A note on the relationship between the precision of classical methods of rock analysis and the concentration of each constituent.

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A GRANITE (G–1) from Westerley, Rhode Island, and a diabase (W–1) from Centerville, Virginia, were recently analysed by some 34 analysts in different countries for the purpose of obtaining thoroughly reliable rock standards for spectrochemical analysis. Most determinations were made by so-called classical methods of chemical analysis. The results of the investigation have been discussed by Fairbairn and others.[1] Fairbairn examined the results statistically and, using the relative deviation (standard deviation expressed as a percentage) as a measure of precision, concluded that precision deteriorated with a decrease in the concentration of a constituent. In the present paper this general observation will be demonstrated quantitatively by means of a graphical presentation, thus providing the petrologist with a guide for rapidly assessing and comparing the precision of classical methods of chemical analysis over considerable concentration ranges. This guide should apply particularly to rock analyses which have been made during the last 60–70 years.

For his statistical calculations, Fairbairn assumed normal (Gaussian) distribution of observations about some central (modal) value. Although replicate chemical determinations rarely follow such a distribution,[2]

[1] H. W. Fairbairn, W. G. Schlecht, R. E. Stevens, W. H. Dennen, L. H. Ahrens, and F. Chayes, A co-operative investigation of precision and accuracy in chemical, spectrochemical and modal analysis of silicate rocks. Bull. U.S. Geol. Surv., 1951, no. 980.

W. G. Schlecht, Co-operative investigation of precision and accuracy. Anal. Chem., 1951, vol. 23, p. 1568.

H. W. Fairbairn and J. F. Schairer, A test of the accuracy of chemical analyses of silicate rocks. Amer. Min., 1952, vol. 37, pp. 744–757. [M.A. 12–33.]

H. W. Fairbairn, Precision and accuracy of chemical analysis of silicate rocks. Geochim. Cosmochim. Acta, 1953, vol. 4, pp. 143–156. [M.A. 12–264.]

[2] Positive skewness, negative skewness, irregular distributions, as well as normal and lognormal type distributions have been observed for the particular series of chemical observations under discussion.

statistical calculations based on assumed normal distribution for all
constituents may nevertheless be used for the purpose of semi-quantita-
tively comparing precision in a general way, such as will be attempted
here. The exact statistical nature of the distribution of chemical
determinations for each individual constituent should, however, be taken
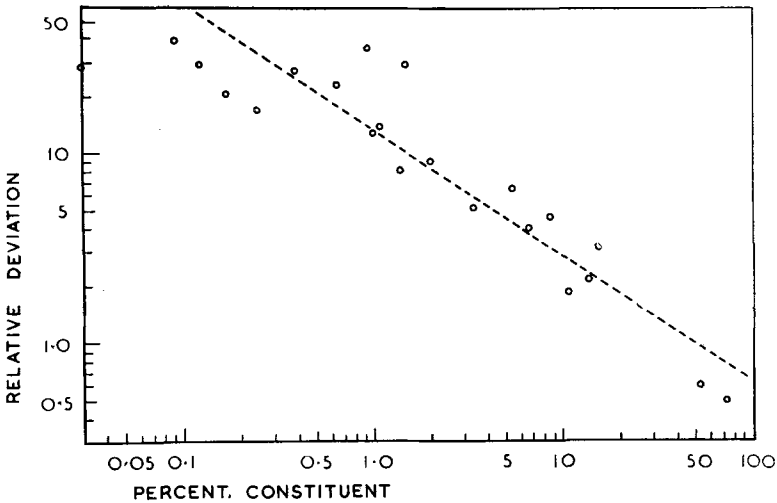

FIG. 1. The precision, as measured by relative deviation, of a chemical determina-
tion is related to the concentration of each constituent in granite (G–1) and
diabase (W–1), using geometric scales; the regularity is quite well developed.

into account when making fully quantitative predictions; this becomes
more important as the dispersion of observations increases.

As we wish to examine the relationship between the relative deviation
(C) and the concentrations of several constituents over wide variations
of both variables (concentration varies from 72·9 % SiO_2 in G–1 to
0·9 % P_2O_5 and C varies from 0·5 % to 39 %) log scales will be used.
They have the advantage also of readily revealing a possible exponential
relationship because this would appear as a straight line—fig. 1 happens
to be a fair example.

