 fall within or are close to the range 1,000 to 1,500 and their average of **1,220** may be recommended. The information on W–1 is less satisfactory; the average of 225 should serve as a good magnitude.

*Beryllium* (Be), *in parts per million*

| G-1 | | W-1 | | Method | Reference |
|---|---|---|---|---|---|
| Average | Value | Average | Value | | |
| ------- | 2 | ------- | ------- | Spectrochemical | MU 51 |
| ------- | <15 | ------- | <15 | do | SH 54 |
| ------- | 4 | ------- | ------- | do | BA 55 |
| ------- | 3 | ------- | ------- | do | HB 56 |
| ------- | 4 | ------- | ------- | do | HM 56 |
| ------- | 2 | ------- | ------- | do | CH 57 |
| ------- | <1 | ------- | ------- | do | SH 58 |
| [1] 2. 5 | ----- | ------- | ------- | do | MY 58 |
| 3. 27 | 3. 00<br>3. 25<br>3. 67<br>3. 37<br>3. 04 | 0. 78 | 0. 76<br>. 56<br>1. 01<br>0. 65<br>. 79<br>. 93 | Isotope dilution | AR 56 |

[1] Average of 9 analyses.

In G–1 the spectrochemical determinations for beryllium (2 to 4) agree in magnitude with the average isotope-dilution value of **3.3,** which is recommended. The isotope-dilution value of **0.8** in W–1 may be recommended also but not with as much confidence, as direct supporting data are not available.

*Cadium* (Cd), *in parts per million*

| G-1 | W-1 | Method | Reference |
|---|---|---|---|
| 5±2 | 6±2 | Polarographic | SG 55 |

These values for cadmium may serve as magnitudes.

*Cerium* (Ce), *in parts per million*

| G-1 | W-1 | Method | Reference |
|---|---|---|---|
| 600 | 70 | Chemical-spectrochemical. | BE 57 |
| 200 | ------ | Spectrochemical | CH 57 |
| 700–1, 400 | ------ | X-ray fluorescence | AA 57 |

The range for cerium in G–1 is considerable and it is difficult to give a preferred value. The average of 600 ppm and the single W–1 value of 70 may serve as general magnitudes.

### *Chlorine* (Cl)

The only determination available (by IW 55) is 50 ppm in G–1.

*Cobalt* (Co), *in parts per million*

| G-1 |  | W-1 |  | Method | Reference |
|---|---|---|---|---|---|
| Average | Value | Average | Value |  |  |
| ------ | 3 | ------- | 40 | Chemical (field) | BL 51 |
| ------ | 10 | ------- | 20 | do | LA 51 |
| ------ | ------- | ------- | 30 | Chemical | GO 56 |
| ------ | ------- | ------- | 35 | Spectrochemical | GA 51 |
| ------ | ------- | ------- | 35 | do | MI 51 |
| ------ | 3 | ------- | 25 | do | MU 51 |
| ------ | $<5$ | ------- | 30 | do | HA 54 |
| ------ | ------- | ------- | 50 | do | NO 54 |
| ------ | 2 | ------- | 55 | do | SH 54 |
| ------ | 2. 5 | ------- | ------- | do | BA 55 |
| ------ | ------- | ------- | 20 | do | SI 55 |
| ------ | 1 | ------- | ------- | do | YA 55 |
| 2. 5 | 2<br>3 | 52 | 43<br>61 | do | HM 56 |
| ------ | ------- | ------- | 20 | do | MB 56 |
| ------ | 2 | ------- | 38 | do | CH 57 |
| ------ | 10 | 60 | 70<br>50 | do | LT 57 |
| ------ | 2 | ------- | 41 | do | TU 57 |
| ------ | 2 | ------- | ------- | do | HL 58 |
| ------ | $<2$ | ------- | 45 | do | MO 58 |
| [1] 2 | ------- | [2] 41 | ------- | do | MY 58 |
| ------ | ------- | ------- | 35 | do | SH 58 |
| ------ | 5 | ------- | 57 | do | YO 58 |
| ------ | ------- | ------- | 23 | Polarographic | SG 55 |
| 2. 1 | 1. 8<br>2. 1<br>2. 1<br>2. 4 | 49 | 45<br>46<br>46<br>50<br>52<br>54 | Neutron-activation | SM 57 |
| 2. 3 | ------- | 54 | ------- | do | CK 59 |

[1] Average of 18 determinations.
[2] Average of 14 determinations.

Agreement between the 21 determinations of cobalt in W–1 is moderately good and two alternative values may be derived—either the average **38** of all determinations or the neutron-activation value of **51** which is distinctly higher. In G–1, the data are less satisfactory. Most values (LA 51 excepted) are within the range 1 to 5 and their average of 2.5 is close to the neutron-activation value **2.2** that is recommended. It should be noted that the MY 58 value of 2 is almost identical and is an average of 18 determinations.

*Chromium* (Cr), *in parts per million*

| G-1 | | W-1 | | Method | Reference |
|---|---|---|---|---|---|
| Average | Value | Average | Value | | |
| ------ | 27 | ------- | 100 | Chemical | HE 51 |
| ------ | 25 | ------- | 110 | Spectrochemical | GA 51 |
| ------ | 10 | ------- | 120 | do | MI 51 |
| ------ | 30 | ------- | 130 | do | MU 51 |
| ------ | 30 | ------- | 140 | do | HA 54 |
| ------ | 20 | ------- | 150 | do | NO 54 |
| ------ | 8 | ------- | 150 | do | SH 54 |
| 26 | 25<br>26 | ------- | ------- | do | BA 55 |
| ------ | 40 | ------- | 100 | do | SI 55 |
| ------ | 10 | ------- | ------- | do | YA 55 |
| 21 | 27<br>19<br>17 | ------- | 116 | do | HM 56 |
| ------ | 20 | ------- | 130 | do | MB 56 |
| ------ | 20 | ------- | 120 | do | CH 57 |
| 13 | 20<br>6 | 145 | 170<br>120 | do | LT 57 |
| ------ | 22 | ------- | 105 | do | TU 57 |
| ------ | 20 | ------- | ------- | do | HL 58 |
| [1] 27 | ------- | [2] 140 | ------- | do | MY 58 |
| 20 | ------- | ------- | 100 | do | SH 58 |
| 21 | ------- | ------- | 130 | do | YO 58 |

[1] Average of 20 determinations.
[2] Average of 9 determinations.

Taken as a whole, agreement for values of chromium in W-1 is exceptionally good and the average of **120** (rounded from 124) is recommended with considerable confidence. Agreement in G-1 is generally less satisfactory but most values are quite close to the average of **22** ppm that is recommended.[11]

*Cesium* (Cs), *in parts per million*

| G-1 | | W-1 | | Method | Reference |
|---|---|---|---|---|---|
| Average | Value | Average | Value | | |
| 2.5 | ----- | ----- | ----- | Spectrochemical | CA 54 |
| 1.5 | 1.51<br>1.48<br>1.54 | 1.08 | 1.03<br>1.13<br>1.07 | Neutron activation | CS 57 |

As the cesium concentration is very close to the detection limit of the spectrochemical procedure, only the neutron-activation values are considered. These should serve as good magnitudes.

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[11] Fröhlich (1960, Zeitschr. anal. Chem., v. 170, p. 383-387) found by a colormetric method, using diphenylcarbazide, 20 ppm Cr in G-1 and 125 ppm Cr in W-1.

*Copper* (Cu) *in parts per million*

| G-1 |  | W-1 |  | Method | Reference |
|---|---|---|---|---|---|
| Average | Value | Average | Value |  |  |
| ------- | 20 | ------- | 130 | Chemical (field) | BL 51 |
| ------- | 10 | ------- | 80 | do | LA 51 |
| ------- | Trace | ------- | 100 | Chemical | HE 51 |
| 15.9±0.4 | ------- | 121±3 | ------- | do | RS 58 |
| ------- | 5 | ------- | 44 | Spectrochemical | GA 51 |
| ------- | 8 | ------- | 130 | do | MI 51 |
| ------- | 15 | ------- | 90 | do | MU 51 |
| ------- | 6 | ------- | 140 | do | SH 54 |
| ------- | 13 | ------- | ------- | do | BA 55 |
| ------- | 10 | ------- | 50 | do | SI 55 |
| 14 | 17<br>11<br>16 | ------- | 160 | do | HM 56 |
| ------- | 11 | ------- | ------- | do | MB 56 |
| ------- | 12 | ------- | 100 | do | CH 57 |
| ------- | 25 | 87 | 44<br>130 | do | LT 57 |
| ------- | 10 | ------- | ------- | do | HL 58 |
| ------- | 15 | ------- | 135 | do | MO 58 |
| [1] 13 | ------- | ------- | ------- | do | MY 58 |
| ------- | 9.5 | ------- | ------- | do | SH 58 |
| [2] 9.5 | ------- | [3] 112 | ------- | Neutron-activation. | SM 57 |
| 17±16 | ------- | 68±10 | ------- | Polarographic | SG 55 |
| ------- | 18 | ------- | 171 | X-ray fluorescence. | HF 57 |

[1] Average of 22 determinations.
[2] Average of 6 determinations.
[3] Average of 8 determinations.

The average values for copper of **13** and **110** (rounded from 107) for G–1 and W–1, respectively, are recommended.

*Fluorine* (F), *in parts per million*

| G-1 |  | W-1 |  | Method | Reference |
|---|---|---|---|---|---|
| Average | Value | Average | Value |  |  |
| ----- | 450 | ----- | ----- | Chemical | HE 51 |
| ----- | 900 | ----- | ----- | do | PE 54 |
| ----- | 900 | ----- | ----- | do | OS 54 |
| ----- | 800 | ----- | ----- | do | SN 54 |
| ----- | 400 | ----- | ----- | do | SU 54 |
| 685 | 670<br>680<br>-------<br>700<br>770 | 200 | 200<br>-------<br>200 | do | GO 56 |
| ----- | ----- | ----- | 170 | do | KO 56 |
| 785 | 770<br>800 | ----- | 200 | do | HG 57 |
| ----- | 920 | ----- | 200 | Spectrochemical | SE 51 |

The average for fluorine of **730** in G-1 is recommended. In W-1 the average of 200 should be a good magnitude.

