

XRF DETERMINATION OF MAJOR ELEMENTAL CONTENTS OF CLAY SAMPLES FROM NORTH-WEST PENINSULAR MALAYSIA *

Ahmad Saat¹, Zaini Hamzah², Zaharidah Abu Bakar²

¹International Education Centre (INTEC),

UiTM Kampus Seksyen 17, 40200 Shah Alam, Malaysia.

²Faculty of Applied Sciences, Universiti Teknologi MARA, 40450 Shah Alam, Malaysia.

Fax: +603 55227065; e-mail: ahmad183@salam.uitm.edu.my

Abstract

Clay has been considered as important material for man, either used as building materials, pottery or as components in material industry and technology. In the present study ten clay samples obtained from various locations in North-West Peninsular Malaysia were used. Majority of the clays were economically manufactured to be used as building materials or pottery. The objective of study was to determine the main elemental contents of the samples, and relate the results to the types of minerals, as well as to compare them with clays from other studies. In the study X-ray Fluorescence (XRF) coupled to samples dilution method and standard calibration samples was used. The elements detected in the study were Si, Al, Fe, Ti, K and Ca. Depending on locations, the percentage concentration ranged between 24.8 – 32.4 for Si, 10.8 – 19.0 for Al, 0.09 – 2.12 for Fe, 0.08 – 1.13 for Ti, 0.45 – 3.39 for K and trace amount of Ca and P. However, Mg that normally found in typical clay was not found in the studied samples. Comparing the oxide of the major elements with other studies, it was found that the clay samples contained mixtures of kaolinite (two-layered structure) and illite (three-layered structure) in which K is found in its interlayer space of the structure.

Keywords: Clay, XRF, elemental contents

INTRODUCTION

Elemental or chemical analysis is an important step of establishing the nature of minerals (Newman, 1987) such as clay. All the elements present in the samples are then expressed in their respective oxides, in such a way their sum and that of water content approaches the sample weight. In the study of clay minerals for their structural formulae elements such as Si, Al, Fe, Mg, Ti, Mn, P, Ca, K and Na are essential (Mermut & Faz Cano, 2001). The most often used instrumental method for multi-elemental analysis of clay samples is neutron activation analysis (NAA). This method is preferred due to its ability to provide the required level of accuracy, automation and coupled with important data bank for comparison purposes. However NAA involved relatively high cost and difficulty to access a suitable nuclear irradiation facility. (Garcia-Heras, *et al.*, 1997). Although x-

* Presented at ICXRI 2008, 2 – 6 June 2008, UMS, Sabah.

ray fluorescence (XRF) analysis could not provide multi-elemental results of the same level as NAA, most researchers (Garcia-Heras, *et al.*, 1997; Dondi, *et al.*, 2001; Papadopoulou, *et al.*, 2007)) prefers XRF as an alternative to NAA since it is less expensive and more accessible.

In Malaysia clay has been used in a wide range of industries, ranging from building materials and pottery up to agricultural and ceramic. All these industries exploit the properties that clay can be molded into any shape and fired to dry without losing its form. Therefore the physico-elemental-mineralogical properties of clay do not only determine the clay samples characteristics, but also influences the physical characteristics such as colour and plasticity, hence determine its economic importance and usage. Study on Malaysian clays mineralogy study began during the end of 1960's together with the development of clay-related industries. Most of the studies were incorporated within the study on soils (Mohd Nordin, 1977, Liew, *et al.*, 1985, Kok, 2000). The present study aimed at the determination of major elemental contents of clay samples from north-western of Peninsular Malaysia by using x-ray fluorescence (XRF) analysis and then estimates the qualitative mineralogical composition of the samples by comparing with typical clay minerals.

METHODOLOGY

Sampling

For the study majority of the samples were collected from factories at various places in the north-western of Peninsular Malaysia, as summarized in Table 1. The origin, locations, physical description and usage of the clays are also listed in the table. Samples were collected in such a way that contamination was minimized, and as far as possible the use of metallic tools was avoided. The raw samples were placed in polythene bags and tied up.

Samples preparation

In the laboratory, visible foreign matters and coarse sand particles were removed manually. After oven dried at 60 °C for 24 hours, the samples were crushed using agate mortar to powder form and then sieved (250 μm sieve) to remove finer sand particles. The fine samples were turned into slurries by mixing adequate amount of distilled water and leaved to settle for 24 hours. Sand particles being relative denser were separated out in the lower portion of the settled slurries, leaving clay sample for study at the top portion.

