ART. XVII.—*The Summation of Chemical Analyses of Igneous Rocks*; by H. H. ROBINSON.

THEORETICALLY the summation of a complete chemical analysis should be 100 per cent; actually it rarely is that. Although an analyst may take every precaution to ensure a strictly accurate result, most of his summations will be either higher or lower than the true one. Are these departures from the mean value distributed in any definite and orderly manner? It is the purpose of this paper to discuss this question in general as well as in individual cases, first touching briefly on some of the analytical errors that may affect such a distribution, and also to show how the probable errors of an analyst's summations may be used as a guide to the quality of the analytical work.

The study is based on the analyses of the Washington and Washington-Roth tables,* as well as on more recent analyses. Their number is 3,391. The only analyses omitted are: (1) those whose summation has been recalculated to 100 per cent, or by estimation of some constituent is equal to 100 per cent, and (2) those whose summation is distinctly low through the non-determination of some constituent. The statistical data are given in Table I. The summations were tabulated, and are here given, on the basis of a 0.05 per cent unit in order to lessen work.

An inspection of the table shows that there are few analyses with low summation, but that the number increases in a striking manner from about 99 per cent to a maximum at 100.15–100.19 per cent. Likewise there is a marked decrease in the number of analyses from the maximum to about 101.50 per cent and then a gradual decrease to the highest summations. The different summations are thus distributed with considerable regularity either side of the maximum. What is the probable character of this distribution?

As a matter of pure chance it would seem probable that the high and low summations should be evenly distributed either side of the maximum, provided no unusual factors affect the summation of the analyses. The fitted distribution or probability curve should be symmetrical with respect to the vertical axis passing through the maximum. It is necessary, therefore, to examine the factors involved before a conclusion can be reached as to the most probable character of the distribution.

It appears most likely that the errors due to the methods used in the determination of the individual constituents of a silicate analysis tend to balance one another, so that, given

* Washington, H. S., *Chemical Analyses of Igneous Rocks*, Prof. Paper, U. S. G. S., Nos. 14 and 28, 1903 and 1904.

TABLE I.

The number of analyses from 97·00% to 103·50% for groups of summations differing by 0·05 per cent.

Summations.	97	98	99	100	101	102	103
·00-·04	1	2	19	139	26	3	--
·05-·09	--	--	15	143	29	4	--
·10-·14	1	1	29	144	10	--	--
·15-·19	--	4	22	151	20	--	--
·20-·24	--	1	30	128	12	3	--
·25-·29	1	1	29	131	18	--	--
·30-·34	--	4	34	133	12	2	1
·35-·39	--	1	36	114	17	2	--
·40-·44	--	2	49	83	8	1	1
·45-·49	1	1	42	88	9	2	1
·50-·54	--	4	49	90	2	1	--
·55-·59	--	3	47	77	7	3	--
·60-·64	1	4	71	69	5	1	--
·64-·69	1	3	82	69	3	--	--
·70-·74	1	4	95	67	3	1	--
·75-·79	--	6	96	59	6	--	--
·80-·84	--	5	116	48	3	1	--
·85-·89	1	2	119	43	2	--	--
·90-·94	2	4	142	36	1	--	--
·95-·99	--	8	131	34	2	--	--
Totals	10	60	1253	1846	195	24	3
Grand total	3391						

sufficient analyses, their effect on the general average is equal to zero. Washington* gives figures for the allowable variation in duplicate determinations of the various oxides, all of which may be either plus or minus, in which case they would tend, of course, to balance one another purely as a matter of chance. Dittrich,† on the basis of special determinations, decided that errors of a certain size and direction were to be expected for six of the common rock elements expressed as oxides. However, part of the analytic work was not done by Dittrich and was poor, and as a whole it hardly warranted quantitative conclusions. The qualitative statement of the results is that a minus error is to be expected for alumina, a plus error for ferric iron, and a plus or minus error for lime,

* Washington, H. S., *Chemical Analysis of Rocks*, p. 24, 1904.

