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QUANTITATIVE ANALYSIS OF A CERAMIC CLAY

JERAPONG TONTRAKOON and DANIEL BREEN

Department of Physics, Faculty of Science, Chiang Mai University, Chiang Mai, Thailand

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Summary

A quantitative analysis of a widely used ceramic clay has been carried out by X-ray diffraction, using the method of internal standards. The analysis is supplemented by chemical and thermal methods. Internal consistency of the results and comparison with other measurements are discussed.

Introduction

The production of ceramics is an important handicraft industry in the Chiang Mai area of northern Thailand. Most or all of the kilns in the area used naturally occurring clay from a deposit in Mae Rim, Chiang Mai province, which is usually referred to as Mae Rim ball clay. From this clay skilled craftsmen produce articles of traditional and modern design, mostly for an export market. At present, demand exceeds supply so that the producers are generally content to continue unchanged successful lines. However, increasing competition, whether within the area or from outside, changing market demands, or dissatisfaction with some defects of the products will force attention to improving quality. A major defect of local products appears to be a lack of strength: even a moderate mechanical shock can cause breakage. Besides, while market success is certainly due to the charm of the traditional green glazed stoneware known as Celadon, the products tend to be thick and heavy, limiting the range of designs which could be made.

A combination of several clays or addition of other minerals to clay can improve the quality of ceramic products[1]. The addition of other minerals would certainly improve the strength of local ceramic products as has already been demonstrated by work carried out at the ceramics division of the Industrial Services Institute, Chiang Mai, and strength tests made by one of the authors[2]. However, to assess systematically the optimum additives required it is necessary to have an accurate analysis of the basic clay. Such an analysis would also form the basis for a study of the phase diagram of the clay, which could lead to optimum firing and fuel economy.

Typically, the principal constituents of ceramic clay include kaolin, quartz and feldspar. Kaolin, an aluminium silicate, is the major constituent in ceramic clays. It occurs in tiny flat plates, roughly hexagonal in outline. Kaolin contributes the plastic and drying properties so important in forming ceramics. Quartz is a hard crystalline mineral which is the most commonly found from of silica. It plays an important role in controlling shrinkage and acts as a refractory backbone constituent of ceramic products. Feldspar is an anhydrous aluminosilicate containing K^+, Na^+, or Ca^{2+}, and acts as the flux that results in a glassy binding component. Ball clay such as is found in Mae Rim also contains organic matter which gives a dark colour to the raw clay. The analysis carried out in this study involved estimating the quantities of these components. Other components are usually present in smaller quantities and play a minor role in the industry.

Methods

Internal Standards

While chemical methods give a convenient analysis of a clay the results are in terms of oxide content which, because of the variable composition of most clays, cannot be related directly to the more important mineral content. X-ray analysis, on the other hand, gives a direct recording of the actual mineral content, each mineral having a distinct X-ray spectrum. Qualitative analysis consists in the matching of the positions and relative intensities of lines of the X-ray spectrum against known mineral spectra until all the components in the clay have been identified. Quantitative analysis requires a comparison of line intensities with the intensity of some standard present in a known amount. There exist several methods involving the measurement of other paramaters such as the absorption coefficient of the sample, which is both inconvenient and a source of error. In the method of internal standards comparison is made between the intensity of lines of the components being analysed and the intensity of lines of a standard introduced in the clay in a known amount. The ratio of these intensities is converted to a quantitative proportion of the unknown to the standard by comparison with calibration curves derived from prepared standard mixtures.

The intensity of an X-ray line in a powder mixture is given by

$$I_{ij} = \frac{K_{ij}v_j}{\mu} \tag{1}$$

where I_{ij} is the intensity of the i^{th} line in the powder pattern of component j whose concentration is sought.

K_{ij} is a constant depending on the apparatus, X-ray wavelength, and the structure of component j;

v_j is the volume fraction of component j;

μ is the linear absorption coefficient of the powder mixture.

