

THE MINERALOGICAL MAGAZINE

AND

JOURNAL OF THE MINERALOGICAL SOCIETY

No. 227

December, 1954

Vol. XXX

*A further note on the presentation of chemical analyses of minerals.*¹

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[Read June 10, 1954.]

SUPPOSE that in the study of a mineral we have determined the cell-dimensions and the density, and made a chemical analysis. From these we can readily calculate the empirical unit-cell contents, which will usually approach integral values and so suggest a probable formula.

But the calculated empirical unit-cell contents, being based on chemical and physical data subject to experimental error, will be subject to numerous sources of error, and in any serious study it is very desirable to have some rough idea of the probable limits of error. Unfortunately, this is a matter of considerable complexity, but the following suggestions may be of assistance, though they will doubtless be considerably improved on.

The 'probable error' of the density and cell-dimensions can usually be assessed without much difficulty, but the errors of the chemical analysis are by no means easy to estimate.

Considering first the errors of the physical data, we may take as an example a monoclinic mineral for which we have the experimental cell-dimensions $(a \pm \delta a)$ Å., $(b \pm \delta b)$ Å., $(c \pm \delta c)$ Å., $(\beta \pm \delta \beta)^\circ$, and specific gravity² $D \pm \delta D$. The cell-weight, $W = abcD \sin \beta$, will be subject to an error δW that may reasonably be assessed, assuming the errors δa ,

¹ M. H. Hey, *Min. Mag.*, 1939, vol. 25, p. 402.

² The specific gravity must, of course, be corrected for all known impurities, including hygroscopic water; and due allowance must be made for uncertainties in the amount of impurity and in the uniformity of its distribution when assessing the probable error in the specific gravity, δD .

$\delta b, \delta c$ are truly independent, by squaring and adding¹ the several relative errors $\delta a/a, \delta b/b, \delta c/c, \{\sin \beta - \sin(\beta - \delta\beta)\}/\sin \beta$, and $\delta D/D$:

$$\left(\frac{\delta W}{W}\right)^2 = \left(\frac{\delta a}{a}\right)^2 + \left(\frac{\delta b}{b}\right)^2 + \left(\frac{\delta c}{c}\right)^2 + (\delta\beta \cot \beta)^2 + \left(\frac{\delta D}{D}\right)^2 \quad . \quad . \quad i$$

If, however, the errors $\delta a, \delta b, \delta c$, are not independent, we shall have a larger value for δW , since then:

$$\left(\frac{\delta W}{W}\right)^2 = \left(\frac{\delta a}{a} + \frac{\delta b}{b} + \frac{\delta c}{c}\right)^2 + (\delta\beta \cot \beta)^2 + \left(\frac{\delta D}{D}\right)^2 \quad . \quad . \quad ia$$

In a tetragonal, hexagonal, or cubic mineral the errors in the two or three equal cell-dimensions are obviously not independent, and

$$\left(\frac{\delta W}{W}\right)^2 = \left(\frac{2\delta a}{a}\right)^2 + \left(\frac{\delta c}{c}\right)^2 + \left(\frac{\delta D}{D}\right)^2$$

for tetragonal and hexagonal minerals, or

$$\left(\frac{3\delta a}{a}\right)^2 + \left(\frac{\delta D}{D}\right)^2$$

for cubic minerals.

Measurements of unit-cell dimensions are subject to error from several sources, some of which, such as errors in the measurement of distances between diffraction spots, are independent for the three different dimensions, while others, such as errors due to uncertainties in camera dimensions, film shrinkage, &c., are likely to affect all three cell-dimensions in the same sense. Where there is no evidence to the contrary, it will usually be desirable to assume that the errors in the unit-cell dimensions are not independent, and to use formula *ia*, since it is better, as a rule, to over-assess the probable error than to under-assess it.

¹ It may be of interest to consider shortly the addition of errors. Where errors are not independent, we can usually say definitely that a positive error in one factor, say δa , will be associated with a positive error in another, δb , and a negative error in a third, δc , and so on; and the total error is clearly obtained by simple addition with due regard to sign, $(\delta a + \delta b - \delta c \dots)$. But when the errors are independent, we do not know how their signs are to be associated—a positive error δa may be associated with a positive δb , or equally likely with a negative δb . If two positive or two negative errors are associated, the total error will be

$$\pm(\delta a + \delta b) = \pm\sqrt{\{(\delta a)^2 + (\delta b)^2 + 2\delta a \cdot \delta b\}};$$

but if one is positive and the other negative, the total will be

$$\pm(\delta a - \delta b) = \pm\sqrt{\{(\delta a)^2 + (\delta b)^2 - 2\delta a \cdot \delta b\}}.$$

Since we do not know the distribution of signs, our best estimate of the probable error will be somewhere between these values, and it can be shown that the best estimate will in fact be $\pm\sqrt{\{(\delta a)^2 + (\delta b)^2\}}$.

Knowing the weight of the unit cell, W , the empirical unit-cell contents are readily calculated from the chemical analysis. For if there is P % of an oxide X_mO_n of molecular weight M , the weight of X_mO_n in the unit-cell must be $PW/100$ and since the weight of a molecule of X_mO_n is $1.6603M \times 10^{-24}$ gm., and W will be in units of 10^{-24} gm. if a , b , and c are in Å., the number of molecules of X_mO_n in the unit cell must be $PW/166.03M$, and the number of atoms of X in the unit cell is $PWm/166.03M$, associated with $PWn/166.03M$ atoms of oxygen. The calculations are simplified and shortened by the use of a conversion factor $F = W/1.6603S$, where S is the net summation of the analysis after deduction of impurities; by incorporating S in the conversion factor instead of 100, the formal step of recalculating the analysis to 100 % after deduction of impurities is avoided; and F will be subject to a relative error, $\delta W/W$, due to errors in the physical data, together with an error due to errors in the estimation of impurities; the latter error affects S , and if it amounts to δi % it will give rise to a relative error of $\delta i/S$. The total relative error in F , $\delta F/F$, is therefore given by $(\delta F/F)^2 = (\delta W/W)^2 + (\delta i/S)^2$.

