

QUANTITATIVE X-RAY POWDER DIFFRACTION ANALYSES OF CLAYS USING AN ORIENTING INTERNAL STANDARD AND PRESSED DISKS OF BULK SHALE SAMPLES

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Abstract—Quantitative analysis of clay minerals by X-ray powder diffraction requires oriented clays in order to increase detection limits of the analyses. This is achieved commonly either by smear or sedimentation techniques; however, these techniques can lead to poor analytical precision when used with an internal standard because they often produce non-homogeneous internal standard–clay mineral mixtures. Compaction of bulk shale material at 8000 psi in an hydraulic press produces preferred orientations comparable to that produced by smear or sedimentation. When used with a suitable platy internal standard which provides an estimate of clay mineral preferred orientation, excellent analytical precision is achieved routinely. Several lines of experimental evidence indicate that 1–5 μm MoS_2 is an ideal orienting internal standard for use with compaction mounts.

INTRODUCTION

Although highly accurate and precise quantitative mineral analyses of soil clay material apparently have been attained recently (Roberts and Johnson, 1974), clay mineral percentages in rocks and soils usually are not determined by such complex, time-consuming, and expensive approaches. The most widely used analytical methods employ X-ray powder diffraction alone. Although X-ray powder diffraction methods will never produce analytical results of the same precision and accuracy as more complex methods, they provide very rapid estimates of major differences in clay minerals between samples. Because rapid analytical methods facilitate the study of many samples, the detection of major stratigraphic and geographic clay mineral trends, which often are important for many geologic studies, is facilitated. Rather than exceptional accuracy and precision, therefore, the major requirements for many clay studies is that speed, good reproducibility, and internal consistency should be achieved easily, and that consistent comparison of results between different laboratories is possible. Interlaboratory comparisons necessitate that a standard analytical method be adopted, but a commonly accepted technique has not yet been developed.

A wide variety of X-ray powder diffraction techniques for quantitative clay mineral analyses have been published in recent years, but none is clearly superior to the others. Some do not utilize an internal standard, as for example the studies of Schultz (1964) who used empirically determined factors which related peak intensities to clay mineral percentages. Other studies eliminate some of the problems resulting from the lack of an internal standard by determining the mass absorption coefficients of samples in

various ways (Carroll, 1970). Some type of internal standard is often used because of numerous difficulties resulting from differences in mass absorption characteristics within samples and between samples and analytical standards, and because of unavoidable variations in instrument operating parameters. Various internal standards have been proposed, including fluorite, tetra-methyl ammonium stannic chloride (R. L. Handy, personal comm., 1975), boehmite (van der Marel, 1960; Gibbs, 1967), aluminum powder (Burtner, 1974), zinc hydroxide (Mossman *et al.*, 1967), and molybdenum sulfide (Quakernaat, 1970).

In quantitative analyses of clays, oriented clay mounts obtained either by smear or sedimentation techniques generally are utilized in order to increase the detection limits of the analyses. These methods, when used in conjunction with an internal standard, may produce poor analytical results because non-homogeneous clay mineral–internal standard mixtures may be produced by the techniques used to obtain orientation of the clays. This may occur whenever the specific gravity and particle size of the internal standard powder are different than those of the clay material being determined. Another problem may develop when sedimentation is used to obtain a specific size fraction for XRD analyses. Analyses of a specific size fraction may introduce bias into the results because of different relative amounts of each clay type in different size fractions (Schultz, 1955; Gibbs, 1965; Towe, 1974). Most geologists are interested in relative or absolute clay mineral percentages in a bulk rock, and not those in a single arbitrarily chosen fraction.