† Dittrich, M., *Ueber Genauigkeit von Gesteinanalysen*, *Neues Jahrb. f. Min. u. Geol.*, vol. ii, p. 69, 1903.

magnesia, potash, and soda. An examination of the best methods used in rock analysis, such as are given by Hillebrand,* shows that the probable character of the errors in the determination of individual oxides is as follows:

SiO ₂	—	MgO	+	H ₂ O	±
Al ₂ O ₃	—	CaO	±	TiO ₂	—
Fe ₂ O ₃	+	Na ₂ O	±	P ₂ O ₅	+
FeO	—	K ₂ O	±	MnO	+

On account of the customary practice of determining Al₂O₃ by difference, the errors for Fe₂O₃, TiO₂, and P₂O₅ have to be considered as a single error the value of which is plus. If, then, the errors as a whole are of about the same size, it is evident that they will tend to balance because the chances for plus and minus errors are equal.

The errors which result from analytic methods alone rarely neutralize one another in individual analyses. They do so only in an average based on a large number of analyses. The size of the unbalanced errors, however, can not well be large because present-day methods of silicate rock analysis are reasonably accurate. No doubt such errors were more pronounced in the older analytic work due to less accurate methods, less well developed technic, and to poorer reagents.

It may be concluded, then, that errors due to methods should bring about a slight dispersion of individual summations on either side of the general average and that this distribution should be symmetrical because there is an even chance for plus and minus errors.

There is not a complete balancing of all the errors affecting a summation. As is well known, analyses commonly add up to more rather than less than 100 per cent. For example, 61 per cent of all the analyses used in this study have summations above 100 per cent. The actual average summation for all the analyses is 100.13 per cent. There is thus a small constant plus error due not to unbalanced errors in methods but to different sources such as impurities derived from reagents or from glass and porcelain vessels and to dust. This error was slightly greater (0.2 per cent) in older analytic work and in the future it may well be smaller than at present. It seems hardly possible, however, that it will ever be entirely eliminated.

The conclusion that errors in methods tend to offset one another presumably holds only for analytic work of the better quality. In poor work there may be unbalanced errors. One such error is found in the determination of magnesia. To illustrate this analyses with more than 20 per cent of magnesia

* Hillebrand, W. F., *The Analysis of Silicate and Carbonate Rocks*, U. S. Geol. Survey Bull. 422, 1910.

and not over 10 per cent of water are used. The high percentage of water is unavoidable because the olivine-bearing rocks, which contain large amounts of this element, are particularly susceptible to alteration. The results are:

Quality of work	Number of anal.	Ave. summation
Superior	29	100·14
Inferior	10	100·60

The analyses in the superior group have the same average summation as the general average; presumably the common plus error in the determination of magnesia is sufficiently small to be counterbalanced. On the contrary, the inferior group has a high summation. It is 0·47 per cent above the general average, which is a significant amount and must largely represent the plus error in the determination of magnesia. In general it is no doubt true, except for the best work, that magnesia has been determined in excess of the real amount by the older analytic methods. Gooch and Austin* have shown the conditions which cause this error, as well as how it may be avoided. On the basis of their special determinations an error of 1 in 40 may be expected. The inferior analyses just given show a smaller average error than this, caused probably by counterbalancing errors in the determination of other constituents. It is possible, of course, that the plus error in the determination of MgO itself might raise the general average summation above 100 per cent. The average igneous rock of the earth's crust contains about 4 per cent of MgO and on the proportion of 1:40 the plus error would be 0·10 per cent. However, so large an average error is not allowable, because in many rocks MgO undoubtedly has been correctly determined. Yet with this qualification a small part of the constant plus error in the general average summation might well be due to this cause.

An unbalanced error might be expected in those analyses in which iron has been determined wholly as ferric or as ferrous oxide. Such a procedure should affect the summation provided the oxide not determined is present in any considerable amount. Theoretically, if an analysis shows a total of 15 per cent of ferric oxide, for example, and this includes 5 per cent of ferrous oxide, the summation will be +0·5 per cent in error. If 15 per cent of ferrous oxide is determined and this includes 5 per cent of ferric oxide, then the summation will be -0·6 per cent in error. To test these errors in actual summations analyses have been selected in which the iron, wholly as one oxide or the other, is greater than 10 per cent and in which magnesia is less than 15 per cent. Magnesia can not be set at

* Gooch, F. A., and Austin, M., The Constitution of the Ammonium Magnesium Phosphate of Analysis, this Journal, 4th ser., vol. vii, p. 187, 1899.

