

QUANTITATIVE CLAY MINERALOGICAL ANALYSES FROM THE BULK CHEMISTRY OF SEDIMENTARY ROCKS

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Abstract—A technique suitable for computer application has been developed whereby whole rock major element analyses are corrected for X-ray detectable nonclay minerals and used to set up simultaneous equations which are solved to give clay mineral abundances. A theoretical evaluation of the approach by graphical methods enables the intrinsic errors to be very clearly assessed. Errors are minimized when SiO_2 , Al_2O_3 , and K_2O are used as variables but only slightly increased if total $\text{Fe}_2\text{O}_3 + \text{MgO}$ is substituted for SiO_2 . Quartz and CO_2 content are the only data normally required which cannot be determined by X-ray fluorescence.

Results compare favorably with estimates obtained by XRD and other methods, being more accurate than XRD and equally precise provided the rock does not contain clay minerals other than the kaolin group, the mica group, and chlorite. Errors are large when the clay mineral phases comprise more than 35% chlorite and as yet undetermined when smectite exceeds 10%.

The method is ideally suited to the analysis of large numbers of mudstones of fairly similar mineralogy especially where XRF equipment with direct output to a computer is available.

Key Words—Mudstones, Sedimentary.

INTRODUCTION

Mineralogical trends in fine-grained sedimentary rocks have until recently been relatively little studied. The principal difficulty has been the identification and quantitative determination of minerals of very fine particle size. Identification of most minerals by X-ray powder diffraction is now routine and good abundance estimates of minerals such as quartz can be obtained from diffraction intensities. Clay minerals, because of their very variable composition and crystallinity still present a major problem. By adopting a standard procedure such as measurement of peak intensities of powder lines from oriented aggregates, reasonably precise ($\pm 5\%$) estimates can be obtained for a suite of rocks of restricted stratigraphical range and geographical distribution. Such estimates usually are not accurate unless steps are taken to establish absolute abundances for a type specimen by an independent method.

Comprehensive chemical methods have been developed for the quantitative analysis of clay minerals (Alexiades and Jackson, 1966) but they consume much time of skilled analysts and cannot be justified for most geological investigations. Recent increased interest of petroleum geologists in clay mineralogy and the long standing problems of quality control in ceramic industries have highlighted the need for a method of clay mineral analysis that is more accurate, equally precise and more easily automated than XRD.

Imbrie and Poldervaart (1959) described a scheme for the recasting of bulk chemical analyses into mineralogical analyses for a limited range of sedimentary rocks. Major differences from X-ray results were recorded. Nicholls (1962) developed a more flexible

scheme in which normative clay minerals bearing no direct relation to actual phases present were computed as a means of comparing a wider variety of sedimentary rocks. Where the composition of phases present was known, norms could be combined into meaningful minerals. Such norms have not seen much application in practice and where mineral compositions are known abundances usually can be calculated more simply.

Mietsch (1962) discussed a graphical method of representing the uncertainty in recast mineral analyses as a function of the uncertainty in the most variable phase: in his case the clay as a whole. By this means the investigator could decide what level of knowledge of the clay composition was necessary to establish meaningful recast mineralogical analyses when undertaking a large scale study.

The present paper will show how similar graphical methods may be used to justify computer solving of a series of simultaneous equations set up to represent realistic clay phases in a carboniferous mudstone sequence. The applicability of this technique to other rock types will be discussed.

THEORETICAL EVALUATION OF THE PROBLEM

The chemical composition of any rock type can be related to its known mineral constituents' compositions by a set of simultaneous equations of the type:

$$a_i x + b_i y + c_i z = 100k_i \quad (1)$$

where a_i , b_i , c_i , and k_i , are the percentages of element i in mineral phases X, Y, Z and the bulk rock respectively. x , y , and z are the percentages of phases X, Y,

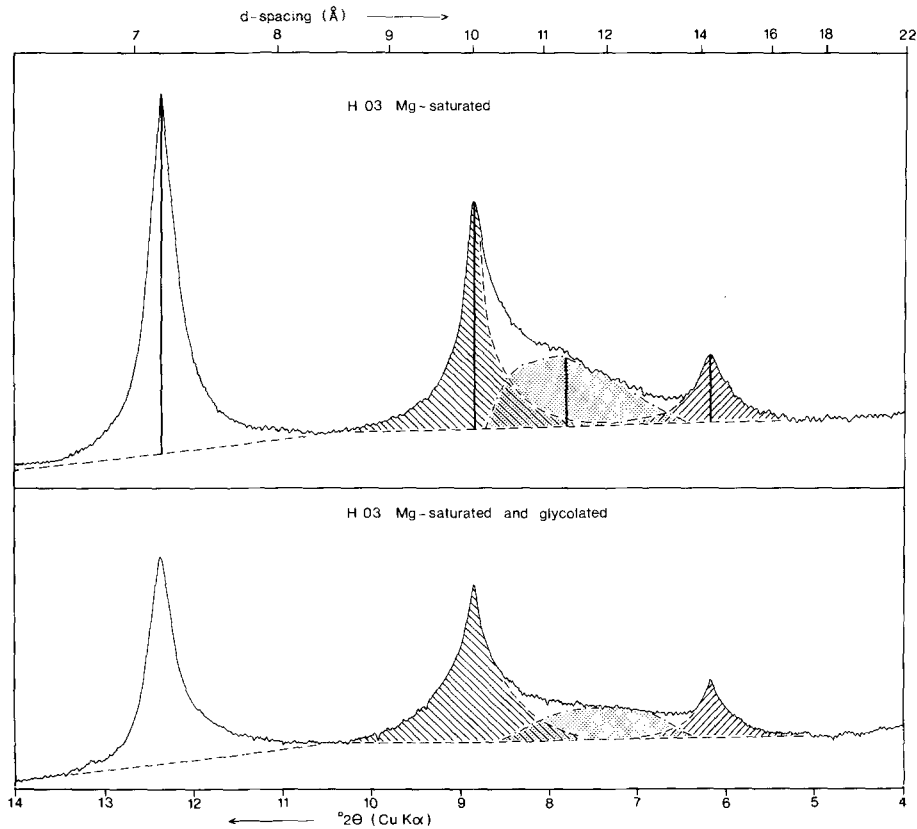


Fig. 1. X-ray diffractometer traces ($\frac{1}{4}^\circ/\text{min}$) of an oriented specimen of typical Hepworth mudstone. Constructed peaks for interlayered illite-smectite are shown in stipple. Positions of peak intensity measurements are indicated by bars.

and Z present in the rock. The equations cannot be solved if there are more phases than elements determined or if the compositions of all phases for the required number of elements cannot be fixed within limits comparable to the experimental error of chemical analysis. In general the susceptibility of many mineral structures to ionic substitution precludes a simple solution.