*Gallium* (Ga) *in parts per million*

| G-1 | W-1 | Method | Reference |
|---|---|---|---|
| 15 | 15 | Chemical | HE 51 |
| [1] 21.3 | [1] 21.5 | do | CR 58 |
| 19 | 13 | Spectrochemical | GA 51 |
| 20 | 15 | do | MI 51 |
| 18 | 12 | do | MU 51 |
| 10 | 20 | do | HA 54 |
| 15 | 20 | do | NO 54 |
| 18 | 11 | do | SH 54 |
| 20 | ------ | do | BA 55 |
| 18 | 15 | do | MB 56 |
| 13 | 8 | do | CH 57 |
| 20 | ------ | do | HL 58 |
| 23 | 23 | do | MO 58 |
| [2] 20 | [3] 15 | do | MY 58 |
| 16 | 8 | do | SH 58 |
| 20 | 24 | X-ray fluorescence | NR 58 |

[1] Average of 5 determinations.
[2] Average of 29 determinations.
[3] Average of 22 determinations.

Eight of the fourteen who determined gallium in both rocks report the gallium content of G-1 as greater than that of W-1, four report the reverse, and two found equal concentrations. The averages of 18 and 16 for G-1 and W-1, respectively, are recommended. These values agree quite closely with MY 58 who carried out a large number of replicate determinations.

*Germanium* (Ge), *in parts per million*

| G-1 | | W-1 | | Method | Reference |
|---|---|---|---|---|---|
| Average | Value | Average | Value | | |
| 1.0 | 0.9<br>1.0 | 1.6 | 1.6<br>1.6 | Chemical | ON 56 |

These values for germanium should serve as reasonable magnitudes.

*Indium* (In), *in parts per million*

| G-1 | | W-1 | | Method | Reference |
|---|---|---|---|---|---|
| Average | Value | Average | Value | | |
| 0. 026 | 0. 024<br>. 026<br>. 026<br>. 025<br>. 029<br>. 029<br>. 025 | 0. 064 | 0. 064<br>. 070<br>. 061<br>. 065<br>. 065<br>. 062<br>. 063 | Neutron-activation-- | SS 57 |

Agreement between the several replicate determinations for indium is very close and provided there is no unforeseen error, the averages of **0.026** and **0.064** for G–1 and W–1, respectively, are recommended.

*Lanthanum* (La), *in parts per million*

| G-1 | W-1 | Method | Reference |
|---|---|---|---|
| 200 | 30 | Chemical-spectrochemical---------- | BE 57 |
| 130 | ------ | Spectrochemical------ | GA 51 |
| 430 | 32 | -----do-------------- | MI 51 |
| 190 | ------ | -----do-------------- | MU 51 |
| 100 | <5 | -----do-------------- | HA 54 |
| 60 | ------ | -----do-------------- | NO 54 |
| 158 | ------ | -----do-------------- | BA 55 |
| 70 | ------ | -----do-------------- | YA 55 |
| 100 | ------ | -----do-------------- | CH 57 |
| 100 | ------ | -----do-------------- | LT 57 |
| 96 | ------ | -----do-------------- | HL 58 |
| [1] 140 | ------ | -----do-------------- | MY 58 |
| 160 | 26 | -----do-------------- | YO 58 |

[1] Average of 16 determinations.

The average **150** of the 13 determinations for lanthanum in G–1 may be recommended but with some reservation because of the considerable spread of values. In W–1 the average 30 of 3 determinations may serve as a magnitude.

*Lithium* (Li), *in parts per million*

| G–1 | | W–1 | | Method | Reference |
|---|---|---|---|---|---|
| Average | Value | Average | Value | | |
| ----- | 23 | ----- | 9 | Spectrochemical | GA 51 |
| ----- | 19 | ----- | 9 | do | MI 51 |
| ----- | 25 | ----- | 20 | do | NO 54 |
| ----- | <25 | ----- | <20 | do | SH 54 |
| ----- | 30 | ----- | 7 | do | CH 57 |
| [1] 23 | ----- | [1] 15 | ----- | do | JU 56 |
| [2] 29 | ----- | [2] 9. 5 | ----- | do | SH 58 |
| [3] 29 | ----- | [1] 9. 7 | ----- | do | SR 59 |
| 23. 5 | 24<br>23 | 14 | 14<br>13<br>15 | Flame photometric | EH 55 |
| ----- | 22 | ----- | 14 | do | HO 56 |
| [4] 21. 3 | ----- | [4] 12. 6 | ----- | Isotope dilution | SW 58 |

[1] Average of 3 determinations.
[2] Average of 6 determinations.
[3] Average of 4 determinations.
[4] Average of 8 determinations.

Agreement for determinations of lithium in G–1 is good and the average value of **24** is recommended. Agreement in W–1 is less satisfactory but the average of **12** is nevertheless recommended with some confidence as it is close to the isotope-dilution value, which is an average of 8 determinations.

*Manganese* (Mn) *in parts per million*

| G–1 | W–1 | Method | Reference |
|---|---|---|---|
| 340 | 1, 300 | Spectrochemical | HA 54 |
| 125 | -------- | do | BA 55 |
| 400 | 2, 000 | do | SI 55 |
| 100 | -------- | do | YA 55 |
| 220 | -------- | do | HM 56 |
| 210 | 1, 300 | do | MB 56 |
| 160 | 1, 200 | do | CH 57 |
| 105 | -------- | do | HL 58 |
| 190 | 1, 450 | do | MO 58 |
| [1] 190 | [2] 1, 200 | do | MY 58 |
| 260 | 990 | do | SH 58 |
| 212 | 1, 400 | X-ray fluorescence | HF 57 |

[1] Average of 26 determinations.
[2] Average of 18 determinations.

The results for manganese average 210 for G–1 and 1,300 (rounded from 1,340) for W–1; the chemical analyses averaged by Stevens and Niles, part 1 of this report, are 230 and 1,320, respectively.

*Molybdenum* (Mo) *in parts per million*

| G-1 | | W-1 | | Method | Reference |
|---|---|---|---|---|---|
| Average | Value | Average | Value | | |
| ------ | 14 | ------- | 5 | Chemical (field) | LA 51 |
| 6.6 | 6.5<br>6.7 | 0.5 | 0.5<br>0.4<br>.5 | Chemical | KS 54 |
| ------ | 6 | ------- | ------- | Spectrochemical | MI 51 |
| ------ | 6 | ------- | ------- | do | MU 51 |
| ------ | 5 | ------- | ------- | do | NO 54 |
| ------ | <4 | ------- | ------- | do | SH 54 |
| ------ | 11 | ------- | ------- | do | BA 55 |
| ------ | 10 | ------- | ------- | do | HB 56 |
| 6.5 | 4<br>9 | ------- | ------- | do | HM 56 |
| ------ | 7 | ------- | ------- | do | CH 57 |
| ------ | 6 | ------- | ------- | do | HL 58 |
| ------ | 7 | ------- | 5 | do | MO 58 |
| [1] 9 | --------- | ------- | ------- | do | MY 58 |
| ------ | <10 | ------- | <4 | do | SH 58 |

[1] Average of 16 determinations.

In G-1 most determinations for molybdenum (14 and <4 excluded) are fairly close to the average of **7**, which is recommended (it matters little if 14 and <4 are actually taken into account). In W-1, two magnitudes involving a factor of 10 are listed. According to JE 58, interference with his tungsten determinations by molybdenum was observed in G-1 only, which suggests the lower value of 0.5 for W-1 as the more likely magnitude.

When these rocks are used as standards it should be recalled that the molybdenum concentration in G-1 is unusually high. (See, for example, the data of KS 54 and the histogram of Ahrens, 1954b.)

*Niobium* (Nb) *in parts per million*

| G-1 | W-1 | Method | Reference |
|---|---|---|---|
| [1] 22 | [1] 10 | Chemical colorimetric | GR 59 |
| 18 | --------- | Spectrochemical | BA 55 |
| 20 | --------- | do | CH 57 |
| [2] 19 | --------- | do | MY 58 |

[1] Average of 10 determinations.
[2] Average of several determinations.

The agreement for determinations of niobium by two methods is very good for G-1 and the average of **20** is recommended; the value of 10 for W-1 should serve as a good magnitude.

*Neodymium* (Nd) *in parts per million*

| G–1 | W–1 | Method | Reference |
|---|---|---|---|
| 80 | ------ | Spectrochemical | GA 51 |
| 100 | 50 | do | BE 57 |
| 50 | ------ | do | CH 57 |
| 100 | 50 | do | YO 58 |

The average of 80 in G–1 and 50 in W–1 should serve as good magnitudes for neodymium until further data are available.

*Nickel* (Ni), *in parts per million*

| G–1 | | W–1 | | Method | Reference |
|---|---|---|---|---|---|
| Average | Value | Average | Value | | |
| ------ | ------- | ------- | 80 | Chemical (field) | BL 51 |
| ------ | 60 | ------- | 150 | do | LA 51 |
| ------ | ------- | ------- | 70 | Chemical | HE 51 |
| ------ | ------- | 73 | 72<br>74 | do | GO 56 |
| ------ | 5 | ------- | 47 | Spectrochemical | MI 51 |
| ------ | ------- | ------- | 80 | do | MU 51 |
| ------ | <10 | ------- | 100 | do | HA 54 |
| ------ | ------- | ------- | 80 | do | NO 54 |
| ------ | <2.5 | ------- | 140 | do | SH 54 |
| ------ | ------- | ------- | 40 | do | SI 55 |
| ------ | 8 | ------- | ------- | do | YA 55 |
| ------ | 1 | ------- | 100 | do | HB 56 |
| ------ | 3–4 | 111 | 120<br>102 | do | HM 56 |
| ------ | ------- | ------- | 30 | do | MB 56 |
| ------ | ------- | ------- | 75 | do | CH 57 |
| ------ | ------- | 115 | 140<br>90 | do | LT 57 |
| ------ | <2 | ------- | 110 | do | TU 57 |
| ------ | <1.5 | ------- | ------- | do | HL 58 |
| ------ | <2 | ------- | 85 | do | MO 58 |
| ------ | ------- | [1] 79 | ------- | do | MY 58 |
| ------ | <3 | ------- | 54 | do | SH 58 |
| ------ | 4 | ------- | 114 | do | YO 58 |
| 1.2 | 1.0<br>1.0<br>1.3<br>1.5 | [2] 73 | ------- | Neutron-activation | SM 57 |
| 2±2 | ------- | 53±2 | ------- | Polarographic | SG 55 |
| 3 | ------- | 68 | ------- | X-ray fluorescence | HF 57 |

[1] Average of 16 determinations.
[2] Average of 6 determinations.