If x_j is the ratio of weight of component j and the mixture sample, v_j may be written

$$\frac{x_j/\rho_j}{\sum_1^n x_i/\rho_i}$$

where ρ_i is the density of component i and the summation in the denominator is carried out over all components in the mixture. Then the equation for the intensity may be written:

$$I_{ij} = \frac{K_{ij}\, x_j/\rho_j}{\sum_1^n x_i \mu_i^*} \qquad (2)$$

where $\mu_i^* = \frac{\mu_i}{\rho_i}$ is the mass absorption coefficient of component i. Then if I_{kn} is the intensity of line k of a standard denoted by the index n,

$$\frac{I_{ij}}{I_{kn}} = \frac{K_{ij}\, \rho_n\, x_j}{K_{kn}\, \rho_j\, x_n} \qquad (3)$$

This is the basic equation of the internal standards method. If x_n is kept constant while x_j is varied, a plot of $\frac{I_{ij}}{I_{kn}}$ against x_j is a straight line. The slope is a unique constant characteristic of components j and n, which is independent of the absorption characteristic of the specimen, or even the other component present. Such a curve is the calibration curve which can be used to estimate the amount of a specific component in a clay, once the intensity ratios have been measured.

The material used as an internal standard must be readily obtainable in good purity and of suitable crystalline size to give sharp diffraction lines not superimposed on the spectrum to be analysed. Calcium fluoride (CaF_2) and calcium hydroxide ($Ca(OH)_2$) were used in the present work.

Sample preparation and diffraction measurements

The principal problem in X-ray analysis of clays lies in sample preparation. Because of the platelike nature of clay particles the crystals tend to align parallel to any flat surface under pressure. Thus great attention is required to make samples give reproducible line intensity.

For identification purposes it is useful to make oriented samples in which the platelets have a preferred orientation. This can be done by transferring some drops from a suspension of the clay in water on to a microscope slide and allowing it to dry. This is repeated until a sufficiently thick layer is formed. In such a sample the basal lines become enhanced and are easily identified.

Non-oriented samples were mounted in sample holders made of 0.16 cm thick aluminium sheeting cut in 3.7 x 3.7 cm squares. A rectangular hole to hold the powder measures 2 x 1½ cm. If the grain size of the clay powder is too large the random nature of the sample surface will give variable line intensity. On the other hand if the grain size is too small there is a reduction in intensity. The optimum grain size was found experimentally as follows. The powder was first passed through a 400 mesh sieve and then ground with an agate pestle and mortar. Five samples were mounted and the line intensities compared. It was found that for kaolin, calcium fluoride and calcium hydroxide, equal line intensities could be produced after 15 minutes grinding while for the harder materials, quartz and feldspar, at least 45 minutes were required. Thus when samples of ceramic clay were being made the powder was ground 15 minutes for kaolin analysis, and up to an hour for quartz and feldspar analysis.

To make an unoriented sample a clean glass slide is bound by tape to one side of the aluminium holder and the ground powder is sieved into the cavity. The powder is pressed gently but firmly with another slide and excess powder sliced off. This process is repeated until the powder is packed sufficiently to give reproducible intensities, but not so tight that orientation is increased leading to variation of relative intensities of spectral lines. Another glass slide is taped to the back of the holder and the front slide removed to give a surface which is exposed to the X-ray beam.

Standard samples were made by mixing 1 g of CaF_2 with 3 g of a mixture of kaolin and quartz. The proportions of kaolin and quartz in the mixture were varied so that for x g of kaolin, (3−x) g of quartz were used, x being varied from 0 to 3 in 10% steps. Since the CaF_2 line overlaps with a feldspar line, standard samples of feldspar and quartz were similarly made using $Ca(OH)_2$ as internal standard. The relative intensities of the lines were measured by sketching in the tails of each line against a background derived from the shape of the trace in the vicinity of the line. The lines were then cut out and weighed on an analytic balance so that the ratio of the weights gives the ratio of the integrated line intensities. A resulting calibration curve for each of the three components is shown in Fig. 1, 2, and 3. A similar procedure was used in making clay samples, 1 g of the standard being mixed with 3 g of the clay. When the ratio of intensities was measured, the actual amount of the constituent being studied in the clay could be read off the calibration curves. All intensity measurements were averages of the results of three traces made on each of a total of five samples. The standard deviation gives a measure of the accuracy of the results.