Igneous petrologists circumvent the problem to some extent by the use of a normative calculation scheme based on knowledge of mineral associations assumed essentially to be equilibrium assemblages. No such assumption can be justified for a sedimentary assemblage. Sedimentary rocks, however, contain a limited range of detrital minerals and simple neofomed phases whose abundances can be related directly to one or more elements in the bulk analysis. The schemes of Imbrie and Poldervaart (1959) and Nicholls (1962) thus satisfactorily account for free SiO_2 , Ti, S, P, and CO_2 in estimating quartz, rutile, pyrite, apatite, and carbonates. Clay minerals present the major problem since, with the exception of kaolinite their compositions vary over wide ranges. Characterization is primarily by X-ray behavior and swelling properties: chemical compositions may overlap and have very different tetra-

hedral and octahedral cation occupancies. Such difficulties can be tackled only by considering rocks of a common type with two or three clay phases whose compositional ranges are well documented in the literature.

The rocks on which the present approach is developed are mudstones of Westphalian age from a freshly exposed quarry face of the Hepworth Iron Company, Penistone, Yorkshire, England. Full wet chemical analyses are given in Pearson (1973) and will be published elsewhere. Quartz has been determined by XRD (method of Till and Spears, 1969). The typical diffractometer trace in Figure 1 (oriented smear on glass) shows kaolinite and mica as the major clay mineral components with subsidiary chlorite. K saturation and glycol treatments suggest that the complex mica peak may be attributed to a 10 Å nonexpandable mineral together with a small amount of a slightly expanding phase, possibly a randomly interstratified illite-smectite with around one third smectite layers (method of Mering, 1949).

Total silicate compositions have been calculated from the bulk chemical analyses by subtraction of quartz, anatase, siderite, apatite, and pyrite making assumptions analogous to those of Nicholls (1962). No other nonclay phases were detected by XRD. Water

Table 1. Chemical composition of the silicate fraction of mudstones (all values weight percent whole rock).

	SiO ₂	Al ₂ O ₃	K ₂ O	MgO	FeO	Fe ₂ O ₃	CaO	Na ₂ O	H ₂ O ⁺	Total	FM*
HAV	30.63	22.06	2.58	1.61	2.47	1.56	0.28	0.41	7.26	68.86	5.64
UCM	28.16	20.60	3.35	1.17	1.43	0.61	0.00	0.62	4.86	60.80	3.21
LPM	23.49	20.96	3.76	1.83	5.27	0.86	0.05	1.16	5.28	62.66	7.96

HAV Average of 16 upper Carboniferous (Westphalian) mudstones, Hepworth (Pearson, 1973).

UCM Upper Carboniferous Mudstone, Bersham borehole (Nicholls, 1962).

LPM Average of 10 lower Palaeozoic Mudstones, mid-Wales (Evans and Adams, 1975).

* FM = MgO + FeO + Fe₂O₃.

soluble Na and K were also subtracted. The average total silicate composition (HAV) for 16 mudstones is given in Table 1. Equivalent data for an Upper Carboniferous mudstone (Nicholls, 1962) and the mean of 10 Lower Palaeozoic mudstones (Evans and Adams, 1975) are also included.

GRAPHICAL APPROACH TO THE SOLUTION

The simplest approach is to assume that the average Hepworth silicate composition (HAV) can be partitioned between three phases: kaolinite, illite, and chlorite and that their compositions can be adequately approximated by analyses from the literature of clay minerals from rocks of a similar age and type. Equations of type (1) can then be applied. Table 2 shows some analyses from Deer et al. (1962) which have been chosen according to the above criteria.

Of the major constituent oxides which could be used to set up equations:

SiO₂/Al₂O₃ ratio is related to lattice type

K₂O resides almost wholly in mica

MgO, FeO reside mainly in chlorite

Fe₂O₃ may reside in mica or chlorite or both

H₂O⁺ is related to lattice type but is subject to the largest experimental error.

Taking K 1, I 1 and C 1 from Table 2 as the compositions of kaolinite, mica, and chlorite respectively and applying equation (1) to SiO₂ for HAV gives:

$$45.77 \text{ KA} + 51.22 \text{ IL} + 25.07 \text{ CH} = 3063$$

and if these are the only clay phases present

$$\text{KA} + \text{IL} + \text{CH} = 68.86 \quad (2)$$

Substituting for CH and simplifying:

$$(\text{SiO}_2) \text{ IL} = 51.2 - 0.79 \text{ KA}$$

applying the same procedure to Al₂O₃, MgO, and K₂O gives further linear equations:

$$(\text{Al}_2\text{O}_3) \text{ IL} = 138.4 - 3.2 \text{ KA}$$

$$(\text{MgO}) \text{ IL} = 72.7 - 1.31 \text{ KA}$$

$$(\text{K}_2\text{O}) \text{ IL} = 42.4 - 0.05 \text{ KA}$$

These four lines have been plotted on Figure 2 producing six widely scattered two variable solutions. The restriction that total clay content must not exceed 69% can be imposed by drawing in the line KA + IL = 69. This reduces the number of possible solutions by one. Clearly one or more of the compositions K 1, I 1, and C 1 must be grossly in error and the solutions are meaningless.

The logical next step therefore is to try and assess the effect on the above lines of varying the compositions

Table 2. Reference analyses of clay minerals selected from Deer et al. (1962) (weight percent).

	SiO ₂	Al ₂ O ₃	K ₂ O	MgO	FeO	Fe ₂ O ₃	CaO	Na ₂ O	H ₂ O ⁺	Total*	FM
K 1	45.77	39.07	0.31†	0.08	0.04	0.30	0.26	0.17	13.68	99.68	0.42
M 1	45.87	38.69	10.08	0.10	0.00	0.00	0.00	0.64	4.67	100.05	0.10
I 2	56.91	18.50	5.10	2.07	0.26	4.99	1.59	0.43	5.98	95.83	7.32
I 1	51.22	25.91	6.09	2.84	1.70	4.59	0.16	0.17	7.14	99.82	9.13
C 1	25.07	19.78	0.50‡	11.67	21.66	7.54	1.04	0.18	10.82	98.26	40.87

K 1 Average of kaolinite analyses 1, 2, 3, and 4 (p. 202).

