Quantitative Analysis of Clay Minerals Using X-ray Diffraction Technique - Part I

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التحليل الكمي لمعادن الطين باستخدام طريقة انعكاس أشعة أكس – الجزء الأول

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خلاصة : يعتبر التحليل النوعي والكمي لمعادن الطين مهما في تقييم قوة الامتصاص للتربة التمددية . يصف هذا البحث بالتفصيل طريقة بسيطة لتحديد كمية معادن طين الخوض (شمالي عُمان) باستخدام طريقة انعكاس أشعة أكس . تعتمد هذه الطريقة على إضافة معادن قياسية داخلية معروفة لعينات الطين . يحتوي الطين الذي تمت دراسته في هذا البحث على معادن المونتمورولونايت . الباليجورسكايت ، الألايت والكيلونايت . تم خلط قياسات داخلية من هذه المعادن مع عينات الطين بنسب مختلفة ثم قياس مساحات الموجة المنعكسة . توصل البحث إلى وجود علاقة خطية بين مساحة الموجة المنعكسة ونسب الخلط القياسية المضافة ومن هذه العلاقة تم تقدير كميات معادن الطين الموجودة في طين الخوض .

ABSTRACT: Qualitative and quantitative analysis of clay minerals are important in the evaluation of the swelling potential of expansive soils. A relatively simple method for the quantification of clay minerals of Al-Khod (Northern Oman) using an X-ray diffraction method is described in detail in this paper. The method is based on the additions of known internal standards to the clay sample. The clay investigated in this study contained montmorillonite, palygorskite, illite and kaolinite. Internal standards of these minerals were mixed with the clay at different proportions and intensities of reflected peak areas were measured. It was found that the peak areas intensities relate linearly with additions of different proportions of standards. From these intensities, the clay minerals present in the clay of Al-Khod were estimated.

Expansive soils are widely spread in Northern Oman associated mainly with Tertiary materials. Expansive soils undergo volumetric changes upon wetting and drying thus causing distress and damage to engineering structures founded on them. A detailed information on their distribution and characteristics is provided by Al-Rawas and Woodrow (1992). Expansive clay minerals such as montmorillonite, illite, palygorskite etc. have great influence on the swelling behaviour of the soil. Montmorillonite is the most "active" mineral and is responsible for most of the swelling problems. Thus, knowledge of the types and amounts of clay minerals present in a soil is essential in the evaluation of the swelling potential of the soil. In Oman, only qualitative and semi-quantitative means of clay minerals analysis using X-ray diffraction were used in the past. There appears to be no published quantitative analysis available in the literature prior to this study which may be due to the complexity of the work, lack of expertise in this field and time needed for such work.

Qualitative and semi-quantitative techniques were mostly used worldwide for the analysis of clay mineralogy, but more accurate quantiative approaches are needed in order to obtain reasonably, accurate estimates of clay minerals in a soil. However, quantitative approaches based on the comparison of diffraction peak heights or peak areas can only be used as estimates due to the differences in :

(i)   mass absorption coefficients of different minerals
(ii)   orientation of particles
(iii)   thickness of samples
(iv)   surface texture of samples
(v)   degree of crystallinity of the minerals
(vi)   chemical composition
(vii)   other factors

In quantitative techniques where internal standards of known minerals are utilized, reasonable estimates can be produced. Researchers who have investigated this work reported that the results obtained must be considered to be ± 2, 5 or 10% (Gibbs, 1965; Carrol, 1970). Moore and Reynolds, Jr. (1989) stated that quantitative analysis should be considered good if errors amount to ± 10% of the proportions present for major components, and ± 20% for minerals whose concentrations are less than 20%.

The following paper describes a quantitative method for the determination of the montmorillonite, illite,

palygorskite and kaolinite concentrations of Al-Khod clay (Northern Oman) based on the additions of proportions of known internal standards. This is part of an ongoing investigation into concentration of clay minerals in samples obtained throughout Oman.

Review of Quantitative Methods

Several quantitative methods using X-ray diffraction technique were attempted by several researchers. The two principal methods that were widely used are reported herein. For detailed information on various quantitative methods, the reader is referred to Burnett (1995).

THE METHOD OF KNOWN ADDITIONS OF AN INTERNAL STANDARD: In this method, differing known weights of a pure standard are added to a sample containing the same component, and the change in the X-ray diffraction intensity is measured. The weight proportion of that component in the original sample can then be estimated. This method was used by Brindley (1961), Klug and Alexander(1974), Jackson (1956) and Dafalla and Ali (1991).

THE METHOD OF KNOWN ADDITIONS OF SOIL CLAY: In this method, increasing proportions of soil clay are added to a constant weight of a standard, and the change in the X-ray diffraction intensity from 100% standard to 100% soil clay is measured. The weight proportions of various components of the soil clay can then be estimated (Ruhe and Olson, 1979).