These considerations led us to attempt to determine clay mineral percentages in dry bulk shale samples

of Pennsylvanian-age rocks from southern Iowa using an orienting internal standard, with orientation of the clay produced by compaction in an hydraulic press (Scott, personal communication, 1975). We have found that gently disaggregated shales compacted into disks at 8000 psi exhibit intense 001 clay reflections, the intensity depending directly on the compaction pressure. A previous study (Fenner and Hartung, 1969) found that the basal reflections of halloysite samples compacted at 20,000 psi were far more intense than oriented mounts produced by sedimentation; we found in our study that lesser pressures were adequate to produce peaks of comparable intensity to those of sedimented clays, without the use of an aqueous dispersion media. When used with an orienting internal standard such as MoS₂, compacted disk mounts of bulk shales routinely provide very good reproducibility. Preparation is rapid compared to sedimentation methods of producing preferred orientation, but comparable orientation is produced. In addition, the method allows an evaluation of the bulk mineral composition rather than that of a specific size fraction. The method investigated in this study has all the advantages resulting from the use of an internal standard, but does not suffer from problems resulting from the use of an internal standard together with sedimentation or smear mounting methods.

THEORETICAL BASIS OF QUANTITATIVE XRD ANALYSIS OF CLAY MINERALS

The integrated intensity of an *hkl* X-ray powder diffraction plane for a single component in a poly-component mixture is affected by numerous factors in addition to the percentage of that component. Among these factors are (1) those related to the component itself; these include its density, chemical composition, crystalline perfection, particle size, and degree of its crystallographic orientation in the mixture, and (2) those related to the other components; these include especially those matrix characteristics which affect the mass absorption coefficient of the mixture, i.e. its density and bulk composition. If any of these factors vary, then the *hkl* diffraction intensity for that component will vary without any change in its actual concentration in the sample. A widely utilized method for minimizing these difficulties is to add a reference or internal standard in constant proportions to all samples and analytical standards. Under this condition, for a completely randomly oriented mineral component and reference standard, it can be shown (Klug and Alexander, 1974) that the component's concentration in an unknown sample can be related to the ratio of the integrated intensity of a selected *hkl* reflection of the component to that of the reference standard

$$x_{JU} = k_U \frac{I_{JU}}{I_{SU}} \quad (1)$$

where *x* refers to weight percentage of the component

J in an unknown sample *U*, the subscript *S* refers to the internal standard, *k_U* is a constant depending on the characteristics of component *J* in the unknown sample and on the geometry of the X-ray diffraction instrument, and the primes indicate that there are no preferred orientations affecting the intensity of either the component or the internal standard reflections.

However, in dealing with platy clay minerals there is a strong but variable, preferred orientation, and there may be preferred orientation of the internal standard if it exhibits good cleavages or a platy or needle-like morphology. Thus:

$$I'_{JU} = \alpha_{JU} I_{JU} \quad (2)$$

$$I'_{SU} = \alpha_{SU} I_{SU} \quad (3)$$

where the α 's are factors used to correct for preferred orientation.

Substituting for the integrated intensities in equation (1) from (2) and (3) gives:

$$x_{JU} = k_U \frac{\alpha_{JU} I_{JU}}{\alpha_{SU} I_{SU}} \quad (4)$$

In the internal standard method usually we have mixed a set of analytical standards containing known amounts of the clay mineral component *J*, and the same proportions of internal standard as added to unknown samples. From this data we draw an analytical standard curve, which then is used to determine the amount of component *J* in the unknown samples by comparing the ratio of clay peak to internal standard peak areas. In the analytical standards, *A*, we have the same relationship as in (4) holding, i.e.

$$x_{JA} = k_A \frac{\alpha_{JA} I_{JA}}{\alpha_{SA} I_{SA}} \quad (5)$$

Dividing (4) by (5) and rearranging gives:

$$\frac{I_{JA} x_{JU}}{I_{SA} x_{JA}} = \frac{k_U \alpha_{JU} \alpha_{SA}}{k_A \alpha_{SU} \alpha_{JA}} \frac{I_{JU}}{I_{SU}} \quad (6)$$

Accurate determination of the concentration of component *J* in an unknown sample requires, when the amount of component *J* in the unknown and in the analytical standards are equal, that the ratio of peak intensities of the component to that of the internal standard be equal in both unknown and in analytical standard mixtures, i.e. when $x_{JU} = x_{JA}$, then $I_{JA}/I_{SA} = I_{JU}/I_{SU}$. For this condition to hold it is necessary that:

$$\frac{k_U \alpha_{JU} \alpha_{SA}}{k_A \alpha_{SU} \alpha_{JA}} = 1 \quad (7)$$