M 1 Clear flawless muscovite crystal. Analysis 1 (p. 16).

I 1 Fithian illite, Illinois. Analysis 9 (p. 219).

I 2 Illitic material fine colloid fraction, Pennsylvanian underclay. Analysis 12 (p. 220).

C 1 Based on chlorite analysis 32 (p. 144) with adjusted K₂O, MgO, FeO, and Fe₂O₃ contents.

* Does not include any TiO₂, MnO, or H₂O⁻ recorded in analysis.

† Taken as zero for Figures 4 to 8.

‡ Taken as zero for Figures 2 to 8.

of the clay mineral phases. Analyses of sufficient specimens are available (and summarized in Deer et al., 1962) to show that compositional variation in the kaolin group minerals is restricted enough to consider kaolinite composition as fixed. Illites and chlorites can vary over wide ranges, but limits can nevertheless be drawn within which the compositions of all but a few uncommon variants fall. Limits for the major constituent oxides are shown in Table 3. The sum of iron and magnesium oxides (designated FM) has a much more restricted range in chlorites than either iron or magnesium individually and will therefore be used together with SiO₂, Al₂O₃ and K₂O in subsequent calculations.

Applying equation (1) to the data in Table 3 now gives four possible lines for each oxide:

(SiO ₂)	I (Max) C (Max)	IL = 37 - 0.6 KA
	I (Min) C (Max)	IL = 62 - 1.0 KA
	I (Max) C (Min)	IL = 45 - 0.7 KA
	I (Min) C (Min)	IL = 65 - 1.0 KA
(Al ₂ O ₃)	I (Max) C (Max)	IL = 35 - 1.0 KA
	I (Min) C (Max)	IL = -104 + 3.0 KA
	I (Max) C (Min)	IL = 48 - 1.0 KA
	I (Min) C (Min)	IL = 365 - 7.7 KA
(K ₂ O)	I (Max) C (Max)	IL = 21 + 0.07 KA
	I (Min) C (Max)	IL = 46 + 0.15 KA
	I (Max) C (Min)	IL = 26 - 0.03 KA
	I (Min) C (Min)	IL = 52 - 0.06 KA
(FM)	I (Max) C (Max)	IL = 74 - 1.3 KA
	I (Min) C (Max)	IL = 57 - 1.0 KA
	I (Max) C (Min)	IL = 79 - 1.5 KA
	I (Min) C (Min)	IL = 52 - 1.0 KA

When all the above are plotted out it is found that the first and fourth equations for each oxide together define the maximum area over which a solution with another oxide is possible. These four pairs of lines are shown in Figure 3, and the shaded area represents the region in which solutions consistent with all oxides simultaneously are possible. The correct mineralogical composition for HAV must therefore lie somewhere within this region.

Thus far no approximation has been made, the only assumption being that kaolinite composition is fixed as in Table 2. If the further assumption is now allowed that in general illites are related to an ideal muscovite end-member by loss of K accompanied by an increase in tetrahedral Si occupancy at the expense of Al then any illite composition can be approximated by a mixture of the appropriate proportions of muscovite and an extreme low K illite such as I 2 in Table 2. Introduction of both M 1 and I 2 together with K 1 and C 1 into a four phase calculation allows the illite composition to adjust by mixing end-members such that all K₂O can be accommodated. The remaining uncertainty then resides in

Table 3. Compositional ranges of illites and chlorites (weight percent).

Oxide	Illite		Chlorite	
	Maximum	Minimum	Maximum	Minimum
SiO ₂	56.91 (I 9)	45.87 (M 1)	30.30 (C 26)	20.82 (C 5)
Al ₂ O ₃	38.69 (M 1)	18.50 (I 9)	24.47 (C 1)	16.14 (C 7)
K ₂ O	10.08 (M 1)	5.10 (I 9)	0.93 (C 32)	Nil
MgO	3.93 (I 13)	Nil (I 4)	37.96 (C 5)	3.79 (C 4)
FeO	1.85 (I 6)	Nil (I 2)	45.36 (C 23)	Nil (C 9)
Fe ₂ O ₃	5.12 (I 13)	Nil (I 1)	18.97 (C 2)	Nil (C 14)
FM	10.57 (I 13)	0.10 (M 1)	46.03 (C 23)	32.40 (C 12)

Characters in brackets refer to the muscovite, illite or chlorite analysis in Deer et al. (1962) from which the value was selected.

the chlorite composition. This can be illustrated graphically in terms of a three phase problem if all K₂O is assumed to reside in illite and the SiO₂, Al₂O₃ and FM contents of illite are represented by linear functions of their values in M 1 and I 2. The following equations can then be derived:

$$K_2O \text{ (illite)} = (100/IL) K_2O \text{ (clay)} \quad (3)$$

$$SiO_2 \text{ (illite)} = 68 - 2.20 K_2O \text{ (illite)} \quad (4)$$

$$Al_2O_3 \text{ (illite)} = -2.2 + 4.05 K_2O \text{ (illite)}$$

$$FM \text{ (illite)} = 14.5 - 1.44 K_2O \text{ (illite)}$$

Equations of type (1) are now set up for the three remaining oxides with their illite values expressed as a function of K₂O. Taking SiO₂ as an example:

$$45.77 KA + SiO_2 \text{ (illite)} IL + SiO_2 \text{ (chlorite)} CH = 3063$$

Substituting for SiO₂ (illite) from equation (4), for K₂O (illite) from equation (3), for CH from equation (2), writing SiO₂ (chlorite) as S and simplifying we obtain:

$$(45.77 - S) KA + (68 - S) IL + 68.86 S = 3631$$

Substituting for S the maximum and minimum SiO₂ contents of chlorite from Table 2 we obtain:

$$SiO_2 \text{ (Max)} \quad IL = 41.0 - 0.41 KA$$

$$SiO_2 \text{ (Min)} \quad IL = 46.5 - 0.53 KA$$

Following the same procedure for Al₂O₃ and FM we may derive:

$$Al_2O_3 \text{ (Max)} \quad IL = 19.8 + 0.55 KA$$

$$Al_2O_3 \text{ (Min)} \quad IL = -2.6 + 1.25 KA$$

$$FM \text{ (Max)} \quad IL = 71 - 1.45 KA$$

$$FM \text{ (Min)} \quad IL = 72 - 1.77 KA$$

These equations have been plotted in Figure 4. The much reduced field of uncertainty can now be compared with the field transferred from Figure 3.