Since the intensity of a particular component is directly proportional to the concentration of that component, it was possible to develop methods for quantitative analysis based on diffracted intensities. Klug and Alexander (1974) derived the following relationship between diffracted intensity and absorption:

$$I = KW/\mu \qquad (1)$$

where I is the measured intensity of a diffraction line of a crystalline component of the sample, W is the weight fraction of the component, K is a constant for any particular line of a particular mineral and μ is the linear absorption coefficient of the specimen.

Instrumentation - X-ray Diffraction

The X-ray diffractometer used in this study was the PW1700 Automated Powder Diffractometer. The generator settings were 40 kV and 40 mA and the CuKα radiation (λ) was equal to 1.5418Å. A scanning rate of 2° 2θ per minute from 2° to 30° 2θ was used for all samples. The X-ray diffractometer used is attached to a computer which gives both a trace of the X-ray patterns

of minerals and a computer output listing the d spacings, angle of diffraction, intensities, etc. This information was used in the identification of the minerals.

Sample Preparation and Treatment

Sample preparation consisted of washing the carbonates, soluble salt, organic matter and iron oxides from the soil, separating the clay fraction, preparing oriented samples, and treatments of oriented samples. The procedures used for washing the soil from the carbonates, soluble salt, organic matter and iron oxides were as described by Kunze and Dixon (1986). This initial treatment is important in order to eliminate or reduce the effect of these components.

The soil obtained for X-ray diffraction was initially air dried for several days. It was then crushed until it passes No. 200 sieve (75 μm). Then 15 g of the sieved material (silt and clay) was placed in a beaker containing 600-800 ml of distilled water and few drops of a dispersing agent (hexametaphosphate) were added. The suspension was then stirred thoroughly and left for at least six to eight hours. The top 4 cm of the suspension was then transferred into 50 ml centrifuge tubes. Clay fractions (<2 μm) were obtained by centrifuge fractionation (5000 rpm for 30 minutes).

For the preparation of oriented samples on glass slides, 60 mg of the clay fraction (after it was ground to a powder form) was mixed with 1 ml of distilled water and stirred thoroughly. Approximately 30 mg of the clay in the suspension was then carefully transferred into a 2.6 x 2.3 cm glass slide. The clay particles were allowed to settle freely on the slide. Similarly, the remaining 30 mg was also transferred onto another slide. For additional information on the samples preparation, the reader is referred to Whittig and Allardice (1986).

The samples mounted on the slides were allowed to dry before examination. Each sample was examined in three forms; as an oriented clay sample (untreated), as an oriented clay sample treated with ethylene glycol and as an oriented clay sample heated to 550°C for two hours. Ethylene glycol and heat treatments were used to provide additional information essential for the identification of clay minerals.

