

Analysis of mineral samples using combined instrument (XRD, TGA, ICP) procedures for phase quantification

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ABSTRACT

Quantitative phase estimation of complicated suites of minerals by any one technique, such as X-ray diffraction, is often difficult or an approximation at best. This paper describes an approach that combines information from several analytical techniques through a nonlinear minimization algorithm. As an example, this technique was applied to quantify phases in several oil-shale samples containing feldspars, carbonates, and clay minerals that have undergone varying degrees of isomorphous substitution. Analytical techniques required for this suite of minerals included XRD for phase identification and setting of upper and lower limits, elemental analysis for cation content, thermogravimetric analysis for CO₂ content, and selective acid dissolution for carbonate mineral content. With appropriate modification, this approach can be tailored to quantify complicated suites of minerals in any geologic material.

The accuracy of this integrated technique was determined on simulated analytical data sets. Analysis of a series of randomly generated mixtures similar to those normally encountered in natural oil-shale samples showed calculated compositions to be within 1%, absolute, of the hypothetical composition. Expected errors in the analytical data, however, decrease this accuracy to 10%, absolute, with the average error being around 5%, absolute. These results suggest that this approach is superior to, i.e., more accurate than, methods that rely entirely on one single method.

INTRODUCTION

Among all techniques available, X-ray diffraction (XRD) has been used most frequently for qualitative identification and quantitative estimation of mineral components in geologic materials. Although qualitative identification by XRD is relatively easy, several factors complicate accurate quantitative estimation. These include inherent sample variables such as particle size, matrix-absorption coefficient, degree of crystallinity of individual components, preferred orientation, differences in chemical composition between phases and reference standards, amount of noncrystalline material, etc. The effects of these variables on quantitative results can be considerable. For example, it has been shown that variations in the quality of reference standards can introduce errors ranging from ± 7 to $\pm 30\%$ (Bayliss, 1986; Pawlowski, 1985).

As an alternative to using X-ray diffraction data, a number of researchers have attempted to use elemental information instead. One technique (Smyth, 1983) involves apportioning elements that have only one source in the sample to calculate the quantity of those phases. The amount of other elements present in these phases would then be calculated and subtracted from the total elemental analysis. The remaining quantity of these elements are then assigned to other phases in the sample, and the procedure is repeated. The drawback of this sequential method is that errors are propagated so that the

accuracy of the last component quantified is significantly lower than for the first mineral.

Another technique, which was developed by Pearson (1978) and modified by Hodgson and Dudeney (1984), uses matrix algebra to solve a set of simultaneous equations to calculate a mass balance for each element in the sample. Equations are of the form

$$\sum_j a_{ij}X_j = P_i, \quad (1)$$

where a_{ij} is the stoichiometric weight fraction of element i in phase j , X_j is the quantity of phase j in the sample, and P_i is the experimental analysis of element i in the sample. As an extension of this technique, parameters need not be limited to elemental information but may include information available from other analytical techniques, such as weight loss by thermogravimetric analysis (TGA) and cation-exchange capacity (Johnson et al., 1985). In order to satisfy the requirement of n equations for n unknowns, algorithms of this type require that the total number of elements and other parameters measured equal the number of phases present in the sample. This is an undesirable restriction since the total number of parameters available frequently does not equal the number of phases present. A third technique, target-transformation analysis, does not have this restriction but instead re-

TABLE 1. Formulae for minerals in shale samples

| Mineral | Formula | Range |
|-------------------|--|-------------|
| Quartz | SiO ₂ | |
| Calcite | CaCO ₃ | |
| Dolomite-ankerite | Ca(Mg _{1-y} Fe _y)(CO ₃) ₂ | 0 < y < 0.7 |
| Feldspar | | |
| Alkali | K _x Na _{1-x} AlSi ₃ O ₈ | 0 < x < 1 |
| Plagioclase | Na _w Ca _{1-w} Al _{2-w} Si _{2+w} O ₈ | 0 < w < 1 |
| Analcite | NaAlSi ₃ O ₈ ·H ₂ O | |
| Illite | K _z Al ₄ (Si _{8-z} Al _z)O ₂₀ (OH) ₄ | 1 < z < 2 |

quires analyzing at least as many subsamples as there are elements in the sample (Starks et al., 1984).

Recently, Slaughter (1984) proposed a technique that uses a linear Simplex optimization routine to combine elemental analysis and X-ray diffraction data for analyzing clay-mineral mixtures. Optimization algorithms offer three distinct advantages compared to the above techniques. First, optimization techniques allow an unlimited number of parameters to be measured and used. Second, these techniques allow the mole fractions of cations in minerals that undergo isomorphous substitution to be included as unknowns and solved for as part of the solution. This is important since unique stoichiometric values cannot be assigned to these cations because of their extreme variation within and among minerals. Third, by requiring the upper and lower bounds of each variable to be constrained, the optimization technique prevents meaningless solutions.

Our paper outlines a similar approach, which was developed independently of Slaughter's work, for quantifying the phases present in oil-shale samples. This approach differs from Slaughter's in that we use a nonlinear minimization algorithm instead of the linear Simplex routine, and we combine the results of several analytical techniques including elemental analysis, thermal analysis, XRD, and selective dissolution.