The calculations are conveniently set out as in table I, with columns for: the percentages, P ; the atomic ratios, Pm/M ; the empirical unit-cell contents, $E = FPm/M$; the errors in the empirical unit-cell contents consequent on the errors in the physical data, and in the estimation of impurities, $\delta E = \delta FPm/M$; and the oxygen atoms associated with each element,¹ En/m . Summing the last column, and subtracting the oxygen equivalent of any anions such as Cl', F', or S'' in the usual way, we obtain the empirical oxygen content of the unit cell, E_0 ; this will be subject to an error² $\delta_p E_0 = E_0 \delta F/F$ deriving from errors in the physical data and in the estimation of impurities.

It should be noticed that the several errors $\delta_p E$ are not independent, but will all be in the same direction since all depend on δW and on δi . Accordingly, the errors from this source in any group of elements believed to be replacing one another must be simply added, or derived by multiplying the sum of the elements in question by $\delta F/F$.

So far, the only allowance made for errors in the chemical analysis has been the inclusion of δi , the assessed error in the estimation of impurities, in the calculation of the probable error δF of the conversion

¹ A slightly different arrangement is, of course, necessary with minerals such as halides, sulphides, &c.

² Here and subsequently, the symbol δ_p is used for an error arising from the errors in the physical data; for errors arising from the chemical analysis alone the symbol δ_c is used, and for the total error from both sources, δ .

deviation for each constituent; and it may then be assumed with reasonable certainty that the analytical data for the mineral will not be farther from the truth than twice the standard deviation of the test analyses. Properly made up synthetic samples have the advantage of showing up systematic errors in the analytical methods, and where a knowledge of the probable errors of the analysis is of importance, a set of test analyses of such samples is the only really satisfactory check.

For most analyses, however, no such check is available, indeed there is often no other check than a duplicate determination of some or all of the constituents. Sometimes it may be possible to derive a check from the balance of anions and cations in an ionic mineral, or from considerations of the known crystal structure, but this type of check is outside the scope of the present discussion, which is concerned with the information that can be derived from the chemical analysis and physical data alone. Accordingly, in the absence of any direct evidence, the best possible estimate must be made of the probable accuracy of the chemical analysis, and it will be desirable to allow generous possible errors for every constituent. It must be remembered that in the case of constituents that have been determined by difference all the errors in the other constituents concerned fall on the one found by difference; thus in the case of Fe_2O_3 , usually determined by difference between the total iron and the ferrous iron, if the error in total iron (as Fe_2O_3) is assessed at t %, and the error in the ferrous iron (as Fe_2O_3) at f %, the error in the ferric iron will be $\sqrt{t^2 + f^2}$ %; but it should also be remembered that in such a case the variance of the sum of those elements initially weighed together is less than the sum of the variances of the several constituents into which the complex precipitate is ultimately resolved—thus the error in the total iron is t %, and not $\sqrt{f^2 + (f^2 + t^2)}$. The special considerations in the case of elements determined by difference will become apparent in the discussion of particular examples, below.

Having assessed the possible errors, δP %, in the several constituents of a mineral whose analysis is reported in terms of oxides, it is a simple matter to calculate the consequent errors in the empirical unit-cell contents, $\delta_c E$, for each element other than oxygen, for as $E = FmP/M$, $\delta_c E = Fm\delta P/M$ (table II). And the total probable error in each element is then obtained by adding the squares of the probable errors derived from the physical and the chemical data, and taking the square root of the sum: $\delta E = \sqrt{\{(\delta_p E)^2 + (\delta_c E)^2\}}$. As only two or three significant places need usually be considered, these calculations are quickly performed. The total error in any group of elements in which we are

interested, such as a group believed to replace one another isomorphously, must be found by summation of squares, or by simple summation, or partly by one and partly by the other according as the data are or are not independent. Thus in the example under consideration (tables I and II) the errors in $\Sigma(\text{Al} + \text{Fe}''' + \text{Mg})$ derived from the physical data are not independent, but those derived from the chemical data are (the Al_2O_3 was determined directly, and not by difference from a mixed precipitate of $\text{Al}_2\text{O}_3 + \text{Fe}_2\text{O}_3$); accordingly,

$$\begin{aligned} & \{\delta(\text{Al} + \text{Fe}''' + \text{Mg})\}^2 \\ &= (\delta_p \text{Al} + \delta_p \text{Fe}''' + \delta_p \text{Mg})^2 + (\delta_c \text{Al})^2 + (\delta_c \text{Fe}''')^2 + (\delta_c \text{Mg})^2. \end{aligned}$$

TABLE II. The errors $\delta_c E$, in the empirical unit-cell contents derived from an analysis of nigerite consequent on the assessed possible errors, δP , in the chemical analysis, together with the total errors, δE , due to both physical ($\delta_p E$, table I) and chemical sources of error.

