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Accurate quantitative analysis of clay and other minerals in sandstones by XRD: comparison of a Rietveld and a reference intensity ratio (RIR) method and the importance of sample preparation

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ABSTRACT: X-ray diffraction is used widely for quantitative analysis of geological samples but studies which document the accuracy of the methods employed are not numerous. Synthetic sandstones of known composition are used to compare a 'routine application' of a Rietveld and a reference intensity ratio (RIR) method of quantitative phase analysis. Both methods give similar results accurate to within ~±3 wt.% at the 95% confidence level. The high degree of accuracy obtained is believed to depend to a large extent on the spray-drying method of sample preparation used to eliminate preferred orientation.

KEYWORDS: XRD, quantitative analysis, Rietveld analysis.

Characterizing the clay minerals present in a reservoir sandstone can be an important aspect in the understanding of petroleum reservoir quality (Eslinger & Pevear, 1988). Along with the textural information that may be obtained by optical and electron microscopy, detailed characterization of the clay minerals present is commonly based on studies of clay-sized fractions by X-ray diffraction (XRD). Accurate determination of the amounts of the different clay minerals present is more difficult (Wilson, 1987; Pevear & Mumpton, 1989; Moore & Reynolds, 1997) and the quantities in a clay fraction are not readily related to those in the whole rock from which it was obtained. Furthermore, from the point of view of reservoir quality it may be far more important to know the absolute amounts of a clay mineral present in a sandstone than just the relative amounts in a clay fraction (Thornley & Primmer, 1995). Although determination of the amounts of clay minerals in whole-rock samples by XRD is frequently attempted, there is a general and quite justifiable perception that the results are often semi-quantitative at best. In part this can be attributed to the well known difficulties inherent in the quantitative analysis of clay minerals, such as compositional variation, variable degrees of structural order/disorder, and their tendency towards preferred orientation in a powder sample (Brindley, 1980). In one way or another, most of these difficulties stem from the very nature of clay minerals which make both the measurement of X-ray intensities and choice of standards difficult. As far as sandstones are concerned, the difficulties are often compounded by the fact that the total clay mineral content is frequently only a very small fraction of the sample which tends to be dominated by other phases, notably quartz. Other mineral groups such as feldspars can also be problematic to

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analyse because of their compositional variations, microstructural intergrowths and preferred orientation as a result of more than one good cleavage (Chipera & Bish, 1995).

One way to tackle some of these problems is to use methods that combine data from other techniques (Calvert *et al.*, 1989; Thornley & Primmer, 1995), but although such an approach can result in accurate analyses the extra effort involved makes their routine application unattractive. For routine quantitative analysis, XRD undoubtedly has the widest capabilities of any single technique. It is probably for this reason that recent advances in computer aided methods (e.g. Bish & Post, 1993; Hill *et al.*, 1993; Mumme *et al.*, 1996) and instrumentation (e.g. Batchelder & Cressey, 1998) seem to have promoted something of a renewed interest in this application as predicted by Snyder & Bish (1989). Nevertheless, there can be no doubt that attention to sample preparation whereby problems such as preferred orientation can be eliminated by methods such as spray drying (Bish & Reynolds, 1989; Hillier, 1999) is preferable to attempting to correct for such effects with sophisticated software routines.

Although general statements about the accuracy to be expected from XRD methods are often quoted in the literature, there are, in fact, relatively few studies on geological samples which demonstrate the degree of accuracy that they actually achieve (Bish, 1994). This may be because in order to test a method it must be applied to samples where the answer is already known. Yet, as concluded by Bish & Chipera (1988), ''it is imperative that investigators assess the accuracy and precision of their analyses through multiple analysis of standard mixtures''. With most real samples such as sandstones this is not without problems since it is necessary to rely on another estimate of composition such as from point counting, and for clay minerals in particular these data may be too unreliable for such an approach. One way around this problem is to prepare synthetic 'sandstones' of known mineral composition.

In the present study, XRD methods are applied to synthetic 'sandstones' prepared as weighed mixtures dominated by quartz, but with various amounts of feldspar, carbonates and clay minerals also present. These samples are analysed by two independent methods: a reference intensity ratio (RIR) method and a Rietveld method. Analysis by the more traditional RIR method is based on measuring the intensity of one or more peaks for each mineral present and the added internal standard. For the increasingly popular Rietveld method the full experimental XRD pattern is fitted with a calculated mutiphase pattern and the difference minimized by a refinement/optimization procedure. Uncertainty is assessed from the results of these analyses by comparison with the known weighed amounts of minerals.