The kaolin used in preparing the standards came from an English clay deposit, while the quartz and feldspar were Thai geological samples. The purity of each was checked by X-ray analysis. The calcium hydroxide and fluoride used were chemicals of reagent purity.

The X-ray spectrometer used was a Philips Wide Angle Diffractometer unit using copper Kα radiation and a nickel filter with a wide range goniometer and sealed proportional counter. Optimum operating conditions were established by trial

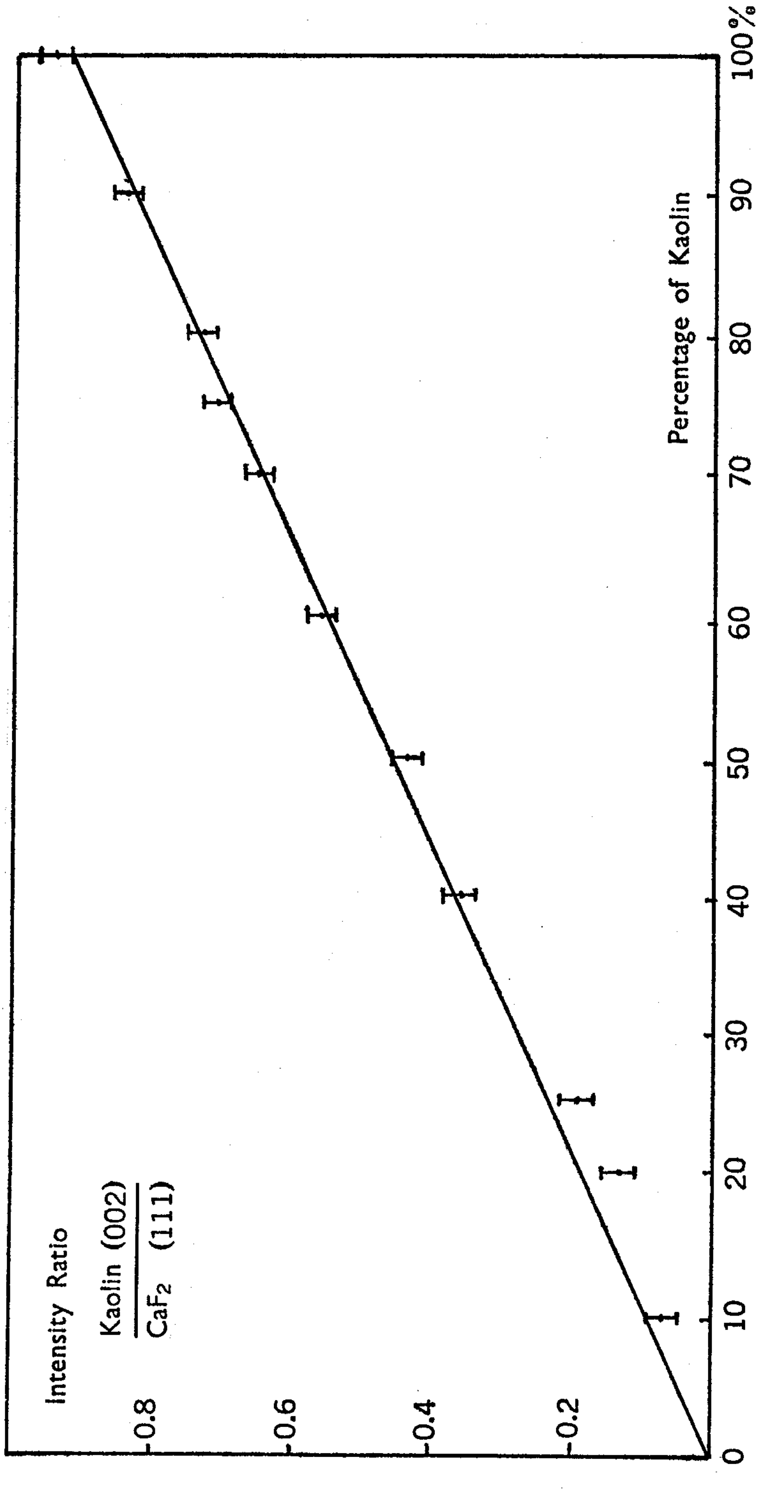

Fig. 1. Standard curve for kaolin

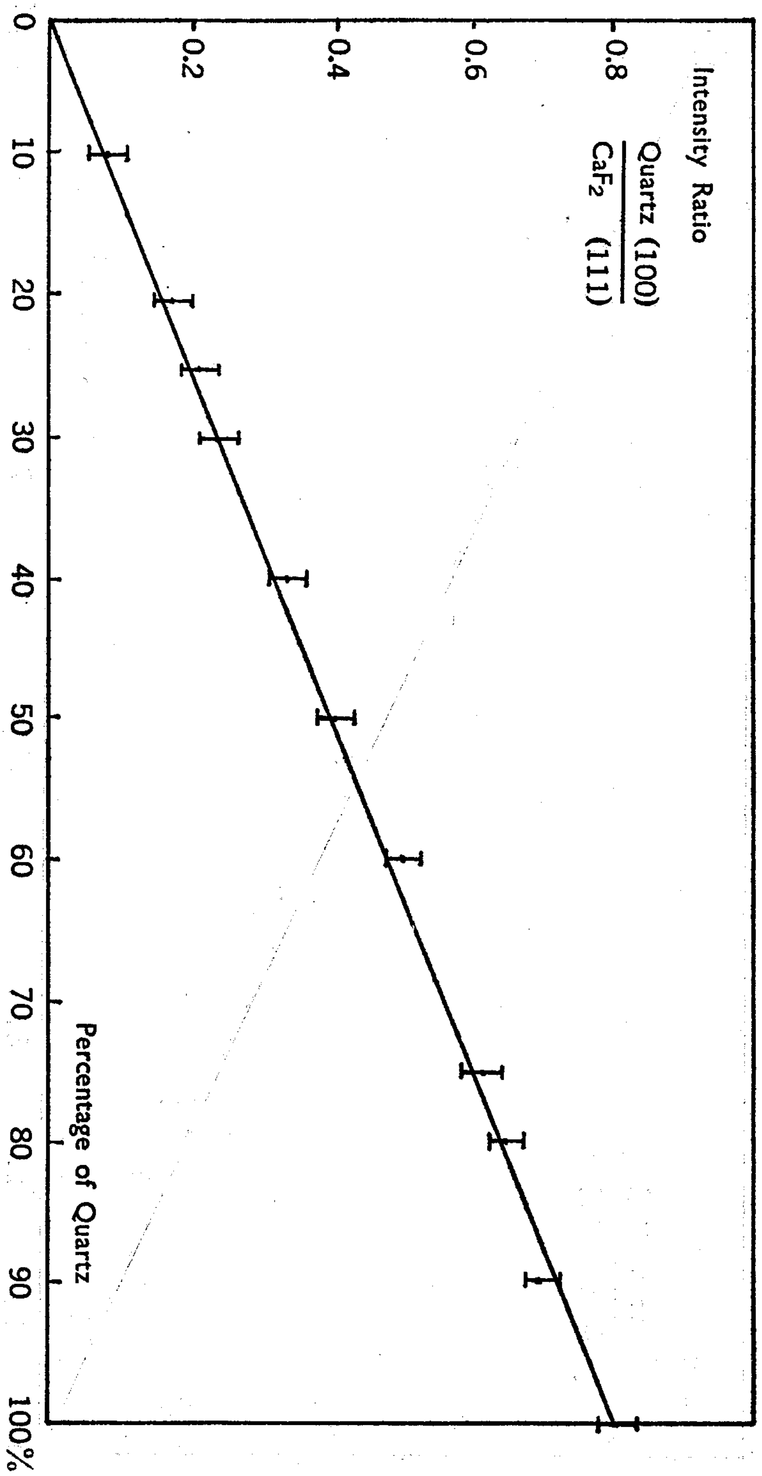

Fig. 2. Standard curve for quartz

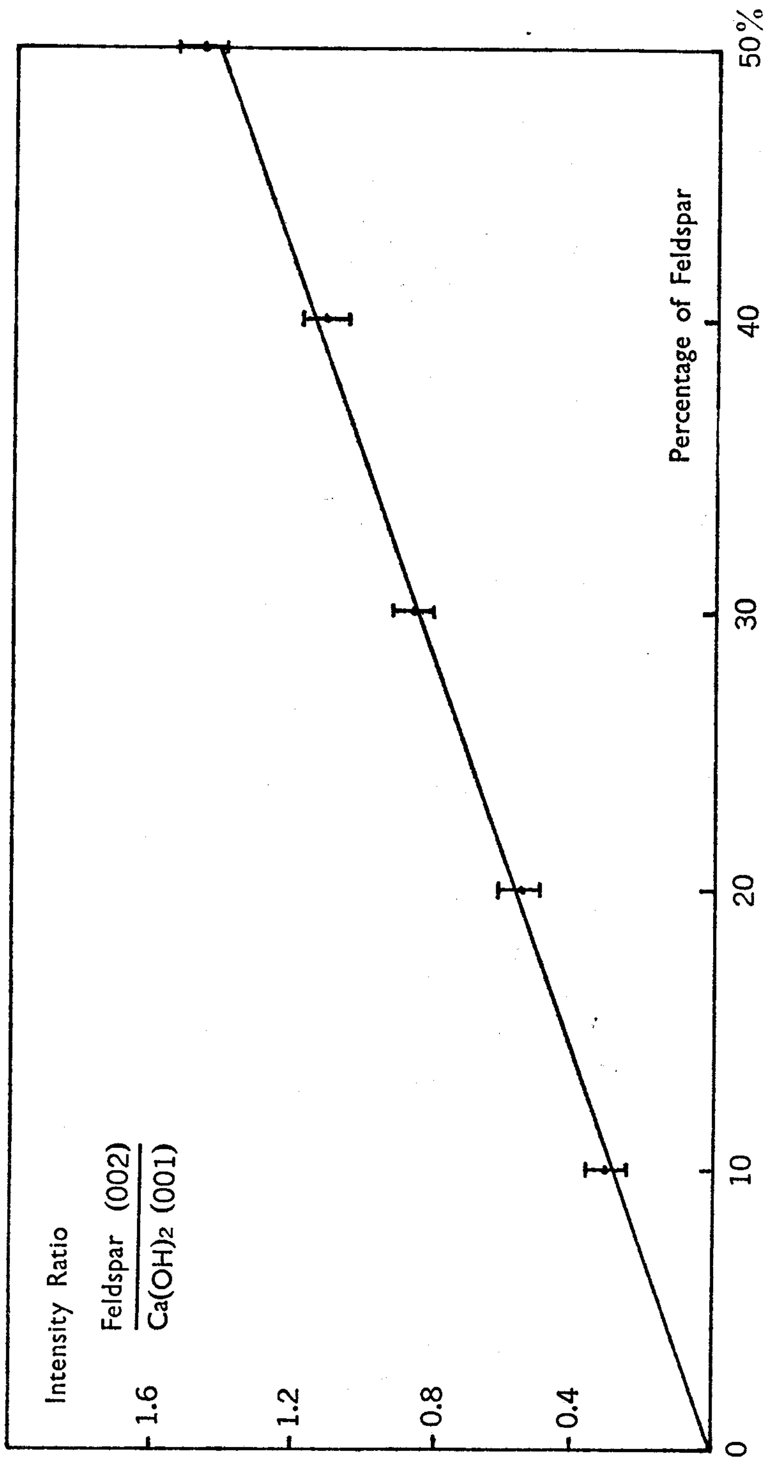

Fig. 3. Standard curve for feldspar

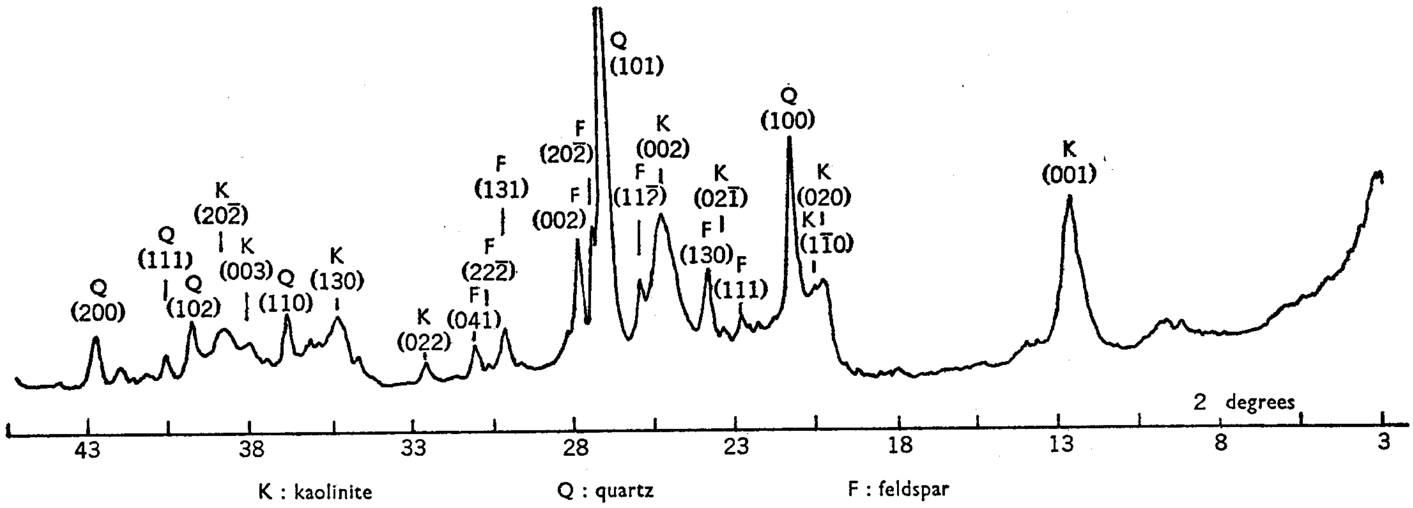

Fig. 4. X-ray diffraction pattern of Mae Rim ball clay