a lower figure because rocks which contain large amounts of iron-bearing minerals are commonly rich in this element. The results are as follows :

Oxide determined	Number of anal.	Ave. summation
Ferric oxide	96	100·13
Ferrous oxide	21	100·04

The average summation for the analyses in which only ferric oxide was determined is the same as the general average, whereas it would be expected to be distinctly higher. An additional plus error due to magnesia would also be expected as a number of the analyses are of inferior quality. The failure of the average summation to show a positive error is no doubt largely due to the actual presence of little, if any, ferrous iron. The basic rocks used in this calculation are especially susceptible to alteration, actually shown by the large amount of water many of them contain, and the ferrous oxide has been raised to ferric form. The average summation for the analyses in which only ferrous oxide was determined is below the general average, an error in the right direction but hardly of significant size unless the summation has been raised by the plus error of magnesia. The result of this test is considerably vitiated by the inferior quality of some of the analyses, taken in connection with their small number. For example, two analyses of the same rock, by the same analyst, have summations of 99·15 and 100·51 per cent. This brings out the point, which will be considered later, that the personal errors of the analyst are sufficiently great to mask any error arising from good analytic methods when the number of analyses averaged is small.

It is possible that the minus error in silica finds expression in the silicic group of rocks (granites and rhyolites), which on the average contain about 70 per cent of this oxide. For example, 135 superior analyses of rocks in this group, selected at random, have an average summation of 100·04 per cent as compared with 100·13 per cent for the general average. The difference may be explained by assuming an actual loss of silica. Such a loss is not unlikely, because many of the analyses, on which the above average is based, were made before the present refinements in the determination of this oxide were introduced.

The foregoing considerations indicate that by far the commonest errors which affect the summation of analyses are of the analyst's own making. The trouble is not so much with methods as with the analyst's ability to use them. Such errors are illustrated by the results of a single chemist's work on rocks of nearly identical composition. The following

examples will suffice: (1) 9 analyses of similar rocks showing summations from 99·86 to 100·54 per cent; (2) 7 analyses, 99·59–101·00; (3) 5 analyses, 99·49–101·05; (4) 8 analyses, 99·86–101·16; (5) 7 analyses, 99·35–100·77; (6) 20 analyses, 99·58–100·72; (7) 21 analyses, 98·85–101·68. The range in the last example is 2·83 per cent and for this analyst's entire work on rocks of almost identical composition it is 3·96 per cent. This, of course, is an extreme example. Commonly the range of an analyst's summations will fall inside of 2 per cent. In general, as shown by the analyses used in this study, the range is from 97 to 103·5 per cent, or 3 per cent and more either side of the general average of 100·13 per cent.

The individual analyst's errors are generally of two kinds. There is commonly a constant error represented by the difference between the analyst's average summation and the general average. There are always accidental (residual) errors represented by the differences between an analyst's single summations and his own average summation. The constant error is of small size compared with the accidental errors. In two-thirds of the above cases it is less than 0·2 per cent and the largest is 0·53 per cent. The accidental errors may be as large as 2 per cent either side of the average, although the great majority range from 0·5 to 0·75 per cent.

The chances appear even that the constant error may be either plus or minus. Thus out of 43 analysts all of whom have made over 15 analyses, 21 have a plus error averaging 0·21 per cent, 20 have a minus error averaging 0·17 per cent, and 2 have no error. The chances are even that the accidental errors will be either plus or minus in so far as they represent errors which lie in analytic methods. The accidental errors due to other causes, such as the incomplete washing or collection of precipitates, may be either plus or minus, apparently with equal chance. It thus appears that the errors which affect the summation of analyses for the most part are evenly distributed and consequently the probability curve for summations will be symmetrical. And it would seem the most probable assumption that this relation holds generally true.

However, whether summations in general are evenly distributed or not will depend on whether the proper unit of measure is employed. Analytic results are expressed to the hundredth place of decimals—not to mention the thousandth place. But a unit of measure (difference) of 0·01 per cent is of no significance. A difference of 0·05 per cent, the unit of Table 1, is below significant size. What then is the unit of most significant size? The requirements are that it shall show a maximum of the same value as the general average (100·13) and shall result in an even distribution of summations either side of the maximum.

