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Identification of clay minerals in mixtures subjected to differential thermal and thermogravimetry analyses and methylene blue adsorption tests

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ABSTRACT

The study of identification methods for clay minerals is very important because of the very fine particle size (less than 2 µm) of these materials, which makes it difficult to recognize them with the naked eye. Because they consist of electrically charged particles, clay minerals exhibit distinct and dynamic behavior. From geotechnical standpoint, clay minerals are present in a wide variety of rocks and soils. Because their behavior is difficult to predict, careful consideration is necessary because they exert great influence on the design and construction of roads, tunnels, foundations, slopes, and many other types of infrastructure. Their characteristics may have a positive effect, e.g., when acting as clay liners, or a negative one, e.g., when their swelling characteristic causes buildings to lose their stability. In this context, the purpose of this work was to compare the reliability of two clay mineral identification methods: combined differential thermal analysis and thermogravimetry (*DTA-TG*) and the methylene blue adsorption test (*MBAT*). Proportional mixtures of kaolinite and bentonite were prepared in order to investigate the two methods. These two types of clay were chosen due to their distinct behaviors: kaolinite is a 1:1 clay mineral, and bentonite is composed mostly of montmorillonite, a 2:1 clay mineral. The two methods showed a positive and highly significant correlation. Moreover, the *MBAT* can provide thermal information related to *DTA-TG* tests.

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1. Introduction

Clay minerals have been used extensively in the production of building materials and ceramics due to their unique properties. More recently, they have become an important element in the composition of plastics, paints, rubbers, and even cosmetics. In geotechnical terms, clays are part of the Earth's substrate and are present in a wide variety of rocks and soils. Therefore, it is of great importance to identify them properly because they exert great influence in the design and construction of many types of buildings. Clays may be used in a positive way, e.g., as barriers against contaminant percolation ("clay liners"). However, if they are part of a soil mass, their swelling properties can lead to slope instability.

Numerous methods have been devised to identify clay minerals, including the methylene blue adsorption test (*MBAT*) and combined differential thermal analysis and thermogravimetry (*DTA-TG*). These methods do not provide the exact mineral composition but offer indirect information about its behavior, allowing for an interpretation of possible minerals. These methods are inexpensive and can be

completed in a short time and may therefore be of interest, depending on the type of clay minerals involved.

The aim of this study was to analyze and compare the two identification methods: the *MBAT* and *DTA-TG*, through the recognition of proportional mixtures of kaolinite and bentonite because the geotechnical behavior of the soil depends on the ratios of different types of clay.

The methylene blue (*MB*) test has long been employed to determine the cation exchange capacity (CEC) and surface area of clay minerals (Fairbairn and Robertson, 1957; Johnson, 1957; Phelps and Harris, 1967; Kahr and Madsen, 1995; Neumann et al., 2002; Chiappone et al., 2004; Yukselen and Kaya, 2006; Petkovsek et al., 2010) but was only fully standardized by Tran Ngoc Lan in 1977. This methodology is based on the measurement of the amount of MB adsorbed by or exchanged on clay from an aqueous solution (Pham Thi and Brindley, 1970), considering that each type of clay mineral has a given range of MB adsorption. According to Stapel and Verhoef (1989), MB is a positively charged organic polymeric molecule (C₁₆H₁₀N₃ClS) that is used in the MBAT in an aqueous solution; thus, all clays capable of swelling are in an expanded state. Therefore, all the external and internal crystal surfaces of the clay minerals are accessible to the MB, which replaces the exchangeable cations. As stated in Appelo and Postma (1994), sorption may be defined as an alteration of the concentration of a solute as a result of mass transfer between the solution and the solids.



Research paper



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Table 1

Characteristics of the samples: columns 2 and 3 describe the proportion of kaolinite and bentonite in each sample; columns 4, 5, and 6 describe the mass used in the methylene blue adsorption test (*MBAT*), the differential thermal analysis (DTA), and thermogravimetry (*TG*), respectively.