MATERIALS AND METHODS

Five synthetic sandstones were prepared from weighed amounts of pure minerals as given in Table 1. The non-clay minerals chosen were quartz, albite, calcite and dolomite whilst minerals chosen to represent clay minerals include a muscovite, a chlorite and a kaolinite. Although both the particular chlorite and the muscovite samples used are not true clay minerals in that they do not occur naturally in a clay size, they were selected because they were easier to obtain in the quantities necessary in a form pure enough for the purpose in hand. Ten percent corundum (Sigma Aldrich aluminium oxide powder <10 μm) was also added to each mixture to act as an internal standard. Additionally, ground glass was added to one mixture to simulate the presence of an amorphous component which can be estimated indirectly by methods that incorporate an internal standard. The weighed samples (2 g total) were carefully transferred to a McCrone mill, to which ~6 ml of a 0.5% solution of polyvinyl alcohol and a single drop of 1-octanol were also added. This mixture was ground for 12 min with a set of agate elements, and the resulting slurries spray dried directly from the McCrone mill, as described by Hillier (1999).

The samples thus obtained were top loaded into 2.5 cm diameter circular cavity holders and run on a Siemens D5000 with a θ/θ goniometer. Divergence and antiscatter slits were 1°, receiving slit 0.3°, and Co-$K\alpha$ radiation was selected by a diffracted beam monochromator. Diffraction patterns were recorded by step scanning from $2-75°2\theta$, with a step size of 0.02° and counting for 2 s per step, with the sample spun continuously throughout. These scan conditions were chosen to represent those that are used in practice for quantitative analysis where there is invariably a compromise between the quality of the data and the need to run many samples on a routine basis. With these conditions, one sample takes ~2 h to run and

Table 1. Mineral composition of the synthetic ‘sandstones’.

Mineral	Mix1	Mix2	Mix3	Mix4	Mix5
Kaolinite AIPB	0.3008	0.2000	0.0604	0.0402	0.1031
Chlorite CCa-1	0.3039	0.1797	0.0813	0.0499	0.0806
Muscovite 14	0.3484	0.1644	0.1000	0.0571	0.0613
Quartz 5	0.7883	0.5890	1.1030	1.1533	0.1985
Calcite 12	0.0208	0.2000	0.3593	0.1012	0.3785
Dolomite 6	0.0218	0.2048	0.1027	0.3010	0.4045
Albite 7	0.0205	0.2636	0.0428	0.1079	0.2028
Ground glass					0.4022
Corundum 3	0.2005	0.2002	0.2055	0.2012	0.2035
Total (g)	2.0050	2.0017	2.0550	2.0118	2.0350
Kaolinite AIPB	15.0	10.0	2.9	2.0	5.1
Chlorite CCa-1	15.2	9.0	4.0	2.5	4.0
Muscovite 14	17.4	8.2	4.9	2.8	3.0
Quartz 5	39.3	29.4	53.7	57.3	9.8
Calcite 12	1.0	10.0	17.5	5.0	18.6
Dolomite 6	1.1	10.2	5.0	15.0	19.9
Albite 7	1.0	13.2	2.1	5.4	10.0
Ground glass					19.8
Corundum 3	10.0	10.0	10.0	10.0	10.0
Total (%)	100.0	100.0	100.0	100.0	100.0

in conjunction with an automatic sample changer running overnight, or all weekend if necessary, it is possible to process as many as a hundred samples in a week without unnecessary use of the diffractometer during the day time when it is required for other tasks. The same samples were also re-loaded and re-run over the same angular range and with the same step size but counting for 4 s per step. This second run was made in order to make some assessment of the effect of counting statistics on precision for this type of sample.

The RIR method of quantitative analysis is also known as the ‘matrix flushing’ method after Chung (1974) since matrix absorption affects are ‘flushed’ out of the equation for quantitative analysis. In its most general form (e.g. see Jenkins & Snyder, 1996) a RIR is given by:

$$\mathrm{RIR}_{\mathrm{i,s}} = \left(\frac{X_{\mathrm{s}}}{X_{\mathrm{i}}}\right)\left(\frac{I_{(hkl)\mathrm{i}}}{I_{(hkl)'\mathrm{s}}}\right)\left(\frac{I^{rel}_{(hkl)'\mathrm{s}}}{I^{\mathrm{rel}}_{(hkl)\mathrm{i}}}\right)$$

where X denotes weight fraction, I intensity, I^{rel} relative intensity and the subscripts i and s indicate phase i and the standard phase s, respectively. When the standard phase is corundum and the intensity ratio is determined according to convention from the most intense corundum line $I_{(113)\mathrm{cor}}$ and from the most intense line from phase i, $I_{(hkl)\mathrm{i}}$ in a 50:50 mixture by weight, RIR values are known as I/I_{cor} or $\mathrm{RIR}_{\mathrm{cor}}$. In terms of $\mathrm{RIR}_{\mathrm{cor}}$ the concentration of any phase i in a sample spiked with a known amount of corundum is given by:

$$X_{\mathrm{i}} = \left(\frac{X_{\mathrm{cor}}}{\mathrm{RIR}_{\mathrm{cor}}}\right)\left(\frac{I_{(hkl)\mathrm{i}}}{I_{(113)\mathrm{cor}}}\right)$$

The $\mathrm{RIR}_{\mathrm{cor}}$ values for the phases used, determined from spray dried mixtures with corundum, are given in Table 2. However, it should be noted that the values given for muscovite, chlorite and kaolin are not true $\mathrm{RIR}_{\mathrm{cor}}$ values as defined, since they are not determined from, nor normalized to, the most intense peak from these phases in each pattern. This is simply a convenience due to problems of resolution with other peaks.