	δP %.		$\delta Pm/M$.	$\delta_c E =$ $F\delta Pm/M$.	$(\delta_c E)^2$ $\times 10^4$.	$(\delta_p E)^2$ $\times 10^4$.	$(\delta E)^2$ $\times 10^4$.	δE .
TiO_2	0.04	Ti	0.0005	0.005	0.25	0	0.25	0.005
SnO_2	0.30	Sn	0.0020	0.021	4.4	4.8	9.2	0.030
Al_2O_3	0.30	Al	0.0060	0.064	41	169	210	0.145
Fe_2O_3	0.40	Fe'''	0.0050	0.054	29	3.6	32.6	0.057
FeO	0.30	Fe''	0.0040	0.043	18.5	0.25	18.8	0.043
ZnO	0.15	Zn	0.0018	0.019	3.6	0.5	4.1	0.020
MgO	0.10	Mg	0.0025	0.027	7.3	0.2	7.5	0.027
MnO	0.02	Mn	0.0003	0.003	0.1	0	0.1	0.003
PbO	0.10	Pb	0.0005	0.005	0.25	0	0.25	0.005
H_2O	0.20	OH	0.0222	0.238	566	5.3	571	0.239
Total iron (as Fe_2O_3)	0.25	Total Fe	0.0031	0.033	10.9	5.6	16.5	0.041

$$\delta\Sigma(\text{Sn,Ti}) = \sqrt{\{(0.022)^2 + (0.25 + 4.4) \times 10^{-4}\}} = 0.031$$

$$\delta\Sigma(\text{Al,Fe}''',\text{Mg}) = \sqrt{\{(0.153)^2 + (41 + 29 + 7.3) \times 10^{-4}\}} = 0.176$$

$$\delta\Sigma(\text{Zn,Fe}''',\text{Mn,Pb}) = \sqrt{\{(0.013)^2 + (3.6 + 18.5 + 0.1 + 0.25) \times 10^{-4}\}} = 0.049$$

$$\delta\Sigma(\text{metals}) = \sqrt{\{(0.19)^2 + (0.25 + 4.4 + 41 + 3.6 + 7.3 + 0.1 + 0.25 + 10.9) \times 10^{-4}\}} = 0.207$$

But in deriving the error in the total metal atoms per unit cell,¹ $\delta\Sigma(\text{metals})$, we must add in $(\delta_c \text{Fe}_{\text{total}})^2$, and not $(\delta_c \text{Fe}''')^2 + (\delta_c \text{Fe}''')^2$, since Fe_2O_3 is determined by difference between total iron and ferrous iron, and the total iron is involved in $\Sigma(\text{metals})$. In general, due consideration should be given to the actual analytical methods employed in their bearing, not only on the individual errors of the several elements, but on the errors of any groups of elements in which we may be interested.

¹ Strictly speaking, the errors added in finding $\Sigma(\text{metals})$ will not all be truly independent, since the total error in all the oxides is necessarily $(100 - S \pm \delta i)$; and δi has already been incorporated in δF .

We have now assessed the probable errors in each element present in the mineral, except oxygen. The most obvious course would be to simply calculate the errors in the oxygen content, $Fn\delta P/M$, for each oxide reported in the analysis, and add them through their squares, as independent errors. But a simple consideration will show that this course is likely to lead to a considerable exaggeration of the error in the oxygen atoms per unit cell consequent on errors in the chemical analysis. For if we consider a mineral in which all the constituent oxides contain the same percentage of oxygen (as, for example, MgO and TiO₂ do approximately), no error of analysis, however gross, will affect the percentage of oxygen found for the mineral and, therefore, the number of oxygen atoms per unit cell found.

Errors of chemical analysis can take two forms—errors of determination and errors of separation, the former being independent for all the oxides present, while the latter are not since an underestimate of one oxide is necessarily coupled with an overestimate of another. In some minerals, particularly when the number of elements present is very small, it may be desirable to take special consideration of the errors of separation, and such a case will be considered below, but in general it will suffice to assume that the analytical errors and their effects on the oxygen figure are independent,¹ and to regard them all as errors of determination that chance to balance out more or less completely.

Regarding the analytical errors, then, as independent errors of determination, each will affect the observed percentage of oxygen in the mineral in proportion to the difference between the percentage of oxygen in the mineral and that in the oxide. The percentage of oxygen in the mineral can readily be calculated by the general relation $E = FP/M$ from the number of oxygen atoms per unit cell, E_0 , which has already been found (table I); from this, the oxygen percentage in the mineral, $P_0 = 16E_0/F$. We now take the differences, Δ , between the percentage oxygen in the mineral, P_0 , and the percentages in the several oxides² (col. Δ , table III); then the error δP in the analytical determination of each oxide will involve an error in the number of oxygen atoms $\delta_c E_0 = F\Delta\delta P/1600$. These errors are squared and summed, the square root of the sum giving the probable total error in the oxygen content due to analytical errors (table III), to which must be added the error

¹ The assumption that the errors of separation are independent is only likely to be serious when two of the oxides concerned in any particular separation, wrongly taken as independent, differ widely in oxygen percentage—e.g. Yt₂O₃ and Ce₂O₃.

² The percentages of oxygen in the principal mineral-forming oxides are listed in table V.

TABLE III. Calculation of the probable error in the oxygen content of the unit cell consequent on the assessed probable errors in the chemical analysis of nigerite, and of the total error in the oxygen due to both physical (table I) and chemical sources of error. For details see text.

	O % = 1600n/M.	Δ .	$F\Delta/1600$ $\times 10^2$.	δP .	$\delta_c E_0 =$ $F\Delta\delta P/1600$ $\times 10^2$.	$(\delta_c E_0)^2$ $\times 10^4$.
TiO ₂	40.05	5.03	3.36	0.04	0.13	0.02
SnO ₂	21.23	-13.79	-9.22	0.30	-2.77	7.67
Al ₂ O ₃	47.09	12.07	8.07	0.30	2.42	5.86
Fe ₂ O ₃	30.76	-4.26	-2.85	0.25	-0.71	0.50
ZnO	19.66	-15.36	-10.27	0.15	-1.54	2.37
MgO	39.70	4.68	3.13	0.10	0.31	0.10
MnO	22.56	-12.46	-8.33	0.02	-0.17	0.03
PbO	7.17	-27.85	-18.62	0.10	-1.86	3.46
H ₂ O	88.81	53.79	35.97	0.20	7.19	51.70
					$\Sigma(F\Delta\delta P/1600)^2$	71.71×10^{-4}
					Σ , excl. H ₂ O	20.01×10^{-4}

% Oxygen in nigerite = $16E_0/F = 35.02\%$.