Sample	Kaolinite (%)	Bentonite (%)	MBAT (g)	DTA (g)	TG (g)
1	100	0	1	1	6.83
2	90	10	1	1	6.83
3	80	20	1	1	6.85
4	70	30	1	1	6.83
5	60	40	1	1	6.83
6	50	50	0.5	1	6.84
7	40	60	0.5	1	6.83
8	30	70	0.5	1	6.83
9	20	80	0.5	1	6.83
10	10	90	0.5	1	6.84
11	0	100	0.5	1	6.84

Numerous studies have focused on analyzing the efficiency of the *MBAT* applied to soils with widely different mineralogy (Brindley and Thompson, 1970; Higgs, 1988; Kahr and Madsen, 1995; Çoçka, 2002), some of them related to soil expansivity (Fityus and Smith, 2000; Yukselen and Kaya, 2008). Erguler and Ulusay (2003) stated that the *MBAT* is a good tool in order to predict the swelling properties of soils. An interesting application of the *MBAT* is in the assessment of the quality of rock aggregates (Stapel and Verhoef, 1989; Yool et al., 1998) used in concrete and mortar. Because these rock aggregates may contain swelling clay minerals that have deleterious effects on buildings, the recognition of these types of minerals is very important.

The thermal analysis is based on the observation of the responses of materials to changes in temperature. While DTA curves show the effect of energy changes (endothermic and exothermic reactions), *TG* curves show weight changes during heating (Guggenheim and Van Groos, 2001). Because clay minerals are highly susceptible to significant compositional changes in response to subtle changes in their environmental conditions, *TG* curves provide interesting information about the reactions that occur during this test because each clay mineral exhibits distinct behavior.

Like the *MBAT*, general studies involving the thermal analyses of clay behavior are also long-standing (Bradley and Grim, 1951; Greene-Kelly, 1957; Grim and Kulbicki, 1961; Mackenzie, 1970; Balek and Murat, 1996; Guggenheim and Van Groos, 2001; Costa et al., 2004; Manoharan et al., 2012; Arsenovic et al., 2014; Tajeddine et al., 2015). Studies related to construction, which consider the effect of various components in cement and concrete composition, are also common (Wild et al., 1996; Stroeven and Dau, 1999; Kakali et al., 2001), as are several works on the composition and strength of ceramics (Brindley and Maroney, 1960; Kingery, 1974; Ramesh et al., 1998; Seifert et al., 2001).

The interpretation of *DTA-TG* curves alone is not sufficient to accurately identify mineralogical species, but it allows for a broad classification of the main clay minerals, particularly of monomineralic clays (Mackenzie, 1970). The *DTA* provides basic information for the

able 2				
alculated	parameters	of	MBA	T.

Sample	Mass (g)	Volume (cm ³)	A (g/100g)	Vb (g/100g)	SSA (m²/g)	CEC (cmol ⁺ /kg)
1	1	10.5	1.58	1.58	38.54	4.92
2	1	35	5.25	5.25	128.45	16.41
3	1	59	8.85	8.85	216.53	27.67
4	1	81	12.15	12.15	297.27	37.99
5	1	106.5	15.98	15.98	390.86	49.95
6	0.5	64	19.2	19.2	469.76	60.03
7	0.5	76.5	22.95	22.95	561.51	71.75
8	0.5	88.2	26.46	26.46	647.39	82.73
9	0.5	101	30.3	30.3	741.34	94.73
10	0.5	117	35.1	35.1	858.78	109.74
11	0.5	133	39.9	39.9	976.22	124.75

identification of the main clay minerals, and *TG* indicates which reactions are associated with mass losses.