In order for this to be true for all samples containing the unknown component being determined, it is necessary that $k_U = k_A$ and that $\alpha_J = c\alpha_S$, where *c* is a fixed constant, under all conditions. For k_U to equal k_A , it is necessary that the chemical and physical characteristics of the mineral component *J* in the unknown be identical to those of the component in

the analytical standards. For example for kaolinite analyses, the kaolinite chosen for an analytical standard must be identical in particle size, crystal perfection, chemical composition, etc. to the kaolinite occurring in all unknown samples. To the degree that this is not true, the ratio k_U/k_S will vary from sample to sample, even though the actual amount of kaolinite might be constant. Likewise, for $\alpha_J = c\alpha_S$, it is necessary that the orientation of the internal standard S mirror that of component J under all conditions. If this is not true, then poor accuracy and precision may occur because of variable preferred orientations of the mineral components being sought compared to that occurring in the analytical standards. For minerals without strong preferred orientation, the orientation factor is negligible; however, for platy clay minerals this factor cannot be ignored if accurate and precise determinations are being sought.

From these considerations, it is clear that two conditions must be satisfied for accurate quantitative XRD analyses of clay mineral mixtures; the clays used in making the analytical standards must be very similar to the clay species that occur in the unknown mixtures, and the internal standard chosen for the study must be similar in morphology and particle size to the unknown clays, i.e. it must be an orienting internal standard.

CHOICE AND EVALUATION OF ORIENTING INTERNAL STANDARD

Although quantitative clay analyses by X-ray powder diffraction involve two fundamental problems, one related to the choice of analytical standard clays used in constructing standard curves, and one related to the choice of internal standard, the present study has attempted to provide information about only the latter problem. Using sample preparation methods discussed in the appendix, and utilizing analytical standard clays considered similar to those encountered in our study of Pennsylvanian clays of southern Iowa, we have studied the suitability of MoS_2 as an orienting internal standard when used in compacted disks of bulk shale samples. The minerals analyzed were three very common components in the shales encountered in our study, kaolinite, mica-clay (illite) and quartz.

There are several requirements for an orienting internal standard, most of which are common to those for any type of internal standard, which severely restrict possible choices. Any internal standard for X-ray powder diffraction analyses should (1) exhibit suitable crystallinity and particle size in order to give sharp diffraction peaks, (2) be readily available, (3) provide intense diffraction lines near the analysis lines, (4) not cause interference by superposition on the analysis peaks, and (5) not already be present in variable amounts in the samples being analyzed. In addition for clay analyses, it should have (6) a platy morphology and a suitable particle size so that it will

orient to the same degree as platy clay particles, (7) stability and non-reactivity to the chemical and physical treatments used to differentiate clay mineral species, and to atmospheric fluctuations and conditions. A last consideration is that the internal standard material should be of similar specific gravity as clay minerals if sedimentation techniques are utilized to obtain oriented clay samples for analysis; otherwise, selective sedimentation will cause a variation in the relative amount of internal standard and the unknown clay components in the surface layers of the mixture after sedimentation onto a support media.

The first workers to suggest an orienting internal standard for use in clay analyses seem to be Mossman *et al.* (1967) who tested $\text{Mg}(\text{OH})_2$, brucite; $\text{Al}(\text{OH})_3$, gibbsite; $\text{Zn}(\text{OH})_2$; CdCl_2 ; SnS_2 ; MoS_2 , molybdenite; and pyrophyllite. They concluded that zinc hydroxide was the most suitable choice because it possessed an intense diffraction peak near the major clay analytical peaks, and because it was of suitable specific gravity for use in standard sedimentation techniques. Pyrophyllite was also suitable in its specific gravity and peak locations, but its diffraction peak was relatively weak, thus requiring the addition of large amounts of the mineral to unknown samples in order to produce usable diffraction lines. They pointed out, however, that $\text{Zn}(\text{OH})_2$ is not stable in contact with moist air or at temperatures above 300°C . Quakernaat (1970) found that artificial MoS_2 seemed more suitable for analyses of clays than zinc hydroxide. He found that the use of a thickener composed of sodium-carboxy-methyl cellulose added to the solutions used in preparing sedimentation mounts minimized selective sedimentation of the heavier MoS_2 compared to the clays being studied; however, he was not able to eliminate this problem completely in his work.