Agreement for nickel in G–1 is unsatisfactory. The very high value of 60 may perhaps be due to reagent impurity and will be omitted. The neutron-activation value of 1.2 should be reliable but is distinctly less than most of the other values including the one of 3 given by the X-ray fluorescence method. Data on W–1 are extensive and agreement is moderate. The average (150 excepted because of possible blank) is 82 and may be recommended. The neutron-activation value is close but distinctly lower.

*Lead* (Pb), *in parts per million*

| G–1 | W–1 | Method | Reference |
|---|---|---|---|
| 14 | 5 | Chemical (field)------ | BL 51 |
| 15 | 5 | -----do------------- | LA 51 |
| 28 | 10 | Chemical----------- | HE 51 |
| [1] 51 | -------- | -----do------------- | WA 55 |
| [2] 46 | -------- | -----do------------- | KP 56 |
| [3] 48 | -------- | -----do------------- | PW 56 |
| [2] 47 | -------- | -----do------------- | WN 56 |
| 23 | 7 | Spectrochemical------ | GA 51 |
| 25 | -------- | -----do------------- | MI 51 |
| 22 | -------- | -----do------------- | MU 51 |
| 50 | -------- | -----do------------- | NO 54 |
| 37 | 20 | -----do------------- | SH 54 |
| 52 | -------- | -----do------------- | BA 55 |
| 55 | -------- | -----do------------- | CH 55 |
| [4] 55 | -------- | -----do------------- | MY 55 |
| [5] 28 | [6] 7 | -----do------------- | WR 55 |
| 28 | -------- | -----do------------- | YA 55 |
| [2] 47 | -------- | -----do------------- | CH 56 |
| 22 | <10 | -----do------------- | HM 56 |
| 50 | -------- | -----do------------- | MB 56 |
| [2] 49 | -------- | -----do------------- | MU 56 |
| [2] 56 | -------- | -----do------------- | MY 56 |
| 26 | 6 | -----do------------- | WE 56 |
| [2] 47 | -------- | -----do------------- | WR 56 |
| 47 | -------- | -----do------------- | CH 57 |
| 48 | <2 | -----do------------- | TU 57 |
| 55 | -------- | -----do------------- | HL 58 |

[1] Average of 16 determinations.
[2] Average of 12 determinations.
[3] Average of 14 determinations.
[4] Average of 48 determinations
[5] Average of 3 determinations.
[6] Average of 2 determinations.

These puzzling results are discussed in some detail by Flanagan (part 5). On the basis of the recent results, the lead content of G–1 seems to be close to **50**; even an order of magnitude can hardly be set for W–1.

*Palladium* (Pd) *in parts per million*

| G-1 | W-1 |  | Method | Reference |
|---|---|---|---|---|
|  | Average | Value |  |  |
| <0.01 | 0.019 | 0.017<br>0.020 | Neutron activation | SV 55 |

The neutron-activation value in W–1 for palladium should serve as a good magnitude.

*Rubidium* (Rb) *in parts per million*

| G-1 |  | W-1 |  | Method | Reference |
|---|---|---|---|---|---|
| Average | Value | Average | Value |  |  |
|  | 550 | ------- | 64 | Spectrochemical | GA 51 |
|  | 590 | ------- | 15 | do | MI 51 |
|  | 250 | ------- | 20 | do | NO 54 |
| 212 | 210<br>213 | ------- | ------- | Flame photometer | GO 56 |
| [1] 205 | ------- | 22 | 19<br>25 | do | HO 56 |
| 217 | 215<br>218 | 28.5 | 27.9<br>29.1 | Isotope dilution | HP 55 |
| [2] 214 | ------- | [3] 21.3 | ------- | do | SW 58 |
| 239 | 221<br>254<br>243 | 27 | 27<br>29<br>26 | Neutron-activation | SC 55 |
| 219 | 217<br>219<br>222 | 21.3 | 20.6<br>21.6<br>21.8 | do | CS 57 |
|  | 248 | ------- | 25 | X-ray fluorescence | HF 57 |

[1] Average of 12 determinations.
[2] Average of 8 determinations.
[3] Average of 16 determinations.

The information on rubidium is of particular interest because several of the determinations are evidently of superior quality. This is due in part to the interest in this radioactive element because of its use for determining geological age. In G–1 the two high values will be omitted as well as the first neutron activation determinations (SC 55) which have been replaced by the later ones of CS 57. The average in G–1 is **220** (rounded from 224) and may be recommended. The average in W–1 (omitting GA 51 and SC 55) is **22** and may also be recommended.

*Antimony* (Sb) *in parts per million*

| G-1 | W-1 | Method | Reference |
|---|---|---|---|
| [1] 0. 6 | [1] 1. 2 | Chemical | WL 54 |

[1] Average of 4 determinations.

These values for antimony may serve as magnitudes.

*Scandium* (Sc) *in parts per million*

| G-1 | W-1 | Method | Reference |
|---|---|---|---|
| 4 | 51 | Spectrochemical | GA 51 |
| | 36 | do | KV 51 |
| | 15 | do | MI 51 |
| 2 | 34 | do | MU 51 |
| <10 | 70 | do | HA 54 |
| | 50 | do | NO 54 |
| <3 | 35 | do | SH 54 |
| 3. 5 | -------- | do | BA 55 |
| 4 | 50 | do | CH 57 |
| | 50 | do | LT 57 |
| | 35. 1 | do | HK 58 |
| 3 | -------- | do | HL 58 |
| [1] 6 | [2] 52 | do | MY 58 |
| 1 | 17 | do | SH 58 |
| 4 | 63 | do | YO 58 |

[1] Average of 15 determinations. [2] Average of 8 determinaitons.

The range of 15 to 70 for scandium in W–1 involves a factor of a little more than 4; most values, however, fall within or very close to the range 35 to 65, and the average of **43** is recommended with reasonable confidence. In G–1 the information is less satisfactory, but the average of 4 should be a good magnitude.[12]

*Tin* (Sn), *in parts per million*

| G-1 | | W-1 | | Method | Reference |
|---|---|---|---|---|---|
| Average | Value | Average | Value | | |
| 2. 3 | 2. 0<br>2. 5 | 2. 8 | 2. 5<br>3. 0 | Chemical | ON 57 |
| ----- | 5 | ----- | ----- | Spectrochemical | CH 57 |
| ----- | <2 | ----- | <2 | do | TU 57 |

The available data indicate that the tin content in G–1 and W–1 is about the same and probably of the order of 2 to 3 ppm.

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[12] Kemp and Smales (1960, Geochim. et Cosmochim. Acta, v. 18, p. 149–150) by neutron activation found 2.8 ppm (average of 5 determinations) in G–1, 34 ppm (average of 4 determinations) in W–1.

*Strontium* (Sr), *in parts per million*

| G-1 | | W-1 | | Method | Reference |
|---|---|---|---|---|---|
| Average | Value | Average | Value | | |
| ----- | 450 | ----- | 450 | Chemical | HE 51 |
| ----- | 250 | ----- | 250 | Spectrochemical | GA 51 |
| ----- | 900 | ----- | 420 | do | MI 51 |
| ----- | 120 | ----- | 120 | do | MU 51 |
| ----- | 200 | ----- | 200 | do | HA 54 |
| ----- | 280 | ----- | 180 | do | NO 54 |
| 395±25 | ----- | ----- | ----- | do | BA 55 |
| ----- | 225 | ----- | 130 | do | TU 55 |
| ----- | 500 | ----- | ----- | do | YA 55 |
| ----- | 440 | ----- | 400 | do | HM 56 |
| ----- | 300 | ----- | 300 | do | MB 56 |
| ----- | 218 | ----- | 158 | do | TK 56 |
| ----- | 200 | ----- | 200 | do | CH 57 |
| 320 | 260<br>380 | 200 | 180<br>220 | do | LT 57 |
| ----- | 287 | ----- | 172 | do | TG 57 |
| ----- | 256 | ----- | 180 | do | GU 58 |
| ----- | 225 | ----- | ----- | do | HL 58 |
| ----- | 250 | ----- | 150 | do | SH 58 |
| [1] 258 | ----- | [1] 151 | ----- | Flame photometer | FG 59 |
| 233 | 230<br>233<br>236 | 177 | 172<br>182 | Isotope dilution | HP 55 |
| ----- | 262 | ----- | 178 | do | TG 57 |
| [2] 236 | ----- | [2] 180 | ----- | do | SJ 57 |
| [2] 252 | ----- | [2] 172 | ----- | Neutron-activation | SL 57 |
| ----- | 263 | ----- | 197 | X-ray fluorescence | HF 57 |

[1] Average of 5 determinations.
[2] Average of 4 determinations.

If the high value of 900 is omitted, the G-1 average for strontium is **280** (rounded from 279). This value may be a little high because of the few values between 400 and 500; alternatively, therefore, the average **250** (rounded from 246) of the isotope-dilution and neutron-activation determinations may be recommended. On this basis, the alternative recommended values for W-1 are **220** and **175**, respectively.

*Tantalum* (Ta), *in parts per million*

| G-1 | W-1 | Method | Reference |
|---|---|---|---|
| [1] 1.59 | [1] 0.47 | Neutron activation | SA 57 |

[1] Average of 4 determinations.

As the agreement of the replicate determinations for tantalum is close (range in G-1, 1.54 to 1.63; and in W-1, 0.45 to 0.49) 1.6 and 0.5 should represent very satisfactory magnitudes unless unforeseen error is present.

*Thorium* (Th) *in parts per million*

| G-1 | W-1 | Method | Reference |
|---|---|---|---|
| ------ | 2. 6 | Chemical | GJ 57 |
| [1] 45 | [2] 1. 9 | ----do | GR 57 |
| [3] 51 | [4] 2. 2 | ----do | GR 58 |
| [5] 52 | [4] 2. 2 | ----do | LG 58 |
| [6] 51 | [6] 2. 1 | Chemical colorimetric | HT 59 |
| 61 | 3. 6 | X-ray fluorescence | HU 58 |

[1] Average of 15 determinations.

[2] Average of 9 determinations.

[3] Average of 14 determinations.

[4] Average of 5 determinations.

[5] Average of 6 determinations.

[6] Average of 4 determinations.

The X-ray fluorescence values for thorium are higher than those provided by the spectrophotometric procedures, but the agreement is nevertheless satisfactory and the averages of 52 and 2.4 for G-1 and W-1, respectively, may be recommended.