Additionally, the RIR used for chlorite requires comment since it is a multiple peak RIR based on the sum of the integrated intensity from both 003 and 004 chlorite peaks. This is a device designed to take account of variation in chemical composition that may otherwise influence RIR values making the choice of standard a crucial step. For example,

TABLE 2. RIR_{cor} values determined from spray-dried mixtures and corresponding peak positions

Mineral	Peak(s) *d*-spacing (Å)	RIR_{cor}
Quartz	3.34	4.04
Albite	3.19 (cluster)	2.07
Calcite	3.03	2.73
Dolomite	2.89	1.94
Muscovite	10.00	0.23
Chlorite	4.75 + 3.52	0.86
Kaolinite	3.58	0.53

see the work of Chipera & Bish (1995) on zeolites and feldspars. The chlorite RIR of 0.86 has a standard deviation of 0.03 based on data for four trioctahedral chlorites that span much of the naturally occurring range in Fe/(Fe+Mg) ratios (0.11, 0.14, 0.40, 0.74). Obviously, in the present study the chemistry of the chlorite in the weighed mixtures was constant and the use of a multiple peak not essential. In natural samples, however, the use of such multiple peak RIRs presents a relatively simple way to account for compositional variation, especially when variation due to preferred orientation is removed.

Furthermore, it must be understood that although RIRs are potentially universal constants, unless calibrated using an instrument sensitivity standard such as NBS SRM 1976 (Schreiner, 1995), to some extent they remain specific to the instrument and conditions under which they are measured. All intensity measurements were integrated intensity, i.e. peak areas, and were measured using the single peak function of the Siemens/Bruker AXS Diffrac AT EVA software. The use of integrated intensity rather than peak height is essential for phases such as clay minerals since peak height may depend on crystallinity and defects. In theory, however, integrated intensity is constant (for example see Moore & Reynolds, 1997).

The Rietveld method of quantitative analysis was applied to the same diffraction data using the commercial program Siroquant (Taylor, 1991). Essentially, the Rietveld method involves fitting the observed diffraction pattern with a synthetic pattern which is a sum of patterns calculated for each phase in the sample; as such this method is known as a full-pattern fitting method (Snyder & Bish, 1989; Bish, 1994). The difference between the synthetic pattern and the observed pattern is minimized by an interactive refinement/optimization procedure. In effect, the Rietveld method uses calculated standards with the advantage that such standards are tailored to the actual minerals present during the refinement process. The amounts of the phases present in the sample are obtained from the final value of the refined scale factor for each phase.

Siroquant is not the most sophisticated of Rietveld refinement programs, e.g. atom site occupancy cannot be refined, but it is designed specifically for quantitative phase analysis with a user friendly interface and a database of >300 phase entries, additions to which can be made easily, if necessary. The refinement strategy employed was relatively simple including just five stages. The first three stages were similar to the automatic pre-scale option available as a setting in the Siroquant program i.e. stage (1) six cycles on phase scales with a damping factor of 0.4; stage (2) six cycles on phase scales and instrument zero with a damping factor of 0.4; and stage (3) six cycles on phase scales with a damping factor of 0.8. Stages (4) and (5) consisted of six cycles on half-widths, and six cycles on unit-cell dimensions both with a damping factor of 0.2. For the first four test samples a linear background was subtracted automatically prior to analysis using the batch processing facilities of the Siemens/Bruker AXS Diffrac AT EVA software. For the fifth test sample, the background was removed manually using Siroquant because of the presence of the amorphous ‘hump’ due to the ground glass. For all samples, intensity in the low-angle region was adjusted using the Siroquant default angular calibration. For each sample the refinement procedure took ~5 min on a 166 mHz Pentium PC. An example of the graphical output from Siroquant for the 2 s/step counted sample for ‘Mix 2’ is shown as Fig. 1.

RESULTS

The results are presented in Table 3 and illustrated by the graphs of % known *vs*. % found in Fig. 2. Both methods give good results with absolute errors typically less than plus or minus a few percent, and in most cases better than this. The frequency distribution of the absolute errors for each of the four sets of analyses is illustrated in Fig. 3. In general these histograms show that there is little difference between all four sets of results although