In order to monitor the effect on the solutions of

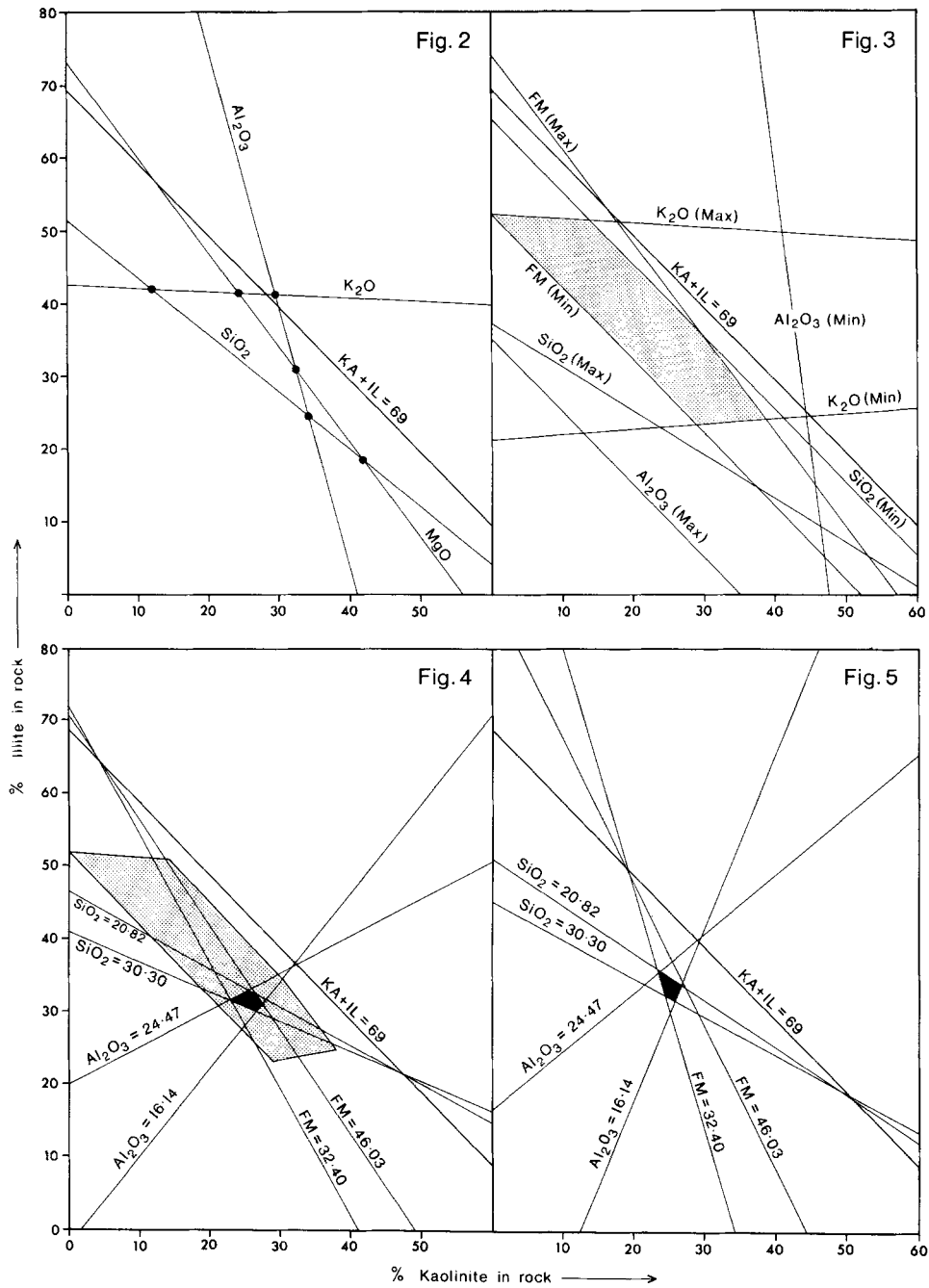


Fig. 2 to Fig. 5. See text for explanation.

choosing a different illite end-member composition the above procedure has been repeated using illite analysis I 1 in place of I 2. The lines are replotted in Figure 5. The slight shift in the field which results can be taken into account when assessing the error of a determination by this method.

The fields in Figures 4 and 5 reflect uncertainty only in chlorite composition. In Figure 6 the field from Fig-

ure 4 has been replotted on coordinates of % Al_2O_3 and % SiO_2 in chlorite. Contours for kaolinite and illite (solutions to the simultaneous equations expressed as % total clay phases) have been drawn in and can be seen to be linearly related to chlorite composition except in the region of both high Al_2O_3 and high SiO_2 .

A chlorite composition near the mean of the range (such as C 1 in Table 2) thus plots near the centers of

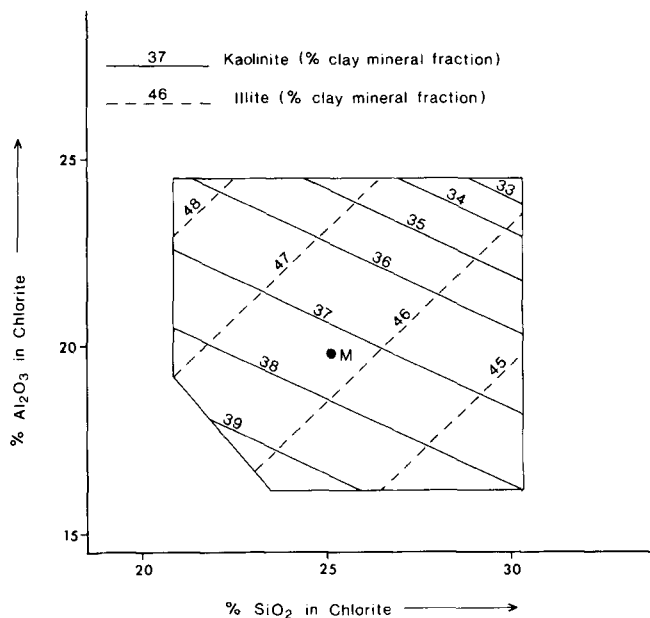


Fig. 6. Replot of solid field from Figure 4 on axes of chlorite composition. M indicates plot of mean chlorite composition C 1.

gravity of the fields in both Figures 4 and 6. Furthermore where chlorite composition is known a precise solution for kaolinite and illite can be read off a plot of the type shown in Figure 6. Where, as in the present case chlorite composition is unknown, use of a mean composition allows a solution with a clearly defined error to be obtained.