EXPERIMENTAL PROCEDURES

Description of technique

The analytical information is analyzed using the ZXMWDM minimization algorithm available from International Mathematical and Statistical Libraries, Inc., 7500 Bellaire Blvd., Houston, Texas 77036-5085, U.S.A. This routine seeks to minimize the function

$$F = \sum w_i F_i^2, \quad (2)$$

where w_i are weighting functions with

$$\sum w_i = 1. \quad (3)$$

The functions F_i are user-defined functions that are characteristic of the sample. For example, minimizing Equation 1 yields

$$F_i = \sum_j a_{ij} X_j - P_i, \quad (4)$$

In mass-balance equations, the parameters a_{ij} are fixed for minerals such as quartz and calcite. For others, such as ankerite, illite, and feldspar, these parameters vary with the degree of isomorphous substitution in the phase. In order to incorporate

TABLE 2. Analytical data for oil shales

| | D10-5 (raw) | D18-5 (raw) | D29-5 (spent) | D40-5 (spent) | D48-5 (spent) |
|-----------------------|----------------------------|----------------|------------------|------------------|------------------|
| Na (wt%) | 1.5 | 1.4 | 1.6 | 2.2 | 1.5 |
| Al (wt%) | 3.3 | 2.8 | 3.5 | 4.1 | 3.7 |
| Ca (wt%) | 12.0 | 13.0 | 15.0 | 13.0 | 14.0 |
| Fe (wt%) | 1.7 | 1.6 | 1.9 | 2.0 | 1.8 |
| Mg (wt%) | 3.4 | 3.2 | 4.0 | 3.8 | 4.1 |
| Si (wt%) | 14.0 | 13.0 | 15.0 | 17.0 | 17.0 |
| K (wt%) | 1.2 | 1.3 | 1.6 | 1.7 | 1.9 |
| CO ₂ (wt%) | 18.2 | 18.1 | 22.0 | 20.5 | 21.1 |
| | Extracted amounts (wt%) | | | | |
| Acetic acid (wt%) | — | 37.8 | 50.0 | 47.8 | 50.3 |
| HCl (wt%) | 51.6 | 50.7 | 58.0 | 54.4 | 56.7 |
| | XRD intensities (relative) | | | | |
| 3.43 Å | 22 | 20 | 9 | 15 | 6 |
| 3.34 Å | 69 | 85 | 74 | 81 | 94 |
| 3.18–3.25 Å | 30 | 24 | 25 | 52 | 34 |
| 3.04 Å | 29 | 55 | 71 | 57 | 69 |
| 2.89–2.91 Å | 100 | 100 | 100 | 100 | 100 |

the isomorphously substituted elements, additional variables can be assigned to the model. For example, in ankerite, Ca(Mg_{1-y}Fe_y)(CO₃)₂,

$$a_{\text{Ca,ankerite}} = 40.1/(184.4 + 31.5y) \quad (5a)$$

$$a_{\text{Fe,ankerite}} = 55.8y/(184.4 + 31.5y) \quad (5b)$$

$$a_{\text{Mg,ankerite}} = 24.3(1 - y)/(184.4 + 31.5y), \quad (5c)$$

where the denominator is the molecular weight of ankerite and 40.1, 55.8, and 24.3 are the atomic weights of Ca, Fe, and Mg, respectively. The value of y is unknown (0.0 < y < 0.7) (Warne et al., 1981), but the minimization routine will allow y to be solved as an additional variable since the F_i functions need not be linear. This treatment can be extended to the other minerals (e.g., illite, feldspar, and montmorillonite) that have undergone isomorphous substitution.

Equation 4 is not limited to mass balances but can also be used for any measured parameter P_i where a_{ij} would be the portions of that parameter attributed to each phase. For example, if P_i is the TGA weight loss between two temperatures, then a_{ij} would be the theoretical weight losses for each component in that temperature range. Other potential parameters include percent extractables, cation-exchange capacity, and surface area.

A final function,

$$F_i = \sum X_j - 100, \quad (6)$$

serves as a constraint to ensure that the sum of the phases equals 100. Since samples may contain unidentified minerals, noncrystalline components, organic matter, and water, the model should include a variable for an unknown phase.

The routine requires upper and lower limits for each variable. Minimally, provisions should be made to ensure that the lower bound for any phase is not less than 0% and the upper bound is not greater than 100%. However, narrowing the bounds further would improve accuracy by increasing the probability of the algorithm converging to the true answer. This could be accomplished by measuring integrated XRD peak intensities for each phase and placing confidence limits on peak-area ratios. Better limits could be set if other factors that affect intensities were incorporated. Bounds on the degree of isomorphous substitution must also be established, and these can be obtained from the literature.

The minimization algorithm can be tailored for any specific suite of minerals. To demonstrate the application of this technique, we selected several samples of oil shale that contained quartz, calcite, dolomite-ankerite, feldspar, analcite, and illite. Thus, F_1 through F_7 , as described by Equation 4, were assigned to mass balances for the elements Na, Al, Ca, Fe, Mg, Si, and K, e.g., P_1 equaled the measured weight percent of Na in the sample. An eighth function, F_8 , was assigned to the quantity of CO_2 as measured by TGA weight loss between 615°C and 840°C. Equation 7 (below) gives the matrix for the eight functions, and Table 1 lists the chemical formulae for the minerals in the sample.