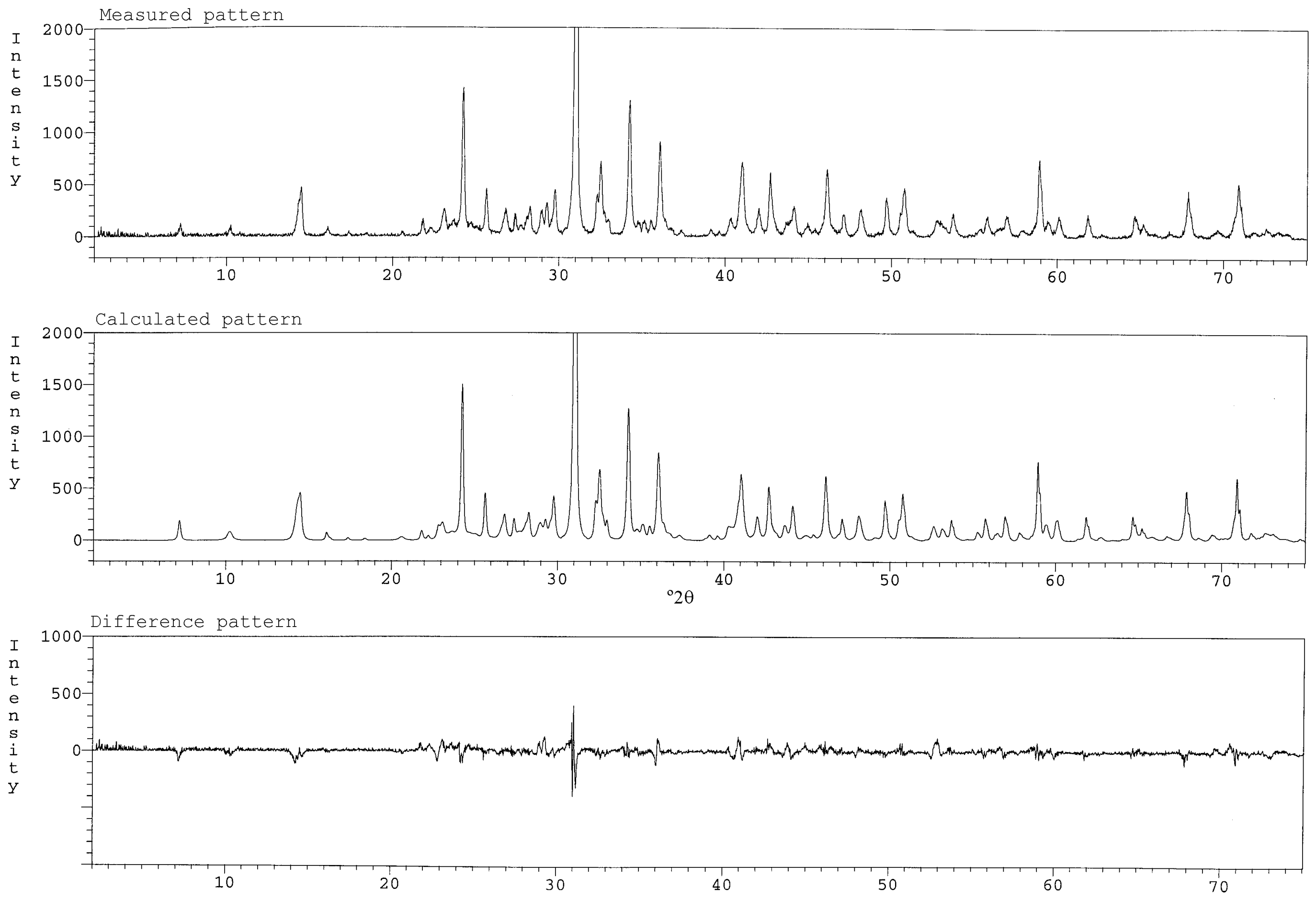

FIG. 1. Example of the graphical output from the Rietveld quantitative analysis program Siroquant showing the measured XRD pattern, the final calculated XRD pattern and the difference pattern for 'Mix 2'.