ASSESSMENT OF ERRORS

In Figure 7 the plot of Figure 4 has been repeated for three Hepworth samples so that their fields of uncertainty may be compared with that of HAV. The solution obtained using chlorite composition C 1 from Table 2 is indicated in each case. The field area is found to vary with CH^2 and the linear uncertainty in illite and kaolinite is thus approximately proportional to the chlorite content of the sample.

A further possible source of error lies in the assumption that all K_2O resides in the mica fraction of the clay. Examination of published analyses for kaolinite and chlorite indicates maximum K_2O contents of 0.5% in kaolinite and 1% in chlorite (though chlorites commonly contain much less). The effect of variation in kaolinite and chlorite K_2O contents on the solutions has been assessed and included in Table 4.

Table 4 shows the maximum error attributable to each source for solutions on HAV using clay mineral compositions K 1, M 1, I 2, and C 1 with SiO_2 , Al_2O_3 , and K_2O as variables. The final column gives the total error resulting when FM, Al_2O_3 , and K_2O are used as variables. The error due to chlorite composition varies

with the proportion of chlorite in the clay fraction and can be expressed as:

$$\begin{aligned} KA (\text{error}) &= 0.241 CH \\ IL (\text{error}) &= 0.146 CH \\ CH (\text{error}) &= 0.193 CH \end{aligned}$$

The total error thus becomes unacceptable (KA error $> \pm 10\%$) in rocks where chlorite constitutes more than around 35% of the total clay mineral. It should be noted, however, that the total error is the maximum error which can possibly arise with a rock in which all clay mineral compositions lie at the extremes of their ranges. For the majority of rocks therefore the errors will be significantly less.

Though the use of FM as a variable gives rise to a slightly enlarged field of uncertainty and therefore increased errors, this may in some circumstances be a worthwhile sacrifice in that a semiquantitative quartz determination will then suffice to estimate total clay

Table 4. Component errors in solutions for HAV.

	Chlorite composition	Illite end-member	Kaolinite K_2O	Chlorite K_2O	Total error	Total* error	Total*† error
Kaolinite	± 2.3	± 1.0	± 0.7	± 0.5	± 4.5	± 6.5	± 6.5
Illite	± 1.5	± 2.0	± 0.7	± 0.5	± 4.7	± 6.8	± 8.7
Chlorite	± 2.0	± 1.5	± 0.0	± 0.0	± 3.5	± 5.1	± 7.3

* Percent clay mineral fraction. Other values percent whole rock.

† Determined on FM, Al_2O_3 , and K_2O variables. All other values determined on SiO_2 , Al_2O_3 , and K_2O .

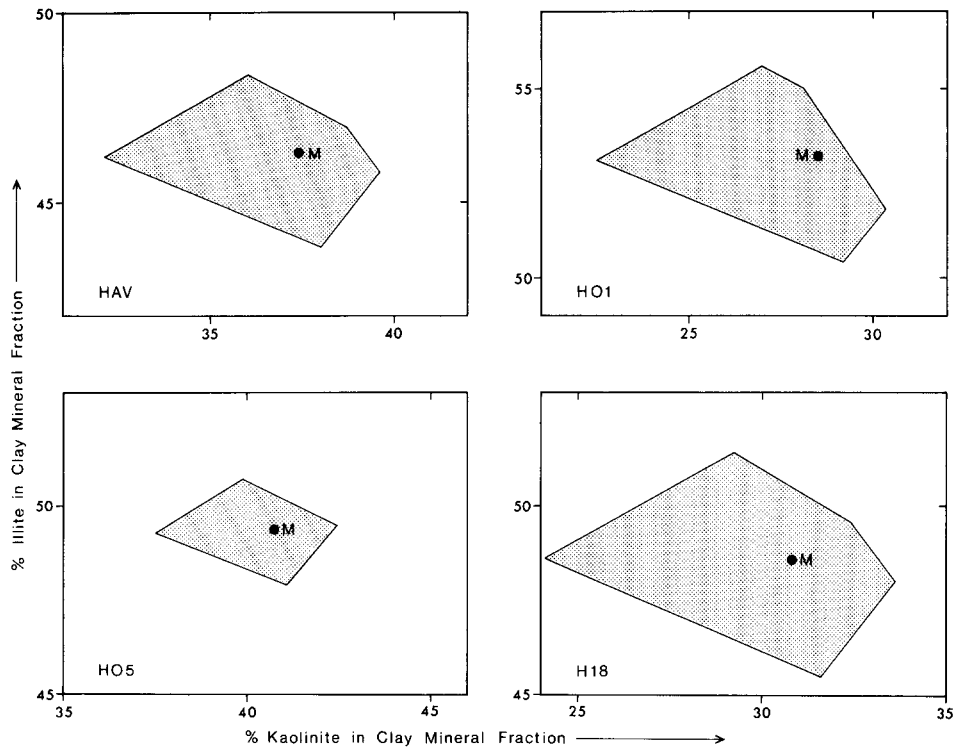


Fig. 7. Solid field of Figure 4 compared to analogous fields for individual Hepworth mudstones. M indicates solutions obtained with chlorite composition C 1 in each case.

mineral content. Little increase in error probably results from the use of total Fe_2O_3 instead of $\text{FeO} + \text{Fe}_2\text{O}_3$ in FM, no separate FeO determination then being necessary.