In our own study, we have evaluated MoS_2 for use as an orienting internal standard when it is used in compacted bulk shale disks. The efficiency of the MoS_2 as an orientation indicator and the factors that affect the relative intensity of clay and MoS_2 diffraction peaks when used in compacted shale disks were evaluated in several ways. The first was by determining the linearity of analytical standard curves when the weight percentages of standard kaolinite, mica-clay and quartz were plotted against the ratio of peak areas of selected analysis peaks to the 6.15 \AA internal standard peak. If the internal standard orients to the same degree as the standard clays, then with constant instrumental conditions, $\alpha_{JA} = c\alpha_{SA}$ of equation (5) and a linear function should be obtained. Initial plotting of data points showed that nearly linear curves were obtained for the clay minerals but not for the quartz, the latter non-linearity being expectable because of the different morphology of quartz compared to the platy internal standard. Because of their evident linearity, a linear regression analysis was used to determine the best fitting linear curve for the clay minerals. In addition, a standard error of regression

Table 1. Statistical evaluation of standard mineral analytical curves

Clay mineral	Standard error of regression	Confidence level (error term) for 50% concentration
Mica-clay	0.00436	± 0.552
Kaolinite	0.081	± 10.931

and an error term, expressed as a confidence level at 50% standard mineral concentration for the 95% level was also calculated (Table 1).

A measure of the variability of the relative orientation of the internal standard compared to that of the minerals being determined is provided by the replication error. Five disks of the same Pennsylvanian shale, each containing constant concentrations of the internal standard, were prepared using 8000 psi pressure, and analyzed with constant XRD settings over a period of about three hours. As can be seen from Table 2, the sample replication error is small for the clay minerals but relatively large for quartz.

In addition to linearity of standard curves and replication errors, another type of test was performed by determining the changes in ratios of peak areas from an unpressed, nearly randomly oriented sample mount compared to the same ratio in samples compacted at different pressures. A Pennsylvanian shale from southern Iowa was prepared and mixed with the internal standard. Ten fractions of this mixture were then mounted in the following manner: (1) five were used in a standard back-filled powder holder (McCreery, 1949) without compaction, and each then X-ray scanned, (2) the other five splits were transferred to aluminum rings and were progressively compacted at 1000 psi, 2000 psi, 4000 psi, 8000 psi and 10,000 psi with X-ray scans after each compaction. If the internal standard maintained constant orientation relative to the clay minerals and quartz in this shale, then the ratio of peak areas for these minerals to the internal standard peak area should remain constant even though preferred orientation of the platy clays increases during the progressive compaction. It is clear (Table 3) from this series of tests that marked increases in orientation of clays and the MoS_2 occurred during compaction. In the back-filled powder mounts for example, in which no compaction occurred and with relatively poor preferred orientation, the mean area of the kaolinite 7 Å peak was 62.6 units compared to a mean of 56 units for the MoS_2 6.15 Å peak; these areas increased to a mean

Table 2. Replication tests for Pennsylvanian shale sample

Mineral	Mean* percentage concentration	S.D.	Coefficient of variation
Kaolinite	51%	0.0122	2.40%
Mica-clay	39%	0.0114	2.89%
Quartz	9.4%	0.0114	12.10%

* Mean of five disks prepared from same bulk shale.

of 126 units for kaolinite and 111 units for MoS_2 when the material was compacted at 1000 psi; and a progressive increase in both peak areas with greater compaction pressure occurred until at 10,000 psi, the mean of the kaolinite peak area was 238 units compared to 231 (estimated since the peaks were slightly offscale) for MoS_2 . These observations, in which progressive orientation of platy minerals develops with progressive compaction pressures, are in accord with numerous published reports on the effects of mechanical compaction upon clay material containing various amounts of pore water (Martin and Ladd, 1975; Tchalenko, Burnett and Hung, 1971; Clark, 1970).