Preliminary studies showed that the samples grain size is a critical factor that affect results of XRF. In the present study samples were ground for twenty minutes until the grain size is lower that two micron. For the XRF elemental analysis, dilution method was used, where the samples as well as the standards was homogenously mixed with analytical grade boric acid, in a 0.6 g to 5.4 g ratio. The homogenized mixture was compressed in stainless steel die, with a 20 ton pressure to form circular disk of diameter 4 cm and thickness about 0.5 cm.

Table 1. Description of samples used in the study

SAMPLE	ORIGIN	LOCATION	PHYSICAL DESCRIPTION	USAGE
SP1	Sungai Petani-Alor Star old road	N05° 40' 21" E100° 30' 28"	Yellowish white, very fine, smooth feel	Bricks, toilet bowl & sinks, sewer pipes
SDB1	Sungai Dua, Butterworth	N05° 25' 42" E100° 28' 12"	Greyish with yellowish brown stains, gritty	Bricks and roof tiles
BS1	Bagan Serai, Perak	N05° 07' 36" E100° 29' 52"	Light Brown with yellowish mottles, smooth feel with fine sand grains	Bricks
S1	Sungai Sayong, Perak	N04° 45' 26" E100° 57' 59"	Brownish grey, gritty	Pottery and clay-based souvenirs
P1	Ipoh, Perak	N04° 37' 59" E101° 07' 04"	Yellowish grey with brownish stains, slightly gritty	Bricks and sewer pipes
V1	Sungai Siput, Perak	N04° 44' 55" E101° 07' 31"	Whitish grey with some organic matter, fine smooth feel	Tiles, sewer pipes and flower pots.
K1	Bidor, Perak	N04° 06' 46" E101° 07' 28"	Pinkish cream color, slightly gritty	Kaolin bricks (for export)
TK1	Teluk Kumbar, Penang	N05° 17' 26" E100° 13' 49"	Brownish grey, slightly gritty	Not economically utilized
TB1	Teluk Bahang, Penang	N05° 27' 33" E100° 12' 22"	Grey with yellowish mottles, gritty	Not economically utilized
KT1	Kampung Bercham, Perak	N04° 38' 10" E101° 06' 46"	Brownish grey with brown patches, slightly gritty	Flower and cooking pots, clay stoves

Instrumentation

For the study, a Philip model PW 1410 XRF machine with chromium target, PE crystal ($2d = 8.742 \text{ \AA}$) analyzer, and gas flow proportional counter was used. The tube rating was 50 kV 40 mA and 2θ range of 58° to 147° . This 2θ range was found to be suitable for major elements determination in clay. The detector is coupled to a recorder to produce the XRF spectrum of the sample.

RESULTS AND DISCUSSIONS

Figure 1 shows a typical spectrum of one of the samples studied. In the spectrum, the K_{α} peaks for the various major elements in the sample are the prominent peaks. In the study only single K_{α} peaks of first or second order were used. These peaks, in which the height is directly proportional to particular elemental contents in the samples and standards were used in the elemental analyses.

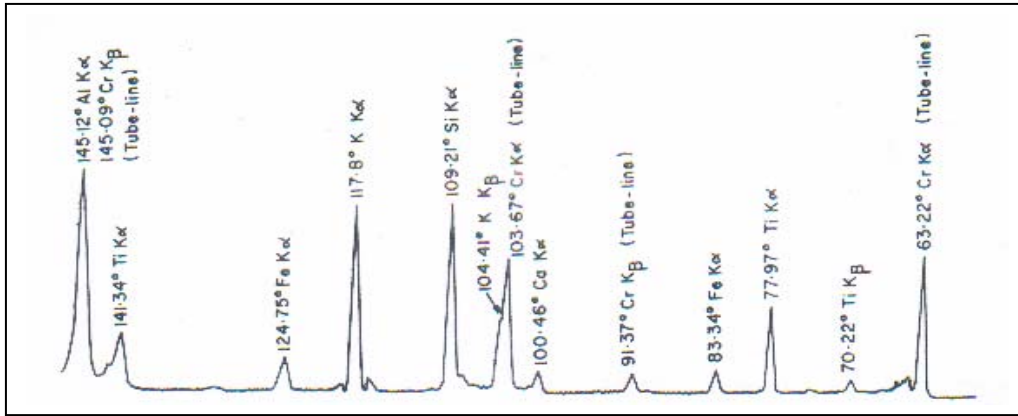


Figure 1. XRF Spectrum of a clay sample studied.

The major elements elemental contents of clay samples in the present study are summarized in Table 2. The uncertainties shown in the results are estimates of experimental errors contributed by calibration and the peak height of the respective spectrum. The values quoted are the average of two analyses of the same sample. Depending on locations, the percentage concentration ranged between 24.8 – 32.4 for Si, 10.8 – 19.0 for Al, 0.09 – 2.12 for Fe, 0.08 – 1.13 for Ti, 0.45 – 3.39 for K. Trace amount of Ca and P are also detected in some samples. However, Mg that normally found in typical clay was not found in the studied samples.