Clay Minerals Identification

The data presented by Brown and Brindley (1980) and Moore and Reynolds (1989) were used as a guide for the identification of clay minerals. The clay mineral groups of montmorillonite, illite, palygorskite and kaolinite were identified in the clay of Al-Khod by their characteristic basal reflections. Non-clay minerals such as quartz and calcite were also identified. The X-ray pattern of Al-Khod Clay is shown in Fig. 1.
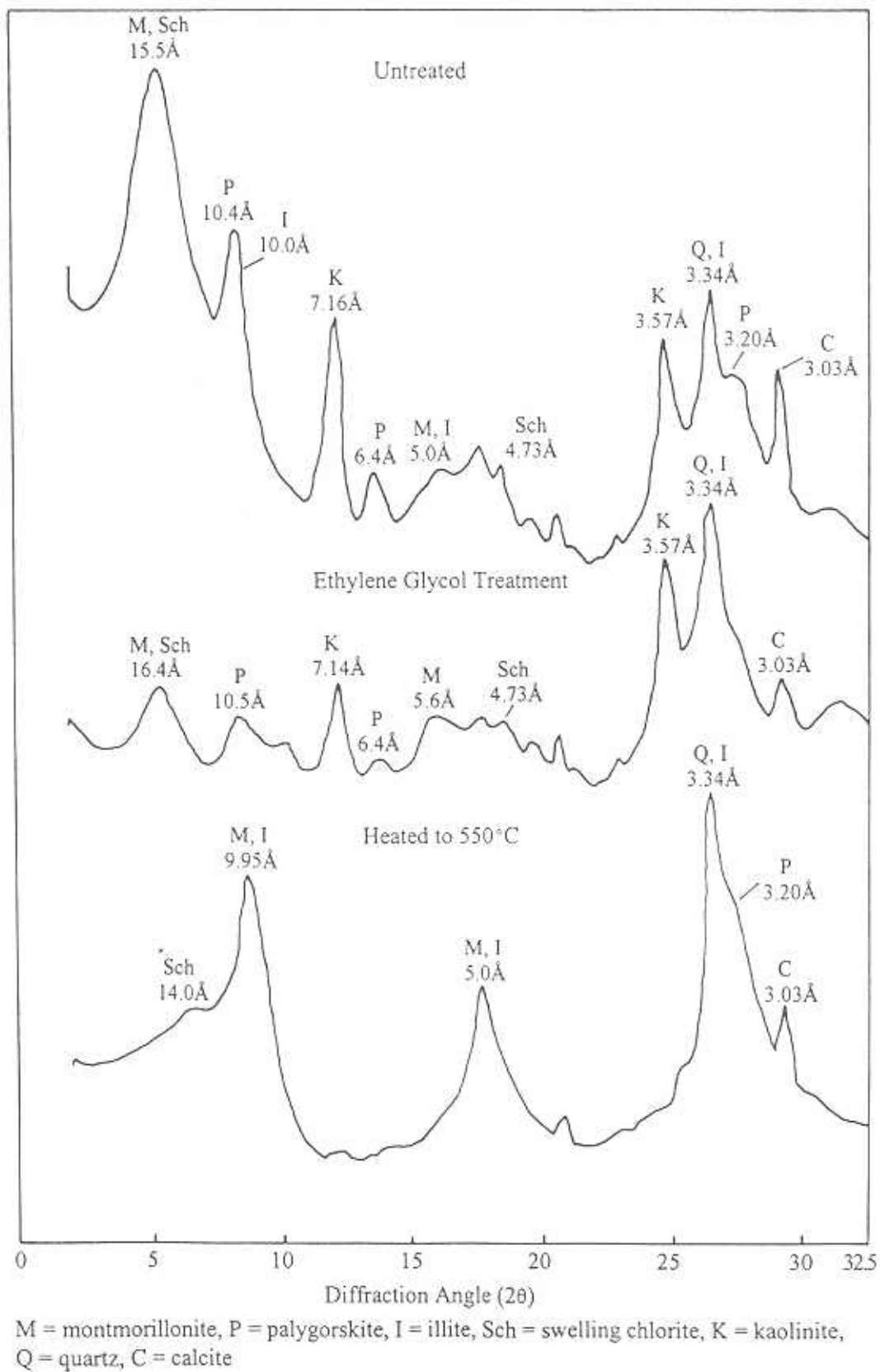
Figure 1. X-ray diffraction patterns of Al-Khod clay sample with different treatments.

MONTMORILLONITE: Sodium montmorillonite and calcium montmorillonite are characterized by 12 and 14-15Å peaks respectively. Montmorillonite expands to 17Å upon glycolation and collapses to 9.5-10Å when heated to 550°C for two hours.

ILLITE: Illite has basal reflections of 10, 5 and 3.3Å which are unaffected by glycolation and heat treatments.

PALYGORSKITE: Palygorskite has basal reflections of 10.5, 6.36 and 4.47Å which are unaffected by glycolation. When subjected to heat treatment at 350°C, the intensity of the main reflection decreases and at 600°C, the 10.5Å completely disappears (Wilson, 1987).

KAOLINITE: Kaolinite is characterized by 7 and 3.5Å peaks. Kaolinite is unaffected by glycolation and disappears when heated to 550°C for two hours.

Adopted Method and Procedures

In this study, the *"Method of Known Additions of an Internal Standard"* for the determination of montmorillonite, illite, palygorskite and kaolinite concentrations in the soil as stated by Dafalla and Ali (1991) was adopted. However, they only considered one component, montmorillonite, whereas in this study four components were analysed.

In this method, pure standards of the four identified clay minerals were added to the soil clay in different percentages of 10, 20, 30, 40%, etc. By plotting the X-ray diffraction intensities or peak areas against the concentrations (percentages) added for each standard mineral, we obtain a linear relationship from which we can predict the concentrations of the actual minerals present in the clay sample.

The internal standards chosen for this study and their chemical compositions are shown in Table 1. The montmorillonite, illite and kaolinite standards were produced by ECC International Ltd of the United Kingdom whereas the palygorskite sample was produced by the Ministry of petroleum and Minerals (Sultanate of Oman). The X-ray patterns of these minerals combined were shown in Fig. 2. The X-ray reflections of these minerals were found to be similar to those produced by Al-Khod clay.

Prior to the addition of the internal standards, three natural samples were tested to establish the repeatability and reproducability of results. A representative sample was chosen as a reference (Fig. 1). The internal standards were added to the natural samples in order to make mixtures of varying proportions. Six mixes having additional concentrations of bentonite, illite, palygorskite and kaolinite (by weight) of 30, 40, 50, 60, 70 and 80% were made.

TABLE 1

Chemical analysis of the standards and clay used in the study.