Error in O due to the FeO determination ($\delta P = 0.30\%$) = $F\delta P/2M = 0.022$.

Error in $\Sigma(O, OH)$ due to other analytical errors = $\sqrt{\{\Sigma(F\Delta\delta P/1600)^2\}} = 0.085$.

Error in O due to other analytical errors = 0.045.

Error in O due to physical sources (table I) = 0.29.

Total error in $\Sigma(O, OH) = \sqrt{\{(0.085)^2 + (0.022)^2 + (0.29)^2\}} = 0.30$.

Total error in O = $\sqrt{\{(0.045)^2 + (0.022)^2 + (0.29)^2\}} = 0.295$.

TABLE IV. The empirical unit-cell contents of nigerite, with their probable errors, based on the assessed errors of the chemical analysis and physical data (from tables I-III).

TiO ₂	0.17 ± 0.04	Ti	0.02 ± 0.01	$\Sigma(\text{Sn, Ti})$	1.81 ± 0.03
SnO ₂	25.33 ± 0.30	Sn	1.79 ± 0.03	$\Sigma(\text{Al, Fe}''', \text{Mg})$	12.62 ± 0.18
Al ₂ O ₃	50.91 ± 0.30	Al	10.69 ± 0.15	$\Sigma(\text{Zn, Fe}', \text{Mn, Pb})$	1.04 ± 0.05
Fe ₂ O ₃	11.90 ± 0.40	Fe'''	1.59 ± 0.06	$\Sigma(\text{metals})$	15.47 ± 0.21
FeO	2.65 ± 0.30	Fe''	0.39 ± 0.04		
ZnO	4.51 ± 0.15	Zn	0.59 ± 0.02	$\Sigma(O, OH)$	24.35 ± 0.30
MgO	1.28 ± 0.10	Mg	0.34 ± 0.03		
MnO	0.09 ± 0.02	Mn	0.01 ± 0.00		
PbO	0.94 ± 0.10	Pb	0.05 ± 0.01		
H ₂ O	1.46 ± 0.20	OH	1.86 ± 0.24		
S	99.35	O	22.49 ± 0.29		
SiO ₂	0.48 ± 0.10				

99.83
Total iron } 14.84 ± 0.25
as Fe₂O₃ }

a 5.71 ± 0.02 Å.

c 13.86 ± 0.04 Å.

D 4.51 ± 0.03

The approximation of $\Sigma(O, OH)$ to the integral 24 is clearly within the limits of probable error, but $\Sigma(\text{metals})$ probably departs significantly from either of the integral values 16 or 15.

due to errors in the physical data. In making this summation, it must be remembered that the quantities directly determined are not the percentages of Fe_2O_3 and FeO , but the total iron (as Fe_2O_3) and the net state of oxidation of the mineral, which in an under-oxidized mineral is normally reported as FeO . Accordingly, the entries in table III are for total iron as Fe_2O_3 , not for Fe_2O_3 and FeO , and a separate calculation is made of the effect of error in the ferrous oxide determination on the oxygen content; the latter will clearly be $F\delta P/2M$, or $\frac{1}{2}\delta_c E_{\text{Fe}^{2+}}$, and is an independent error to be added to the others. The final results of these calculations are summarized in table IV.

TABLE V. Percentages of oxygen in the principal mineral-forming oxides.

H_2O	88.81	NiO	21.42	As_2O_3	24.26	UO_2	11.85
Li_2O	53.55	CuO	20.12	Sb_2O_3	16.47	N_2O_5	74.07
Na_2O	25.81	ZnO	19.66	Bi_2O_3	10.30	P_2O_5	55.64
K_2O	16.99	PbO	7.17	CO_2	72.71	As_2O_5	34.81
Cu_2O	11.18	B_2O_3	68.92	SiO_2	53.28	Sb_2O_5	24.73
BeO	63.97	Al_2O_3	47.09	GeO_2	30.59	Nb_2O_5	30.10
MgO	39.68	Cr_2O_3	31.58	SnO_2	21.23	Ta_2O_5	18.11
CaO	28.53	Mn_2O_3	30.41	TiO_2	40.05	SO_3	59.55
SrO	15.44	Fe_2O_3	30.06	ZrO_2	25.97	CrO_3	49.00
BaO	10.43	Yt_2O_3	21.25	HfO_2	15.20	MoO_3	33.34
MnO	22.56	La_2O_3	14.73	ThO_2	12.12	WO_3	20.70
FeO	22.27	Ce_2O_3	14.62	MnO_2	36.81	UO_3	16.78
CoO	21.35	Lu_2O_3	12.06	CeO_2	18.59		

Considering the results of these calculations as applied to the analysis of nigerite, we note that: the total error in the oxygen content from chemical sources is comparable with that in any other major constituent element such as Al; despite a fairly generous assessment of the probable error of the chemical analysis, the physical data remain the main source of error in the cell-contents as far as the major constituents and their sums are concerned; and the analysis appears to afford substantial evidence that there are vacancies in one or other of the sets of lattice positions occupied by metal ions, since $\Sigma(\text{metals}) = 15.47 \pm 0.21$, while the oxygen positions are probably completely occupied, since $\Sigma(\text{O,OH}) = 24.35 \pm 0.30$.