According to the typical thermal behavior of kaolinite, it starts to lose both moisture and adsorbed water at a temperature of 100 °C. Subsequently, a dehydroxylation reaction occurs in the range of 450 °C and 650 °C, represented by a second endothermic peak in its curve. At this point, the clay mineral loses its plasticity, and as temperature increases, it forms an amorphous kaolinite known as metakaolinite (Grim, 1953). The vitrification phase starts at temperatures higher than 900 °C, where mullite and high temperature silica polymorphs crystallize.

In smectites, the loss of adsorbed and coordinated water occurs between 100 °C and 250 °C. These clay minerals have a high CEC, so the shape of their peaks depends on the nature of the adsorbed cations (Hendricks et al., 1940). Dehydroxylation occurs between 400 °C and 700 °C, with Fe-rich smectites showing an endothermic peak at approximately 500 °C, while Fe-poor smectites show the same peak at approximately 700 °C. Smectites lose their structure at 900 °C, whereupon the vitrification phase begins with the crystallization of mullite, tridymite, and cristobalite.

2. Materials and methods

2.1. Materials

Kaolinite and bentonite were chosen because these materials behave quite differently. While kaolinite has a 1:1 structure, bentonite is a commercial designation for a clay blend composed predominantly of montmorillonite, which has a 2:1 structure, characterizing it as a swelling type mineral. This study involved clay mixtures; hence, the choice of completely different clay minerals favored a better comparative analysis of the two methods under analysis.

Eleven mixtures were prepared in pre-established proportions, as shown in Table 1, which also describes the mass quantities used in each test. Both materials were characterized by x-ray diffraction with oriented specimens and a copper-target tube as showed in Fig. 1.



Fig. 1. Diffractograms of (A) kaolinite and (B) bentonite.



Fig. 2. Correlations between the Vb index and kaolinite/bentonite percentages, $R^2 = 0.9971$.

2.2. The methylene blue adsorption test (MBAT)

The *MBAT* was performed using the filter paper method described by Pejon (1992), which is a modification of the original method proposed by Tran Ngoc Lan (1977). The preparation of the samples consisted of first air drying them before weighing. A suspension of each sample in approximately 10 cm³ of deionized water was then prepared and placed on a magnetic stirrer.

A burette was filled with a *MB* solution (0.0015 g/cm^3) and positioned over the suspension beaker. Then, a quantity of the blue methylene solution was added to the suspension, which was stirred for another 3 minutes. Using a glass rod, a drop of the mixture was picked up and placed on Whatman #42 filter paper. The test was considered negative if only a dark blue spot appeared. Whenever a light blue halo appeared around the dark blue spot, the test was considered positive and concluded.



Fig. 3. DTA (left) and TG (right) curves for mixtures: a) 0% kaolinite – 100% bentonite, b) 10% kaolinite – 90% bentonite, c) 20% kaolinite – 80% bentonite, and d) 30% kaolinite – 70% bentonite.



Fig. 4. DTA (left) and TG (right) curves for mixtures: a) 40% kaolinite – 60% bentonite, b) 50% kaolinite – 50% bentonite, c) 60% kaolinite – 40% bentonite, and d) 70% kaolinite – 30% bentonite.

Based on this test, valuable properties of clay minerals and soils in general can be determined, namely, the *Vb* index "blue value," activity (*A*), specific surface area (*SSA*), and cation exchange capacity (*CEC*).

Tran Ngoc Lan (1977) defines the *Vb* index as the *MB* mass needed to produce a cover of one molecular layer on the particles contained in a soil mass of 100 g. The *Vb* index is calculated for the soil mass as a whole, considering more than just the present clay minerals. A higher *Vb* index indicates a greater quantity of methylene blue was adsorbed by the soil, thus creating two possibilities: a high content of clay minerals or the presence of clay minerals with high activity.