*Titanium* (Ti) *in parts per million*

| G-1 | W-1 | Method | Reference |
|---|---|---|---|
| 1, 000 | 10, 000 | Spectrochemical | HB 56 |
| 1, 500 | 6, 700 | ----do | MB 56 |
| 1, 200 | 6, 000 | ----do | CH 57 |
| [1] 1, 400 | [2] 6, 700 | ----do | MY 58 |
| 1, 450 | 8, 520 | ----do | SH 58 |
| 1, 800 | 6, 600 | ----do | YO 58 |

[1] Average of 20 determinations.

[2] Average of 10 determinations.

For titanium the values are given here merely to make the record complete. The averages of 1,400 and 7,400 may be compared with 1,500 and 6,400 averaged from the chemical analyses by Stevens and Niles, part 1.

*Uranium* (U) *in parts per million*

| G-1 |  | W-1 |  | Method | Reference |
|---|---|---|---|---|---|
| Average | Value | Average | Value |  |  |
| [1] 3. 8 | ----- | [2] 0. 52 | ----- | Fluorimetric | JM 58 |
| 3. 55 | 3. 5<br>3. 6 | 0. 53 | 0. 52<br>0. 54 | Neutron activation | HT 56 |
| [3] 3. 2 | ----- | [4] 0. 51 | ------- | Fluorimetric | HT 59 |
| [5] 3. 9 | ----- | 0. 50 | 0. 4<br>0. 5<br>0. 6 | Gamma-ray spectrometry. | HU 58 |

[1] Average of 46 determinations.

[2] Average of 40 determinations.

[3] Average of 17 determinations.

[4] Average of 13 determinations.

[5] Average of 4 determinations.

Agreement for determinations of uranium is very good and, as some of the values represent averages of many determinations, the averages of the three procedures **3.7** and **0.52** for G–1 and W–1, respectively, are recommended with some confidence.

*Vanadium* (V) *in parts per million*

| G-1 | | W-1 | | Method | Reference |
|---|---|---|---|---|---|
| Average | Value | Average | Value | | |
| ----- | 20 | ----- | 220 | Chemical | HE 51 |
| 25 | 24<br>25 | ----- | 180 | do | HR 54 |
| ----- | 18 | ----- | 340 | Spectrochemical | GA 51 |
| ----- | 17 | ----- | 220 | do | MI 51 |
| ----- | 26 | ----- | 220 | do | MU 51 |
| ----- | <20 | ----- | 300 | do | HA 54 |
| ----- | 20 | ----- | 250 | do | NO 54 |
| ----- | 8 | ----- | 170 | do | SH 54 |
| ----- | 17–18 | ----- | ----- | do | BA 55 |
| ----- | ----- | ----- | 200 | do | SI 55 |
| ----- | 20 | ----- | ----- | do | YA 55 |
| ----- | 30 | ----- | 100 | do | HB 56 |
| 18 | 16<br>19 | 285 | 260<br>310 | do | HM 56 |
| ----- | 18 | ----- | 240 | do | MB 56 |
| ----- | 25 | ----- | 250 | do | CH 57 |
| ----- | <25 | 325 | 360<br>290 | do | LT 57 |
| ----- | 38 | ----- | 310 | do | MO 58 |
| ----- | 20 | ----- | ----- | do | HL 58 |
| [1] 20 | ----- | [2] 250 | ----- | do | MY 58 |
| ----- | 14 | ----- | 230 | do | SH 58 |
| ----- | ----- | ----- | 320 | X-ray fluorescence | NR 58 |

[1] Average of 20 determinations.
[2] Average of 17 determinations.

Agreement for determinations of vanadium is for the most part reasonable and the averages of **21** and **240** for G–1 and W–1, respectively, are recommended.[13]

*Tungsten* (W) *in parts per million*

| G-1 | W-1 | Methods | References |
|---|---|---|---|
| (0. 3) | 0. 3±0. 2 | Chemical | JE 58 |
| [1] 0. 47 | [2] 0. 46 | Neutron-activation | SA 57 |

[1] Average of 7 determinations.
[2] Average of 8 determinations.

Because of molybdenum interference in G–1, the spectrophotometric chemical determination for tungsten is not reliable and the reported value of 0.3 can be regarded only as a general magnitude.

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[13] Kemp and Smales (1960, Geochim. et Cosmochim. Acta, v. 18, p. 149–150) by neutron activation found 13 ppm V (average of 8 determinations) for G–1, 246 ppm V (average of 6 determinations) for W–1.

The replicate neutron-activation determinations agree closely (range in G–1, 0.40–0.52; and in W–1, 0.41–0.50) and their averages should be very satisfactory magnitudes.

*Yttrium* (Y) *in parts per million*

| G–1 | W–1 | Methods | References |
|---|---|---|---|
| 24 | ------ | Spectrochemical ----- | GA 51 |
| 30 | ------ | -----do--------------- | MI 51 |
| 25 | ------ | -----do--------------- | MU 51 |
| <20 | 30 | -----do--------------- | HA 54 |
| 10 | ------ | -----do--------------- | NO 54 |
| 20 | 35 | -----do--------------- | SH 54 |
| 26 | ------ | -----do--------------- | BA 55 |
| 22 | ------ | -----do--------------- | CH 57 |
| 15 | 40 | -----do--------------- | HL 58 |
| [1] 19 | [2] 35 | -----do--------------- | MY 58 |
| 20 | 30 | Spectrochemical + chemical enrichment-------------- | BE 57 |
| ------ | 30–50 | X-ray fluorescence---- | AA 58 |

[1] Average of 21 determinations.
[2] Average of 15 determinations.

Taken as a whole, the agreement of the 10 spectrochemical determinations for yttrium is fairly good in G–1 and the average of all determinations, **21**, may serve as a recommended value or at least as a good magnitude. The position is not so clear for W–1. Agreement between the 6 determinations is very good. However, some analysts who determined yttrium in G–1 did not detect it in W–1. The possibility that error in some of the spectrochemical determinations could have arisen as a result of interference of Mn 4374 with sensitive Y 4374 in W–1 (average Mn in G–1 and W–1 is 0.021 and 0.13 percent, respectively; see Fairbairn and others, 1951 and this publication) has been discussed (Ahrens, 1954a, footnote e, table 3–2 (B)). Determinations by BE 57 and AA 58 are free from such error and the available evidence indicates that 35 ppm, the average of all values, should be a satisfactory magnitude.

*Ytterbium* (Yb) *in parts per million*

| G–1 | W–1 | Methods | References |
|---|---|---|---|
| 1 | 2 | Spectrochemical------ | BE 57 |
| 1 | 3 | -----do--------------- | CH 57 |
| [1] 1 | [2] 4 | -----do--------------- | MY 58 |

[1] Average of 16 determinations.
[2] Average of 8 determinations.

The averages of 1 and 3 should serve as reasonable magnitudes for ytterbium for G–1 and W–1, respectively. Ytterbium and to a lesser degree yttrium, seem to be at higher concentration in W–1 than in G–1, whereas the reverse holds for lanthanum and cerium (see above).

*Zinc* (Zn) *in parts per million*

| G-1 | W-1 | Methods | References |
|---|---|---|---|
| 55 | 90 | Chemical (field)______ | BL 51 |
| 41 | 78 | Chemical____________ | HN 58 |
| 38±14 | 81±6 | Polarographic________ | SG 55 |
| 26 | 78 | X-ray fluorescence____ | HF 57 |

Agreement for determinations of zinc in W–1 is good and the average, **82,** may be recommended with reasonable confidence. Agreement in G–1 is less satisfactory and the average, 40, may serve as a magnitude.

*Zirconium* (Zr) *in parts per million*

| G-1 | | W-1 | | Methods | References |
|---|---|---|---|---|---|
| Average | Value | Average | Value | | |
| ------ | 200 | ------- | 70 | Chemical___________ | HE 51 |
| ------ | 162 | ------- | 58 | -----do____________ | DE 57 |
| ------ | 200 | ------- | ------- | -----do____________ | GS 57 |
| ------ | 280 | ------- | 90 | Spectrochemical_____ | GA 51 |
| ------ | 200 | ------- | 50 | -----do____________ | MI 51 |
| ------ | 190 | ------- | 90 | -----do____________ | MU 51 |
| ------ | 300 | ------- | 100 | -----do____________ | HA 54 |
| ------ | 180 | ------- | 100 | -----do____________ | NO 54 |
| ------ | 130 | ------- | 150 | -----do____________ | SH 54 |
| 200±10 | ------- | ------- | ------- | -----do____________ | BA 55 |
| ------ | 200 | ------- | ------- | -----do____________ | SI 55 |
| ------ | 100 | ------- | ------- | -----do____________ | YA 55 |
| ------ | 300 | ------- | 100 | -----do____________ | HB 56 |
| ------ | 220 | ------- | 30? | -----do____________ | HM 56 |
| ------ | 200 | ------- | 90 | -----do____________ | MB 56 |
| ------ | 220 | ------- | 90 | -----do____________ | CH 57 |
| 200 | 210<br>190 | 123 | 120<br>125 | ----do____________ | LT 57 |
| | 180 | ------- | ------- | -----do____________ | TU 57 |
| ------ | 230 | ------- | ------- | -----do____________ | HL 58 |
| ------ | 230 | ------- | 150 | -----do____________ | MO 58 |
| [1] 190 | ------- | ------- | [2] 110 | -----do____________ | MY 58 |
| ------ | 145 | ------- | 86 | -----do____________ | SH 58 |
| ------ | 326 | ------- | ------- | -----do____________ | YO 58 |
| ------ | 220 | ------- | ------- | X-ray fluorescence___ | HM 56 |
| ------ | 268 | ------- | 94 | -----do____________ | HF 57 |
| ------ | 213 | ------- | 98 | -----do____________ | NR 58 |

[1] Average of 24 determinations.
[2] Average of 18 determinations.

Twenty-six analysts have determined zirconium in G-1 and their average of **210** may be recommended. A frequency distribution diagram (fig. 7) indicates however that this value may be slightly high, as the modal value is close to 185, which could be considered as an alternative. If the doubtful value of the HM 56 determination is excluded, the average in W-1 is **100** and is recommended. The MY 58 averages of many determinations are close to the recommended values of 185 and 100. The averages of the chemical determinations agree well with these for G-1 and are a little low for W-1; the averages by X-ray fluorescence are high for G-1 and agree for W-1.