Table 2. Major elemental content and loss on ignition of clay samples.

Elemental Content (%)						
Sample	Si	Al	Fe	Ti	K	LOI
SP1	30.6 ± 2.1	13.5 ± 1.2	0.16 ± 0.01	1.13 ± 0.08	3.39 ± 0.23	5.2 ± 0.1
SDB1	32.4 ± 2.3	13.8 ± 1.2	0.16 ± 0.01	0.38 ± 0.03	0.49 ± 0.03	6.4 ± 0.1
BS1	27.9 ± 2.0	10.8 ± 1.0	2.06 ± 0.14	0.33 ± 0.02	0.84 ± 0.06	9.7 ± 0.2
S1	27.7 ± 1.9	12.6 ± 1.1	0.57 ± 0.04	0.08 ± 0.01	2.32 ± 0.16	8.2 ± 0.2
P1	30.1 ± 2.1	15.9 ± 1.4	0.53 ± 0.04	0.19 ± 0.01	2.08 ± 0.15	6.8 ± 0.1
V1	24.8 ± 1.7	17.3 ± 1.6	0.29 ± 0.02	0.21 ± 0.01	0.82 ± 0.06	8.2 ± 0.2
K1	31.8 ± 2.2	15.5 ± 1.4	0.09 ± 0.01	0.11 ± 0.01	0.45 ± 0.03	4.7 ± 0.1
TK1	26.9 ± 1.9	19.0 ± 1.7	0.36 ± 0.03	0.13 ± 0.01	2.50 ± 0.18	4.9 ± 0.1
TB1	26.7 ± 1.9	16.4 ± 1.5	0.26 ± 0.02	0.13 ± 0.01	2.47 ± 0.18	8.9 ± 0.2
KT1	27.4 ± 1.9	16.6 ± 1.5	2.12 ± 0.15	0.27 ± 0.02	1.49 ± 0.10	7.7 ± 0.2

In the table, the percentage loss on ignition (LOI), accomplished by firing the sample at 600 °C in a furnace for two hour, are also shown. The LOI percentage may be considered as the amount of organic materials present in the samples (Beaudoin, 2003).

Figure 2 shows three elemental ratios Si/Al, Fe/Ti, and K/Ti of the samples and typical kaolinite and illite (from Weaver & Pollard, 1975). For all samples the Si/Al ratio, remain relatively stable at around 1.9 as in typical illite and kaolinite. Fe/Ti ratios for samples BS1, S1 and KT1 show that iron is the dominant element indicating that these are iron-rich clay samples. This might explain the brownish colour of the samples (Table 1). As can be seen from the figure except for samples S1, TK1 and TB1, the K/Ti ratios of other samples are almost stable. The high K/Ti ratios for the three samples go along with that for typical illite. Based on these observations it may leads to a conclusion that the samples studied contained mixtures of kaolinite and illite in different proportions. This is in agreement with earlier study using XRD (Ahmad & Zaini, 2006). However the exact proportions are not determined in the present study.

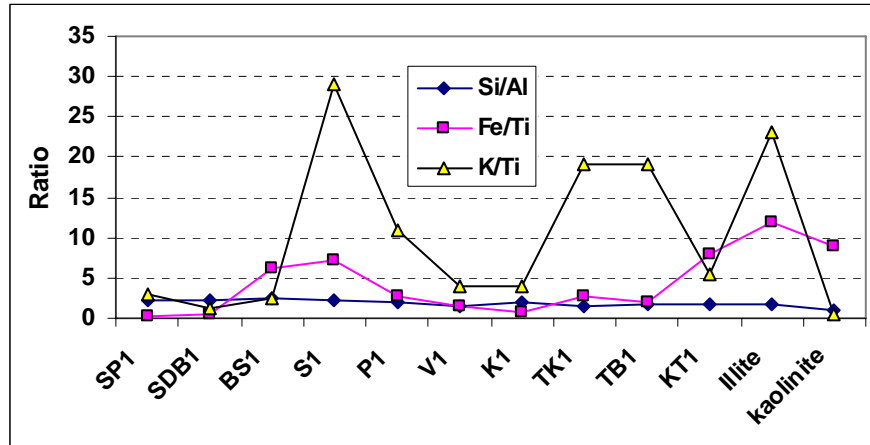


Figure 2. Variation of three elemental ratios between samples.