SOLUTION BY COMPUTER

The above graphical approach is invaluable as a means of evaluating the proposed technique of clay mineral analysis but is far too time consuming to be used routinely. A simple Fortran 4 computer program (SIM2)* has been written whereby solutions for up to eight phases can be conveniently obtained by matrix inversion. For a four phase solution as in the present example, three oxides must be specified as variables on which the equations are to be solved provided the total clay mineral percentage is known. Examination of Figures 4 and 5 suggests that SiO_2 and Al_2O_3 (with K_2O) are likely to give the most reliable solutions as their intersection gives the smallest area of uncertainty. Where H_2O^+ has not been determined and total clay percentage is not accurately known then FM may be used as a fourth variable. The program has a facility whereby oxides not used in solving the equations can be recalculated and compared with their input values, any large deviation indicating that one or more of the clay mineral

compositions chosen is a poor approximation to the real phase for the oxide in question. Clay mineral compositions can be amended to minimize deviations. In this way the ferromagnesian components in C 1 (Table 2) have been adjusted from chlorite analysis 32 in Deer et al. (1962) to give zero deviation. The total FM remains virtually unchanged. Na_2O and CaO are minor components and not readily assignable to any particular phase. H_2O^+ likewise has not been recalculated because of uncertainty in the assignment of whole rock H_2O to structural or possible interlayer sites and larger error in its determination.

Table 5 lists clay mineral analyses obtained as output from SIM2 in four phase solutions using K 1, M 1, I 2, and C 1 as phase compositions and SiO_2 , Al_2O_3 , and K_2O as variables. The estimates obtained by Nicholls (1962) and Evans and Adams (1975) for their own samples are included for comparison.

Table 5. Clay mineral abundances as weight percent whole rock.

	Kaolinite	Muscovite	Illite	Chlorite	Total mica
HAV	27.17	17.78	12.71	11.21	30.48
UCM	18.70	26.99	10.78	4.33	37.77
LPM	6.41	38.43	-4.84	22.65	33.59
UCM*	12.63	—	—	5.17	41.83
LPM†	nil	—	—	26.20	37.20

* Estimates of Nicholls (1962).

† Estimates of Evans and Adams (1975).

* The program package can be obtained from the author.

Table 6. Clay mineral abundances as weight percent clay fraction.

	Kaolinite	Muscovite	Illite	Chlorite	Total mica
H01	30.34	31.82	19.52	18.31	51.35
H02	28.75	31.60	20.49	19.16	52.09
H03	28.59	32.20	22.53	16.68	54.73
H04	39.73	28.85	18.08	13.34	46.93
H05	42.49	29.98	17.61	9.92	47.59
H08	48.86	18.68	19.27	13.19	37.95
H10	36.55	25.87	21.57	16.02	47.43
H11	42.31	25.28	15.92	16.48	41.20
H12	49.93	16.92	20.78	12.37	37.70
H13	53.96	17.84	13.24	14.97	31.07
H14	47.75	22.29	12.55	17.41	34.84
H15	40.41	27.08	15.48	17.03	42.56
H16	36.62	29.45	14.01	19.92	43.46
H17	38.05	21.34	25.24	15.37	46.58
H18	32.82	26.78	19.85	20.55	46.63
H19	32.32	27.73	21.07	18.89	48.80
HAV	39.45	25.82	18.45	16.28	44.27

Table 6 lists solutions for all Hepworth mudstones as percent clay mineral fraction and Table 7 the deviations from input values for the recalculated oxides not used as variables.

Comparison of solutions with XRD and other methods

X-ray powder diffraction estimates of clay mineral abundances were made by measuring peak intensities on diffractometer charts obtained from oriented whole rock powder on glass slides. For this purpose the 10 Å peak was drawn in symmetrically (see Figure 1) and the residual after subtraction attributed to expanded micas and recorded as 11 Å material. Peak intensity percentages (p. i. p.) for all Hepworth samples are given in Table 8.

XRD estimates have been plotted against computed chemical estimates in Figures 8, 9, 10, and 11. Linear regression equations and correlation coefficients are also given. In Figure 9 the combined 10 Å and 11 Å p.i.p. is plotted against computed total mica since this is found to give a better correlation than either 10 Å vs. muscovite or 11 Å vs. illite. The computed mica phases thus cannot individually be equated directly with their XRD counterparts. This may be a result of differing degrees of smectite interlayering in the illite or of the presence of discrete 10 Å illite.

The estimates of Nicholls (1962) for the Bersham mudstone (Table 5) were obtained by recombination of his normative silicates on the assumption that all K₂O, Na₂O is in illite, all MgO, FeO in chlorite, and that residual Al₂O₃, SiO₂ can be partitioned between kaolinite and a smectitelike illite component. No Al₂O₃ is attributed to chlorite.

Evans and Adams (1975) determined the quantitative mineralogy of their Lower Paleozoic mudstones by the methods described in Alexiades and Jackson (1966). Chlorite in particular is determined thermogravimetri-

Table 7. Deviation of recalculated oxides from input values (percent whole rock).

	MgO	FeO	Fe ₂ O ₃	FM
H01	0.02	-0.04	0.40	0.38
H02	-0.25	-0.09	0.26	-0.09
H03	-0.08	-0.00	-0.05	-0.13
H04	-0.10	-0.34	0.16	-0.27
H05	0.02	-0.42	0.22	-0.18
H08	0.69	0.24	-0.25	0.68
H10	0.05	0.60	-0.32	0.34
H11	-0.03	-0.11	-0.24	-0.39
H12	-0.01	0.46	-0.74	-0.29
H13	-0.02	-0.44	0.07	-0.39
H14	-0.02	-0.39	0.24	-0.17
H15	0.00	0.01	0.01	0.02
H16	-0.16	-0.48	0.44	-0.21
H17	0.06	0.39	0.09	0.53
H18	-0.20	0.37	-0.17	0.00
H19	0.03	0.40	-0.12	0.31
HAV	-0.00	-0.00	-0.00	-0.00
UCM	0.40	0.46	-0.31	0.55
LPM	-0.76	0.37	-0.63	-1.01

cally during dehydroxylation up to 950°C. Illite is determined as the bulk analysis residual after accounting for all other minerals detected by XRD.

DISCUSSION

The excellent correlation seen in Figures 8 and 9 is good evidence that the computed kaolinite and mica estimates bear a close relationship to the abundances of the real phases present. Though the correlation between computed chlorite and 14 Å peak is less good this almost certainly reflects the errors inherent in both the measurement of small peaks from X-ray charts and in the assumption that abundance is directly proportional to peak height. Indeed it is generally true that over a wide range XRD peak height is not linearly related to abundance and the apparent linearity in Figures 8 to 11 cannot be extrapolated to the ordinate. The apparent

Table 8. X.R.D. clay mineral estimates as peak intensity percent clay phases.