It should be added that the limits of error calculated in this way from the assessed errors of a single analysis and set of physical data have no statistical significance, and are mere estimates (it is for that reason that they have been referred to as 'probable errors' and not variances); too much weight should not be attached to the actual figures found. On the other hand, when taken in conjunction with a considerable number of similar calculations made on minerals for which both chemical

and X-ray data have been obtained, there is clear evidence that the errors in empirical unit-cell contents are not usually so great as some recent studies of rock and mineral analyses might suggest, and in particular that analytical error will rarely affect the observed oxygen atoms per unit cell seriously. Thus in the case of the nigerite analysis discussed above, 24.35 ± 0.30 may be taken as a reasonable approach to 24.00; but on the other hand, 15.47 ± 0.21 is probably a truly significant departure from 16.00. In general, we may say that if we can assume a certain probability that the true value is within the assigned range, there is something like ten times that probability that it is within twice the assigned range.

TABLE VI. Empirical unit-cell contents for matlockite (Min. Mag., 1934, vol. 23, p. 589).

	$P \%$.	δP .	P/M .	$\delta P/M$.	$E = FP/M$.	$\delta_p E = \delta FP/M$.	$\delta_c E = F\delta P/M$.	$(\delta_p E)^2 \times 10^4$.	$(\delta_c E)^2 \times 10^4$.	$(\delta E)^2 \times 10^4$.	δE .
Pb	79.55 ± 0.5		0.3839	0.0024	1.979	0.0315	0.0124	9.9	1.5	11.4	0.034
F	7.11 ± 0.5		0.3742	0.0263	1.929	0.0307	0.135	9.4	182	191	0.138
Cl	13.44 ± 0.1		0.3791	0.0028	1.954	0.0311	0.0144	9.7	2.1	11.8	0.034
	100.10								$\Sigma \delta E_{(F,Cl)}$	203	0.142
D	7.05 ± 0.07		$\delta D/D$	0.010							
a	$4.10 \pm 0.02 \text{ \AA}$.		$\delta a/a$	0.005							
c	$7.23 \pm 0.02 \text{ \AA}$.		$\delta c/c$	0.003							
								$(\delta F/F)^2 = (\delta W/W)^2$			
								$= (2\delta a/a + \delta c/c)^2 + (\delta D/D)^2$			
								$= (10+3)^2 \times 10^{-6} + 100 \times 10^{-6} = 269 \times 10^{-6}$			
	$W = a^2cD = 856.8 \times 10^{-24} \text{ g.}$							$\delta F/F = 0.016$			
	$F = W/1.6603 S = 5.155$							$\delta F = 0.082$			
Pb	1.98 ± 0.03	} + valencies = 2Pb = 3.96 ± 0.06 - valencies = $\Sigma(F+Cl) = 3.88 \pm 0.14$									
F	1.93 ± 0.14										
Cl	1.95 ± 0.03										

The low value for both + and - valencies suggests that either one of the cell-sides or the density is a little too low. Since there are only three constituent elements, any positive error in one constituent must have been compensated by a negative error in another; but the column $\delta_c E$ shows that (owing to the great difference in their atomic weights) a 0.5% increase in F would increase the F atoms per unit cell by 0.13% while a balancing 0.5% decrease in Pb would only reduce the Pb atoms per unit cell by 0.01%. It is clear that the experimental data agree with an ideal of 2PbFCl per unit cell within their assessed probable error.

A number of further examples have been worked out to illustrate the method. In table VI calculations have been made for a particularly simple analysis, matlockite. Table VII illustrates the procedure when the constituent believed to be most liable to error (here B_2O_3) has an oxygen percentage markedly different from that of the mineral as a whole; a positive error in the percentage of B_2O_3 , with more oxygen than the mineral as a whole, will entail a positive error in the observed oxygen atoms per unit cell, and will necessarily be accompanied by negative errors in some of the other constituents since the summation is

nearly 100 %; but the other constituents have oxygen percentages less than that of the mineral as a whole and so their negative percentage errors entail a positive error in the oxygen atoms per unit cell; therefore in this case we add the $\delta_c E_0$ values themselves, and not their squares as we should if the errors were fully independent.

TABLE VII. Empirical unit-cell contents for sinhalite (Min. Mag., 1952, vol. 29, p. 848). Here it is found more appropriate to add the partial errors in the oxygen content due to errors in the chemical analysis directly rather than through their squares, for reasons given in the text.

	P	δP	Pm	δPm	$E =$	$\delta_p E =$	$\delta_c E =$	$\% O =$	$\delta_c E_0 =$				
	$M.$	$M.$	FPm	FPm	En	$F\delta Pm$	$P\delta Fm$	$1600n$	$F\Delta\delta P$				
	$\Delta.$	$\Delta.$	$M.$	$M.$	$m.$	$M.$	$M.$	δE	$1600.$				
B ₂ O ₃	24.2 ± 1.5	0.6950	0.0430	B	3.55	5.32	0.220	0.015	0.22	68.93	19.52	0.096	
Al ₂ O ₃	41.0 ± 0.5	0.8044	0.0098	Al	4.10	6.15	0.050	0.017	0.05	47.09	—	2.32	0.004
Fe ₂ O ₃	2.0 ± 0.2	0.0250	0.0025	Fe ^{'''}	0.13	0.20	0.013	0.000	0.01	30.76	—	18.65	0.012
MgO	32.3 ± 0.5	0.8014	0.0124	Mg	4.09	4.09	0.063	0.017	0.07	39.70	—	9.71	0.016
S	99.5			E_0	15.76							$\Sigma\delta_c E_0$	0.128
H ₂ O	0.3 ± 0.3 = δi												
	99.8			$\% \text{ oxygen in sinhalite} = 16E_0/F = 49.41$ $\delta E = \sqrt{(\delta_p E)^2 + (\delta_c E)^2}$ $\delta\Sigma(\text{Mg, Fe, Al, B}) = \sqrt{(\Sigma\delta E)^2} = 0.24$ $(\delta W/W)^2 = (\delta a/a + \delta b/b + \delta c/c)^2 + (\delta D/D)^2$ $= 0.0026^2 + 0.0015^2$ $\delta W/W = 0.0030$ $(\delta F/F)^2 = (\delta W/W)^2 + (\delta i/S)^2$ $= 0.0030^2 + 0.0030^2$ $\delta F/F = 0.0042$ $F = W/1.6603S = 5.103$ $\delta F = 0.021$ $\delta_p E_0 = E_0 \delta F/F = 0.066$ $\delta E_0 = \sqrt{(\delta_p E_0)^2 + (\delta_c E_0)^2}$ $= \sqrt{(0.066)^2 + (0.128)^2}$ $= 0.144$ $\Sigma(\text{Mg, Al, Fe, B}) = 11.87 \pm 0.24$									