Figure 3 shows a web-plot to compare the SiO₂, Al₂O₃ and other oxides percentage contents in samples and typical illite and kaolinite minerals. In the study, iron assumed to be in Fe₂O₃ form only is combined with TiO₂ and K₂O under other oxides category. The figure is plotted in a log-scale. In terms of SiO₂ contents, all samples show higher percentage than those in typical illite and kaolinite. However, the Al₂O₃ contents of samples are somewhat lower than that of kaolinite. These observations might be attributed to the higher sand content in the samples, as indicated by the gritty feel of the samples (Table 1).

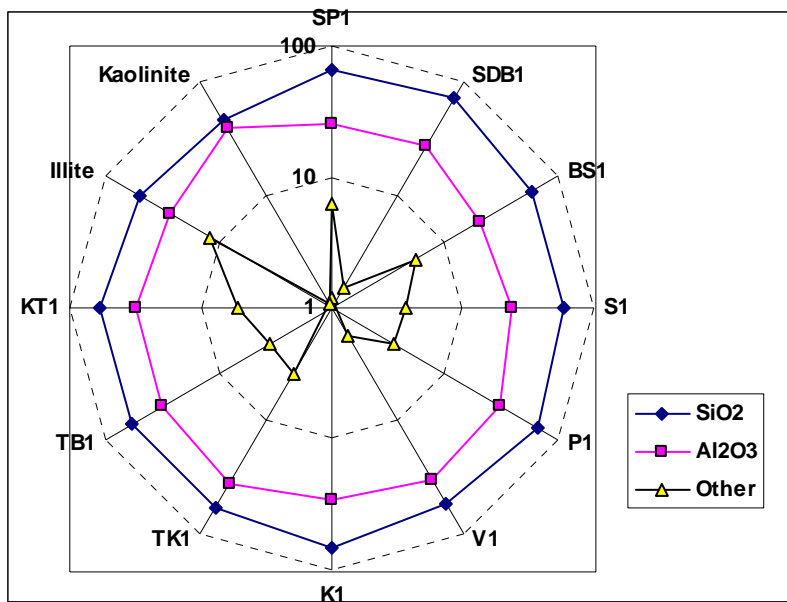


Figure 3. Comparison of SiO₂, Al₂O₃ and other oxides percentage contents in samples and typical illite and kaolinite minerals (Weaver & Pollard, 1975).

CONCLUSIONS

The major elemental contents of clay samples detected in the study were Si, Al, Fe, Ti and K. Based on comparison with typical clay minerals, indicated that the samples are mixtures of kaolinite and illite in various proportions, depending on samples locations.

Acknowledgement

The authors would like to thank Universiti Teknologi MARA (UiTM), Malaysia for providing the fund to present this paper at the ICXRI 2008, Kota Kinabalu, Sabah.

REFERNCES

Ahmad Saat & Zaini Hamzah, (2006) *X-ray Diffraction Study of Clay from North-West Peninsular Malaysia*, presented at the International Conference on X-ray Application in Research and Industries (ICXRI 2006), 6 – 8 August 2006, Putrajaya, Malaysia.

Beaudoin, 2003

Dondi, M., Guarini, G., Ligas, P., Palomba, M., Raimondo, M. (2001) *Chemical, Mineralogical and Ceramic Properties of Kaolinite materials from Tresnuraghes Mining District (Western Sardinia, Italy)*, Applied Clay Science, 18, 145 – 155.

Garcia-Heras, M., Fernandez-Ruiz, R., Tornero, J.D. (1997) *Analysis of Archeological Ceramics by TXRF and Contrasted with NAA*, Journal of Archeological Science, 24, 1003 – 1014.

Kok Kai Chern, (2000) *Physical, geochemistry and mineralogical studies on the strength development of lime stability cohesive soils*; MSc Thesis, Universiti Teknologi Malaysia (UTM), Unpublished.

Liew, K.Y., Khoo, L.E., Bong, K.T., (1985) *Characterization of Bidor kaolinite and illite*; Pertanika, Vol. 8. No. 3, 323-330.

Mohd Noordin Hj Wan Daud (1977) *Clay mineralogy of soils under rubber in Peninsular Malaysia Part I – Identification and Distribution*; Rubber Research Institute of Malaysia Journal, Vol. 1, No. 1, 19-32.

Mermut, A.R. and Cano, A.F. (2001), *Baseline Studies of the Clay Minerals Society Source Clay: Chemical Analysis of Major Elements*, Clays and Clay Minerals, Vol 49, No. 5, 381-386.

Newman, A.C.D. (1987), *Chemistry of Clays and Clays Minerals*, Mineralogical Society Monograph, 6, Longman Scientific and Technical, Harlow, Essex, England, 480 p.

Weaver, C.E. and Pollard, L.D. (1975), *The Chemistry of Clay Minerals*; Elsevier Scientific Publishing Company, Amsterdam, 213 p.