	7 Å	10 Å	11 Å	14 Å	10 Å + 11 Å
H01	52	28	9	11	37
H02	49	31	11	9	42
H03	46	36	8	9	44
H04	58	26	9	8	35
H05	63	27	6	4	33
H08	66	16	8	9	24
H10	56	24	8	13	32
H11	58	25	8	8	33
H12	68	17	7	8	24
H13	73	13	5	9	18
H14	68	16	5	11	21
H15	64	21	7	8	28
H16	58	24	6	11	30
H17	60	23	7	10	30
H18	54	26	6	13	32
H19	57	26	8	10	34

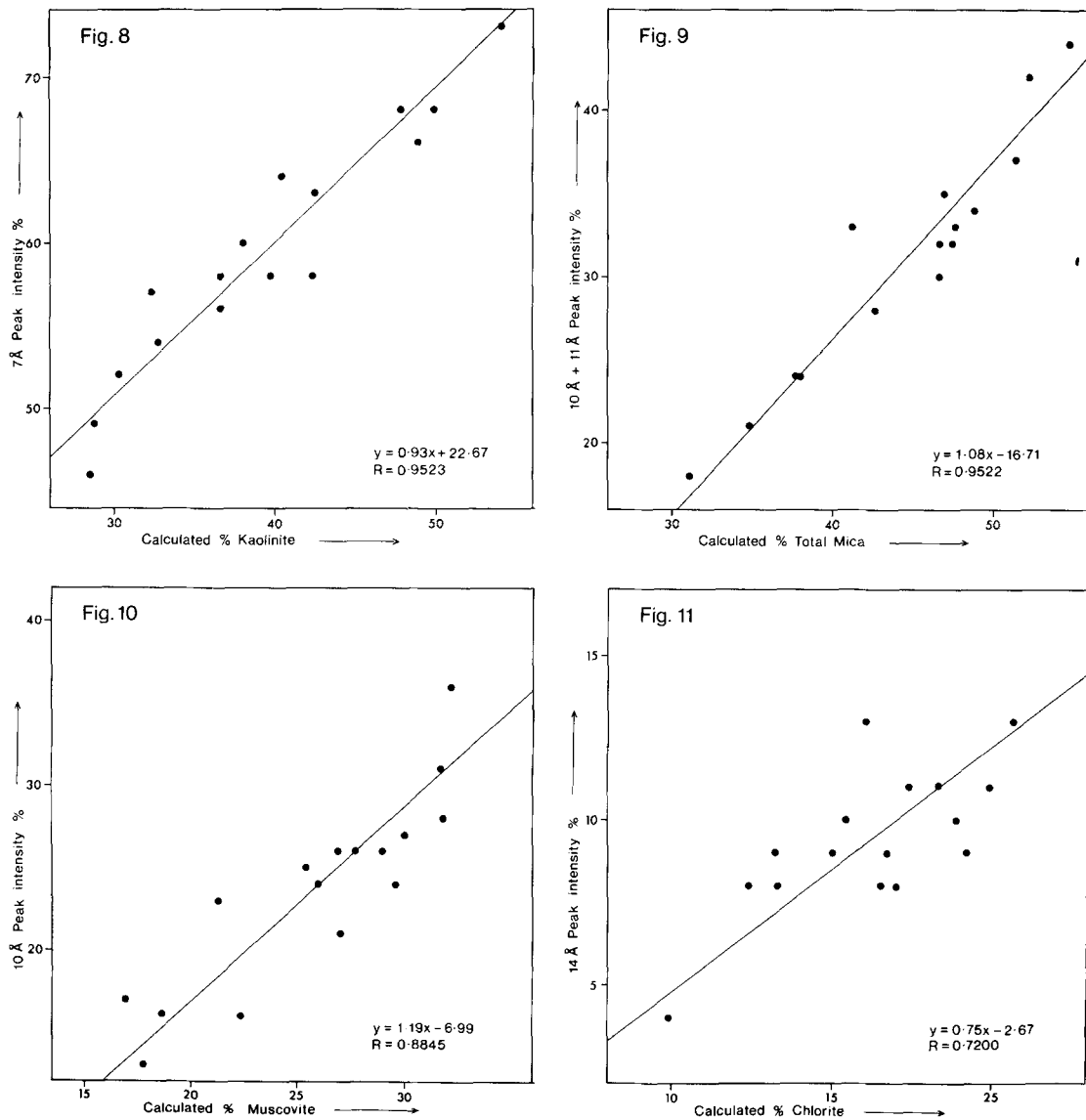


Fig. 8 to Fig. 11. Relationships of X.R.D. estimates to calculated chemical estimates for kaolinite, total mica, muscovite, and chlorite. Reduced major axis linear regression equation and correlation coefficient (R) given in each case.

22.67% overestimate of kaolinite and 16.71% underestimate of mica by XRD are thus unlikely to be physically meaningful.

Whilst the precision of the present method is likely to be comparable to that of XRD for the dominant clay mineral phases, its reliability as an estimator of absolute abundance is certainly far superior. The limit of detection is probably about the same in each case but whilst errors in XRD are ill defined and operator-dependent the computation method allows errors to be accurately assessed.

Application of the present method to the data of Nicholls (1962) produces results significantly different from (though broadly similar to) those of that author.

This is entirely due to the different assumptions made concerning the compositions of illite and chlorite. The present estimates fall well within the range of possible mineralogical compositions suggested by Nicholls (1962) in his discussion (KA: 9-26, IL: 32-45, CH:3-6), lie close to the means of the ranges proposed and are at least as good estimates of the actual mineral contents.

Recalculation of Evans and Adams (1975) data by the present method likewise gives abundances for illite and chlorite somewhat lower than those authors' independent estimates. The differences in this case can be attributed to the admitted unusual compositions of the illites and chlorites in these Lower Palaeozoic sedi-

ments, most of which, if Evans and Adams (1975) calculations are correct, lie outside the normal ranges proposed in this paper. Even so, the estimates are not too dissimilar: an indication that the present technique is applicable to rocks of a variety of ages and types other than those of the study.

The evidence above suggests that this technique can be applied to common mudstone mineralogies with the possible exception of those which are smectite rich. Any small interlayer smectite component in the Hepworth mudstones is assumed to have been accommodated by the flexibility allowed to the illite composition. It is with this in mind that I 2 has been used for the computation rather than I 1 since it allows a wider illite compositional range. Smectite compositions are very variable indeed and where smectite makes up more than around 10% of the clay fraction of a rock then the present method probably cannot be applied without further information on smectite composition. The maximum smectite content in the Hepworth mudstones is probably about 8%, with most samples containing a maximum of 5 to 6%. Further work is needed to establish the optimum way of incorporating smectite into this type of analysis. Such work is currently in progress.