Fig. 1 relates C (after Fairbairn, 1953) and percentage constituent
(SiO_2, Al_2O_3, CaO, &c.) in granite G–1 and diabase W–1. The plotted
points are purposely not labelled as the relationship in fig. 1 is intended
to be perfectly general. The regularity is well developed and, in fact,
hardly short of amazing when the variety of chemical procedures and the

range of concentration is taken into consideration. Thus, for example, most analysts determined Si, Al, Ca, Mg, and P gravimetrically, Fe volumetrically, Na and K by the Lawrence Smith procedure, and Mn and Ti by colorimetric methods. The slope of the curve of best fit is about 33°, the tan of which is 0·65; in other words, the general relationship may be expressed approximately by

$$C \alpha \frac{1}{\text{concentration}^{0.65}}.$$

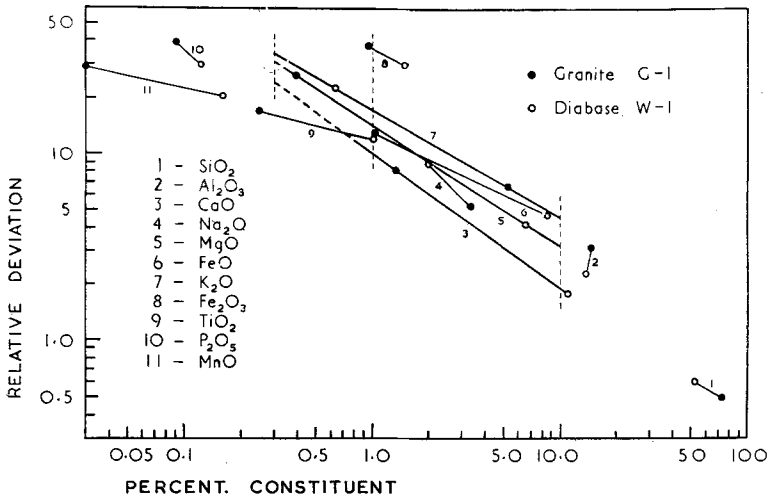The value of the exponent would be unity had the slope been 45°.

FIG. 2. As in fig. 1, but showing details of constituents.

Details for each constituent are shown in fig. 2. As in fig. 1 of Fairbairn (1953) this plot shows that precision deteriorates with decrease of concentration of each individual constituent, with the exception of Al_2O_3. It is of interest to note that the slopes of lines joining pairs of plotted points are often similar to the slope for the stream of points (cf. fig. 1) as a whole. As might be expected, the slopes of such lines for titanium and manganese are less than those of the others as these two elements are usually determined colorimetrically.

Figs. 1 and 2 may be of some aid to a petrologist for roughly assessing and comparing the accuracy with which individual constituents may be determined by means of classical methods of chemical analysis. Fig. 2 shows clearly that Fe_2O_3 determinations are conspicuously inferior to any

others at a given concentration (for example 1 %) and that lime deter-
minations are decidedly superior to both potash and magnesia over the
concentration range covered by W–1 and G–1. A fairly critical com-
parison involving some extrapolation may be made for some constituents,
as indicated by CaO, MgO, and K_2O in fig. 2. Table I compares relative
deviations for these constituents at 0·3, 1, and 10 % as obtained from
the extrapolations in fig. 2.

TABLE I. A comparison of relative deviations at three different concentrations of
K_2O, MgO, and CaO.

Concentration.	Relative deviation.		
	K_2O.	MgO.	CaO.
0·3 %	35 %	32 %	(25 %)*
1·0	18	15	10
10·0	4·8	3·3	2

* Very rough, as it is based on considerable extrapolation.

At a concentration of 0·3 % K_2O, as in olivine-basalt, for example, C
is large (35 %) and indicates that there must be considerable error in
many published determinations. Statistical prediction thus indicates that
two-thirds of the determinations should fall within 0·3±0·1 %, that is,
0·2 to 0·4 % K_2O, but that the remaining one-third would be outside
these limits; 95 % of the determinations should fall within 0·1 to 0·5 %
K_2O. It must be emphasized again that these calculations can only be
regarded as approximate, particularly as they are based on assumed
normal distributions; nevertheless, they should indicate the error magni-
tudes which are expected for different constituents at different con-
centrations. Caution must be exercised to confine such comparisons and
calculations to classical methods of chemical analysis of rocks having a
composition approximating granite or diabase, basalt and gabbro, or
something intermediate.

The regularities of figs. 1 and 2 make an interesting comparison with
spectrochemical methods where reproducibility remains independent of
concentration. Figs. 1 and 2 also provide an example of the power of
the geometric scale for revealing regularities which might otherwise
remain hidden.