Two additional, optional functions capitalized on the ability of this algorithm to handle nonelemental information. These functions minimized (1) the difference between the total carbonate content and the weight percent extracted with acetic acid,

$$F_9 = X_{\text{Ankerite}} + X_{\text{Calcite}} - P_{\text{extd, acetic acid}} \quad (8)$$

and (2) the difference between the total carbonate plus analcite content and the weight percent extracted with hydrochloric acid,

$$F_{10} = X_{\text{Ankerite}} + X_{\text{Calcite}} + X_{\text{Analcite}} - P_{\text{extd, HCl}} \quad (9)$$

The program asked the user to input whether one or both acids were used and then selected Equations 8 and/or 9 as appropriate.

The upper and lower limits for quartz, calcite, dolomite-ankerite, feldspar, and analcite were taken as the normalized intensity ratio for each phase $\pm 20\%$. The normalized intensity ratios were obtained from dividing the measured X-ray intensities of peaks at 3.34, 3.04, 2.89–2.91, 3.18–3.25, and 3.43 Å, respectively, by the total intensity of these five peaks and multiplying by 100.

Since micaceous minerals are platy in nature, the peak around 10 Å, due to illite, is often not observed in random-mount diffractograms when present in small amounts. Therefore, rather than using the intensity of this peak to estimate the bounds for illite as above, the lower bound was set at 0% and the upper bound estimated directly from an X-ray diffractogram of an oriented mount.

It is difficult to distinguish by powder XRD between alkali feldspar ($\text{K}_x\text{Na}_{1-x}\text{AlSi}_3\text{O}_8$ with up to 10% substitution of Ca), and plagioclase feldspar ($\text{Na}_w\text{Ca}_{1-w}\text{Al}_2\text{Si}_{2+w}\text{O}_8$ with up to 10% substitution of K) (Deer et al., 1966) when both are present in a multicomponent mixture. Because of this problem, when key reflections for feldspar were present, the algorithm assumed that both alkali and plagioclase feldspars were present. This was done because it was difficult to set upper bounds on the amount of Ca and K present if the ternary system ($\text{K}_x\text{Na}_{1-x}\text{Ca}_w\text{Al}_{2-w}\text{Si}_{2+w}\text{O}_8$) were used instead. However, the final output combined the results and only reported the weight fraction for one feldspar.

Since it was difficult to assign an individual X-ray intensity to each feldspar phase, both phases were assigned identical bounds. The boundary was calculated from the sum of the intensities in the 3.18–3.25-Å range. Consequently, when the algorithm summed

the two feldspar phases, it could have overestimated the amount of feldspar present since the upper bound for each feldspar was equivalent to what the upper bound for total feldspar should have been. Therefore, an additional function minimized the difference between total feldspar content ($X_{\text{Ca-F}} + X_{\text{K-F}}$) and the product of quartz content (X_{Q}) times the ratio of feldspar to quartz ($X_{\text{F/Q}}$):

$$F_{10} = X_{\text{Ca-F}} + X_{\text{K-F}} - X_{\text{F/Q}}X_{\text{Q}} \quad (10)$$

This allowed introduction of a constraint on the total amount of feldspar based on the ratio of the XRD intensities for feldspar (3.18–3.25 Å) to quartz (3.34 Å). The lower and upper bounds for $X_{\text{F/Q}}$ were set at $0.5\times$ and $1.5\times$ the intensity ratio, respectively.

Analytical techniques

Five Green River oil-shale samples were analyzed for their mineral content; two were raw (i.e., unprocessed), and three were spent shales that had been collected after the retorting process.

Whole-rock XRD analyses (<45- μm fraction) were carried out on a packed, random mount in a Rigaku XRD using $\text{CuK}\alpha$ radiation and a graphite-crystal monochromator. TGA was performed with a DuPont 1090 thermal analyzer using a DuPont 951 TGA cell. Approximately 15–20 mg were heated at 20 deg/min under a flowing N_2 atmosphere. Differential thermal analysis was obtained with the DuPont DTA cell under both N_2 and CO_2 atmospheres. Total elemental analyses were obtained by ICP atomic emission spectroscopy.

Two methods were used for selectively dissolving the carbonate materials. With one, the samples were digested in 3% acetic acid for 1 h; with the other method, samples were digested in 6 N HCl for 15 min. After digestion, the samples were washed with distilled water, and the filtrates were made up to a known volume. The washed residues were weighed after drying at 110°C, and the difference in weight was used to compute the total amount of carbonate minerals in the sample.

RESULTS

The XRD results showed that both the raw and spent shales contained the same suite of minerals: calcite, Fe-substituted dolomite or ankerite, quartz, feldspar, analcite, and illite. The presence of ankerite rather than dolomite was confirmed by DTA, which revealed three endothermic peaks characteristic of ankerite decomposition in a CO_2 environment (Warne et al., 1981). The weight loss after acetic acid digestion ranged from 38% to 50%, indicating that the carbonate minerals were the major components of these samples.