Although the absolute intensities of clay and MoS_2 peak areas increased markedly during compaction, the ratio of the peak areas remained nearly constant over the entire series of runs, giving 7.2% and 4.2% coefficients of variation for kaolinite/ MoS_2 and mica-clay/ MoS_2 peak area ratios. A much different result, again expectable, was found for quartz which resulted in 68% coefficient of variation. The large changes in quartz/ MoS_2 indicates that progressive orientation of the MoS_2 developed whereas quartz remained nearly unaffected during compaction.

We believe these several lines of evidence clearly prove the suitability of MoS_2 as an orienting internal standard in compacted disks of bulk shales, but all these experiments were performed using either our standard analytical mixtures or similar Pennsylvanian shales, all prepared in the same manner. Thus the effects of sample preparation, particle size, and bulk mineralogy on the peak area ratios had not yet been evaluated; these effects were next investigated.

The effects of sample grinding are summarized in Table 4. Two separate splits of the same Pennsylvanian shale were prepared in different manners with regard to grinding. One of the splits already containing MoS_2 was ground for six hours in a mechanical mortar and pestle. The other split, not containing MoS_2 , was ground for two hours in the mechanical mortar and pestle. For this split, the internal standard MoS_2 was added after grinding and the two substances gently mixed in an agate mortar and pestle. Each of the two splits was then analyzed in duplicate using constant XRD conditions. In these analyses the effects of comminution on the ratio of clay peak areas to that of the internal standard will be evident. For the first split, comminution occurred both for the clay components and the internal standard since they were mixed together before grinding took place; if equal comminution occurred for both materials, then there should be no change in the peak area ratios. For the second split, comminution was limited to the clay minerals since MoS_2 was not present in the sample during grinding; we should expect to find a major change in the diffraction intensity ratios since changes in particle sizes are known to affect X-ray powder diffraction intensities. The results show that comminution of the clays followed by addition of MoS_2 to the ground material produces large effects on the

Table 3. Results of progressive compaction of sample disks on peak areas of minerals and internal standard, MoS₂

Mineral	Compaction pressure	Peak area* arbitrary units	Ratio of mineral peak area to area of 6.15 Å MoS ₂ peak	S.D.	Percentage coefficient of variation
Kaolinite	0	7Å; 62.6	1.26	0.15	12%
	1000	126	1.14	0.08	7
	2000	168	1.09	0.06	5.6
	4000	196	1.09	0.025	2.3
	8000	225	1.10	0.03	2.9
	10000	238	1.02	0.05	4.8
Percent coefficient of variation of areas of 7 Å/6.15 Å peaks—7.2%					
Mica-clay	0	10Å; 45.5	0.91	0.13	14%
	1000	110	0.99	0.11	11
	2000	144	0.93	0.045	5
	4000	174	0.97	0.098	10
	8000	196	0.96	0.03	3
	10000	203	0.87	0.16	1.8
Percent coefficient of variation of areas of 10 Å/6.15 Å peaks = 4.6%					
Quartz	0	4.26Å; 35	0.73	0.23	31
	1000	42	0.37	0.08	20
	2000	38	0.25	0.03	13
	4000	38	0.21	0.02	11
	8000	41	0.20	0.014	7.5
	10000	38	0.15	0.03	18
Percent coefficient of variation of areas of 4.26 Å/6.15 Å peaks = 68%					

* Mean of five splits of prepared bulk sample, Pennsylvanian shale from southern Iowa.

analytical results compared to those obtained on the same shale which had been gently disaggregated in a mortar and pestle rather than ground. Comminution of both the clay and internal standard by grinding them together produces some changes in analytical results compared to that obtained on unground shale material, but the difference is comparatively minor.