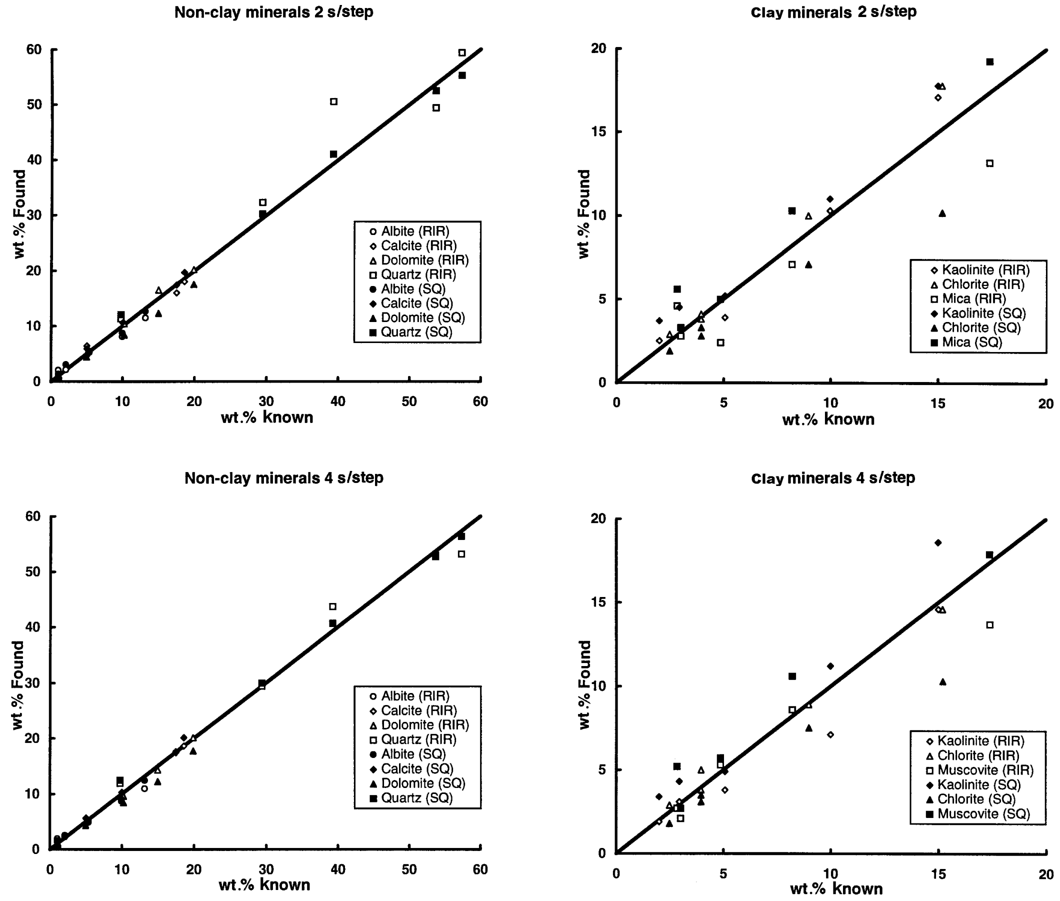

FIG. 2. Graphs of %known *vs.* %found for the four data sets.

there is some indication that the RIR method is slightly more accurate than the Siroquant method and that the accuracy of both methods is slightly improved when applied to XRD patterns counted for 4 s per step compared to those counted for only 2 s per step. For both techniques the errors appear to be normally distributed. If a single outlying error of 11.2 wt.% is excluded from the analysis of the RIR 2 s counted set, the standard deviations for all four sets of data range between 1.7 and 1.5 wt.%. Thus an uncertainty of ±3 wt.% is a reasonable estimate of the maximum uncertainty at the 2s or 95% confidence level for all and any of the phases analysed, smaller errors being much more likely given their apparent normal distribution. The limited results for estimation of amorphous content indicate that the RIR method was much more accurate than the Siroquant method. This may be related to error in estimation and removal of the amorphous background 'hump' which was necessary using Siroquant.

Although the data points are limited, Table 4 shows a statistical analysis of the absolute errors broken down by phase for each of the four sets of data. For each phase, uncertainty at the 95% confidence level is equal to ± the 2s values listed in the table. The values range from ±0.5 wt.% for the RIR method for calcite from patterns scanned for 4 s per step to ±6.6 wt.% for the RIR method for quartz from patterns scanned at 2 s per step. However, most values are <±3 wt.%, i.e. the estimate of uncertainty at the 95% confidence level when all the data are considered as a whole. Notably, the two largest estimates of uncertainty are both for quartz which is by far the largest component in four of the five mixtures. This

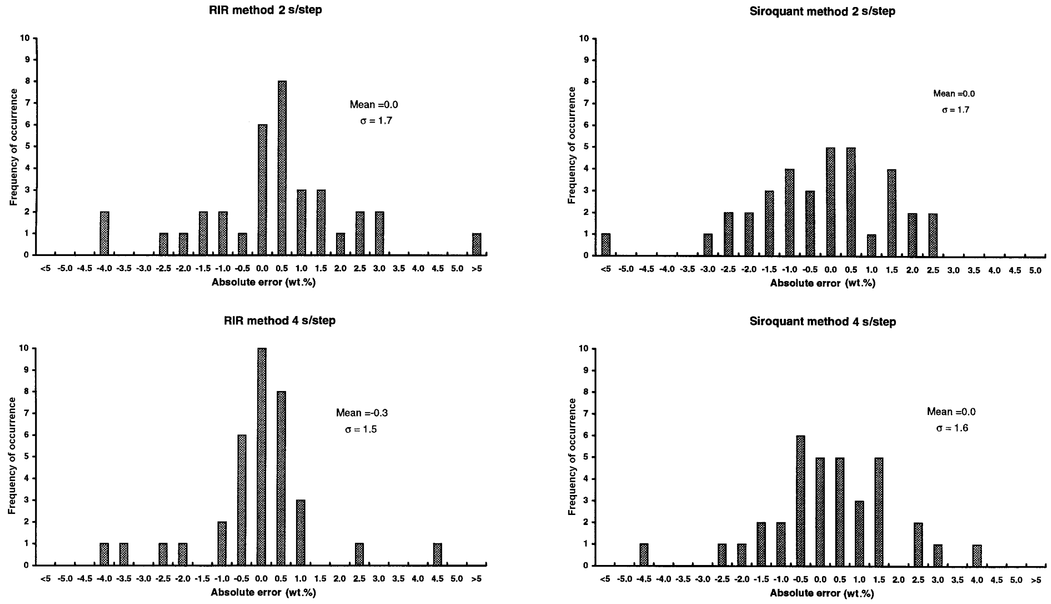

FIG. 3. Frequency distribution of absolute errors for the four data sets.

probably reflects the fact that absolute errors tend to be positively correlated with abundance, but it would require considerable effort to conduct a study based on many more mixtures covering a much wider range of compositions to test this.