The empirical unit cell contents clearly indicate some substitution of (Al, Mg) for B; they also suggest that the sum (Mg + Al + Fe + B) is integral and that there are some vacancies in the oxygen lattice, but the evidence is not conclusive in this respect.

Doubts concerning the function of water in a mineral, or its true amount, are probably the commonest cause of uncertainty in the unit-cell contents. Water is tenaciously adsorbed by many minerals, especially in fine powder, so that it is often very difficult to decide whether small amounts of water found on analysis are constitutional or impurities. The problem is all the more troublesome because water contains a higher percentage of oxygen (89 %) than any other oxide, so that uncertainties in the water content have a particularly serious effect on the oxygen atoms per unit cell, because water has a particularly low molecular weight, and because its accurate determination is often unexpectedly difficult. Accordingly, it is often desirable not only to assign

an ample probable error to the water determination, but to make special calculations of the effect on the unit-cell contents of a mistake in the allocation of the water found to constitutional or adsorbed water.

If the mineral contains h % of water which was either not determined or was accounted an impurity (adsorbed or included water), the net sum, S , will be low by h %; the observed density will be correct if the presence of the water was not recognized, but if it was regarded as an impurity and a density correction made, this correction will have to be subtracted from the 'corrected' density. The first factor will reduce the conversion factor F by $Fh/(S+h)$, while the latter will also reduce F , by $Fh(D-1)/\{100D+h(D-1)\}$, where S is the net sum excluding the water, and D the 'corrected' density. Thus the corrected value of F will be:

$$F - \Delta F = F - \frac{Fh}{S+h}$$

if the density D had not been 'corrected' for the supposedly adsorbed water, but

$$F - \Delta F = F - \frac{FhD}{100}$$

if the correction had been made.¹ All the unit-cell contents except the oxygen will now be reduced by $\Delta F P m / M$; the corrected total oxygen will be:

$$\Sigma(\text{O,OH}) = E_0 - E_0 \Delta F / F + Fh/18.$$

If the water is to be reported as hydroxyl, it will amount to $hF/9$ atoms per unit cell. The water determination will, of course, have been subject to an error, say δh %, and this must be taken account of in the usual way; it will often be an appreciable fraction of h , and will affect the corrections in all the other elements present, through F ; as these errors will all be in the same direction, it will be appropriate to incorporate the error with the errors in F arising from uncertainties in the physical data.

In table VIII the empirical unit-cell contents have been calculated

¹ More exactly

$$F - \Delta F = F \left(1 - \frac{h}{S+h} \right) \left(1 - \frac{h(D-1)}{100+h(D-1)} \right);$$

if h is less than about 5% and $S+h$ does not depart seriously from 100%, the simpler expression is adequate. It is perhaps appropriate to mention here that the density correction for x % of an impurity of density d is

$$D_c - D_0 = x D_0 (D_0 - d) / (100 d - x D_0),$$

where D_c is the corrected and D_0 the observed.

from an analysis of kornerupine (J. P. Girault, Amer. Min., 1952, vol. 37, p. 535, analysis 5b [M.A. 12-227]), assuming the water is an impurity, and also assuming the water is present as hydroxyl groups, using the above procedure to make the appropriate corrections. A comparison with Girault's table 5 raises several interesting points. The two tables agree fairly well when the water is assumed to be an essential constituent (table VIII, col. E^+ ; Girault's table 5, col. 6), but there are small differences, especially in the oxygen atoms per unit cell; these arise from three sources: the values of a , b , and c in table VIII have been calculated from the original measurements, which are in kX , by use of the factor 1.0022 and then rounded off to 0.01, but if the original kX values are used with the appropriate factor for the weight of a hydrogen atom, we find a value for F^+ 0.02 greater; then the value of ΔF has been calculated in table VIII from the rounded off figure for the density as 'corrected' for 0.97 % H_2O , but if F^+ is calculated direct using the observed density of 3.37, we find a value another 0.03 greater; that is, the values of F^+ , and therefore of E^+ in table VIII, are 0.15 % low (F^+ should be 29.81), which will increase the discrepancies as compared with Girault's table 5. With these corrections, the difference between the values of E^+ in table VIII and col. 6 of Girault's table 5 amounts to 0.7 %, suggesting that Girault has used the wrong value for the weight of a hydrogen atom (1.6603 if Å. are in use, but 1.649 if kX are used, a difference of 0.7 %).