This unit has been found by taking different sized units, from necessity, as multiples of 0.05 per cent, and determining which gives the best distribution. It is thus found that a unit of 0.15 per cent most nearly meets the requirements for the entire range of summations. The units of 0.20 and 0.25 per cent also produce a symmetrical distribution between the restricted limits of 99.50 and 100.74 per cent, which is better than that given by the 0.15 per cent unit. As three-quarters

FIG. 1.

of all summations fall within the foregoing limits there is practically little choice between the 0.15, 0.20, and 0.25 per cent units. A study of a larger number of analyses than here used might show the 0.15 per cent unit to be less suitable than the 0.20 or possibly the 0.25 per cent unit. The 0.15 per cent unit has been used to show the distribution of summations in general and the 0.25 per cent unit has been chosen, purely as a matter of convenience, to show the distributions for individual analysts which are later given.

For the unit of 0.15 per cent there are three possible combinations of the 0.05 per cent unit. The values for these three combinations have been plotted, as is customary, and a symmetrical curve has been fitted to them, as shown in fig. 1. In this figure the ordinates are the actual number of analyses, but

in those following they are percentages of the total number of analyses; in all the figures the summation groups are plotted by their mean value.

In general the departures from the fitted curve would appear small in view of the fact that the analyses (1) are the work of some hundreds of different chemists; (2) that they cover a period of 32 years, although the great majority fall in the last 6 years of that period, during which time many changes in methods of analysis were made; (3) that there is the certainty of some constant errors, and a possibility of others being present; and (4) that all the summations are not a matter of pure chance. Such departures as are shown are to some extent, though not wholly, due to the unit of measure being below significant size. This is evident when the data are plotted by the 0.20 per cent unit; the irregularities are much smoothed out, although the curve as a whole becomes slightly asymmetric.

The different proportions of the entire number of analyses which may be expected to fall into the several groups of summations on the basis of the 0.15 per cent unit are given below. Corresponding figures are also given for groups by differences of 0.25 per cent on the assumption of an entirely symmetrical distribution.

TABLE II.

0.15 per cent unit		0.25 per cent unit	
Summation groups	Proportion of analyses	Summation groups	Proportion of analyses
100.05-100.19	12.8%	100.00-100.24	20.8%
100.20-100.34	11.8	100.25-100.49	17.0
99.90-100.04		99.75-99.99	
100.35-100.49	9.6	100.50-100.74	10.5
99.75-99.89		99.50-99.74	
100.50-100.64	7.1	100.75-100.99	6.0
99.60-99.74		99.25-99.49	
100.65-100.79	5.1	101.00-101.24	3.1
99.45-99.59		99.00-99.24	
100.80-100.94	3.6	101.25-101.49	1.3
99.30-99.44		98.75-98.99	
100.95-101.09	2.4	101.50-101.74	.6
99.15-99.29		98.50-98.74	
101.10-101.24	1.5	Beyond above limits	2.2
99.00-99.14			
101.25-101.39	.8		
98.85-98.99			
101.40-101.54	.5		
98.70-98.84			
101.55-101.69	.3		
98.55-98.69			
101.70-101.84	.2		
98.40-98.54			
Beyond above limits	1.5		

The general distribution curve (fig. 1) is based, of course, on the work of many analysts. Some of these, however, have contributed much more greatly than others. This is particularly true of the chemists of the United States Geological Survey; fully one-third of all the analyses here used have been made by them. Thus a distribution curve for the summations of the analyses made by the Survey chemists may be drawn. Such a curve for the work of five Survey chemists is shown by I, fig. 2. For comparison the distribution curve (II) for the work of all chemists, exclusive of those five analysts, is

FIG. 2.

added. The number of analyses used for I is 1,012; for II it is 2,497. For convenience the analyses are grouped by differences of 0.25 per cent, the significance of which unit has been noted in an earlier paragraph.

Clearly the Survey chemists have a much larger proportion of summations at or near the maximum than have other chemists. The relative percentages of analyses falling in the several summation groups are as given on the following page.