DISCUSSION

Even though XRD is widely used to estimate the composition of geological samples, studies which provide a reliable indication of the accuracy of the methods used are few. As mentioned previously, the difficulty of assessing accuracy can at least be partly attributed to the lack of well characterized test samples. As a consequence, a large proportion of the studies which do attempt to assess accuracy often still have to rely on a comparison with other estimates of composition, such as those made by point counting or from normative calculations. Undoubtedly, quantitative mineralogical analysis by XRD of geological samples is unlikely ever to achieve the levels of accuracy of chemical analysis, but what then is the level of accuracy that we can hope to achieve? According to Calvert *et al.* (1989) results within 3 wt.% absolute or 10% relative of the true concentration constitute ''highly accurate'' results. In the same publication Reynolds (1989) suggested that 10% relative should be considered ''excellent''. According to Calvert *et al.* (1989) this suggestion is not entirely arbitrary but based on the experience that 3 wt.% absolute ''is about the best that can be done for typical natural rock samples containing many phases''. Notably, a blind test of five commercial laboratories in 1988 produced results in which from 26% to as much as 54% of the reported values were less accurate than this (Calvert *et al.*, 1989).

Perusal of some studies where accuracy is assessed indicates that the suggested definition of 'highly accurate' is reasonable. For example, Bish & Post (1993) using the Rietveld method to analyse prepared binary mixtures of minerals obtained results within ±2.5 wt.% of the true concentration. If it is reasonable to consider all the errors for the binary mixtures as a group (excluding Fe-rich phases where results were affected by microabsorption) then a generalized estimate of uncertainty at the 95% confidence level would be ±3.6 wt.%. Using a position sensitive detector, Cressey & Schofield (1995) and Batchelder & Cressey (1998) also reported results for prepared mixtures of two to three phases with errors typically ±2% or better. Similarly, examination of the study by Chipera & Bish (1995) based on the RIR method applied to prepared test rocks of known composition shows that ~75% of the absolute errors are

Table 3. Comparison between wt.% known and wt.% found for the five different test mixtures analysed by both the RIR and the Siroquant methods for patterns obtained by counting for both 2 and 4 s per step; also given are absolute and relative errors (%).

Method and s/step		RIR 2			Siroquant 2			RIR 4			Siroquant 4		
	%known	%found	abs. error	rel. error	%found	abs. error	rel. error	%found	abs. error	rel. error	%found	abs. error	rel. error
Mix 1													
Kaolinite	15.0	17.1	2.1	14.0	17.8	2.8	18.7	14.6	−0.4	−2.7	18.6	3.6	24.0
Chlorite	15.2	17.8	2.6	17.1	10.2	−5.0	−32.9	14.6	−0.6	−3.9	10.3	−4.9	−32.2
Muscovite	17.4	13.2	−4.2	−24.1	19.3	1.9	10.9	13.7	−3.7	−21.3	17.9	0.5	2.9
Quartz	39.3	50.5	11.2	28.5	41.0	1.7	4.3	43.7	4.4	11.2	40.7	1.4	3.6
Calcite	1.0	1.2	0.2	20.0	1.1	0.1	10.0	1.2	0.2	20.0	1.2	0.2	20.0
Dolomite	1.1	1.1	0.0	0.0	0.7	−0.4	−36.4	1.1	0.0	0.0	0.9	−0.2	−18.2
Albite	1.0	2.0	1.0	100.0	1.3	0.3	30.0	1.9	0.9	90.0	1.5	0.5	50.0
Mix 2													
Kaolinite	10.0	10.3	0.3	3.0	11.0	1.0	10.0	7.1	−2.9	−29.0	11.2	1.2	12.0
Chlorite	9.0	10.0	1.0	11.1	7.1	−1.9	−21.1	8.9	−0.1	−1.1	7.5	−1.5	−16.7
Muscovite	8.2	7.1	−1.1	−13.4	10.3	2.1	25.6	8.6	0.4	4.9	10.6	2.4	29.3
Quartz	29.4	32.3	2.9	9.9	30.2	0.8	2.7	29.4	0.0	0.0	30.0	0.6	2.0
Calcite	10.0	10.7	0.7	7.0	10.6	0.6	6.0	9.9	−0.1	−1.0	10.3	0.3	3.0
Dolomite	10.2	10.4	0.2	2.0	8.4	−1.8	−17.6	9.6	−0.6	−5.9	8.4	−1.8	−17.6
Albite	13.2	11.4	−1.8	−13.6	12.6	−0.6	−4.5	10.9	−2.3	−17.4	12.4	−0.8	−6.1
Mix 3													
Kaolinite	2.9	2.8	−0.1	−3.4	4.5	1.6	55.2	3.1	0.2	6.9	4.3	1.4	48.3
Chlorite	4.0	4.1	0.1	2.5	3.3	−0.7	−17.5	5.0	1.0	25.0	3.5	−0.5	−12.5
Muscovite	4.9	2.4	−2.5	−51.0	5.0	0.1	2.0	5.3	0.4	8.2	5.7	0.8	16.3
Quartz	53.7	49.4	−4.3	−8.0	52.5	−1.2	−2.2	53.0	−0.7	−1.3	52.7	−1.0	−1.9
Calcite	17.5	16.0	−1.5	−8.6	17.4	−0.1	−0.6	17.6	0.1	0.6	17.4	−0.1	−0.6
Dolomite	5.0	5.1	0.1	2.0	4.4	−0.6	−12.0	5.0	0.0	0.0	4.3	−0.7	−14.0
Albite	2.1	2.1	0.0	0.0	3.0	0.9	42.9	2.2	0.1	4.8	2.5	0.4	19.0
Mix 4													
Kaolinite	2.0	2.5	0.5	25.0	3.7	1.7	85.0	1.9	−0.1	−5.0	3.4	1.4	70.0
Chlorite	2.5	2.9	0.4	16.0	1.9	−0.6	−24.0	2.9	0.4	16.0	1.8	−0.7	−28.0
Muscovite	2.8	4.6	1.8	64.3	5.6	2.8	100.0	2.7	−0.1	−3.6	5.2	2.4	85.7
Quartz	57.3	59.4	2.1	3.7	55.3	−2.0	−3.5	53.2	−4.1	−7.2	56.4	−0.9	−1.6
Calcite	5.0	6.4	1.4	28.0	5.9	0.9	18.0	5.6	0.6	12.0	5.7	0.7	14.0
Dolomite	15.0	16.5	1.5	10.0	12.3	−2.7	−18.0	14.3	−0.7	−4.7	12.2	−2.8	−18.7
Albite	5.4	5.4	0.0	0.0	5.2	−0.2	−3.7	4.8	−0.6	−11.1	5.0	−0.4	−7.4