The effects of grinding on the relative intensities

of clay and internal standard diffraction peaks probably can be attributed to changes in the relative numbers of diffracting particles by the grinding process. When both types of materials are ground together, the number of diffracting particles of both materials is increased, thus increasing the diffraction intensities of both. Under the grinding method utilized in our experiments, however, clay particles apparently are slightly more affected by grinding than

Table 4. Effect of grinding shale sample on analytical X-ray powder diffraction results

Peak areas (arbitrary units)			Ratio of peak areas, Clay/MoS ₂	
Kaolinite 001	Mica 001	MoS ₂ 002	Kaolinite/MoS ₂	Mica-Clay/MoS ₂
(A) Sample containing MoS ₂ ground together for 6 hr in automatic mortar and pestle. Single analyses of two sample disks compacted at 8000 psi.				
235	211	189	1.24 (68%)*	1.12 (55%)
235	181	200	1.18 (65%)	0.91 (45%)
(B) Sample ground for 2 hr in automatic mortar and pestle, then MoS ₂ added to ground sample. Single analyses of two sample disks compacted at 8000 psi.				
306	227	161	1.91 (102%)	1.41 (72%)
285	209	155	1.84 (99%)	1.36 (69%)

* The percentage figures in parentheses after each peak area ratio correspond to the clay mineral percentage as determined from these ratios—using an analytical curve based on known mixtures of kaolinite and mica-clay. When percentages were greater than 100% they were obtained from extrapolation of the linear analytical curves.

The percentages of kaolinite and mica clay for this shale were determined previously to be 51% kaolinite and 37% mica-clay, using routine procedures described in the appendix on analytical procedures.

MoS₂ particles as shown by the slightly greater enhancement of clay peak intensities compared to those of the internal standard. When grinding is limited to shale material, the number of diffracting clay particles is greatly increased relative to that of the internal standard so that a large change in the diffraction intensity ratios of the two materials occurs.

Because grinding proved to be so significant, we have concluded the gentle disaggregation of shale samples without rigorous grinding or pulverizing probably is advisable in order to obtain consistent analytical results. It is clear that clay particle sizes within unknown samples exert major effects on analytical accuracy. If unknown sample clays differ greatly in particle sizes compared to the clays used in analytical standards, then relatively large errors in analysis will result. This conclusion, however, does not indicate lack of efficiency of MoS₂ as an orienting internal standard; similar effects will occur with any potential internal standard because the difficulty arises from differences within the clays themselves, rather than from characteristics of the internal standard material.

A final test of the internal standard used in the present study was for evaluating the effects of dilution and of changes in the mass absorption characteristics of sample material upon analytical results. A mixture containing a known amount of Beaver's Bend illite and kaolinite was mixed with three different dilutants chosen to give a range in X-ray absorption characteristics. The dilutants were quartz, a relatively poor absorber; calcite, a stronger absorber; and pyrite, a very strong absorber of X-rays (Carroll, 1970). According to theoretical arguments, dilution and mass absorption effects should not affect analytical results provided the internal standard substance is suitable for reference purposes. The results (Table 5) showed that dilution and X-ray absorption effects produced relatively minor analytical discrepancies. Discrepancies between expected and observed results were especially small with quartz as dilutant; with calcite, the discrepancies were small for kaolinite but larger for the mica-clay; with pyrite, relatively large discrepancies were found for both clays. Although pyrite produced significant effects on analytical results, such large pyrite concentrations as used in the test are very uncommon in shales. These results indicate that the techniques used in the present study should provide acceptable analytical results regardless of bulk sample composition as long as the samples are not strongly enriched in heavy X-ray absorbers.

EVALUATION OF COMPACTED DISKS MOUNTING METHOD

On the basis of our work we found that very strong preferred orientation of clay minerals develops when a bulk shale is subjected to strong unidirectional compaction. This preferred orientation produces basal X-ray powder diffraction peaks for platy clay particles

Table 5. Effect of dilution with different compounds on analytical results

Dilutant	Percent clay found		Percent clay expected	
	Kaolinite	Illite	Kaolinite	Illite
Calcite	36%	12%	35%	15%
Quartz	34%	17%	35%	15%
Pyrite	27%	11%	35%	15%