The superior results as to summation shown by the chemists of the U. S. Geological Survey are due to several reasons among which not the least is the experience gained from continuous work. Also, poor analyses (supposing such may occasionally be made) are evidently not allowed to leave the laboratory until their errors have been found and corrected. And it may be said that if all chemists followed this same

Summation groups	Proportion of analyses	
	U. S. G. S. chemists	All others
99·00– 99·24	·8	4·2
99·25– 99·49	1·6	6·6
99·50– 99·74	7·5	11·0
99·75– 99·99	24·4	15·9
100·00–100·24	35·7	17·7
100·25–100·49	22·9	13·9
100·50–100·74	5·4	12·1
100·75–100·99	1·7	6·8
	100·0	88·2
Beyond above limits	0·0	11·8
	100·0	100·0

practice their distribution of summations would more nearly approach that of the Survey chemists. In fact, the lower grade for the work of other chemists is due to the inexperience of many of the analysts. It is absolutely essential for a beginner to make analyses in duplicate, no matter what may be the nature of the rock, until he can secure accordant results. The writer has been told by a teacher of quantitative analysis that out of several hundred students the number who had obtained uniformly good results could be counted on the fingers of one hand. As Hillebrand has stated, "too great stress can not be laid upon the importance, especially for the analyst of limited experience, of consistently testing most of his final precipitates and filtrates as carefully as possible in order to be sure, on the one hand, that the substances reported by a given name are wholly such and, on the other, that all is reported. In no other way can an analyst so soon acquire the needed confidence in himself and his methods."*

A comparison of the distribution of summations for all other chemists with that for the five chemists of the U. S. Geological Survey (fig. 2) shows beyond argument how great is the room for improvement in the general quality of silicate rock analysis. The efficiency of the Survey chemists, which is fairly expressed by their distribution curve for summations, may well be taken as the standard.

An idea of the general quality of silicate rock analyses may also be obtained from the proportion of analyses that fall within certain proposed limiting summations, as shown in the following table:

* *Op. cit.*, p. 28.

Limits	Proposed by	Proportion of analyses in
99·75–100·50	Hillebrand*	55
99·75–100·75	Hillebrand†	66
99·50–100·75	Washington‡	76

Hillebrand says: "Given the purest obtainable reagents, an ample supply of platinum, facilities for working, and a reasonably clean laboratory, there is little excuse for the failure on the part of a competent chemist to reach a summation within the limits 99·75–100·50 per cent."§ Washington states: "If, therefore, the analysis of a rock is satisfactorily complete, there is no excuse . . . for a summation that does not fall within the somewhat liberal limits here assigned."|| Interpreted in the light of these statements the figures in the last column of the above table are a striking commentary on the quality of a large proportion of the analyses of igneous rocks. Dr. Hillebrand's narrower limits are presumably based on his own experience; 90 per cent of his summations fall within them. For the work of the chemists of the U. S. Geological Survey, exclusive of Dr. Hillebrand, the proportion is 77 per cent. For all chemists, exclusive of those of the Geological Survey, the proportion is less than 50 per cent. These limits of 99·75–100·50 per cent, therefore, might well be considered too narrow; yet the writer prefers them because they furnish an additional stimulus to good work. And, indeed, they are of little value, and may be actually harmful, except when looked at in that way.

Having considered the general problem, the distribution of the summations of individual analysts may now be taken up. From a practical standpoint—improvement in analytic skill—such examples are most interesting.

As already stated, an analyst may have, in addition to the ever-present residual errors, a constant personal error which causes his average summation to be either above or below the general average. The following examples (fig. 3) show the effect of such errors in comparison with a normal curve. In this figure, and those following, the coördinate points are connected simply by straight lines, as sufficient for purposes of illustration. The number of analyses in each summation group is expressed as a percentage of the total number in each case so that the results for different analysts may be comparable.

* Bull. U. S. G. S., No. 148, 1897, p. 62.

† Bull. U. S. G. S., No. 422, 1910, p. 28.

‡ Prof. Paper, U. S. G. S., No. 14, 1903, p. 34.

§ Bull. U. S. G. S., No. 422, 1910, p. 28.

|| Idem, p. 36.