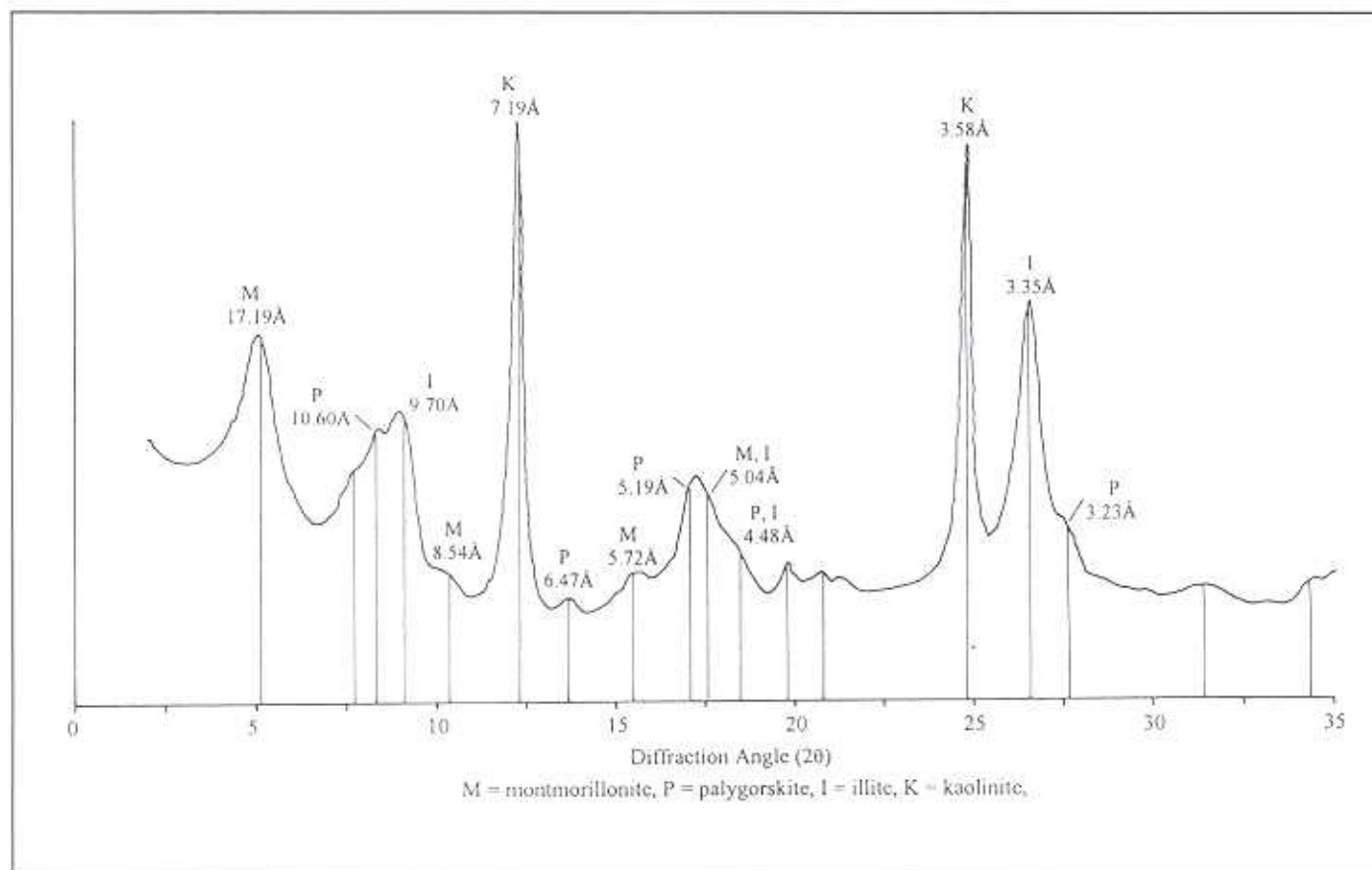| Sample/ Chemical Analysis	Montmorillonite Bentonite Fulgel (Surrey)	Illite (Hungarian)	Kaolinite SPS (England)	Palygorskite ATT-22 (Oman)	Clay Al-Khod (Oman)
SiO₂	59.4	52.1	48.0	48.30	46.94
Al₂O₃	16.1	31.1	37.0	12.40	8.25
Fe₂O₃	6.40	0.69	0.70	5.80	5.60
TiO₂	0.91	0.09	0.03	0.61	1.65
CaO	2.59	0.28	0.06	1.20	12.65
MgO	3.52	1.50	0.24	10.70	2.52
K₂O	0.69	8.91	1.50	0.70	0.92
Na₂O	3.27	0.16	0.13	0.19	1.22
L.O.I.	7.10	4.90	12.3	18.50	18.95

Figure 2. X-ray diffraction patterns of the internal standards used in the study treated with ethylene glycol.