Analyzing a mineral mixture with the minimization algorithm requires a number of assumptions depending on the phases present. For the oil shales, elements were

$$\begin{array}{l} F_1 \\ F_2 \\ F_3 \\ F_4 \\ F_5 \\ F_6 \\ F_7 \\ F_8 \end{array} = \begin{array}{ccccccc} 0 & 0 & 0 & a_{14} & a_{15} & 0.104 & 0 \\ 0 & 0 & 0 & a_{24} & a_{25} & 0.122 & a_{27} \\ 0 & 0.400 & 0 & a_{33} & a_{34} & 0 & 0 \\ 0 & 0 & a_{43} & 0 & 0 & 0 & 0 \\ 0 & 0 & a_{53} & 0 & 0 & 0 & 0 \\ 0.468 & 0 & 0 & a_{64} & a_{65} & 0.256 & a_{67} \\ 0 & 0 & 0 & 0 & a_{75} & 0 & a_{77} \\ 0 & 0.440 & a_{83} & 0 & 0 & 0 & 0 \end{array} \begin{array}{l} X_{\text{Quartz}} \\ X_{\text{Calcite}} \\ X_{\text{Ankerite}} \\ X_{\text{Ca-Feldspar}} \\ X_{\text{K-Feldspar}} \\ X_{\text{Analcite}} \\ X_{\text{Illite}} \end{array} - \begin{array}{l} P_{\text{Na}} \\ P_{\text{Al}} \\ P_{\text{Ca}} \\ P_{\text{Fe}} \\ P_{\text{Mg}} \\ P_{\text{Si}} \\ P_{\text{K}} \\ P_{\text{CO}_2} \end{array} \quad (7)$$

TABLE 3. Composition of oil shales (%)

| | D10-5 | D18-5 | D29-5 | D40-5 | D48-5 |
|---|-------|-------|-------|-------|-------|
| A. (Using acetic acid and HCl digestions) | | | | | |
| Quartz | — | 17 | 19 | 18 | 21 |
| Calcite | — | 18 | 19 | 15 | 17 |
| Ankerite | — | 20 | 31 | 32 | 33 |
| Feldspar | — | 7 | 10 | 17 | 11 |
| Analcite | — | 12 | 8 | 7 | 7 |
| Illite | — | 2 | 7 | 8 | 9 |
| Other | — | 24 | 7 | 3 | 2 |
| Total | | 100 | 101 | 100 | 100 |
| B. (Using HCl digestion) | | | | | |
| Quartz | 17 | 17 | 19 | 18 | 22 |
| Calcite | 12 | 18 | 18 | 14 | 16 |
| Ankerite | 28 | 23 | 31 | 32 | 31 |
| Feldspar | 11 | 7 | 10 | 18 | 12 |
| Analcite | 11 | 10 | 9 | 9 | 10 |
| Illite | 2 | 4 | 6 | 5 | 5 |
| Other | 18 | 22 | 7 | 5 | 4 |
| Total | 99 | 101 | 100 | 101 | 100 |
| C. (Using acetic acid digestion) | | | | | |
| Quartz | — | 18 | 18 | 16 | 20 |
| Calcite | — | 18 | 19 | 14 | 17 |
| Ankerite | — | 21 | 31 | 34 | 33 |
| Feldspar | — | 8 | 9 | 15 | 11 |
| Analcite | — | 9 | 13 | 20 | 14 |
| Illite | — | 4 | 4 | 0 | 4 |
| Other | — | 24 | 6 | 1 | 1 |
| Total | | 102 | 100 | 100 | 100 |
| D. (Without acid digestion) | | | | | |
| Quartz | 17 | 16 | 18 | 17 | 21 |
| Calcite | 13 | 18 | 19 | 13 | 16 |
| Ankerite | 28 | 23 | 30 | 32 | 31 |
| Feldspar | 11 | 7 | 9 | 16 | 12 |
| Analcite | 13 | 11 | 13 | 19 | 12 |
| Illite | 2 | 3 | 4 | 0 | 4 |
| Other | 18 | 21 | 6 | 3 | 4 |
| Total | 102 | 99 | 99 | 100 | 100 |

assigned to the various minerals according to Table 1 and the following requirements:

1. Only the identified minerals contributed to the analyzed chemistry, i.e., unidentified material did not contain these elements.

2. Only ankerite and pure calcite were allowed as carbonates, i.e., all Mg and Fe were assigned to ankerite with other solid solutions not being allowed. If the X-ray diffractograms had shown other end members, such as siderite or magnesite, to be present, then the input to the algorithm would have been modified to include them.

3. All K present in the feldspars was assigned to alkali feldspar, and all Ca was assigned to plagioclase feldspar.

An additional assumption was that acetic acid digestion is selective in removing only calcite and dolomite-ankerite, whereas hydrochloric acid digestion removes not only these two minerals but also analcite. X-ray diffraction of the residue and elemental analysis of the leachate confirmed the validity of the assumption.

Finally, it was assumed that the intensity of the 3.34-Å peak was due only to quartz. In reality, it also included a small contribution from illite. If illite had been a major component of the sample, a different quartz peak (e.g., 1.82 Å) would have been used with appropriate scaling.