As may be seen, analyst A has a very symmetrical distribution of summations as 28·5 per cent of the analyses have summations above and 31·3 per cent below that of the maximum group. His average summation of 100·11 per cent practically coincides with the general average, the constant error being only 0·02 per cent. Also the proportion of analyses (40·2) falling in the group of maximum frequency is high. In fact, having regard for the large number of analyses made by this chemist, this proportion may be considered as high as is obtainable in ordinary practice. Analyst B has an evident constant minus

FIG. 3.

error; it amounts to 0·22 per cent, as his average summation is 99·91. The constant error is, indeed, sufficiently large to throw the group of maximum frequency to 99·75–99·99 per cent. The distribution curve of B is somewhat asymmetric and a larger proportion of summations lie above the group of maximum frequency than below; the percentages are, respectively, 37·8 and 25·0. The proportion of summations (36·4) in the maximum group is good. Analyst C has a constant plus error of 0·12 per cent, his average summation being 100·25. His group of maximum frequency is 100·25–100·49 per cent, but the group 100·00–100·24 per cent contains nearly as large a proportion of analyses. The actual maximum for the fitted

curve thus would lie between these two groups and the curve would be flatter topped than those of A and B. Disregarding this fact, it may be noted that 46·8 per cent of C's summations lie below his actual group of maximum frequency, whereas 19·5 per cent are above. It will be observed that both B and C, whose groups of maximum frequency are, respectively, below and above the average group of 100·00–100·24 per cent, have the larger proportion of summations on the side of their maximum group which is toward the general average of 100·13 per cent.

The three curves of fig. 3 are based on a sufficiently large number of analyses in each case to make them fairly reliable. There is no great choice between the curves as to form, although that of A is evidently better than those of B and C. The work of these three analysts has been chosen for illustration because it typifies certain general features which may be stated as follows:

1. When the group of maximum frequency, on the basis of the 0·25 per cent unit, coincides with the average group (100·00–100·24 per cent), then (1) the number of analyses in the groups above and below that of maximum frequency will be equal, or (2) commonly a greater proportion will lie either above or below as the case may be. That is to say, most analysts have a slightly asymmetrical distribution of summations about the maximum which indicates the existence of a "personal equation." In general, however, the number of analyses on opposite sides of the maximum group should be equal. This is approximately true for the work of those analysts, fourteen in number, who fall in this category, the figures being 32·3 per cent above and 31·5 per cent below.

2. When the group of maximum frequency lies below the common maximum group then a larger proportion of summations will lie above the group of maximum frequency. Six out of eight analysts whose maximum group is below the average maximum group show this feature. For the eight analysts taken together 40·9 per cent of their summations are above and 21·8 per cent are below their group of maximum frequency.

3. When the group of maximum frequency lies above the average group then a larger proportion of summations will lie below the group of maximum frequency. This feature is shown by all the analysts, nine in number, who fall in this category. The proportion of summations are 50·2 per cent below and 18·9 per cent above their group of maximum frequency.

The foregoing characteristics may be taken as guides for testing the normality of the distribution of an analyst's summations. The explanation of the relations noted under (2) and

(3) would seem to be that an analyst naturally works toward the general average rather than away from it.

Distribution curves with a single maximum, as illustrated at their best in fig. 3, are the common type. A less common type is a double distribution curve—one with two maxima. Triple distribution curves, due to pure chance, probably do not occur.

Several examples of double distribution curves are shown in fig. 4. There is no doubt as to the reality of such distributions, the data are ample. In fact, the best curve of the four (D) rests on the smallest number of analyses. Just what conditions influence an analyst to get summations thus distributed

FIG. 4.

is difficult to say. They may be entirely personal, and the problem is then one for the psychologist, or they may result from such causes as changes in analytic methods, technic or quality of reagents, or to differences in the composition of the rocks analyzed.

Referring to fig. 4, it is seen that analyst D has larger proportions of summations in the two groups lying either side of the common maximum group than in that group itself. His tendency, also, is to get more summations in the lower group (99.75–99.99) than in the higher (100.25–100.49). The distribution of the summations under the circumstances, as shown by the form of the curve, is excellent. It must be concluded that such results are not in any sense haphazard. The tendency of analyst E toward double maxima is less marked than that of D. This analyst's upper maximum is the group 100.50–100.74 per cent, his lower is strictly in 99.75–99.99 per cent, but practically covers that group and the next lower. His maxima are thus farther apart than those of D and his

It also appears that the same chances hold for the occurrence of distributions with double maxima.