Turning to the unit-cell contents counting the water as an impurity (table VIII, col. E^- ; Girault's table 5, col. 2), Girault's figure of 24.3 for Al is an arithmetical slip for 24.0, and involves a reduction in the oxygen content to 85.6. The figures in table VIII are again 0.06 % low owing to the conversion of the original kX units to Å. and rounding off of the results, and Girault's figures are 0.7 % low owing to the use of 1.6603 instead of 1.649 in the calculation of F , but there remains a discrepancy of about 1.7 %. This is probably due to the use by Girault of the measured density of 3.37 in calculating the unit-cell contents with water taken as an impurity, which would make his results 2.3 % low; if the water is an impurity, the density must be corrected for it.

Finally, it will be clear from the values of δE in table VIII that no conclusion can be drawn concerning the role of the water in kornerupine unless much more accurate data can be obtained. To bring δE_0 down to 0.4, which is probably the maximum value that would allow of safe deductions, the chemical analysis, cell-dimensions, and density would all have to be more accurate; if the relative error in the cell-dimensions

TABLE VIII. An analysis of kornerupine (Amer. Min., 1952, vol. 37, p. 535), interpreted assuming the water is an impurity (E^-) and also assuming it is an essential constituent (E^+).

	$P\%$	δP	Pm/M	$\delta Pm/M$	$\delta_p E$	$\delta_e E$	O %	Δ	$\delta_e E_0$	E^-n/m	E^+n/m	E^-	E^+	δE
SiO ₂	30.32 ± 0.30	Si	0.5047	0.005	0.15	0.15	53.26	7.38	0.042	31.08	30.04	Si	15.54	15.02 ± 0.21
B ₂ O ₃	3.51 ± 0.20	B	0.1008	0.003	0.03	0.18	68.93	23.05	0.088	4.65	4.50	B	3.10	3.00 ± 0.18
Al ₂ O ₃	40.97 ± 0.30	Al	0.8038	0.006	0.24	0.15	47.09	1.21	0.007	37.12	35.88	Al	24.75	23.92 ± 0.28
Fe ₂ O ₃	0.42 ± 0.40	Fe ^m	0.0053	0.005	0.00	0.15	30.76	-15.12	0.058	0.24	0.24	Fe ^m	0.16	0.15 ± 0.15
FeO	8.52 ± 0.30	Fe ^e	0.1186	0.004	0.04	0.12	—	—	—	3.65	3.58	Fe ^e	3.65	3.58 ± 0.13
MgO	14.91 ± 0.10	Mg	0.3700	0.0025	0.11	0.08	39.70	-6.18	0.012	11.04	11.02	Mg	11.04	11.02 ± 0.15
CaO	0.06 ± 0.03	Ca	0.0053	0.0006	0.00	0.02	28.53	-17.35	0.010	0.03	0.03	Ca	0.03	0.03 ± 0.02
Na ₂ O	0.08 ± 0.05	Na	0.0026	0.002	0.00	0.06	25.81	-20.07	0.009	0.04	0.04	Na	0.08	0.08 ± 0.06
P ₂ O ₅	0.09 ± 0.03	P	0.0013	0.0004	0.00	0.01	56.32	10.44	0.006	0.10	0.10	P	0.04	0.04 ± 0.01
S^-	98.88						$\sqrt{(\sum(\delta_e E_0)^2)0.13}$					O	88.31	83.83 ± 0.89
H ₂ O	0.97 ± 0.20	OH	0.1077	0.022	0.03	0.66	88.81	42.93				OH	—	3.20 ± 0.66
S^+	99.85						$\sqrt{(\sum(\delta_e E_0, OH)^2)0.21}$					$\Sigma(O, OH)$	—	87.03 ± 0.90
Total iron as Fe ₂ O ₃	9.88 ± 0.20;											$\Sigma(Si, B)$	18.64	18.02 ± 0.30
	$\delta_p E(\text{Fe total}) = 0.10$											ΣR	40.11	38.83 ± 0.45
												$\Sigma(Al, Fe^m)$	24.91	24.08 ± 0.32
												$\Sigma(Mg, Fe^e, Ca, Na, P)$	15.20	14.75 ± 0.22

TABLE VIII (contd.)

$D_{\text{corr.}}$ 3.45 ± 0.01 (corrected for 0.97 % H ₂ O taken as impurity)	$\delta D/D$ 0.003	$\Delta F/F = \frac{0.97 \times 3.45}{100}$
$[D$ 3.37 ± 0.01]	$\delta i/S$ 0.002	$= 0.0334$
a 13.72 ± 0.04 Å.	$\delta a/a$ 0.003	$\Delta F = 1.04$
b 15.97 ± 0.04 Å.	$\delta b/b$ 0.003	$F^+ = 29.76$
c 6.69 ± 0.02 Å.	$\delta c/c$ 0.003	% oxygen in kornepine = 88.31 × 16/F
		$= 45.88 \%$
$F^- = abcD/1.6603S$	$(\delta F/F)^2 = (0.009)^2 + (0.003)^2 + (0.002)^2$	$\delta_c E_0$ due to error in FeO = $\frac{1}{2} E_{\text{Fe}}^*$
$F^+ = 30.80$	$\delta F/F = 0.010$	$= 0.06$
	$\delta F = 0.30$	$\delta \Sigma(\text{Si, B}) \sqrt{\{(0.15 + 0.03)^2 + (0.15)^2 + (0.18)^2\}}$
$\delta_p E_0 = 88.31 \times 0.010 = 0.88$		$= 0.30$
$(\delta E_0)^2 = (\delta_p E_0)^2 + \Sigma(\delta_c E_0)^2 + (\frac{1}{2} \delta E_{\text{Fe}})^2$		$\delta \Sigma(\text{Al, Fe}^{''}) = \sqrt{\{(0.24)^2 + (0.15)^2 + (0.15)^2\}}$
$= 0.76 + 0.017 + 0.004$		$= 0.32$
$\delta E_0 = 0.89$		$\delta \Sigma(\text{Mg, Fe}', \text{Ca, Na, P}) = \sqrt{\{(0.15)^2 + (0.12)^2 + (0.08)^2 + (0.02)^2\} + (0.06)^2 + (0.01)^2}$
		$= 0.22$