TABLE 4. Calculated fraction of isomorphously substituted elements in oil shales

| | D10-5 | D18-5 | D29-5 | D40-5 | D48-5 |
|---|-------|-------|-------|-------|-------|
| A. (Using acetic acid and HCl digestions) | | | | | |
| Fe in ankerite | — | 0.13 | 0.18 | 0.21 | 0.19 |
| K in feldspar | — | 0.38 | 0.43 | 0.27 | 0.51 |
| Na in feldspar | — | 0 | 0.23 | 0.73 | 0.49 |
| K in illite | — | 2 | 2 | 2 | 2 |
| B. (Using HCl digestion) | | | | | |
| Fe in ankerite | 0.18 | 0.18 | 0.17 | 0.19 | 0.16 |
| K in feldspar | 0.49 | 0.53 | 0.48 | 0.34 | 0.61 |
| Na in feldspar | 0 | 0 | 0.03 | 0.51 | 0 |
| K in illite | 2 | 2 | 2 | 2 | 2 |
| C. (Using acetic acid digestion) | | | | | |
| Fe in ankerite | — | 0.14 | 0.18 | 0.21 | 0.19 |
| K in feldspar | — | 0.27 | 0.66 | 0.77 | 0.88 |
| Na in feldspar | — | 0 | 0 | 0.08 | 0 |
| K in illite | — | 2 | 2 | n.a. | 2 |
| D. (Without acid digestion) | | | | | |
| Fe in ankerite | 0.18 | 0.19 | 0.17 | 0.19 | 0.16 |
| K in feldspar | 0.53 | 0.57 | 0.61 | 0.69 | 0.67 |
| Na in feldspar | 0 | 0 | 0 | 0.02 | 0 |
| K in illite | 2 | 2 | 2 | n.a. | 2 |

Note: n.a. = not applicable.

Table 2 lists the analytical data obtained for the five oil shales; Table 3 shows the compositions calculated by integrating the data into the minimization algorithm. Table 3 also compares the composition calculated for the set of samples using four different options with respect to data on selective-acid dissolution (HCl plus acetic, HCl, acetic, none). The values obtained for quartz, calcite, and ankerite by the four different computations agreed within 2%, absolute. The largest discrepancies were for analcite and illite, especially for sample D40-5, which contained a significantly higher level of Na. Analcite contains Al and Si, which are variables in illite and feldspar, and Na, which is present as a variable in feldspar. Without the additional constraint of the HCl treatment, the algorithm apparently placed this excess Na in analcite rather than feldspar. This used up the Al and Si required by illite. But when the analcite content was constrained by the weight percent digested by HCl, the algorithm assigned the excess Na to feldspar, thereby leaving sufficient Al and Si for illite. This showed the advantage of this acid treatment used alone or with an acetic acid treatment, and the values for these options were probably the most accurate.

The higher quantity of unidentified material in samples D10-5 and D18-5 was expected since these were raw shales, which contain significant amounts of organic matter and water. This was substantiated by the relatively lower quantities of each of the elements present in these two samples as compared to the spent shales (Table 2). Deviations from 100% for total content were due to round-off.

Table 4 reveals the calculated fractions for the isomorphously substituted cations in ankerite, feldspar, and illite. The Fe for Mg substitution in ankerite varied between 14% and 21%. The constant value of 2.0 for K suggests that the mica species present in the samples was muscovite rather than illite. This, however, could not be confirmed

TABLE 5. Calculated composition of hypothetical mineral mixtures in percent

| Phase | T | CB | CH | CA | CO | T | CB | CH | CA | CO | T | CB | CH | CA | CO |
|----------|------------|----|----|----|----|------------|----|----|----|----|------------|----|----|----|----|
| | Mixture 1 | | | | | Mixture 2 | | | | | Mixture 3 | | | | |
| Quartz | 25 | 25 | 25 | 25 | 25 | 10 | 10 | 10 | 10 | 10 | 40 | 40 | 40 | 40 | 40 |
| Ankerite | 40 | 40 | 40 | 40 | 40 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 | 15 |
| Calcite | 20 | 20 | 20 | 20 | 20 | 40 | 40 | 40 | 40 | 40 | 20 | 20 | 20 | 20 | 20 |
| Feldspar | 15 | 15 | 15 | 15 | 15 | 30 | 29 | 30 | 29 | 30 | 0 | 0 | 0 | 0 | 0 |
| Illite | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 |
| Analcite | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 0 | 20 | 20 | 20 | 20 | 20 |
| Other | 0 | 0 | 0 | 0 | 0 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 | 5 |
| | Mixture 4 | | | | | Mixture 5 | | | | | Mixture 6 | | | | |
| Quartz | 30 | 30 | 30 | 30 | 30 | 20 | 20 | 20 | 20 | 20 | 55 | 55 | 55 | 55 | 55 |
| Ankerite | 10 | 10 | 10 | 10 | 10 | 15 | 15 | 15 | 15 | 15 | 5 | 5 | 5 | 5 | 5 |
| Calcite | 40 | 40 | 40 | 40 | 40 | 30 | 30 | 30 | 30 | 30 | 20 | 20 | 20 | 20 | 20 |
| Feldspar | 0 | 0 | 0 | 0 | 0 | 25 | 25 | 25 | 23 | 23 | 5 | 5 | 5 | 5 | 6 |
| Illite | 10 | 10 | 10 | 10 | 10 | 0 | 0 | 0 | 0 | 0 | 10 | 10 | 10 | 10 | 10 |
| Analcite | 0 | 0 | 0 | 0 | 0 | 10 | 10 | 10 | 11 | 12 | 0 | 0 | 0 | 0 | 0 |
| Other | 10 | 10 | 10 | 10 | 10 | 0 | 0 | 0 | 0 | 0 | 5 | 5 | 5 | 5 | 5 |
| | Mixture 7 | | | | | Mixture 8 | | | | | Mixture 9 | | | | |
| Quartz | 40 | 40 | 40 | 40 | 40 | 20 | 20 | 21 | 22 | 19 | 20 | 21 | 20 | 21 | 21 |
| Ankerite | 15 | 15 | 15 | 15 | 15 | 30 | 30 | 30 | 30 | 30 | 35 | 35 | 35 | 35 | 35 |
| Calcite | 15 | 15 | 15 | 15 | 15 | 10 | 10 | 10 | 10 | 10 | 15 | 15 | 15 | 15 | 15 |
| Feldspar | 0 | 0 | 0 | 0 | 0 | 15 | 16 | 15 | 10 | 20 | 10 | 10 | 11 | 10 | 5 |
| Illite | 10 | 10 | 10 | 10 | 10 | 5 | 5 | 5 | 4 | 5 | 10 | 9 | 9 | 9 | 9 |
| Analcite | 10 | 10 | 10 | 10 | 10 | 5 | 4 | 5 | 9 | 1 | 5 | 5 | 5 | 6 | 10 |
| Other | 10 | 10 | 10 | 10 | 10 | 15 | 15 | 15 | 15 | 15 | 5 | 5 | 5 | 5 | 5 |
| | Mixture 10 | | | | | Mixture 11 | | | | | Mixture 12 | | | | |
| Quartz | 40 | 40 | 40 | 41 | 40 | 15 | 15 | 16 | 16 | 15 | 15 | 15 | 16 | 14 | 16 |
| Ankerite | 10 | 10 | 10 | 10 | 10 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 | 30 |
| Calcite | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 | 10 |
| Feldspar | 10 | 10 | 10 | 9 | 10 | 20 | 20 | 19 | 16 | 22 | 15 | 16 | 15 | 19 | 9 |
| Illite | 20 | 20 | 20 | 20 | 20 | 10 | 10 | 11 | 10 | 10 | 5 | 5 | 4 | 4 | 4 |
| Analcite | 10 | 10 | 10 | 11 | 10 | 5 | 5 | 5 | 8 | 3 | 5 | 5 | 5 | 2 | 10 |
| Other | 0 | 0 | 0 | 0 | 0 | 10 | 10 | 10 | 10 | 10 | 20 | 20 | 20 | 20 | 20 |