Table 3 (*contd.*)

Method and s/step		RIR 2			Siroquant 2			RIR 4			Siroquant 4		
	%known	%found	abs. error	rel. error	%found	abs. error	rel. error	%found	abs. error	rel. error	%found	abs. error	rel. error
Mix 5													
Glass	19.8	22.0	2.2	11.1	30.7	10.9	55.1	21.0	1.2	6.1	30.0	10.2	51.5
Kaolinite	5.1	3.9	−1.2	−23.5	5.2	0.1	2.0	3.8	−1.3	−25.5	4.9	−0.2	−3.9
Chlorite	4.0	3.8	−0.2	−5.0	2.8	−1.2	−30.0	3.8	−0.2	−5.0	3.1	−0.9	−22.5
Muscovite	3.0	2.8	−0.2	−6.7	3.3	0.3	10.0	2.1	−0.9	−30.0	2.7	−0.3	−10.0
Quartz	9.8	11.3	1.5	15.3	12.1	2.3	23.5	11.9	2.1	21.4	12.5	2.7	27.6
Calcite	18.6	18.0	−0.6	−3.2	19.7	1.1	5.9	18.6	0.0	0.0	20.1	1.5	8.1
Dolomite	19.9	20.2	0.3	1.5	17.5	−2.4	−12.1	20.1	0.2	1.0	17.7	−2.2	−11.1
Albite	10.0	8.0	−2.0	−20.0	8.7	−1.3	−13.0	8.6	−1.4	−14.0	9.0	−1.0	−10.0

TABLE 4. Statisical analysis of absolute errors by phase.

Mineral		RIR 2 abs. error	Siro 2 abs. error	RIR 4 abs. error	Siro 4 abs. error
Albite	Mean	−0.6	−0.2	−0.7	−0.3
	2s	2.6	1.7	2.5	1.4
Calcite	Mean	0.0	0.5	0.2	0.5
	2s	2.3	1.0	0.5	1.2
Chlorite	Mean	0.8	−1.9	0.1	−1.7
	2s	2.2	3.6	1.2	3.7
Dolomite	Mean	0.4	−1.6	−0.2	−1.5
	2s	1.2	2.1	0.8	2.1
Kaolinite	Mean	0.3	1.4	−0.9	1.5
	2s	2.4	2.0	2.5	2.7
Muscovite	Mean	−1.2	1.4	−0.8	1.2
	2s	4.5	2.4	3.4	2.4
Quartz	Mean	0.6	0.3	0.3	0.6
	2s	6.6	3.7	6.4	3.1

s: standard deviation

within ±3 wt.% of the known concentration. Again if the errors are taken as a group, a generalized estimate of uncertainty at the 95% confidence level is ±5.2 wt.%.