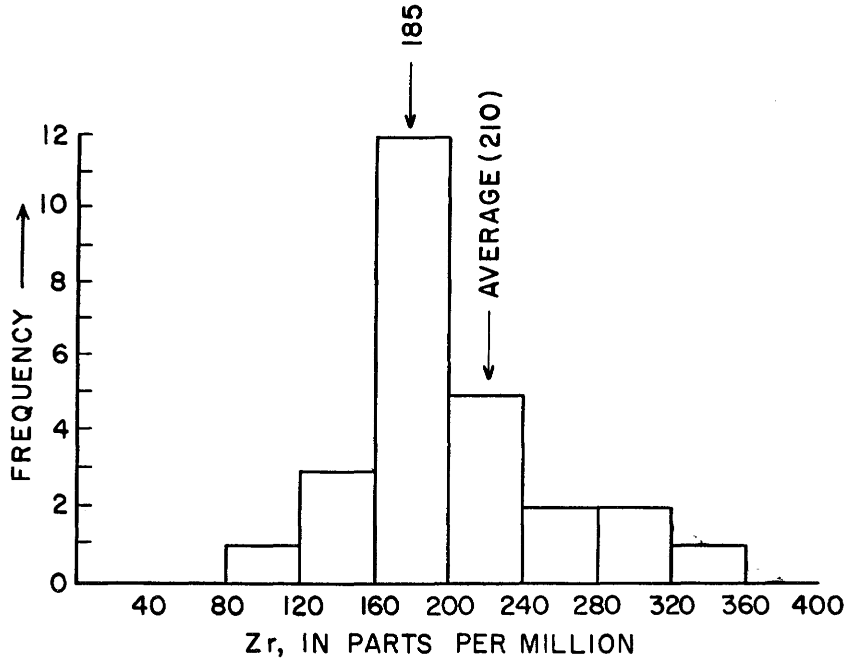

FIGURE 7.—The distribution of the determination of zirconium in the rock G-1 (26 determinations).

### *Code of analysts*

[The number refers to the year in which the analysis was reported]

AA 57 Adler, I., and Axelrod, J. M., U.S. Geol. Survey, Washington, D.C., quoted by Berman (1957).
X-ray fluorescence ------ Ce, Y

AR 56 Arnold, J. R., Princeton Univ., Princeton, N.J., written communication, 1956.
Isotope dilution ------ Be

BA 55 Barnett, Paul, U.S. Geol. Survey, Denver, Colo., written communicacation, 1955.
Spectrochemical ------ Ba, Be, Co, Cr, Cu, Ga, La, Mn, Mo, Nb, Pb, Sc, Sr, V, Y, Zr

BE 57 Berman, S. (1957), U.S. Geol. Survey, Washington, D.C.
Chemical-spectrochemical ------ Ce, La, Nd, Y, Yb

BL 51 Bloom, H., U.S. Geol. Survey, Denver, Colo., quoted by Ahrens (1951, 1954a).
Chemical colorimetric (field method) ------ Co, Cu, Ni, Pb, Zn

CA 54 Canney, F. C., Massachusetts Inst. Technology, Cambridge, quoted by Ahrens (1954a).
Spectrochemical ------ Cs

CH 55 Chodos, A. A., California Inst. Technology, Pasadena, written communication, 1955.
Spectrochemical ------ Pb

CH 56 Chodos, A. A., California Inst. Technology, Pasadena, written communication, 1956. See Flanagan, part 5.
Spectrochemical ------ Pb

CH 57 Chodos, A. A., California Inst. Technology, Pasadena, written communication, 1957.
Spectrochemical ------ B, Ba, Be, Ce, Co, Cr, Cu, Ga, La, Li, Mn, Mo, Nb, Nd, Ni, Pb, Sc, Sn, Sr, Ti, V, Y, Yb, Zr

CK 59 Carr, M. H., and Turekian, K. K. (1959), Yale Univ.
Neutron activation ------ Co

CR 58 Culkin, F., and Riley, J. P. (1958), Liverpool Univ., England.
Spectrophotometric ------ Ga

CS 57 Cabell, M. J., and Smales, A. A. (1957), Atomic Energy Research Establishment, Harwell, England.
Neutron activation ------ Cs, Rb

DE 57 Degenhardt, H. (1957), Univ. of Göttingen, Germany.
Colorimetric ------ Zr

EH 55 Ellestad, R. B., and Horstman, E. L. (1955), Lithium Corp. of America and Univ. of Minnesota, Minneapolis.
Flame photometer ------ Li

EU 54 Eugster, H. P., quoted by Ahrens (1954a).
Spectrochemical ------ B

FG 59 Fornaseri, M., and Grandi, L., written communication, 1959, Univ. Rome.
Flame photometer ------ Sr

*Code of analysts*—Continued

GA 51 Gorfinkle, L. G., and Ahrens, L. H., Massachusetts Inst. Technology, Cambridge, quoted by Ahrens (1951).
Spectrochemical ---------------------------- Ba, Co, Cr, Cu, Ga, La, Li, Nd, Pb, Rb, Sc, Sr, V, Y, Zr

GJ 57 Grimaldi, F. S., Jenkins, L. B., and Fletcher, M. H. (1957), U.S. Geol. Survey, Washington, D.C.
Spectrophotometric ------------------------ Th

GO 56 Goldich, S. S., and Oslund, E. H. (1956), Univ. of Minnesota, Minneapolis.
Chemical ---------------------------------- F by E. H. Oslund
Co and Ni by R. A. Burwash
Rb by H. Baadsgaard

GR 57 Grimaldi, F. S., Levine, H., Jenkins, L. B., and Campbell, Esma, U.S. Geol. Survey, Washington, D.C., written communication, 1957.
Spectrophotometric ------------------------ Th

GR 58 Grimaldi, F. S., Campbell, Esma, and Jenkins, L. B., U.S. Geol. Survey, Washington, D.C., written communication, 1958.
Spectrophotometric ------------------------ Th

GR 59 Grimaldi, F. S., U.S. Geol. Survey, Washington, D.C., written communication, 1959.
Chemical colorimetric --------------------- Nb

GS 57 Geiger, R. A., and Sandell, E. B. (1957), Univ. of Minnesota, Minneapolis.
Fluorimetric ------------------------------- Zr

GU 58 Grabowski, R. J., and Unice, R. C. (1958), Shell Development Co., Houston, Texas.
Spectrochemical ---------------------------- Ba, Sr

HA 54 Harvey, C. O., Great Britain Geol. Survey, London, quoted by Ahrens (1954a), and by Guppy and Sabine (1956); the figures given in the latter reference have been used.
Spectrochemical ---------------------------- Ba, Cr, Co, Ga, La, Mn, Ni, Sc, Sr, V, Y, Zr

HB 56 Hodge, E. S., and Baer, W. K. (1956), Mellon Inst., Pittsburgh.
Semiquantitative spectrochemical ------------ Ba, Be, Mo, Ni, Ti, V, Zr

HD 59 Harder, Hermann (1959), Univ. Göttingen, Germany.
Spectrochemical ---------------------------- B

HE 51 Hey, M. H., British Museum of Natural History, quoted by Ahrens (1954a).
Chemical ---------------------------------- Ba, Cr, Cu, F, Ga, Ni, Pb, Sr, V, Zr

HF 57 Hower, J., and Fancher, T. W. (1957), Stanolind Oil and Gas Co., Tulsa, Okla.
X-ray fluorescence ------------------------- Cu, Mn, Ni, Rb, Sr, Zn, Zr

HG 57 Hollingsworth, R. P. (1957), Univ. of Durham, England.
Spectrophotometric ------------------------ F

HK 58 Hamaguchi, Hiroshi; Tomura, Kenji; and Kuroda, Rokuro (1958), Tokyo Univ. of Education.
Spectrochemical ---------------------------- Sc

*Code of analysts*—Continued

| | | |
|---|---|---|
| HL 58 | Hall, W. L., The Texas Co., Bellaire, Texas, written communication (1958). | |
| | Spectrochemical | B, Ba, Co, Cr, Cu, Ga, La, Mn, Mo, Ni, Pb, Sc, Sr, V, Y, Zr |
| HM 56 | Hawley, J. E., and MacDonald, G. (1956), Queens Univ., Kingston, Ontario. | |
| | Semiquantitative spectrographic | Ba, Be, Co, Cr, Cu, Mn, Mo, Ni, Pb, Sr, V, Zr |
| | X-ray fluorescence | Zr |
| HN 58 | Huffman, Claude, and Lipp, H. H., U.S. Geol. Survey, Denver, Colo., written communication, 1958. | |
| | Chemical | Zn |
| HO 56 | Horstman, E. L., (1956), Univ. of Minnesota, Minneapolis. | |
| | Flame photometer | Li, Rb |
| HP 55 | Herzog, L. F., and Pinson, W. H., Jr. (1955), Massachusetts Inst. Technology, Cambridge; also in Herzog (1956). | |
| | Isotope dilution | Rb, Sr |
| HR 54 | Hammer, A. J., Bowling Green State Univ., Bowling Green, Ohio, written communication, 1954. | |
| | Chemical spectrophotometric | V |
| HT 56 | Hamilton, E., Oxford Univ., written communication, 1956 and 1958, and Hamilton (1959). | |
| | Radioactivation | U |
| HT 59 | Hamilton, E., Greenland Geol. Survey, Copenhagen, written communication, 1959, and Hamilton (1959). | |
| | Chemical colorimetric | Th |
| | Fluorimetric | U |
| HU 58 | Hurley, P. M., Massachusetts Inst. Technology, written communication, 1958. Th quoted by Levine and Grimaldi (1958). | |
| | X-ray fluorescence | Th |
| | Gamma-ray spectrometry | U |
| HW 59 | Hahn-Weinheimer, P., Univ. at Frankfurt, Germany, written communication, 1959. | |
| | Chemical colorimetric | B |
| IW 55 | Iwasaki and others (1955), Tokyo Inst. Technology. | |
| | Chemical colorimetric | Cl |
| JE 58 | Jefferey, P. G., Univ. of Cape Town, South Africa, written communication, L. H. Ahrens, 1958. | |
| | Chemical colorimetric | W |
| JM 58 | Joslyn, M. A., Molloy, M., Warr, J., Sherwood, A. M., Schnepfe, M., Moore, R., and Caemmerer, A., U.S. Geol. Survey, Washington, D.C., written communication, 1958. | |
| | Fluorimetric | U |
| JU 56 | Jury, R. V. (1956), Atomic Energy Research Establishment, Harwell, England. AERE-C/M-269, quoted by Smales and Webster (1958b). | |
| | Spectrochemical | Li |
| KO 56 | Kokubu, N. (1956), Kyūshū Univ., Japan. | |
| | Chemical colorimetric | F |