Note: T = True values for hypothetical lab mixtures. CB = Values calculated with algorithm using both acid digestions. CH = Values calculated with algorithm using HCl digestion. CA = Values calculated with algorithm using acetic acid digestion. CO = Values calculated with algorithm without acid digestion.

by XRD. Some of the shales showed significant quantities of both K and Ca present in the feldspar. These elements cannot exist in solid solution in feldspar except in small quantities. Thus, the calculated chemistry appears to in-

dicate the presence of two discrete feldspars—a plagioclase and an alkali feldspar. A shoulder on the main feldspar peak at 27.8° in the X-ray diffractogram supported the presence of two feldspar phases.

TABLE 6. Calculated fraction of isomorphously substituted elements in hypothetical mineral mixtures

| Phase | T | CB | CH | CA | CO | T | CB | CH | CA | CO | T | CB | CH | CA | CO |
|----------------|------------|------|------|------|------|------------|------|------|------|------|------------|------|------|------|------|
| | Mixture 1 | | | | | Mixture 2 | | | | | Mixture 3 | | | | |
| Fe in ankerite | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| K in feldspar | 0.05 | 0.04 | 0.04 | 0.04 | 0.04 | 0.05 | 0.05 | 0.05 | 0.05 | 0.05 | n.a. | n.a. | n.a. | n.a. | n.a. |
| Na in feldspar | 0.71 | 0.70 | 0.71 | 0.71 | 0.72 | 0.71 | 0.70 | 0.71 | 0.71 | 0.71 | n.a. | n.a. | n.a. | n.a. | n.a. |
| K in illite | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. | n.a. |
| | Mixture 4 | | | | | Mixture 5 | | | | | Mixture 6 | | | | |
| Fe in ankerite | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| K in feldspar | n.a. | n.a. | n.a. | n.a. | n.a. | 0.05 | 0.05 | 0.50 | 0.05 | 0.05 | 0.05 | 0.00 | 0.02 | 0.03 | 0.15 |
| Na in feldspar | n.a. | n.a. | n.a. | n.a. | n.a. | 0.71 | 0.72 | 0.72 | 0.70 | 0.69 | 0.71 | 0.75 | 0.68 | 0.73 | 0.59 |
| K in illite | 1.25 | 1.24 | 1.22 | 1.24 | 1.24 | n.a. | n.a. | n.a. | n.a. | n.a. | 1.25 | 1.26 | 1.30 | 1.23 | 1.08 |
| | Mixture 7 | | | | | Mixture 8 | | | | | Mixture 9 | | | | |
| Fe in ankerite | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| K in feldspar | n.a. | n.a. | n.a. | n.a. | n.a. | 0.05 | 0.08 | 0.00 | 0.02 | 0.05 | 0.05 | 0.01 | 0.05 | 0.04 | 0.26 |
| Na in feldspar | n.a. | n.a. | n.a. | n.a. | n.a. | 0.71 | 0.67 | 0.73 | 0.57 | 0.75 | 0.71 | 0.69 | 0.65 | 0.65 | 0.15 |
| K in illite | 1.25 | 1.25 | 1.25 | 1.25 | 1.24 | 1.25 | 1.12 | 1.79 | 1.82 | 1.32 | 1.25 | 1.47 | 1.36 | 1.39 | 1.13 |
| | Mixture 10 | | | | | Mixture 11 | | | | | Mixture 12 | | | | |
| Fe in ankerite | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 | 0.1 |
| K in feldspar | 0.05 | 0.05 | 0.01 | 0.05 | 0.08 | 0.05 | 0.03 | 0.00 | 0.06 | 0.06 | 0.05 | 0.09 | 0.00 | 0.04 | 0.12 |
| Na in feldspar | 0.71 | 0.70 | 0.74 | 0.71 | 0.67 | 0.71 | 0.72 | 0.75 | 0.65 | 0.74 | 0.71 | 0.66 | 0.73 | 0.75 | 0.44 |
| K in illite | 1.25 | 1.24 | 1.30 | 1.31 | 1.19 | 1.25 | 1.31 | 1.44 | 1.23 | 1.09 | 1.25 | 1.00 | 1.83 | 1.42 | 1.12 |

Note: Column headings as in Table 5.