TABLE 2

Peak areas of Different Minerals for Different Additions of Standards.

Percentages of standards	Peak areas (cm²)			
	Montmorillonite	Illite	Kaolinite	Palygorskite
0	2.50	0.56	0.60	0.56
30	5.95	1.23	3.81	1.23
40	6.00	1.36	3.80	1.36
50	8.16	1.40	4.39	1.40
60	8.17	1.40	5.60	1.40
70	8.25	1.80	5.40	1.80
80	8.32	1.75	6.25	1.75

Results

The peak areas of minerals for different additions of standards are given in Table 2. These peak areas were plotted against the different additions of standards used and the change in X-ray diffraction patterns of the six mixes are shown in Fig. 3. The traces were clean and smooth which indicate the effectiveness of the chemical pretreatment. Also, it is evident that the intensities of the components increased as the concentrations of the internal standards increased. Montmorillonite and kaolinite showed distinctive and separated peaks
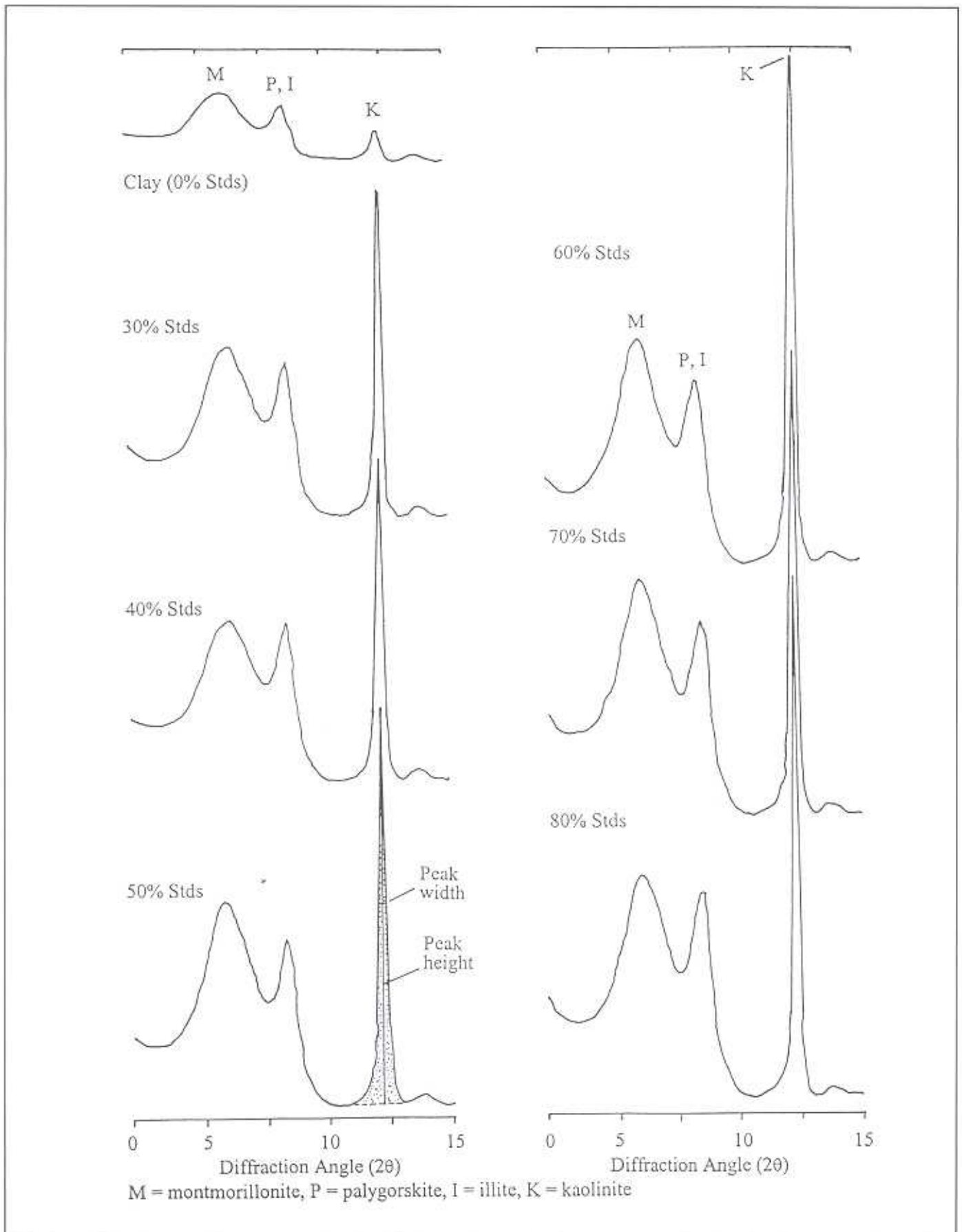
Figure 3. X-ray diffraction patterns showing progressive changes from the clay, through a sequence of increasing additions of internal standards to the clay.