to produce maximum peak area, smoothness and high resolution. Significant instrument paramaters are: divergence slit, 2°; receiving slit, ½°; scanning speed, ½° ($= 2\theta$) per minute; time constant, 4 seconds.

The amounts of organic and soluble matter in the sample were determined by chemical methods. 40 ml of 30% H_2O_2 were added to 10 g of clay which was kept in a hot water bath for one to two days. The clay colour was observed to change from black to light grey. The sample was washed and dried, cooled in a desiccator and reweighed. To determine the fraction of soluble matter 6 g of the clay were dispersed in 600 ml of distilled water and allowed to stand. After filtering and drying as before the sample was reweighed.

A useful comparison can be made with the results of thermal treatment. A clay sample was heated to a temperature between 105° and 110°C, when moisture on the surface of the particles is driven off. Heating to 400°C for two hours causes organic matter to combust, while heating at 600°C for one hour causes decomposition of the structural hydroxils in kaolin. Pure kaolin changes weight by 13.9% on lossing structural hydroxils. Thus loss of weight at each stage allows an estimate of surface water, organic matter, and kaolin content.

Results

Fig. 4 shows the X-ray diffraction pattern of Mae Rim ball clay with identification of the main component lines. The results of the analysis by the method of internal standards are given in Table I. In the case of kaolin two different peaks were compared with a CaF_2 line and one with a $Ca(OH)_2$ line. The error quoted is the standard deviation of the fifteen individual measurements in each case. Table I shows the results of determination of organic and soluble matter content. Table II shows the results of thermal analysis with the quantities of components deduced by

TABLE I: X-RAY ANALYSIS OF MAE RIM CLAY COMPONENTS

Component	Intensity ratio	Content (%)
Kaolinite	$\frac{I_{001}}{I_{111}(CaF_2)} = 0.355$	40.5 ± 2.5
	$\frac{I_{002}}{I_{111}(CaF_2)} = 0.332$	40.5 ± 2.5
	$\frac{I_{001}}{I_{001}(Ca(OH)_2)} = 0.933$	36.5 ± 3.0
Quartz	$\frac{I_{101}}{I_{111}(CaF_2)} = 0.222$	27.25 ± 1.5
Feldspar	$\frac{I_{002}}{I_{001}(Ca(OH)_2)} = 0.515$	18.0 ± 2.5

calculating the weight loss between each temperature step following the interpretation given in the previous section. Errors quoted in Tables II and III are standard deviations for five samples.