TABLE 7. Range of values obtained for 100 iterations giving lowest values of F (sample 8, Table 5)

| | Lower bound | Range | Upper bound | Value at F_{\min} | Actual value |
|----------------|-------------|-----------|-------------|---------------------|--------------|
| Quartz (wt%) | 5.0 | 19.6–20.7 | 45.0 | 20.7 | 20.0 |
| Calcite (wt%) | 0.0 | 9.9–11.2 | 32.5 | 9.9 | 10.0 |
| Ankerite (wt%) | 17.5 | 29.0–30.2 | 57.5 | 30.1 | 30.0 |
| Feldspar (wt%) | 0.0 | 11.9–16.0 | 38.8 | 14.7 | 15.0 |
| Analcite (wt%) | 0.0 | 4.8–5.0 | 26.2 | 5.0 | 5.0 |
| Illite (wt%) | 0.0 | 4.5–7.7 | 20.0 | 4.6 | 5.0 |
| Unknown (wt%) | 0.0 | 14.9–15.4 | 20.0 | 15.0 | 15.0 |
| Fe in ankerite | 0.00 | 0.10–0.10 | 0.70 | 0.10 | 0.10 |
| K in feldspar | 0.00 | 0.00–0.06 | 1.00 | 0.00 | 0.05 |
| Na in feldspar | 0.00 | 0.29–0.85 | 1.00 | 0.73 | 0.71 |
| K in illite | 1.00 | 1.03–1.79 | 2.00 | 1.79 | 1.25 |

TABLE 8. Effect of variations in the analytical data on calculation of composition of hypothetical mineral mixtures (sample 8, Table 5)

| Analytical data | | Calculated composition (using HCl extraction) | | |
|-----------------|-----------|---|-----------|------------|
| Parameter | Range (%) | Phase | Range (%) | Actual (%) |
| Na | 1.3–1.6 | Quartz | 13–23 | 20 |
| Al | 2.9–3.8 | Ankerite | 28–37 | 30 |
| Ca | 9.7–11.6 | Calcite | 6–12 | 10 |
| Fe | 0.9–1.0 | Feldspar | 9–17 | 15 |
| Mg | 3.2–3.8 | Analcite | 1–6 | 5 |
| Si | 14.0–17.2 | Illite | 0–11 | 5 |
| K | 0.4–0.5 | Other | 10–18 | 15 |
| TGA wt. loss | 17.4–20.9 | | | |
| HCl wt. loss | 43.0–47.0 | | | |

DISCUSSION

In order to determine the accuracy of the analysis, major-element content, CO_2 weight loss, and acetic and hydrochloric acid weight losses were calculated for hypothetical mixtures of the above minerals. The phase composition of each hypothetical mixture was then determined by using the algorithm with the simulated analytical information as input. Table 5 shows that the calculated compositions of four-, five-, and six-component mixtures were within 1%, 2%, and 5%, absolute, respectively, of the hypothetical compositions when either the acetic acid digestion was used or when all acid digestion was omitted. Using the HCl digestion either alone or with the acetic acid digestion reduced the deviations to less than 1% irrespective of the number of components! These results demonstrated the accuracy of the algorithm for determining phase composition and were independent of the accuracy of the analytical techniques.

Except for Fe in ankerite, the algorithm did not work quite as well for calculating the isomorphously substituted cations in the other minerals. Table 6 shows that the algorithm calculated the fraction of Fe in ankerite precisely in all of these mixtures. This was due to Fe and Mg being present only in this phase. The accuracy for the fractions of K and Na in alkali feldspar and K in illite depended on the number of phases present and the acid treatment used. K and Na were reported to within 0.04 for four-component mixtures where only one of the minerals alkali feldspar, illite, or analcite was present. When two of these three components were present, as in the five-component mixtures, these fractions were calculated to within 0.05 if an acid treatment was used. The difference between hypothetical and calculated K and Na widened to as much as 0.17 if an acid treatment was not used. In the six-component mixtures, the fractions for alkali feldspar were calculated to within 0.06 when an HCl treatment was used, widened to 0.14 when the acetic acid treatment was used alone, and became unreliable without the acid extraction. Finally, the calculated fraction of K in illite for a six-component mixture was generally unreliable.

The reason for this inability to report the correct chem-

istry in the substituted minerals could be discerned by examining the optimization process in more detail. For example, the algorithm optimized Equation 5 for the data (using HCl digestion) of sample 8 of Table 5 to $F = 0.0002$ in 94 000 iterations, with 100 iterations giving values less than $F = 0.0022$. Table 7 reports the range of values obtained for each variable during these 100 iterations. Since they were extremely close to the minimum value of F , all the values reported in Table 7 were possible solutions to the algorithm. Apparently, the algorithm would only be able to optimize to the physically correct solution if further constraints were imposed by additional analytical data.