whereas palygorskite and illite were overlapped in one peak (Fig. 3). The peak areas were calculated by multiplying the peak height above background times the peak width at half height. This simple method yields superior results and is used by many researchers. Since palygorskite and illite were overlapped, their peak was divided equally between them. Next, the percentages of internal standards added were plotted against the peak areas as shown in Figs. 4, 5, 6 and 7. From these figures, linear relationships can be seen. Similar results were obtained by Dafalla and Ali (1991) in their study on the quantification of montmorillonite clay mineral.

The assumption made by Dafalla and Ali (1991) was used for the calculations of the natural components in thesample. Assuming that the concentration of montmorillonite was (C), natural concentration of montmorillonite was (C_o), initial sample weight was (w) and additional bentonite was (b), C can be written as:

$$C=[b \cdot w + C_o (w - b \cdot w)]/w \tag{2}$$

resulting in

$$C = b + C_o (1-b) \quad \text{and} \quad b = (C - C_o)/(1 - C_o)$$
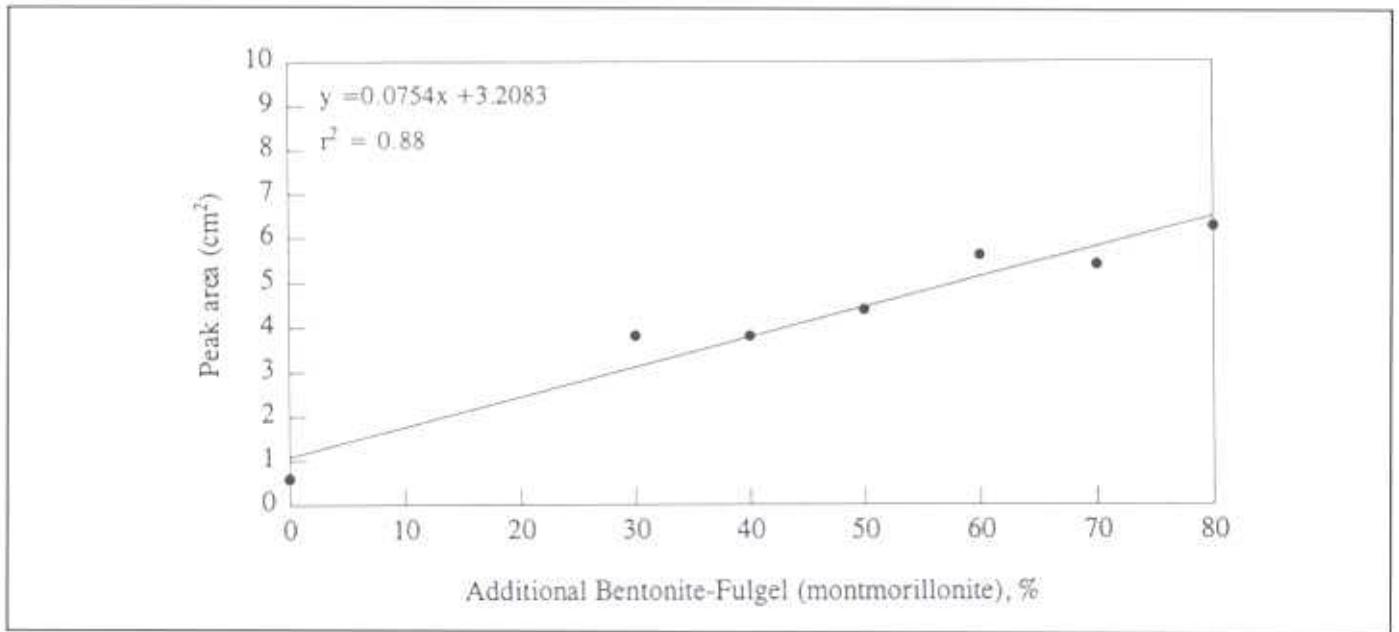