TABLE II: WEIGHT LOSS FOLLOWING SOLUTION TREATMENT OF MAE RIM CLAY

Treatment	Weight loss (%)
Organic solvent	8.66 ± 0.35
Distilled water	2.44 ± 0.14
Deduced organic content	6.22 ± 0.38

TABLE III: WEIGHT LOSS FOLLOWING THERMAL TREATMENT OF MAE RIM CLAY

Temperature (°C)	Weight loss (%)	Deduced component content (%)	
100	1.35 ± 0.08	Moisture	1.35 ± 0.08
400	7.15 ± 0.33	Organic matter	5.80 ± 0.34
600	13.20 ± 0.35	Structural water	6.05 ± 0.48

TABLE IV: FINAL ANALYSIS RESULTS OF MAE RIM CLAY

Component	Content (%)
Kaolinite	39.2 ± 3.2
Quartz	27.3 ± 3.4
Feldspar	18.0 ± 3.7
Organic Matter	6.0 ± 0.5
Moisture	1.4 ± 0.1
Water Soluble Matter	2.4 ± 0.1
Total	94.3 ± 6.0

The overall accuracy of the X-ray results can best be derived from the linearity of the calibration curves. For a straight line given by $y = ax$ the error in the dependent variable x is given in terms of the error in slope Δa and independent

TABLE V: CHEMICAL ANALYSIS AND EQUIVALENT CONTENT

Source	SiO_2(%)	Al_2O_3(%)	Fe_2O_3(%)	CaO(%)	K_2,Na_2O(%)	MgO(%)
Poosawang[4]	59.96	25.23	1.06	0.04	2.75	0.12
Buntanimit[5]	69.72	25.06	1.42	0.59	–	0.20
Thongchai[6]	55.0	27.9	2.1	0.28	4.1	0.44
Ratanasthien[3]	56.2	31.3	–	–	1.8	–
Present work	57.0	19.1	–	–	3.0	–

variable Δy by the equation

$$\Delta x = \frac{1}{a}\sqrt{(x_n^2 \Delta a^2 + \Delta y^2)} \qquad (4)$$

where x_n is an individual result. Using this method of calculating error the final results are listed in Table IV where results derived from Tables II and III are also included. Using known chemical formulae of the clay minerals the chemical content of the clay can be estimated, and the results are included with results from other sources in Table V.

Discussion

Considering the overall result the percentages derived are accurate within the 5% error usually ascribed to such results. The measurements carried out on several samples were reproducible within the limits of error, showing that a satisfactory standardization of sample preparation and precedure have been achieved.

The basic reliability of the X-ray results is confirmed by an estimate of kaolin content derived from the percentage of structural water loss measured by heating to 600°C. A 6% loss corresponds to a 43% kaolin content. While this method is approximate, it does set an upper limit on kaolin content, a valuable indication in making comparison with another analysis which gave a much higher figure. The percentage of organic matter derived from thermal treatment is also confirmed by that obtained by the solvent method.

The sum of detected components shows a total of 94.3%. Although the diffraction pattern of other crystalline component could not be detected, it is highly likely, and confirmed by chemical analysis to be discussed below, that other minerals are present in quantities of the order of 1%. The diffraction pattern of Mae Rim clay also shows a background scattering not seen in the pattern of the standard mixtures. This background is understood to be scattering from amorphous components of the clay and amounts to a few percent of the total. The presence of small quantities of undetected minerals and of amorphous components accounts satisfactorily for the shortfall of the estimated percentages.