Next, the simulated elemental analyses and weight losses due to acid digestion were randomly varied by $\pm 15\%$ and $\pm 5\%$, respectively, to elucidate the sensitivity of the calculated results to expected experimental errors. (A lower variance was used for the acetic acid-digestion weight losses since significantly higher confidence was developed for that analytical method than for the elemental analysis.) Sample 8 from Table 5—20% quartz, 30% ankerite, 10% calcite, 15% feldspar, 5% illite, 5% analcite, and 15% other—was chosen for this analysis. Table 8 tabulates the range of the randomly varied analytical data as well as the range of compositions calculated from this data. When used with the hypothetically correct data and the HCl digestion, the algorithm had calculated the composition within 1% for this sample. However, Table 8 reveals that expected inaccuracies of the analytical data introduced as much as a 10% error, absolute, in the calculated quantity of a phase—with the average error being 5%. These results still compared quite well with accuracies obtained with traditional XRD quantitative methods.

The influence of potential inaccuracies in the XRD data was elucidated in a similar manner. Randomly varying the intensities of the simulated data by 10%, absolute, gave values within 2% of the true value as long as the true quantity was within the bounds established with the X-ray intensities. In other words, the potential errors in determining phase abundances were not nearly as significant as they were with the elemental and thermal data.

CONCLUSIONS

Phases in a mineral mixture can be quantified by integrating elemental analysis, thermal analysis, X-ray diffraction, and data on selective-acid dissolution through a nonlinear minimization algorithm. When used with accurate analytical data, the algorithm can calculate the composition to within 1%, absolute, of the correct value. However, expected variance in the analytical data can introduce average errors of 5%, absolute.

Use of a nonlinear minimization algorithm also allows calculation of the mole fractions of isomorphously substituted cations in minerals. These calculations are quite reliable for determining the ratio of two elements in a phase when the elements are present only in that phase. The calculations are not dependable, however, when the substituting elements are present in more than two phases in the mixture.

The procedure was demonstrated for samples containing quartz, calcite, dolomite-ankerite, feldspar, analcite, and illite. Analytical information required for determining the proportion of each mineral in this suite included (1) elemental analysis for Na, Al, Ca, Fe, Mg, Si, and K; (2) TGA weight loss between 615 and 840°C for CO₂ content; (3) weight fraction of material extracted by acetic and/or hydrochloric acid; and (4) XRD intensities of the characteristic peaks for quartz (3.34 Å), calcite (3.04 Å), dolomite-ankerite (2.89–2.91 Å), feldspar (3.18–3.25 Å), and analcite (3.43 Å).

Hydrochloric acid treatment selectively dissolved carbonate minerals and analcite, whereas acetic acid only dissolved the former. Although the HCl treatment provided more accurate analyses than did the acetic acid, HCl must be used with great care as it is more aggressive and can attack other phases in the mixture. Using both hydrochloric and acetic acid treatments as part of the analysis did not significantly improve the accuracy over that obtained with the hydrochloric acid treatment alone.

Finally, the procedure developed here provides quantitative analysis of mineral mixtures with an accuracy better than existing procedures that use only X-ray dif-

fraction. However, as a combined instrument technique, it may be more time consuming than less-accurate techniques. The user will need to decide whether the situation requires the higher degree of accuracy that this procedure offers.

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REFERENCES

- Bayliss, P. (1986) Quantitative analysis of sedimentary minerals by X-ray powder diffraction. *Powder Diffraction*, 1, 37–39.
- Deer, W.A., Howie, R.A., and Zussman, J. (1966) An introduction to the rock-forming minerals, p. 281–340. Longman Group, London.
- Hodgson, M., and Dudeney, A.W.L. (1984) Estimation of clay proportions in mixtures by X-ray diffraction and computerized mass balance. *Clays and Clay Minerals*, 32, 19–28.
- Johnson, L.J., Chu, C.H., and Hussey, G.A. (1985) Quantitative clay mineral analysis using simultaneous linear equations. *Clays and Clay Minerals*, 33, 107–117.
- Pawlowski, G.A. (1985) Quantitative determination of mineral content of geological samples by X-ray diffraction. *American Mineralogist*, 70, 663–667.
- Pearson, M.J. (1978) Quantitative clay mineralogical analysis from the bulk chemistry of sedimentary rocks. *Clays and Clay Minerals*, 26, 423–433.
- Slaughter, M. (1984) Quantitative determination of clays and other minerals in rocks. *Clay Minerals Society, Program with Abstracts*, 106.
- Smyth, C.P. (1983) Mineralogical correction factors applied to X-ray fluorescence analysis of manganese ore in powder brickette form. *Geological Society of South Africa Special Publication*, 7, 425–434.
- Starks, T.H., Fang, J.H., and Zevin, L.S. (1984) A standardless method of quantitative X-ray diffractometry using target-transformation factor analysis. *Mathematical Geology*, 16, 351–367.
- Warne, S.St.J., Morgan, D.J., and Milodowski, A.E. (1981) Thermal analysis studies of the dolomite, ferroan dolomite, ankerite series. Part 1. Iron content recognition and determination by variable atmosphere DTA. *Thermochimica Acta*, 51, 105–111.

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