*Code of analysts*—Continued

| | | |
|---|---|---|
| KP 56 | Kinser, C. A., Powell, R. A., and Warr, J. J., U.S. Geol. Survey, Washington, D.C., written communication, 1956. See Flanagan, part 5. | |
| | Chemical colorimetric | Pb |
| KS 54 | Kuroda, P. K., and Sandell, E. B., (1954), Univ. of Minnesota, Minneapolis. | |
| | Chemical colorimetric | Mo |
| KV 51 | Kvalheim, A., Statem Rastoff Laboratory, Oslo, Norway, quoted by Ahrens (1951, 1954a). | |
| | Spectrochemical | Sc |
| LA 51 | Lakin, H. W., Almond, H., Reichen, L., and Ward, F., U.S. Geol. Survey, Washington, D.C., quoted by Ahrens (1951, 1954a). | |
| | Chemical colorimetric (field method) | Co, Cu, Mo, Ni, Pb |
| LG 58 | Levine, Harry, and Grimaldi, F. S. (1958), U.S. Geol. Survey, Washington, D.C. | |
| | Spectrophotometric | Th |
| LT 57 | Leininger, R. K., and Taylor, S. R., Indiana Geol. Survey, Bloomington, written communication, 1957. | |
| | Spectrochemical | Ba, Co, Cr, Cu, La, Ni, Sc, Sr, V, Zr |
| MB 56 | McBurney, T. C., Smith-Emery Co., Los Angeles, California, written communication, 1956. | |
| | Spectrochemical: | |
| | quantitative | Ba, Cr, Cu, Ga, Mn, Ti, V, Zr |
| | semiquantitative | B, Co, Ni, Pb, Sr |
| MI 51 | Mitchell, R. L., Macaulay Inst. Soils Research, Aberdeen, Scotland, quoted by Ahrens (1951). | |
| | Spectrochemical | Ba, Co, Cr, Cu, Ga, La, Li, Mo, Ni, Pb, Rb, Sc, Sr, V, Y, Zr |
| MO 58 | McKenzie, R. M., Oertel, A. C., and Tiller, K. G. (1958), Div. Soils, Commonwealth Sci. Indus. Research Organization, Adelaide, South Australia. | |
| | Spectrochemical | Co, Cu, Ga, Mn, Mo, Ni, V, Zr |
| MU 51 | Murata, K. J., U.S. Geol. Survey, Washington, D.C., quoted by Ahrens (1951). | |
| | Spectrochemical | B, Ba, Be, Co, Cr, Cu, Ga, La, Mo, Ni, Pb, Sc, Sr, V, Y, Zr |
| MU 56 | Murata, K. J., and Bastron, H., U.S. Geol. Survey, Washington, D.C., written communication, 1956. See Flanagan, part 5. | |
| | Spectrochemical | Pb |
| MY 55 | Myers, A. T., U.S. Geol. Survey, Denver, Colo., written communication, 1955. | |
| | Spectrochemical | Pb (analysts, Paul Barnett, Polly Dunton, and R. G. Havens) |

*Code of analysts*—Continued

| | | |
|---|---|---|
| MY 56 | Myers, A. T., and Havens, R. G., U.S. Geol. Survey, Denver, Colo., written communication, 1956. See Flanagan, part 5.<br>Spectrochemical | Pb |
| MY 58 | Myers, A. T., U.S. Geol. Survey, Denver, Colo., written communication, 1958.<br>Spectrochemical | Be, Co, Cr, Cu, Ga, La, Mn. Mo, Nb, Ni, Sc, Ti, V, Y, Yb, Zr (analyst, Nancy M. Conklin) |
| NO 54 | Nockolds, S. R., Cambridge Univ., England, quoted by Ahrens (1954a).<br>Spectrochemical | Ba, Co, Cr, Ga, La, Li, Mo, Ni, Pb, Rb, Sc, Sr, V, Y, Zr |
| NR 58 | Norrish, K., Div. Soils, Commonwealth Sci. Indus. Research Organization, Adelaide, South Australia, quoted by McKenzie, Oertel, and Tiller (1958).<br>X-ray fluorescence | Ga, V, Zr |
| ON 55 | Onishi, H., and Sandell, E. B. (1955), Univ. of Minnesota, Minneapolis.<br>Chemical colorimetric | As |
| ON 56 | Onishi, H. (1956), Government Indus. Research Inst., Nagoya, Japan.<br>Chemical colorimetric | Ge |
| ON 57 | Onishi, H., and Sandell, E. B. (1957), Univ. of Minnesota, Minneapolis.<br>Chemical colorimetric | Sn |
| OS 54 | Oslund, E. H., Univ. of Minnesota, quoted by Ahrens (1954a).<br>Chemical | F |
| PE 54 | Peck, L. C., U.S. Geol. Survey, Denver, Colo, quoted by Ahrens (1954a).<br>Chemical | F |
| PW 56 | Powell, R. A., and Warr, J. J. (1956), U.S. Geol. Survey, Washington, D.C.<br>Chemical colorimetric | Pb |
| RS 58 | Riley, J. P., and Sinhaseni, P. (1958), Liverpool Univ.<br>Spectrophotometric | Cu |
| SA 57 | Smales, A. A., and Atkins, D. H. F., Atomic Energy Research Establishment, Harwell, England, written communication, 1957.<br>Neutron activation | Ta, W |
| SC 55 | Smales, A. A., and Cabell, M. J., Atomic Energy Research Establishment, Harwell, England, *in* Smales (1955).<br>Neutron activation | Rb |
| SE 51 | Seraphim, R. H. (1951) thesis, Massachusetts Inst. Technology.<br>Spectrochemical | F |
| SG 55 | Smythe, L. E., and Gatehouse, B. M. (1955). Univ. of Tasmania, Hobart.<br>Polarographic | Cd, Co, Cu, Ni, Zn |
| SH 54 | Shaw, D. M., and Webber, G. R., McMaster Univ., Hamilton, Ontario, quoted by Ahrens (1954a).<br>Spectrochemical | Be, Co, Cr, Cu, Ga, Li, Mo, Ni, Pb, Sc, V, Y, Zr |

*Code of analysts*—Continued

SH 58 Shaw, D. E., Filby, R. H., Siroonian, H., and Yip, C., McMaster Univ., Hamilton, Ontario, written communication, 1958.
Spectrochemical ---------- B, Ba, Be, Co, Cr, Cu, Ga, Li, Mn, Mo, Ni, Sc, Sr, Ti, V, Zr

SI 55 Shilstone, H. M., Jr., Shilstone Testing Laboratory, Houston, Texas, written communication, 1955.
Semiquantitative, spectrochemical ---------- Ba, Co, Cr, Cu, Mn, Ni, V, Zr

SJ 57 Smales, A. A., Webster, R. K., and Morgan, J. W., Atomic Energy Research Establishment, Harwell, England, written communication, 1957.
Isotope dilution ---------- Sr

SL 57 Smales, A. A., and Loveridge, B. A., Atomic Energy Research Establishment, Harwell, England, written communication, 1957.
Neutron activation ---------- Sr

SM 57 Smales, A. A., Mapper, D., and Wood, A. J. (1957), Atomic Energy Research Establishment, Harwell, England, partly *in* Smales (1955)
Neutron activation ---------- Co, Cu, Ni

SN 54 Scoon, J. H., Cambridge, Univ. England, quoted by Ahrens (1954a)
Chemical ---------- F

SR 59 Siroonian, H. A., Shaw, D. M., and Jones, R. E. (1959), McMaster Univ., Hamilton, Ontario.
Spectrochemical ---------- Li

SS 57 Smales, A. A., Smit, J. van R., and Irving, H. (1957), Atomic Energy Research Establishment, Harwell, and Oxford Univ., England
Neutron activation ---------- In

SU 54 Sunkel, W., Div. Chem. Services, Pretoria, Union of South Africa quoted by Ahrens (1954a).
Chemical ---------- F

SV 55 Smales, A. A., and Vincent, E. A., Atomic Energy Research Establishment, Harwell, and Oxford Univ., England, *in* Smales (1955), Vincent and Smales (1956).
Neutron activation ---------- Au, Pd

SW 58 Smales, A. A., and Webster, R. K. (1958a, b), Atomic Energy Research Establishment, Harwell, England.
Isotope dilution ---------- Li, Rb

TG 57 Turekian, K. K., Gast, P. W., and Kulp, J. L. (1957), Columbia Univ., New York, N. Y.
Spectrochemical and isotope dilution ---------- Sr

TK 56 Turekian, K. K., and Kulp, J. L. (1956), Columbia Univ., New York, N. Y.
Spectrochemical ---------- Sr

TU 55 Turekian, K. K. (1955), Columbia Univ., New York, N. Y.
Spectrochemical ---------- Sr

TU 57 Turekian, K. K. (1957), Yale Univ., New Haven, Conn.
Spectrochemical ---------- Co, Cr, Ni, Pb, Sn, Zr

WA 55 Ward, F. N., U. S. Geol. Survey, Denver, Colo., written communication 1955.
Chemical colorimetric ---------- Pb

*Code of analysts*—Continued

| | | | |
|---|---|---|---|
| WE 56 | Wedepohl, K. H. (1956), Univ. of Göttingen, Germany. | Spectrochemical | Pb |
| WL 54 | Ward, F. N., and Lakin, H. W. (1954), U. S. Geol. Survey, Denver, Colo. | Chemical colorimetric | Sb |
| WN 56 | Ward, F. N., and Nakagawa, H. M., U. S. Geol. Survey, Denver, Colo., written communication, 1956. See Flanagan, part 5. | Chemical colorimetric | Pb |
| WR 55 | Waring, C. L., U. S. Geol. Survey, Washington, D. C., written communication, 1955. | Spectrochemical | Pb |
| WR 56 | Waring, C. L., and Worthing, H. W., U. S. Geol. Survey, Washington, D. C., written communication, 1956. See Flanagan, part 5. | Chemical colorimetric--#Pb | |
| YA 55 | Yamasaki, K., Iida, C., and Yokoi, H. (1955), Nagoya Univ., Japan. | Spectrochemical | Ba, Co, Cr, La, Mn, Ni, Pb, Sr, V, Zr |
| YO 58 | Young, E. J. (1958), Massachusetts Inst. Technology. | Spectrochemical | Co, Cr, La, Nd, Ni, Sc, Ti, Zr |

# SECOND REPORT ON A COOPERATIVE INVESTIGATION OF THE COMPOSITION OF TWO SILICATE ROCKS

## PART 5. THE LEAD CONTENT OF G–1

By FRANCIS J. FLANAGAN [14]

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### ABSTRACT

In 1954 the lead content of rock sample G–1 was thought to be 27 ppm, but results differing considerably from this were reported by several laboratories. To test the validity of the recommended value of 27 ppm, a cooperative investigation of the lead content of sample G–1 was undertaken by six laboratories, using six bottles, prepared in 1951, which had never been opened, and a sampling that insured equal treatment of all analysts.