Figure 4. Peak area versus additional Bentonite - Fulgel (montmorillonite).
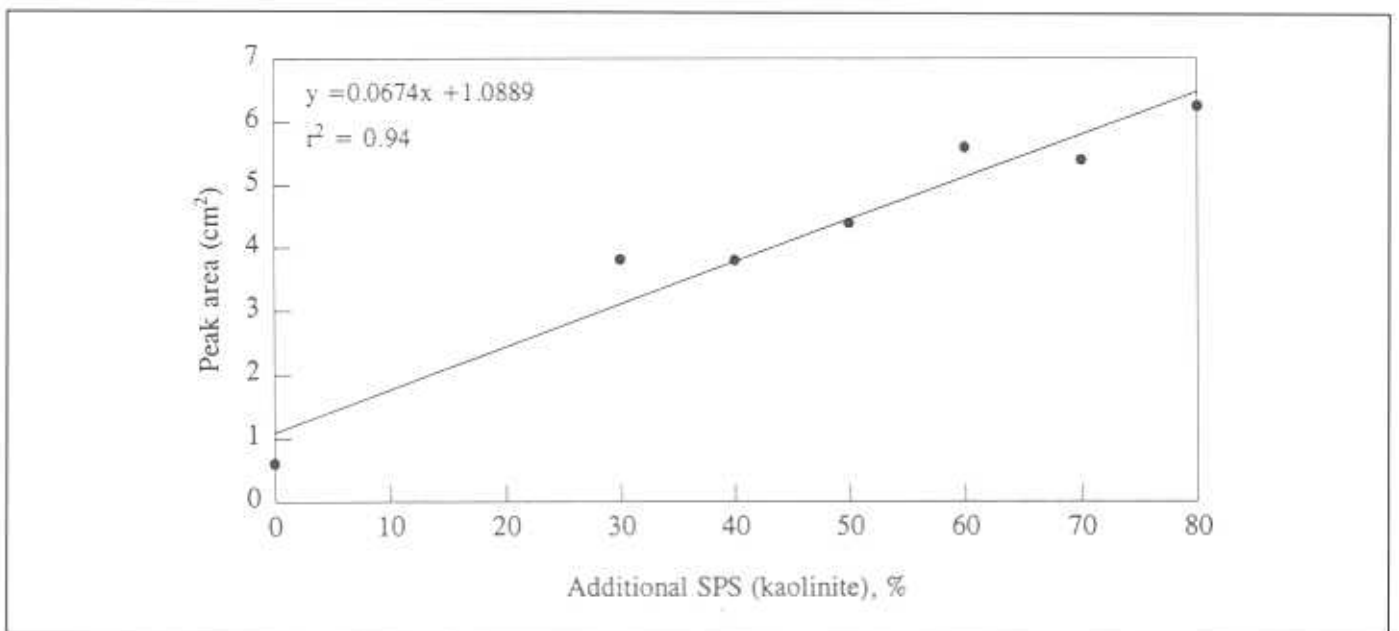