The *Vb* index is obtained through Eq. (1), where *Vb* is the *MB* value in g/100 g of soil, *C* is the concentration of the *MB* solution (g/cm^3), *V* is the volume of the *MB* (cm^3), and *M* is the dry soil mass (g):

$$V_b = \frac{CV}{M}.100\tag{1}$$

The activity (A) of a soil is calculated for its clay fraction based on the Vb index, as indicated by Eq. (2), where CM is the percentage of clay minerals (%). The activity of a soil is, in part, responsible for its cohesion, which affects its consistency. It also influences the water retention of the soil. High values of activity indicate the presence of swelling clay minerals.

$$A = \frac{Vb.100}{CM} \tag{2}$$

The total active (internal plus external) specific surface area (*SSA*) of the soil particles that may be reached by water is calculated from Eq. (3) (Beaulieu, 1979), knowing that a molecule of *MB* has a surface area of 130 Å², and Avogadro's number *N* is 6.02×10^{23} . *M_{MB}* is the anhydrous *MB* molecular mass (g), *m* is the dry *MB* mass (g), and *SSA* is given in



Fig. 5. DTA (left) and TG (right) curves for mixtures: a) 80% kaolinite – 20% bentonite, b) 90% kaolinite – 10% bentonite, and c) 100% kaolinite – 0% bentonite.

 $\rm m^2/g.$ Because clay minerals present a very fine particle size, they will have higher SSA values.

$$SSA = \left(\frac{130.10^{-20}.6.02.10^{23}.m.V}{M_{MB}.M.1000}\right)$$
(3)

The *CEC* is calculated through Eq. (4) (Chen et al., 1974), where the *CEC* is given in cmol⁺/kg and *C*, the concentration of the *MB* solution, is given in normality (N):

$$CEC = \frac{V.C.100}{M} \tag{4}$$

2.3. Differential thermal analysis (DTA)

The temperature gradient and final temperature of the test are adjusted. In this study, a variation of 12.5 °C/min and a final temperature of 1000 °C were adopted. The *DTA* device is a model RB 3000–20 from BP Engenharia, and the test is controlled by its data acquisition system, which detects temperature variations in the sample compared to alumina.

The system is calibrated so that the beta-quartz inversion, which occurs at 573 °C, is recorded as a deflection to the right in the galvanometer, with a maximum at 570 °C (Faust, 1948). Therefore, based on a comparison with quartz, a *DTA* curve (temperature versus galvanometer deflection) can be obtained, on which the positive ordinates correspond to exothermic transformations and the negative ordinates to endothermic transformations. The system has a repeatability of 0.2%.

2.4. Thermogravimetry (TG)

Like the *DTA* equipment, the *TG* is heated at a rate of 12.5 °C/min. The balance then registers the sample's mass loss, which is the result of its loss of water and other volatiles. The *TG* temperature versus mass loss curves complement the interpretation of the *DTA* curves. *TG* is more limited than the *DTA*, so it serves as a complement. The *DTA* and *TG* curves are highly representative of monomineral clays, but both the position and intensity of the endothermic and exothermic transformation



Fig. 6. Correlation between the mass loss of kaolinite and its percentages at a temperature close to 600 °C and the correlation between the mass loss of bentonite and its percentages at a temperature close to 150 °C, obtained from *TG*.



Fig. 7. Correlation between total mass loss and the percentages of kaolinite and bentonite.



Fig. 8. Example of software interface with the automatic calculation of peak areas (the black arrow indicates the number of calories corresponding to the peak).

peaks are altered when the sample under analysis contains more than one type of clay (Mackenzie, 1970).

3. Results and discussion

3.1. The methylene blue adsorption test (MBAT)

The calculated parameters of the eleven samples are listed in Table 2. Because all parameters are directly related to the *MB* volume, the *Vb* index was chosen to correlate to the clay percentage as shown in Fig. 1.