Notable amongst studies which compare XRD results to modal and/or chemical data are that on granitoids by Davis & Walawender (1982), that on igneous and metamorphic rocks by Hill *et al.* (1993), and that on sedimentary rocks by Mumme *et al.* (1996). Davis & Walawender (1982) used an RIR method and calculated variance by a rigorous procedure for error propagation. A generalized estimate of uncertainty calculated from the reported variances is ±3.1 wt.% at the 95% confidence level. In the study of Hill *et al.* (1993) and the related study of Mumme *et al.* (1996), absolute errors were estimated from the Rietveld analysis. Generalized as groups, estimates of uncertainty at the 95% confidence level derived from the reported standard deviations are ±1.6 wt.% for the igneous rocks and ±1.3 wt.% for the sedimentary rocks. However, accuracy cannot be evaluated explicitly in those studies because the true compositions of the rocks which were analysed are unknown. For the igneous study, if the optical and normative modes were assumed to be the true concentrations, the estimate of uncertainty at the 95% confidence level would be ±6.7 wt.%. For the sedimentary study, such a direct comparison cannot be made because the rocks were too fine grained to determine modes by point counting and the normative approach was not deemed to be applicable.

Thus this selection of some very careful studies based on both the traditional RIR approach and on full-pattern methods seem to lend support to the suggestion that results within 3 wt.% absolute represent ‘highly accurate’ results. In the present investigation, >90% of the results fall within this definition. Indeed >75% are within 2% absolute of the known weighed amounts. Improvement in accuracy between the data sets counted for 2 s per step compared to 4 s per step was evident but not especially significant. Perhaps more importantly, the two sets of analyses demonstrate something of the reproducibility of the methods employed since the samples were stored in vials between runs so that the two sets are from independent loadings of the sample holders. This reproducibility is believed to be largely a result of the method of sample preparation whereby McCrone milling for 12 min ensures an adequate reduction of particle size and spray drying of the resulting slurry provides a powder free from the effects of preferred orientation. Proper reduction of particle size reduces the likelihood of serious errors due to particle statistics, microabsorption, and extinction (Brindley, 1980;

Snyder & Bish, 1989; Bish, 1994), whilst the combination of particle size reduction and spray drying ensures that preferred orientation is eliminated.

No matter how sophisticated the process of data treatment, there can be no doubt that sample preparation is the first key step in quantitative analysis, not only in terms of reducing potential sources of error but also in terms of its practical application. For example, although the application of Rietveld quantitive analysis by Hill *et al.* (1993) and of Mumme *et al.* (1996) demonstrate the wonderful potential of this method for complex geological samples, they were not successful in applying corrections to account for severe problems with preferred orientation in normal back-loaded or side-drifted cavity mount samples. Instead they resorted to dealing with preferred orientation by using small samples mounted in rotating capillary tubes but with the result that the XRD patterns took an average of ~45 h to collect. Undoubtedly, the Rietveld method advocated by these and other authors has many potential advantages but such long times for data collection do little to popularize its application to the routine. If preferred orientation is tackled by spray drying, however, samples of the usual size can be presented to the X-ray beam and data collection times are no longer prohibitive, as demonstrated herein.

Even though the Rietveld method has its advantages, it is likely that less sophisticated methods will continue to have their place. The results of this study suggest that accuracy may not be the factor that determines which method is used. Indeed, where true (disordered) clay minerals are concerned, the application of the Rietveld method is still limited principally because of two-dimensional diffraction effects (Bish, 1993). Methods to simulate the complex diffraction patterns of disordered clay minerals have yet to be incorporated into Rietveld type software codes. The approach taken by Siroquant uses an additional database of ‘observed’ patterns to deal with clay minerals (Taylor & Matulis, 1994), but the database is limited and in practice the ability to match the clay minerals in any particular sample often appears less than satisfactory. With the RIR method, accurate clay mineral analysis depends on an accurate measurement of the RIR, and an appropriate strategy for measuring integrated intensity and dealing with interferences from other phases. Even though non-clay-sized mica and chlorite were used in this study, this was for convenience of available quantities only and does not mean that there would be shortcomings in applying the methods to more disordered clays. Additionally, intrinsic variation in the RIR for various clay mineral species needs to be evaluated (Reynolds, 1989) and if methods of sample preparation such as spray drying are used and RIRs related to intensity standards (Schreiner, 1995) there is the potential to determine RIRs of universal application. Furthermore, with preferred orientation eliminated from the problem, use can be made of multiple peak RIRs to account for variable chemical composition (cf. Chipera & Bish, 1995). The RIR for chlorite reported in Table 2 based on the integrated intensity of both the 003 and 004 reflections is an example of this.

CONCLUSIONS

Quantitative XRD analysis of clay and other minerals in sandstones, and indeed geological samples generally, is routinely capable of an accuracy to within ±3 wt.% at the 95% level. Both RIR and Rietveld methods applied in a routine fashion provide similar results. The success of both is believed to depend on sample preparation and the importance of this aspect cannot be overstated. Essentially, through attention to the necessary reduction of particle size and the elimination of preferred orientation by spray drying, sample preparation is standardized to a degree that is not possible by other routine techniques.

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