It would be possible to determine with considerable accuracy from the work of Dr. W. F. Hillebrand, because of its magnitude, what the chances are in favor of various types of symmetry. The results, however, would apply only to the work of analysts whose skill equals that of Dr. Hillebrand. The number of such analysts is, unfortunately, too small to compensate for the labor involved in the calculation of results. For example, from a study of the work of analysts in general the chances appear about 1 : 3 for the occurrence of double maxima, whereas on the basis of Dr. Hillebrand's work they are about 1 : 15. The discrepancy is due in part, certainly, to the lower grade work of a considerable number of the chemists whose analyses were studied.

There is, presumably, a fairly close relationship between the amount of work a chemist does and his technical skill. No doubt there are many analysts whose skill, and reputation, would improve noticeably with increased work. It is unfortunate that silicate rock analysis is so time-consuming that it has become customary to depend on single determinations of constituents for a final result. This custom works out most unfavorably with those chemists who make but a few analyses. It would redound to their credit, and be an excellent thing for petrology, if these analysts did all their work in duplicate. Mineral analyses commonly have been made in duplicate because of the importance of an accurate result for establishing a formula. It is by no means impossible that increased knowledge of rock composition, derived from physico-chemical study, eventually will call for duplicate determinations in rock analysis. At least it will call for work of greater accuracy than much that has been done in the past or is, indeed, being done at present.

The probable error of his single summations, and to a less extent that of his average summation, indicates with considerable accuracy the technical skill of the chemist.* It is not a complete measure because there are possible errors which do not affect the summation, a very persistent one being the incomplete separation of magnesia and alumina. The number of a chemist's analyses has a marked effect on the probable error of his average summation because the calculation involves the quantity $N \times N - 1$. The number affects the probable error

* It will be recalled that the formula for the probable error of an arithmetical mean is $E_a = 0.6745 \sqrt{\frac{[r^2]}{N(N-1)}}$, whereas for a single measurement $E = \sqrt{\frac{r^2}{N-1}}$, where r = residual error and N the number of measurements.

of a single summation only so far as a large amount of work conduces to more accordant results than a small amount. Thus the difference between the probable error of the average summation of a chemist who has done much work and of one who has done little may be as great as 200 per cent, whereas the difference in the probable errors of their single summations may not exceed 25 per cent. For this reason the probable error of a single summation is the more valuable guide to the quality of a chemist's work.

The probable errors for single summations and the average summations of 43 analysts, who have made 15 or more analyses, weighted according to their relative amount of work, are:

Single summation, ± 0.30 per cent.
Average summation, ± 0.02 per cent.

The effect of a considerable difference in the number of analyses on the values of the probable errors is shown by the following figures:

1. For those chemists who have made 50 or more analyses. Single summation, ± 0.20 per cent; average summation, ± 0.01 per cent.

2. For those chemists who have made between 15 and 50 analyses. Single summation, ± 0.40 per cent; average summation, ± 0.07 per cent.

It is the opinion of the writer, based on all available data, that the probable error of ± 0.30 per cent for a single summation furnishes a fair guide for judging a chemist's technical skill, so far as it may be judged by the summation of analyses. If a closer estimate of a chemist's work is desired, then the values based on the amount of work done should be used.

To give point to the foregoing general values, the probable errors, and also the constant errors, for the work of those chemists whose distribution curves have been presented in figures 3-5 may be stated:

Analyst	No. of anal.	Constant error	P. e. single sum.	P. e. ave. sum.
A	450	-0.02	± 0.16	± 0.01
B	140	-0.22	.26	.02
C	77	+0.12	.20	.02
D	37	-0.08	.24	.04
E	147	-0.02	.30	.02
F	46	-0.39	.39	.06
G	50	+0.45	.43	.06
H	21	0.00	.18	.04
I	24	+0.01	.20	.04
J	17	-0.11	.26	.06
K	31	+0.19	.28	5

summations are more uniformly distributed between his two maxima. However like D, he has more summations in the lower maximum group than in the upper one. Analysts F and G have distributions which are quite similar, although F's summations lie largely on the negative side of the general axis (100.13 per cent), whereas those of G are largely on the positive side.

The foregoing double probability curves may be resolved into their two component single probability curves and it then

FIG. 5.

appears that the two parts may be classified under the three heads noted in an earlier paragraph, practically all falling under (2) and (3).