Fig. 2 reveals a linear tendency between the *Vb* index and clay mineral percentages. The result is consistent with the proportions of the mixtures. Bentonite is composed predominantly of clay minerals with a high swelling capacity; thus, its volume may increase when in contact with liquids. On the other hand, kaolinite is a dioctahedral clay with almost no swelling capacity. This characteristic is entirely related to the cation exchange capacity (*CEC*), which is also related to the *Vb* index. High *CEC* values indicate a clay mineral with a high swelling capacity. Therefore, a clay mineral with high swelling capacity indicates that a high volume of *MB* is needed to cover a molecular layer of the particles contained in a given mass of soil.

While the typical *CEC* of bentonite is $80-150 \text{ cmol}^+/\text{kg}$, that of kaolinite is $3-15 \text{ cmol}^+/\text{kg}$. Present calculations show values compatible with those reported in the literature, with a *CEC* of 124.75 and 4.92 cmol^+/kg for bentonite and kaolinite, respectively (Grim, 1953).

3.2. Differential thermal analysis (DTA) and thermogravimetry (TG)

The *DTA* and *TG* curves obtained in this study are consistent with the data presented in the literature on the thermal behavior of kaolinite and bentonite. The main endothermic and exothermic peaks of each mineral were identified, as illustrated in Figs. 3, 4, and 5.

The curve of 100% bentonite (Fig. 3a) shows an intense endothermic peak at 175 °C, which is typical of bentonite, corresponding to the loss of adsorbed water between the layers and the loss of water coordinated to the exchangeable cations. A distinctive, albeit low intensity, endothermic band of sodic bentonite occurs between 580 °C and 610 °C, indicating the loss of structural hydroxyls. This sample may contain a small amount of iron in view of the intermediate location of this peak when compared to the typical behavior of bentonite as described in the introduction. When rich in iron, montmorillonite has endothermic peaks at approximately 500 °C–550 °C, and when it is not iron-rich, this peak moves to 700 °C (Santos, 1989). The mineral's crystalline structure is preserved up to 820 °C, after which its destruction occurs at a small endothermic peak. The *TG* curve is consistent with the *DTA* curve because it registers mass losses as endothermic reactions occur.

In the curve of 100% kaolinite (Fig. 5c), the first small endothermic peak at 130 °C is related to loss of adsorbed water. Dehydroxylation begins at 575 °C and ends at 605 °C, at which point there is an intense endothermic peak. Metakaolinite, which does not have a clearly crystal-line structure, is then formed, and at 990 °C, the nucleation of mullite occurs.

The intermediate curves between 100% bentonite and 100% kaolinite show mainly the decrease of the most intense and typical endothermic peak of bentonite, while the typical endothermic peak of kaolinite emerges, increasing in intensity as the percentage of bentonite decreases.

Fig. 6, which was obtained using the *TG* results, shows the correlation between mass losses (g) and kaolinite–bentonite percentages. It can be inferred that mass losses increase as each percentage of clay increases. Bentonite has a slightly higher mass loss because its swelling capacity is greater than that of kaolinite. Fig. 7 also shows that the total mass loss is greater with higher percentages of bentonite.



Fig. 9. Correlation between clay percentages and the calorific variation of the characteristic endothermic peak: a) bentonite in the DTA, which is equivalent to the energy of the adsorbed water loss shown in the heating-rate curves; b) kaolinite in the DTA, which is equivalent to the energy of dehydroxylation shown in the heating-rate curves.



Fig. 10. Correlation between clay percentages and calorific variation due to mullite crystallization.

3.2.1. Peak area analysis

According to Mackenzie (1970), Norton (1939) was the first to demonstrate experimentally that, under certain conditions and in certain materials, the endothermic peaks of a sample are proportional to the amount of reactive material it contains. Based on the measured heat of reaction, comparisons can be made between the thermal energy, in terms of calorific loss and gain, in each experiment. All the material used in this study is reactive because it blends bentonite and kaolinite.