Using the analysis of variance, it was shown that laboratories yield results significantly different. When the data were classified by sampling order, the variation was also significant but the data contained no recognizable trends that might indicate the cause of the difference. There was, however, no significant difference between the six samples. The best estimates at present of the lead content are grand average, 49 ppm; spectrographic average, 50 ppm; and chemical average, 47 ppm.

### INTRODUCTION

Chemical, spectrographic, and modal analyses of two rock samples, G–1 and W–1, were reported by Fairbairn and others (1951) with the hope that eventually the two samples could be used as standards for these types of rock analysis. Lead is one of the trace elements listed in the analyses and the importance of the correct determination

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[14] U.S. Geological Survey.

of this element is emphasized by its significance in geochemical interpretation.

The first determinations of the lead content of G–1 were listed by Ahrens (*in* Fairbairn and others, 1951) and in Ahrens (1954a, p. 25). On the basis of the first eight determinations listed in table 19, he recommended (1954a, p. 28) the arithmetic mean, 27 ppm, as the lead content of G–1. Although some analyses reported up to 1956 agreed with this figure, others differed markedly. All the analyses made before June 1956 are assembled in table 19.

Inspection of the data in table 19 seems to indicate that, except for the determination of Shaw and Webber, there exist two distinct sets of samples. In general the early determinations seem to center at approximately 25 ppm, whereas a rough average of the later determinations is about 50 ppm. One might conclude that there are two distinct sets of samples; that this is incorrect is shown by the fact that of the five bottles which were sampled by Dunton, Barnett, Havens, and Ward, three had been used in the laboratory since the first distribution of the samples whereas the other two bottles were unopened until sampled for the analyses listed. These determinations, in addition to the earlier high determinations of 50 ppm by Nockolds and 37 ppm by Shaw and Webber, suggest the possibility that some of the earlier determinations were incorrect.

TABLE 19.—*Lead content of sample G–1 determinations prior to present work*

[C, chemical determination; S, spectographic determination]

| Pb (ppm) | Determinations | | Analyst | Reference |
|---|---|---|---|---|
| | Number | Type | | |
| 25 | | S | Mitchell | In Ahrens, 1954a. |
| 22 | | S | Murata | Do. |
| 23 | 10 | S | Gorfinkle and Ahrens | Do. |
| 15 | | [1] C | Lakin and others | Do. |
| 14 | | [1] C | Bloom | Do. |
| 28 | | C | Hey | Do. |
| 50 | | S | Nockolds | Do. |
| 37 | | S | Shaw and Webber | Do. |
| 52 | | S | Barnett | Written communication, 1955. |
| 55 | | S | Chodos | Do. |
| 51 | 16 | C | Ward | Written communication, Myers, 1955. |
| 55 | 48 | S | Barnett, Dunton, and Havens. | Do. |
| 28 | 3 | S | Waring | Written communication, 1955. |
| 28 | | S | Yamasaki and others | 1955. |
| 20–24 | | S | Hawley and MacDonald | 1956. |
| 26 | | S | Wedepohl | 1956. |
| 48 | 14 | C | Powell and Warr | 1956. |

[1] Field method.

Three spectrographic and two chemical laboratories of the U.S. Geological Survey and the spectographic laboratory of the Division of Geological Sciences of the California Institute of Technology agreed in June 1956 to participate in a cooperative investigation of the lead content. Although two laboratories were to make chemical analyses of the samples, their results had been comparable to those of the spectographic laboratories which had reported results with an approximate mean of 50 ppm. The laboratories and the analysts who participated in the investigation are as follows:

| *Laboratory* | *Analysts* | *Type of determination* |
|---|---|---|
| A | A. T. Myers and R. G. Havens | Spectographic. |
| B | K. J. Murata and H. Bastron | Do. |
| C | C. A. Kinser, R. A. Powell, and J. J. Warr | Chemical. |
| D | A. A. Chodos | Spectographic. |
| E | C. L. Waring and H. W. Worthing | Do. |
| F | F. N. Ward and H. M. Nakagawa | Chemical. |

## DETERMINATION OF LEAD

As there are two sets of analyses with means at approximately 25 and 50 ppm, the possibility exists that there might be differences from sample to sample which could cause the apparent bimodal distribution of the lead results reported. One could postulate that either contamination or mineral separation during the filling of the bottles might cause this distribution, but, on the other hand, one would expect that more results would have been reported between the two approximate means. Whether or not such differences actually exist, the conflicting sets of results indicate the obvious need for a redetermination of the lead content of G-1.

The primary purpose of the investigation is to determine whether the lead content of the samples is the same. If there are differences in results, the design of the investigation should also provide a means for estimating these differences and for giving information about the variables that might cause them. Six laboratories were engaged in the test. As it is well known that different laboratories will determine the same quantity differently and perhaps with different precision, it should be possible to separate effects due to laboratories as well as to estimate the precision of each laboratory. It was also suggested that contamination might occur during and between samplings and that a sampling order should be included as one of the variables. Hence there are three factors, samples, laboratories, and sampling order, that may influence the determinations and the test should be designed so that the possible effects of these factors could be estimated.

One of the most popular of the experimental designs in which three factors can be varied simultaneously is the Latin square. You-

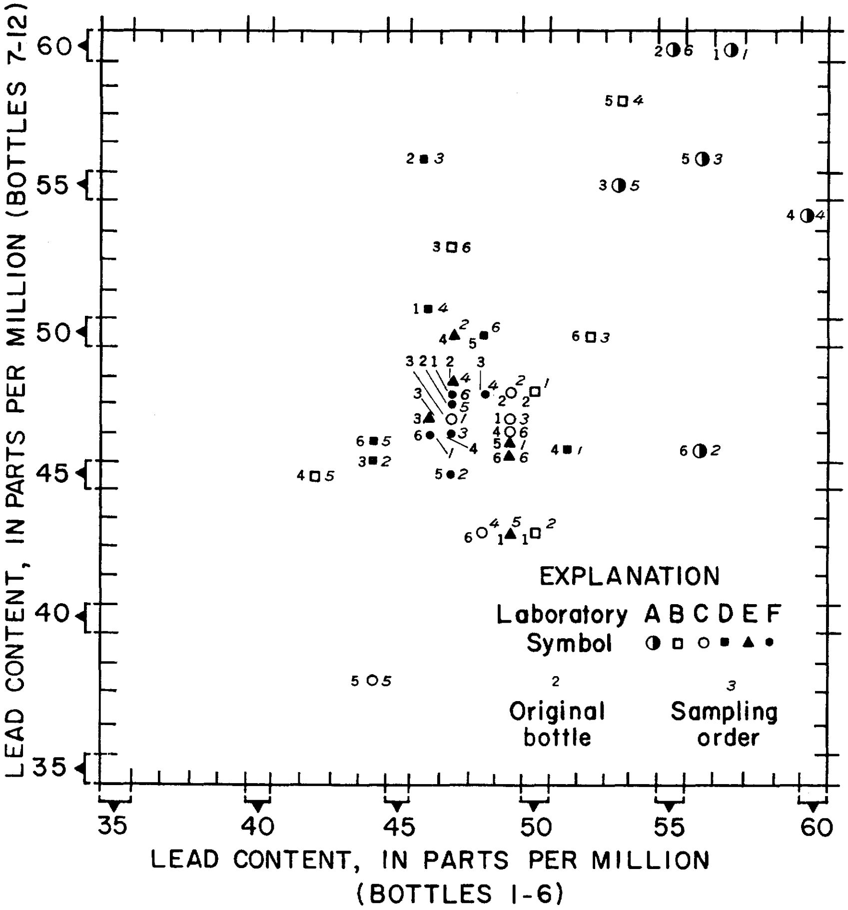

FIGURE 8.—Scatter diagram of the lead content, in parts per million, of duplicate test samples of G–1.

den and Hunter (1955) pointed out the dangers of the indiscriminate use of the Latin square and showed that the partially replicated Latin square will indicate whether the requirement of additivity in the analysis of variance has been met. The extension to a fully replicated Latin square will also indicate compliance with this condition and the three factors above can be accommodated in one experimental design.

As six laboratories had agreed to participate, a 6×6 Latin square, with each determination duplicated, was necessary to meet the requirements of the test. Six bottles were randomly selected from the remaining stock of G–1 and the contents of the bottles were halved, rebottled, and numbered from 1 to 12 so that samples 1 and 7 corresponded to the halves of original sample I, samples 2 and 8 to sample

II, and so forth. The halving of the contents of the six original samples was unknown to all analysts.

As all participants in the investigation would be expected to sample from the same bottles, a sampling order to insure equitable treatment of all laboratories was arranged. To minimize time of travel between samplings, a set of duplicate samples (1 and 7, 2 and 8, and so forth) was sent initially to each of the laboratories. These two bottles were then sampled and sent to the next laboratory on a list accompanying the bottles. The letters "A" through "F" were assigned randomly to the laboratories and the order of sampling is designated by the position of the letters in table 20.

After sampling was completed, the samples were analyzed for lead in a previously determined random order. Laboratories C and F determined lead chemically and laboratories A, B, D, and E spectrographically. The chemical method for both laboratories consisted of a double extraction with dithizone and a subsequent colorimetric determination as described by Powell and Kinser (1958). The analytical data are shown in table 20 classified by sampling-order sequence and original samples and again in table 21 reclassified by laboratories and samples, and are plotted in figure 8. Arabic instead of Roman numerals have been used for convenience in plotting figure 8 to designate original samples and order of sampling.