A distribution of summations to be significant must rest, of course, on sufficient data, and this is essentially true for the examples already cited. The number of analyses necessary to give such a result will vary widely, depending upon the analytic skill of the individual chemist. The minimum number can be determined approximately by examining the work of different analysts. In fig. 5 are given four examples to show that a very good distribution of summations, as indicated

by the symmetry of the curves, may be obtained from as few as 18 analyses (J) and not over 30 (K). The number of analyses for H and I are about midway between those for J and K.

The curves in the above figure are about as symmetrical as those shown in fig. 3, although based on very much smaller numbers of analyses. That none of the curves at their extremities approach the abscissa axis closely is due to the latter fact. For example, one analysis equals 5 per cent of 20 analyses so that if no more than two analyses fell in a limiting group they would equal 10 per cent as plotted on the diagram. The curves have not been extended to zero ordinate values in order to emphasize the limiting summation groups.

The distribution of summations of analysts H and I is distinctly better than for J and K. In fact H has a greater proportion of summations in his maximum group than analyst A (fig. 3); I has a greater proportion than B or C. The limits of their summations, also, are more restricted than for either A, B, or C. These facts, in connection with the small number of analyses, make it practically certain that analysts H and I exercised more than usual care in their work. They may have made some of their analyses in duplicate as well as made special redeterminations in some instances. Such a procedure means, of course, that their results have more than the average chance of being good. Analysts H and I, then, almost certainly could not obtain such favorable results on a large amount of work. It seems likely that the distribution shown by analysts J and K, disregarding the constant errors, more nearly represents the best that should be expected in ordinary practice with a small number of analyses.

The foregoing examples (figs. 3, 4, and 5) show some of the more symmetrical distributions of analyses which have come under the observation of the writer. They indicate, for the most part, what may be expected in good analytic work.

A study of the work of 43 analysts indicates the following chances in favor of a more or less symmetrical distribution of summations:

1. When the number of analyses is over 35, the chances are entirely in favor.

2. When it is between 20 and 35, the chances are as 4 : 5.

3. When it is between 15 and 20, the chances are as 2 : 3.

Below 15 analyses the chances are almost wholly against a symmetrical distribution so that this number is the minimum for a test of this character.

For distributions with a single maximum the chances are about 1 : 3 that the group of maximum frequency will fall outside the average group (100.00–100.24 per cent).

A small probable error for a single summation means that the summations as a whole fall within narrow limits and that a large proportion are in the group of maximum frequency, whereas a large probable error indicates the opposite. As a general rule a small constant error is associated with a small probable error for a single summation. A large constant error is almost always associated with large probable errors for both a single and also the average summation, as shown by analysts F and G and to a less extent by B and K. When particularly large it is an almost sure mark of inferior analytic skill. In but one case out of ten, which have come under observation, has a large constant error been accompanied by small probable errors.

Referring to the probable errors for single summations, all are below the average value of ± 0.30 per cent except those of analysts F and G, and one (E) which is on the average. Probable errors of ± 0.18 – 0.26 per cent are not uncommon for chemists who have made less than 30 analyses, thus comparing well with the value of this error for analysts A, B, and C who have done much work. For this reason the single value of ± 0.30 per cent has been adopted rather than the two values of ± 0.20 and ± 0.40 per cent, depending upon a large or small number of analyses.

As already stated, the size of the probable error for the average summations depends on the number of analyses. It must be judged accordingly. Thus the error of ± 0.02 per cent for B and C is about equal to the value of ± 0.01 per cent for A. Likewise the error of ± 0.04 per cent for analysts D, H, and I should be considered of equal value to the smaller errors for A, B, and C.

It may be said in conclusion, then, that a probable error for a single summation much less than ± 0.30 per cent in connection with a probable error for the average summation of ± 0.01 – 0.03 per cent, when the number of analyses is large, or of ± 0.04 – 0.06 per cent when it is small (less than 50), indicates good technical skill on the part of the chemist. On the other hand, if the probable error for a single summation is much over ± 0.30 per cent and the error for the average summation is in excess of the upper limits just given, then a lack of technical skill is indicated.

Peabody Museum, New Haven, Conn.