To analyze the peak areas, the differential thermal analyzer had to be calibrated before the experiments to obtain a standard reference. This calibration was done based on quartz *DTA* heating-rate curves, whose endothermic peak at 573 °C is well defined. The software of the analyzer recognizes the *DTA* peaks, automatically calculating their areas and giving the corresponding number of calories, as shown in Fig. 8. Based on the measured peak areas, the heat of reaction was determined for the three reactions presented in the heating-rate curves: adsorbed water loss, dehydroxylation, and mullite nucleation (the first two are endothermic reactions and the latter is an exothermic reaction). Fig. 9 illustrates the correlation between the calorific loss and gain with bentonite–kaolinite proportions and the reactions of adsorbed water

loss (a typical bentonite peak at approximately 175 $^{\circ}$ C) and dehydroxylation (a typical kaolinite peak at approximately 600 $^{\circ}$ C).

In Fig. 9, note that the energy of the adsorbed water loss tends to decrease with lower quantities of bentonite. This is consistent with the fact that bentonite is an expansive clay mineral, which has a higher water adsorption capacity. In fact, because of this direct correlation between the amount of bentonite and the loss of adsorbed water during *TG*, this is considered the characteristic peak for this bentonite. The same reasoning applies to the amount of kaolinite and the energy of dehydroxylation, both of which increased during the test.

Fig. 10 shows the correlation between clay percentage and calorific variation due to mullite crystallization. Because the reactions that lead to mullite crystallization are dependent on the presence of kaolinite, it was expected that mullite would be absent or minimal at lower percentages of this clay mineral. The presence of mullite is only evident in the mixture containing 30% kaolinite.

For the *MBAT* correlations, the coefficient of determination was 0.9971, whereas the *DTA* showed 0.9862 for adsorbed water loss, 0.9703 for dehydroxylation, and 0.9731 for mullite crystallization. The two methods showed a positive and highly significant correlation, despite the fact that the MBAT is more subject to human error than the DTA.

The *MBAT* method adopted in this study, which is described by Pejon (1992), substituted the original *MB* concentration of 0.01 g/cm^3 used by Tran Ngoc Lan (1977) for a concentration of 0.0015 g/cm^3 in order to adapt the test to tropical soils, which are more abundant in Brazil and tend to be more kaolinitic. It is believed that the accuracy of the *MBAT* obtained in this study was due to the use of this lower concentration, which led to a lower margin of error when adding the *MB* to the *MB* plus clay dispersion.

3.2.2. Correlations between the MBAT and DTA-TG results

Because the *MBAT* is a simpler identification method than *DTA-TG*, establishing correlations between them in order to obtain heat-related information from the *MBAT* may be of interest in the field of ceramics, for example, in which data on the loss of clay mass and the heat of reaction are important because they are tied to the final quality of ceramics. Therefore, Fig. 10 shows the correlation between the *Vb* and bentonite mass loss (a) and the *Vb* and kaolinite mass loss (c). Note the good linear



Fig. 11. Correlations between a) Vb and bentonite mass loss; b) Vb and adsorbed water loss; c) Vb and kaolinite mass loss; d) Vb and dehydroxylation.

correlation, which enables information on mass loss to be obtained simply from the *Vb* values of the bentonite–kaolinite mixtures. A good correlation was also observed between the *Vb* and heat of reaction due to the loss of adsorbed water and dehydroxylation reactions, as illustrated in Fig. 11b and d.

4. Conclusions

Both the *MBAT* and *DTA-TG* are excellent methods for the indirect identification of kaolinite and bentonite mixtures because they show a positive and highly significant correlation. However, unlike *DTA-TG*, the *MBAT* is a lower cost test that does not require specific equipment, using only ordinary chemistry laboratory equipment. However, it is important to emphasize that quite reliable results may only be obtained through a meticulous and methodic procedure, in order to reduce human error. In some fields, e.g., engineering geology, information about clay composition and percentage is essential, and the *MBAT* proved to be an efficient and inexpensive test. In addition, the thermal data of mass loss and heat of reaction, which are crucial in the use of clays in ceramics, can easily be estimated using the correlation with *Vb*.

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