TABLE 20.—*Lead content classified by sampling order and sample numbers*

| | | Original sample | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | | I | | II | | III | | IV | | V | | VI | | |
| Analyzed sample | | 1 | 7 | 2 | 8 | 3 | 9 | 4 | 10 | 5 | 11 | 6 | 11 | Totals |
| Order of sampling | I | A | | B | | C | | D | | E | | F | | |
| | | 57 | 60 | 50 | 48 | 47 | 47 | 51 | 46 | 49 | 46 | 46 | 47 | 594 |
| | II | B | | C | | D | | E | | F | | A | | |
| | | 50 | 43 | 49 | 48 | 44 | 46 | 47 | 50 | 47 | 45 | 56 | 46 | 571 |
| | III | C | | D | | E | | F | | A | | B | | |
| | | 49 | 47 | 46 | 56 | 46 | 47 | 47 | 47 | 56 | 56 | 52 | 50 | 599 |
| | IV | D | | E | | F | | A | | B | | C | | |
| | | 46 | 51 | 47 | 48 | 48 | 48 | 60 | 54 | 53 | 58 | 48 | 43 | 604 |
| | V | E | | F | | A | | B | | C | | D | | |
| | | 49 | 43 | 47 | 48 | 53 | 55 | 42 | 45 | 46 | 38 | 44 | 46 | 556 |
| | VI | F | | A | | B | | C | | D | | E | | |
| | | 47 | 48 | 55 | 60 | 47 | 53 | 49 | 47 | 48 | 50 | 49 | 46 | 599 |
| Analyzed sample total | | 298 | 292 | 294 | 308 | 285 | 296 | 296 | 289 | 299 | 293 | 295 | 278 | |
| Original sample total | | 590 | | 602 | | 581 | | 585 | | 592 | | 573 | | 3, 523 |

TABLE 21.—*Lead determinations, classified by laboratories and original sample numbers*

| Original sample Nos. | Results of analyses at indicated laboratories | | | | | | | | | | | | Totals |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | A | | B | | C | | D | | E | | F | | |
| I | 57 | 60 | 50 | 43 | 49 | 47 | 46 | 51 | 49 | 43 | 47 | 48 | 590 |
| II | 55 | 60 | 50 | 48 | 49 | 48 | 46 | 56 | 47 | 48 | 47 | 48 | 602 |
| III | 53 | 55 | 47 | 53 | 47 | 47 | 44 | 46 | 46 | 47 | 48 | 48 | 581 |
| IV | 60 | 54 | 42 | 45 | 49 | 47 | 51 | 46 | 47 | 50 | 47 | 47 | 585 |
| V | 56 | 56 | 53 | 58 | 46 | 38 | 48 | 50 | 49 | 46 | 47 | 45 | 592 |
| VI | 56 | 46 | 52 | 50 | 48 | 43 | 44 | 46 | 49 | 46 | 46 | 47 | 573 |
| Column totals | 337 | 331 | 294 | 297 | 288 | 270 | 279 | 295 | 287 | 280 | 282 | 283 | 3, 523 |
| Laboratory totals | 668 | | 591 | | 558 | | 574 | | 567 | | 565 | | 3, 523 |
| Laboratory means | 55. 7 | | 49. 2 | | 46. 5 | | 47. 8 | | 47. 2 | | 47. 1 | | ------ |
| Laboratory standard deviation | 3. 9 | | 4. 5 | | 3. 1 | | 3. 5 | | 1. 9 | | . 9 | | ------ |

One of the chemical laboratories, F, reported duplicate determinations for all samples, using both reagent grade and purified hydrofluoric acid. The set of determinations made with purified hydrofluoric acid was chosen, because the other chemical laboratory had also used the purified reagent. (It was subsequently shown by applying a "t" test, using the differences between the determinations by laboratory F with both reagents, that there was no difference between the results by the two reagents and hence that it was unimportant which set of results was used.) One spectrographer, D, reported some results to 0.5 ppm and these were rounded, using the odd-even rule. Laboratory E reported triplicate results for some samples and of the two complete sets of data, the first set was chosen randomly for this investigation.

The plotted points in the scatter diagram (fig. 8) are the determinations of one-half of the original samples plotted against those of the remaining half. For example, the observation (42, 45) on the left of the diagram represents the determinations by laboratory B on both halves of the original bottle numbered 4, for which 42 ppm were obtained for test bottle 4 and 45 ppm for test bottle 10. In addition to the obviously higher values of laboratory A, figure 8 also shows that the bottles sampled fifth tend to be outside of the main cluster of results.

Inspection of the means in table 21 shows that the mean of laboratory A is about 10 percent higher, and that of laboratory B about 4 percent higher than the grand mean of laboratories C through F. The standard deviations listed in table 21 and the much smaller spread of the results of laboratory F in figure 8 show that the latter laboratory made the determinations with much better precision than the others. This is surprising as usually one laboratory cannot be so much better than the consensus of all the others. It can, in fact, be shown that the variance of the determinations by this laboratory is significantly smaller than the remainder by calculating $F_{max}$ ratios (Pearson and Hartley, 1956).

Although it is obvious that the results of laboratory A are much higher than the remainder, it is more difficult to decide from either the tabulated or plotted data if effects due to the nature of the samples or sampling order are present. To answer these questions the analysis of variance serves as a valuable tool.

## ANALYSIS OF VARIANCE

Because of the heterogeneous variance of laboratory F, the data of this laboratory could be removed from the design and the remaining pattern, which is still a valid experimental design (Kempthorne, 1952, p. 201), treated as a Youden square. However, as the variances of the laboratories may have been inflated by effects due to the samples and to the sampling order and, as the analysis of variance is not seriously affected by a little heterogeneity, the simpler computations for a Latin square were made, which resulted in the analysis of variance in the following table.

*Analysis of variance*

[SS, sum of squares; DF, degrees of freedom; MSS, mean sum of squares; S, significant; NS, not significant]

| Source of variation | SS | DF | MSS | F ratio | Conclusion |
|---|---|---|---|---|---|
| Original samples | 41.2 | 5 | 8.25 | $<1$ | NS; $F_{.95}(5, 56)=2.38$ |
| Laboratories | 705.9 | 5 | 141.2 | 16.0 | S |
| Sampling order | 153.6 | 5 | 30.7 | 3.48 | S |
| Interaction | 177.4 | 20 | 8.87 | $\sim 1$ | NS |
| Error (duplicates) | 316.5 | 36 | 8.79 | | |
| Total | 1,394.6 | 71 | | | |

As could be noted from inspection of the raw data, the variation when the data are classified by laboratories is highly significant and hence it must be inferred that the means of the six laboratories are significantly different. The standard deviation of a single determination by these laboratories is the square root of the error mean sum of squares or approximately 3 ppm. The 95 percent confidence limits for the true mean, $\mu$, can be calculated from the inequality

$$\bar{\bar{x}} - ts/\sqrt{n} < \mu < \bar{\bar{x}} + ts/\sqrt{n} \tag{1}$$

where $\bar{\bar{x}}$ is the grand mean of all laboratories, $t$ is the fractile of Student's "$t$" distribution such that the inequality will contain the true mean 95 percent of the time, $s$ is the standard deviation of a single determination by the laboratories and $n$ is the number of observations from which each laboratory mean was calculated. Substitution in (1) yields the upper and lower limits, 50.4 and 47.4 ppm, which would include the true mean, $\mu$, in 95 percent of the cases. This confidence interval includes the means of only two laboratories, B (49.2 ppm) and D (47.8 ppm).

When the determinations were classified by original samples the variation was not significant and hence it can be inferred that the lead content of the six samples is the same. Because of the random selection of these bottles from the remaining stock, it can also be inferred that the lead content of all remaining bottles is approximately 50 ppm and not 27 ppm as previously recommended. In addition the early determination of 50 ppm makes it seem reasonable to extrapolate this conclusion to the original lot of samples. Although the six bottles may be considered to have the same lead content, the slight differences which do occur can be seen in the adjusted averages for these samples (following table). The similarity of the average lead contents of these samples seems to obviate the possibility of mineral segregation during the original filling of the bottles, a possibility which had seemed reasonable in view of the discordant results of table 19.

*Average lead content of test samples*

| *Sample* | *Lead content (ppm)* | *Sample* | *Lead content (ppm)* |
|---|---|---|---|
| I | 49. 2 | IV | 48. 8 |
| II | 50. 2 | V | 49. 3 |
| III | 48. 4 | VI | 47. 9 |

Although the variation whose source is sampling order was judged significant in the analysis of variance, there seems at present to be no assignable cause for the significance. One would suspect that significance due to sampling order would take the form of some fairly regular change in the lead content of each sample. However, neither the determinations on the individual samples nor the totals for order of sampling indicate any recognizable trend and it is believed at present that the significance obtained is due to chance.

## DIFFERENCES BETWEEN SPECTROGRAPHIC AND CHEMICAL LABORATORIES

It had been assumed during the planning stage of the experiment that significant differences might occur between the six laboratories involved and that, having obtained these differences, one could then determine whether differences existed between the four spectrographic laboratories or between the two chemical laboratories. However, the variances of the four spectrographic laboratories are significantly different, thus precluding a further analysis of variance. The best solution to the problem would therefore seem to accept the overall spectrographic average, 50.0 ppm, as the best spectrographic value. This furnishes one result for lead with which other spectrographic laboratories could compare their own determinations.

Four additional spectrochemical determinations, made since the work reported here, are reported by Ahrens and Fleischer, this report, part 4, p. 96. Three of them, 48, 50, and 55 ppm (TU 57, MB 56, and HL 58, respectively), agree well with the overall spectrographic average.

The question of whether a significant difference exists between the two chemical laboratories is easily resolved. The determinations by the two laboratories on samples 1 through 12 can be paired as shown by Youden (1951) and the differences taken. The average difference, $\bar{d}$, and its standard deviation, $s_d$, can be calculated and their values used to compute Student's "*t*" in the form $t=\bar{d}\sqrt{n}/s_d$, where $n$ is the number of pairs of duplicates. The computed value of "*t*" for the two sets of chemical determinations is 0.66 and this is not significant. It can then be inferred that the average difference is not significantly different from zero—or its equivalent—that there is no difference between the means of the determinations by the two laboratories. Their determinations were then pooled and a value of 47 ppm was calculated as the average of the chemical determinations.

## CONCLUSIONS

It is evident from the raw data that the mean of the lead content of these samples of G–1 is not 27 ppm. Because of the randomization that was introduced into every step where a choice was necessary, it can be inferred that the best estimate of the lead content of the remaining samples of G–1 is 48.9 ppm.

Whether it is reasonable to extrapolate this mean value to all samples of G–1, including those for which 27 ppm have been reported, is indeterminate at this time, but in view of the earlier determination of 50 ppm by Nockolds, redetermination of the lead content by those laboratories that have received samples is indicated.

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