Original analytical standard: 30% Beaver's Bend illite, 70% kaolinite (A. P. Green, 211) Ratio of Dilutant to clay mixture = 50:50; internal standard added after dilution.

of comparable intensity to that produced by sedimentation mounts. The use of compacted disks will be applicable to a wide variety of rock types, but we have found that compacted disks are not suitable for use with very fine-grained material. Using the techniques outlined by Jackson (1956) we obtained < 2 μm fractions of Beaver's Bend illite, and attempted to determine if the use of fine fraction clay material has major effects on the ratio of clay to internal standard peak areas. We found exceptional difficulty in producing good quality compacted disks for this material because disk surfaces became deformed upon release of compaction pressures, thus producing convex upper surfaces. After attempting to obtain flat-surfaced disks by using several different compaction pressures on different samples, we were finally able to obtain one apparently flat disk using 2000 psi pressure. Analysis of this disk gave results consistent with those obtained with unfractionated illite. The difficulty in obtaining the disk indicates that very fine-grained materials are not suitable for quantitative analyses using compaction because non-planar disk surfaces lead to anomalous X-ray results, including changes in peak intensities, line widths, and peak maxima locations. For the large majority of bulk shale samples, this problem is insignificant, but occasionally very fine-grained shales will be encountered which will not be suitable for compared disk mounts.

In addition to this limitation, we have obtained anomalous analytical results with a few samples, about two percent of the total samples studied. One anomaly is that the amount of clay determined occasionally totaled more than 100%. In all cases this error resulted from a gross difference between the analytical standard and unknown sample clays. This source of error is not a result of the compacted disk method employed, but rather results from a commonly observed feature of clay analyses in general; only rarely will the diffraction characteristics of sample clays be closely similar to those of clays chosen as analytical standards. A second type of anomaly that we have occasionally encountered are poorly defined, weak clay diffraction patterns which result in anomalously small clay mineral percentages even though the samples were clay rich. We are not certain of the cause of this anomaly, but we have found that these samples will not provide intense XRD peaks using standard smear mounts either.

These weak diffraction peaks may be caused by poor clay crystallinity or mixed-layer clay diffraction interferences. However, it may be that some clays will not orient well during compaction. A lack of orientation will also reduce the intensities of the basal reflections for the clays.

CONCLUSIONS

As with nearly any analytical method, we have found that there are limitations and potential difficulties inherent in the use of compacted disks of bulk shales in which MoS_2 is used as an orienting internal standard. However, on the basis of our studies we have concluded that the general method, as outlined in the appendix, provides an alternative, highly reproducible, analytical procedure for quantitative X-ray powder diffraction analyses of platy clay minerals. The use of compacted bulk samples eliminates any possibility of selective sedimentation of the internal standard compared to the shale minerals, and leads to an evaluation of total sample components rather than that of a specific size fraction as obtained with sedimentation clay mounting procedures. The use of 1–5 μm MoS_2 as an orienting internal standard increases analytical precision and accuracy by correcting for variable clay mineral preferred orientation, and by minimizing sample matrix effects. Although problems remain in attempting to quantify clay mineral analyses, the main one being that of obtaining clays for use as analytical standards, we believe that the procedures proposed here will minimize many of the difficulties in quantitative analysis of clay minerals by X-ray powder diffraction.

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APPENDIX I: ANALYTICAL TECHNIQUES FOR QUANTITATIVE ANALYSIS

Sample preparation

Approximately 1–1.5 g bulk shale samples were disaggregated with a minimum of grinding in an iron mortar and pestle to < 100 mesh size. The ground sample was then saturated with 40 ml of 1N $\text{MgCl}_2 \cdot 6\text{H}_2\text{O}$ solution and allowed to remain in contact with the solution for approximately 15 min. At the end of this interval, the supernatant liquid was poured off and the clay rinsed twice with distilled water. This Mg^{2+} treatment develops uniform cation saturation, necessary since the nature of cations in interlayer spaces can affect the expansion of expandable clay minerals. The washed residue was then mixed with two ml of tri-*n*-hexylammonium acetate solution (Burtner, 1974), prepared from trihexylamine, $(\text{CH}_3(\text{CH}_2)_5)_3\text{N}$ by procedures outlined by Rex and Bauer (1965). The amine, which expands smectite clay to about 17 Å, was used rather than the standard ethylene glycol or glycerol because it is so tightly bound that treated clays can be dried without causing contraction of previously expanded material. Dried clays should be used for compacted disks, otherwise shrinkage of the drying clays will produce poor analytical results. Preliminary trials with various