CONCLUSION

A method of computing clay mineral analyses from bulk chemistry has been developed which is likely to be applicable to many mudstones in common industrial use. It is restricted in its present form to mudstones in which smectite does not exceed 10% of the total clay mineral and which do not contain significant quantities of clay minerals other than kaolinite, micas, and chlorite. Errors become serious when chlorite exceeds 35% of the total clay mineral unless the chlorite composition can be determined by microprobe or chemically.

The method is ideally suited for use where whole rock analysis of large numbers of fairly similar mudstones is carried out routinely by XRF and results are processed directly by computer or electronic calcula-

tor. Although the use of SiO_2 , Al_2O_3 , and K_2O as variables has been found to minimize errors, only slightly inferior results are obtained if total $\text{Fe}_2\text{O}_3 + \text{MgO}$ (FM) is used instead of SiO_2 . Acceptable clay mineral analyses can be produced, therefore, from XRF analyses supplemented by quartz and CO_2 data. Access to XRD equipment is otherwise necessary only for occasional qualitative checks on the clay mineralogy.

Clay mineral analyses computed by this technique have shown good correlation with XRD estimates and are considered to be far more accurate and equally precise. Precision is improved in a suite of rocks if individual mineral compositions are approximately constant. The technique has been tested on three mudstones of rather different compositions and found to give results comparable with other methods. Differences can be satisfactorily accounted for in terms of the different assumptions underlying the calculations or extreme compositions of the mineral phases.

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Резюме— Разработан удобный для использования компьютера метод, с помощью которого корректируется анализ всех главных элементов пород за влияние неглинистых минералов, обнаруживаемых рентгеноскопическим методом, и одновременно выводятся уравнения, решение которых дает относительное содержание глинистых минералов. Теоретическая оценка этого подхода графическими способами показывает, что он позволяет очень хорошо выявлять существенные ошибки. Ошибки уменьшаются, если SiO_2 , Al_2O_3 и K_2O используются как переменные, но только немного увеличиваются, если $\text{Fe}_2\text{O}_3 + \text{MgO}$ полностью замещает SiO_2 . Содержание кварца и CO_2 являются обычно единственными необходимыми данными, которые не могут быть определены методом флуоресценции рентгеновских лучей.

Сравнение результатов с оценками, полученными с помощью ДРЛ и другими методами, показало, что предлагаемый метод является более точным, чем ДРЛ и в такой же мере воспроизводим при условии, что порода не содержит глинистых минералов кроме каолиновой группы, группы слюд и хлорита. Ошибки велики, ког-

да глинистые минеральные фазы включают более 35% хлорита, и неопределенны, когда содержание смектита превосходит 10%.

Метод идеально подходит для анализа большого числа аргиллитов с примерно одинаковым минералогическим составом особенно, когда в наличии имеется оборудование ФРЛ с прямым выходом на компьютер.

Kurzreferat- Eine passende Methode für Computer-Anwendung wurde entwickelt indem Hauptelementanalysen für mit Röntgenstrahlen auffindbare Nicht-Tonminerale korrigiert wurde und dazu benutzt wurden, Gleichungen mit drei Unbekannten aufzustellen, welche für Häufigkeiten der Tonminerale gelöst wurden. Eine theoretische Auswertung der graphischen Bestimmungsmethoden macht es möglich, die wesentlichen Fehler klar zu sehen. Fehler sind auf ein Minimum reduziert, wenn SiO_2 , Al_2O_3 und K_2O als Variable benutzt werden, aber werden leicht erhöht, wenn Fe_2O_3 und MgO zusammen für SiO_2 substituiert werden. Die Quarz- und Kohlendioxidgehalte sind normalerweise die einzigen notwendigen Daten, die nicht durch Röntgenfluoreszenz bestimmt werden können. Resultate schneiden im Vergleich mit Bestimmungen, die durch XRD und andere Methoden erhalten wurden, günstig ab, weil sie exakter als XRD sind und genau so präzise vorausgesetzt, keine sonstigen Mineralien als die zu den Kaolin- und Glimmergruppen gehörigen und Chlorit anwesend sind. Grosse Fehler erscheinen, wenn die Tonphasen mehr als 35% Chlorit enthalten und sind noch nicht bestimmt worden, wenn mehr als 10% Smektit vorhanden ist. Die Methode ist ideal für die Analyse einer großen Anzahl von Schluffsteinen mit ziemlich ähnlichen mineralogischen Eigenschaften, besonders wenn ein Röntgenfluoreszenzapparat mit direktem Ausgang in einen Computer erhältlich ist.

Résumé- Une technique a été développée qui peut être adaptée à des applications à l'ordinateur. Dans celle-ci, les analyses d'élément principal de roche entière sont corrigées pour les minéraux non-argileux détectables aux rayons-X et utilisées pour établir des équations simultanées qui sont résolues pour donner les abondances des minéraux argileux. Une évaluation théorique de l'approche par méthode graphique permet l'assestement clair des erreurs intrinsèques. Les erreurs sont les moindres lorsque SiO_2 , Al_2O_3 , et K_2O sont utilisés comme variables, et seulement légèrement plus importantes lorsque tout le $\text{Fe}_2\text{O}_3 + \text{MgO}$ est substitué pour du SiO_2 . Les contenus de quartz et de CO_2 sont les seules données normalement requises qui ne peuvent pas être déterminées par la fluorescence aux rayons-X.

Les résultats peuvent être favorablement comparés à des estimations obtenues par diffraction aux rayons-X (X.R.D) et par d'autres méthodes, étant plus exacts que la diffraction aux rayons-X et tout aussi précis que celle-ci, à condition que la roche ne comprenne pas de minéraux argileux autres que ceux du groupe kaolin, ou des groupes des micas et des chlorites. Les erreurs sont grandes quand les phases de minéral argileux comprennent plus de 35% de chlorite, et l'importance de ces erreurs est jusqu'à présent indéterminée lorsque le contenu de smectite dépasse 10%.

Cette méthode s'adapte idéalement à l'analyse de grands nombres d'argilites de minéralogie relativement semblable, particulièrement dans les cas où l'équipement de fluorescence aux rayons-X (X.R.F) directement relié à l'ordinateur est disponible.