Comparison with other results

A semiquantitative analysis of the same clay has been made by B. Ratanasthien *et al.*[3]. Their results are as in Table VI. It is seen that these results show poor agreement with the results of the present study. However the results of B. Ratanasthien *et al.*[3] had poor reproducibility, while the method used also appears unsatisfactory. It involved an estimate of the total spectrum area, and percentages were derived by taking the percentage of area for the spectral lines of each constituent to this total area. Areas were estimated by multiplying peak height by half width. Difficulties in this method, said to be semi-quantitative, are that the estimate of the total area is likely to be inaccurate due to the impossibility of including the effect of broad background lines which should be included in the area. The total area being underestimated, the percentage for each component content is exaggerated. Overlap and the presence of smaller lines would also hinder the measurement of line area due to an individual component.

TABLE VI: ANALYSIS RESULTS FROM RATANASTHIEN *ET AL.*[3]

Sample	Kaolinite	Illite	Quartz	Feldspar	Calcite
S–1	77%	2%	18%	3%	–
S–2	69%	trace	13%	17%	trace

The lower figure for kaolinite has been confirmed by the estimate from structural water content. A kaolinite content as high as 69% or 77% would certainly be excluded. Finally, it is possible that there is in fact a large variation in content for clay samples taken from different parts of the deposit. Further work is necessary to decide this point. If the differences are indeed so great it implies a serious difficulty in providing estimates of content to the ceramic industry that would apply to the material used over a long period.

A comparison may also be made with results available from chemical analysis. Results from three different sources are listed in Table V. For comparison chemical content derived from our results and those of Ratanasthien *et al.* are also included. Apart from noting a reasonable consistency (excepting the result of Buntanimit[5] for SiO_2 which must be considered suspect) little conclusion can be drawn. As previously mentioned the variable composition of clay minerals prohibits an exact correlation of mineral and chemical content. Thus while the Al_2O_3 equivalent of the mineral analysis appears rather low, the fact that this component derives from both the kaolinite and feldspar fractions makes its estimate more liable to error. The alkali oxides percentage, derived from feldspar only, allows a better comparison, and the agreement with the chemical analysis figures can be considered a satisfactory confirmation of our result.

TABLE VII: COMPOSITION OF PORCELAIN BODIES[a]

Place	Clay (%)	Quartz (%)	Feldspar (%)	Limestone (%)
Japan	38.7	48.3	18.0	
Japan	54.8	19.8	25.4	–
China	44.86	22.09	33.05	–
France	66.39	15.11	12.05	6.47
Germany	54.92	21.56	23.52	–
Belgium	57.92	26.56	16.02	–
Denmark	47.0	20.0	33.0	–
Mae Rim	39.2	27.3	18.0	–

[a] All figures except in the last line (present work) are from ref. 7.

A final comparison may be made with the results of a microscopic study of ceramic products made from Mae Rim clay[2]. Under a low power microscope polished sections of the ceramics show a phase structure. A dark phase, which may be identified as the clay fraction, is seen in a light matrix. Measurements of the dark phase for several samples from different kilns show an average of 40%. Taking the results shown in Table IV as a basis we can calculate that the proportion of kaolinite in a fired product would be 39%. The excellent agreement again discriminates against a higher kaolinite content of the original clay.

The results of the present analysis may be shown in interesting perspective by comparison with figures of porcelain body content used in different countries (Table VII).

Conclusion

The internal consistency of the results presented, together with the accuracy expected from the method of internal standards indicate the reliability of the results presented. The relatively low kaolinite content found is confirmed by results from thermal treatment and microscopic study of ceramic products. It is hoped that the details of the method given may help others to extend the present measurements to other clay deposits available to the ceramic industry and thus provide a basis for systematic improvement of clay body used.

Acknowledgement

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บทคัดย่อ

การวิจัยครั้งนี้เป็นการหาปริมาณของส่วนประกอบของดินเหนียวที่ใช้ทำผลิตภัณฑ์เครื่องปั้นดินเผาส่วนใหญ่แล้วจะใช้ X-ray diffraction โดยวิธี internal standards พร้อมทั้งใช้วิธีทางเคมีและวิธีการเผาเข้าช่วยในการหาปริมาณ ส่วนประกอบที่หาได้นำไปเปรียบเทียบและวิเคราะห์ส่วนกับผลที่หาได้จากวิธีอื่น