amounts of the amine solution showed that two ml were enough to expand samples composed solely of smectite clays, so this amount is more than sufficient to cause complete expansion of unknown sample clays. The treated samples were then dried on a hot-plate under a fume hood at 50–60°C, temperatures insufficient to contract the expanded clays. The dried samples were then reground to <100 mesh size.

Ten percent of the internal standard mixture, composed of 85% diatomaceous earth and 15% lubricant grade 1–5 μm MoS_2 , obtained from Atlantic Equipment Engineering, Bergenfield, New Jersey, was then added to all samples and standards and mixed together thoroughly to produce a homogeneous sample–internal standard mixture. The internal standard was first mixed with diatomaceous earth because the extremely intense MoS_2 peak at 6.15 Å requires that very small amounts of this substance be added to produce peaks similar in height to those of the minerals being analyzed. When very small amounts of a substance are added to another powder, both weighing errors and mixing difficulties are reduced if the substance is first mixed with a dilutant such as diatomaceous earth which has little effect upon analyses.

The final mixture was then pressed into an aluminum ring, 2.5 cm i.d. using a hydraulic press at 8000 psi using a two stage increase in pressure; the pressure was first increased to 4000 psi and held for 5 sec, and then brought to 8000 psi for an additional 5 sec. The two stage procedure seemed to enhance clay and internal standard peak intensities slightly, although the amount of time that pressure is exerted has only minor effects on peak intensities. The sample disk was then placed in a specially-manufactured holder for insertion into a standard Norelco goniometer. Occasionally a backing of reagent grade NaCl was used for the pressed disks to prevent relatively coarse-grained materials from falling apart after being pressed. NaCl was used rather than the more commonly used boric acid powder because the latter exhibits an XRD peak at nearly the same location as MoS_2 .

Samples were then scanned from 2° to 30° at 1°/min using a high intensity copper tube at 40 Kv and 20 Ma, with a two and one-half second time constant and 10^4 cps. Cu K_β was removed using a single crystal monochromator composed of lithium fluoride.

Analytical standards and standard curves

The present study chose clays for analytical standards which were believed to be similar to those of the unknown samples of Pennsylvanian shales of southern Iowa. The kaolinite standard was a Pennsylvanian-age plastic clay, designated as type 211 by the supplier, A. P. Green. Several different kaolinites were obtained from this company, but the 211 seemed to have diffraction characteristics most similar to unknown sample kaolinites. Two different micaclays were tested for potential standards; the first was Beaver's Bend illite, obtained from the Oklahoma Geological Survey, which is composed of well crystallized 2M clay with no detectable mixed-layering. The second was Goose Lake Grundite, obtained from Illinois Clay Products, Joliet, Illinois, which is composed of poorly crystallized 1Md clay with 25–30% mixed layering. The Beaver's Bend illite proved to have diffraction characteristics more similar to unknown sample mica-clays than the other clay. Some mixed-layering was present in many of the unknown sample mica-clays, but generally was much less abundant than in the grundite. Powdered quartz, from Baker Chemical Company, was used for the quartz standard.

In determining standard analytical curves, the percentage of standard mineral was plotted against the ratio of a selected clay peak to that of the 6.15 Å MoS_2 peak, for standard mixes compacted to 8000 psi. The analysis peaks were the 7 Å kaolinite, 10 Å mica-clay, and 4.26 Å quartz peaks. Standard mixes contained 10, 30, 50, 70 and 90% standard component with a single component dilutant. For kaolinite, the dilutant was Beaver's Bend illite, for the mica-clay and quartz, it was finely ground orthoclase. The choice of dilutant seemed to have no significant effect on the standard curves.