Figure 5. Peak area versus additional SPS (kaolinite).
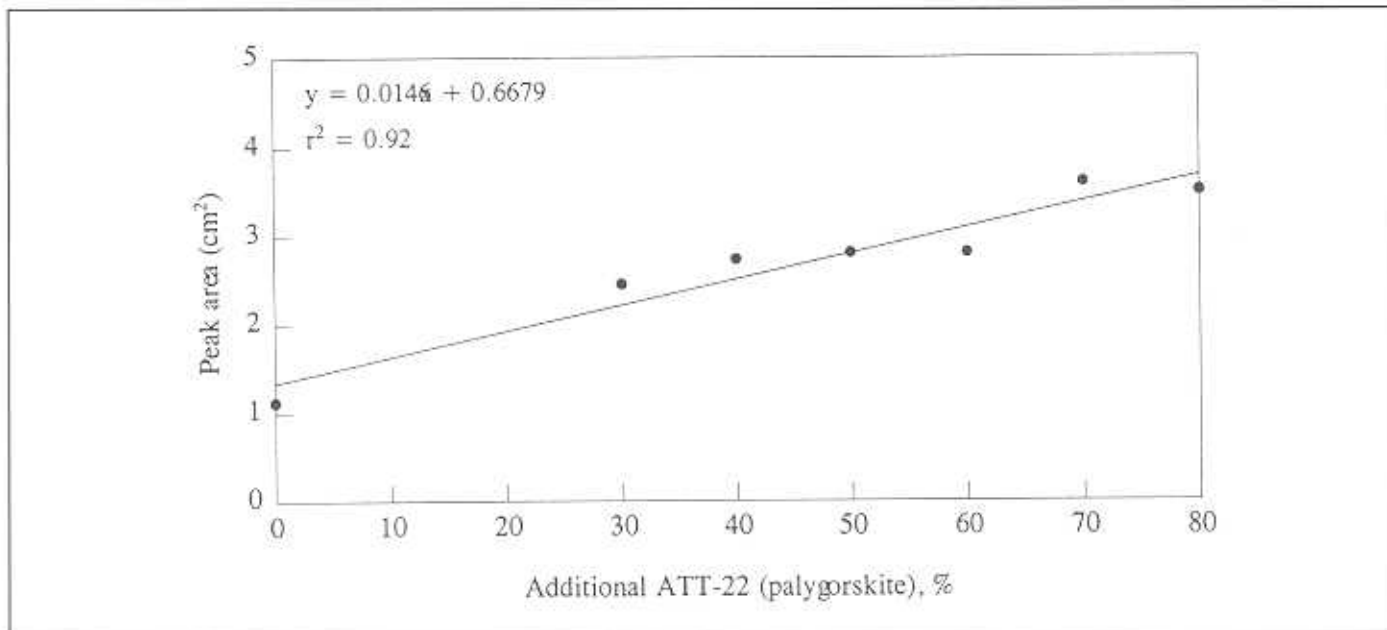
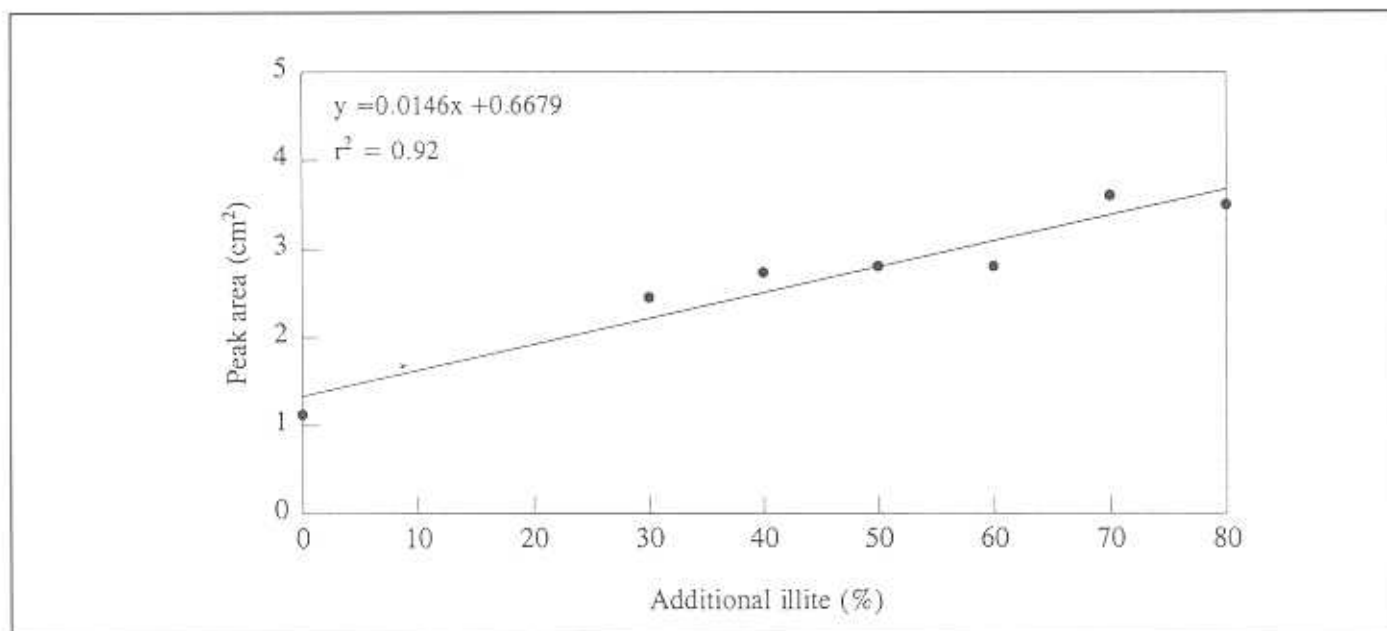Figure 6. Peak area versus additional ATT-22 (palygorskite).

Figure 7. Peak area versus additional illite.

Using linear regression, the best fitting line is defined by the equation:

$$I = 0.0754 \, b + 3.2083 \qquad (3)$$

For I=0 and C=0, then b = 3.2083/0.0754 and C_o = 43%.

The same method was used for calculations of the illite, palygorskite and kaolinite. The natural soncentrations of montmorillonite, kaolinite, palygorskite and illite in the clay sample were calculated to be 43, 16, 23 and 23% respectively. The total concentrations of the four minerals was 105% which indicates an error of only 5%.

This size of error is within the acceptable limits quoted for good quantitative analyses (Moore and Reynolds, Jr. 1989). Therefore, this method seems to be very successful not only for the quantification of a single clay mineral, but also for a mixture of clay minerals (montmorillonite, palygorskite, illite and kaolinite.

Conclusions

This paper describes a relatively simple experimental method of qualitative and quantitative analysis of clay minerals. The method was applied to a sample of Al-Khod clay and the percentages were

found, montmorillonite 43%, kaolinite 16%, palygorskite 23% and illite 23%. The intensities of diffraction peaks measured through peak areas relate directly to the concentration of clay minerals in a clay sample. Furthermore, a linear relationship between additions of proportions of internal standards and increase of peak areas was established.

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