Since the major error in all the sums arises from δF , the sign of all these errors is likely to be the same.

$$\{\delta \Sigma(\text{O, OH})\}^2 = (\delta_p E_0)^2 + \Sigma(\delta_c E_0)^2 + (\frac{1}{2} \delta E_{\text{Fe}})^2$$

$$= 0.77 + 0.044 + 0.004$$

$$\delta \Sigma(\text{O, OH}) = 0.90$$

$$(\delta \Sigma R)^2 = (0.40)^2 + (0.15)^2 + (0.10)^2 + (0.08)^2 + (0.02)^2 + (0.06)^2 + (0.01)^2$$

$$\delta \Sigma R = 0.45 \text{ (R includes Al, Fe, Mg, Ca, Na, P)}$$

could be reduced to 0.001, and that in the density to 0.002, a little improvement in the analysis, especially in the boron and water determinations, might allow the role of the water to be established.

The above example suggests that we should give some consideration to the matter of calculating and rounding off the results of quantitative observations. On the one hand, it is clearly pointless to quote results to four or more significant figures when inevitable sources of error may affect the second significant figure; but on the other hand it is equally undesirable to add unnecessarily to the errors in calculating the published results from the actual measurements. For example, it is usual in a rock analysis to take about 1 gram of rock powder for the 'main portion'; this is weighed on a balance that is usually adjusted to weigh to 0.1 mg., and the silica obtained is weighed on the same balance; the four weighings involved, each to ± 0.1 mg., involve a total error of the order of ± 0.02 in the percentage of silica; accordingly, even if there were no other sources of error, a third decimal place in the silica percentage could have no significance. But on the other hand, if 1.0045 gram of rock powder yielded 0.5372 gram of silica, the percentage of silica comes to 53.50 % if four-figure logarithms are used in the calculations, but 53.48 % if five-figure logarithms are used; clearly four-figure logarithms are not adequate where the measurements run to four significant figures.

An idea that appears to be widely held is that if the actual measurements are known to be liable to an error in, say, the first decimal place, it is justifiable to round them off to that place before working out the results dependent on them, in the expectation that the relative error in the results will be unaffected, while much labour will have been saved. This is not strictly true, and the relative error will commonly be appreciably increased.

The reason is readily seen from the above example. If the weighing of rock powder, 1.0045 gram, was liable to an error which we estimate at ± 1 mg., or a relative error of 0.001, this implies that we estimate the true weight to fall between 1.0035 and 1.0055 gram; if we round-off the weight to 1.005 gram before calculation of the silica percentage, we must increase the assessed relative error to 0.0015, since our lower limit (1.0035 gram) differs by that much from our rounded-off weight. In fact, calculation with ± 1 mg. in both the weight of rock and that of SiO_2 yields SiO_2 53.50 % ± 0.13 % if no rounding-off is carried out, but 53.4 % ± 0.2 % if we round-off the weighings before calculation.

Again, it is often held that although rounding-off may affect the result

appreciably when only a few measurements are involved, if the final result involves a large number of measurements the effects of rounding-off will necessarily tend to cancel out. This is a confusion with the well-known fact that independent errors tend to cancel out when compounded, and is quite untrue, as the calculations¹ summarized in table IX show. We assume that n measurements have been made, and that the quantity sought is their sum; each of the measurements will be liable to error, and since the first place of decimals was uncertain, each measurement has been rounded-off to the nearest integer before summation. If now we compare the sums obtained by this method and by adding the measurements without any rounding-off, and then rounding-off the sum, we find that in fact the results are liable to differ, and the probability of a difference increases the greater the number of measurements; with 7 or more measurements, the sum of the rounded-off measurements is as likely to differ from the rounded-off sum of the actual measurements by at least one unit as it is to agree (see table IX).

TABLE IX. A table of the probability that the sum of n measurements each of which has been rounded-off to the nearest integer will differ by ϵ units from the rounded-off sum of the same n measurements summed before rounding-off. The probabilities for negative values of ϵ are, of course, the same as those here tabulated for positive values.

$n \rightarrow$	1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
$\epsilon \downarrow$											
0	1	0.75	0.670	0.600	0.550	0.510	0.482	0.456	0.429	0.408	0.390
1		0.125	0.165	0.1975	0.217	0.230	0.236	0.241	0.244	0.246	0.247
2				0.0025	0.008	0.015	0.023	0.031	0.041	0.048	0.055
3						2×10^{-5}	2×10^{-4}	6×10^{-4}	0.0013	0.0024	0.0027
4								5×10^{-8}	2×10^{-6}	1×10^{-5}	4×10^{-5}
5										1×10^{-10}	1×10^{-8}

We conclude that it is generally desirable, since the additional time spent in calculations will never be comparable with the time spent on the analysis, to carry out all calculations to at least one place beyond the first significant figure liable to be affected by known sources of error, and to take care that the mathematical instruments (tables or slide-rules) used are adequate to this task. It will also usually be desirable to attempt some estimate of the accuracy of the several measurements made, and to calculate the effect on the final results of the several assessed errors.

¹ If the frequencies of observations in the ranges $A-0.50$ to $A-0.40$, $A-0.40$ to $A-0.30$, ..., $A+0.40$ to $A+0.50$ are all equal, then a random sample of n observations will have a probability p of giving a sum $nA \pm \Delta/10$, where p is the coefficient of $x\Delta$ in the expansion of $G(x) = \left(\frac{1+x+x^2+\dots+x^9}{10x^{9/2}} \right)^n$.