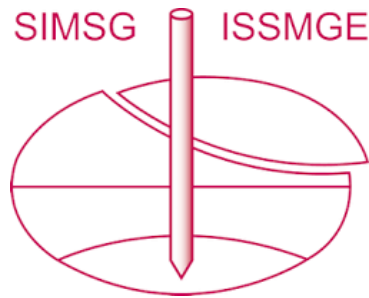


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XRD quantification of clay minerals: impact of sample preparation and quantitative interpretation methods choice

Quantification XRD des minéraux argileux: impact de la préparation et choix des méthodes d'interprétation quantitative

Giorgia Di Remigio, Irene Rocchi & Varvara Zania

Civil Engineering Department, Technical University of Denmark, Denmark, gidire@byg.dtu.dk

ABSTRACT: The detailed knowledge of the mineralogy of a natural clay formation can support the understanding and prediction of its hydraulic and mechanical characteristics. X-Ray diffraction analysis has been widely used in order to obtain the mineralogical composition of natural clays. The quantification of clay mineral composition depends on the sample preparation technique and the data interpretation approach. Despite the great advances in XRD analysis, the data interpretation of multi-mineral soils is still cumbersome and lacks a standard procedure. This study analyses the effect of three different sample preparation methods and four different data interpretation approaches, on the quantification of a series of artificial clay mixtures of known mineral composition, in order to determine the combination that provides the most accurate results. The investigation outcomes show that utilizing fast, easy to perform preparation methods, generally leads to errors up to 40% in the mass percentage calculation. However, using more refined techniques, such as the vacuum based preparation method, decreases the error down to 1%. Finally, the quantification method based on the minerals X-Ray absorption, shows a prediction error up to 4% when performed on vacuum prepared samples.

RÉSUMÉ : La connaissance détaillée de la minéralogie d'une formation argileuse naturelle peut aider à la compréhension et à la prédiction de ses caractéristiques hydrauliques et mécaniques. L'analyse par diffraction des rayons X a été largement utilisée afin d'obtenir la composition minéralogique des argiles naturelles. La quantification de la composition minérale des argiles dépend de la technique de préparation des échantillons et de l'approche d'interprétation des données. Malgré les grands progrès de l'analyse XRD, l'interprétation des données des sols multi-minéraux est encore lourde et manque d'une procédure standard. Cette étude analyse l'effet de trois méthodes différentes de préparation des échantillons et de quatre approches différentes d'interprétation des données, sur la quantification d'une série de mélanges d'argile artificielle de composition minérale connue, afin de déterminer la combinaison qui fournit les résultats les plus précis. Les résultats de l'étude montrent que l'utilisation de méthodes de préparation rapides et faciles à exécuter entraîne généralement des erreurs allant jusqu'à 40 % dans le calcul du pourcentage de la masse. Cependant, l'utilisation de techniques plus raffinées, telles que la méthode de préparation sous vide, réduit l'erreur à 1%. Enfin, la méthode de quantification basée sur l'absorption des rayons X des minéraux montre une erreur de prédiction allant jusqu'à 4% lorsqu'elle est réalisée sur des échantillons préparés sous vide.

KEYWORDS: XRD, X-Ray diffraction, mineralogy, quantification, clay

1 INTRODUCTION

The mineralogical composition of clays affects significantly their electrical and physical characteristics, as showed by numerous studies (Moore and Reynolds, 1997; Środoń and McCarty, 2008; Yuan et al., 2009). This strong correlation is due to the minerals structure, and to their interaction with water, so that 2:1 clay minerals show a significant sensitivity to water, while those with a 1:1 structure have a weaker reactivity to water (Moore and Reynolds, 1997). Having information on the clay mineral composition is therefore useful to forecast the soil mechanical behaviour, before any mechanical test is performed.

The most common technique to qualitatively or quantitatively characterize the clay mineralogical composition is X-Ray Diffraction (XRD) (Ross and Kerr, 1931; Schultz, 1958; Taylor, 1999; Bish and Post, 1993; Środoń, 2002; Zhou et al., 2018). When a crystal is exposed to X-Rays, it reacts by both absorbing and diffracting them. The diffracted wave is then collected and its intensity recorded, showing peaks at certain specific positions, which depend on the crystal structure. The intensity of the diffraction peaks is directly related to the abundance of a certain mineral in the mixture. However, this correlation is not obvious as different minerals are more or less prone to diffract X-Rays, showing therefore different absorption coefficients. These can be calculated if the clay mineral chemical composition is known, however, natural clay deposits are rarely composed of a single, pure, mineral but they are more generally made of a mix of inter-grown clay crystals, so that they do not show a unique, repeatable

structure. For this reason, it is impossible to determine a standard XRD pattern for all the clay minerals existing in nature, especially referring to the Smectite clay group, for which the frequent substitutions and vacancies suggest the existence of a potentially infinite set of these 2:1 minerals. Moreover, the natural clay minerals are rarely fully crystallized, but they are often observed in a transitional phase, causing a shift and a change in the diffraction pattern (Moore and Reynolds, 1997). Also, due to their platy shape, the clay particles show clear orientation patterns, that strongly affect the creation of a randomly oriented specimen (Moore and Reynolds, 1997). This could seem to help when oriented samples need to be generated, however, a unique preparation method has not been developed yet. Moore and Reynolds (1997) described four different methods to prepare this type of samples, namely the Glass slide preparation, the Smear mount method, the Vacuum method and the Centrifuged porous plate method, each showing different downsides, especially concerning the technical difficulties in the sample preparation and its homogeneity. Finally, using different setups for the same XRD equipment leads to the generation of different XRD patterns. For these reasons, even though the main four families of clay minerals can be easily detected from a qualitative analysis of the XRD pattern, a conclusive model for the clay mineral quantification has not been developed yet.

Several attempts were made, trying to create an analysis method able to accurately quantify the clay mineralogical content, specifically Whole Pattern and Single Reflection based approaches were developed. For the former group the most used

is the Rietveld method (Moore and Reynolds, 1997), consisting in the iterative fitting of the known diffraction patterns of one or more minerals, with the XRD pattern of the unknown material. Different software for the clay mineral quantification based on this method were developed with time. SIROQUANT, GSAS, WYRIET, BRENDA, Highscore and TOPAS are some of them. However, a deep knowledge of clay mineral crystallography and X-Ray diffraction theory is needed in order to use them properly, as they give the possibility of manipulating the XRD pattern by changing the crystallographic structure of the clay, a procedure that can lead to the creation of structures that, even though allow for a good fit of the diffractogram, cannot exist in nature. For this reason, the use of these software is recommended only to expert users as every pattern correction needs to be understood and physically justified. About the Single Reflection approach, this consists of analysing the properties of a single characteristic reflection and it is widely used, so that several methods based on this approach are available (Schultz, 1958; Moore and Reynolds, 1997; Mbia et al., 2014).

This study compares the results obtained from a set of tests performed on mixtures of commercial clay prepared with three of the four preparation methods described by Moore and Reynolds (1997) for oriented clay samples, and quantifies the error obtained by quantifying the mineral composition using four different analysis methods, namely the Mineral Intensity Factor (MIF), the method proposed by Bjørnslev (B), that based on the curves fitting (CF), and that based on the absorption coefficients (AC). The results are therefore discussed to take into consideration the effect of the sample preparation on the final results, together with that of the analysis method utilized, in order to suggest the combination that shows the smallest error.

2 METHODOLOGY.

A series of XRD tests were performed on mixtures of commercial kaolinite (K) and bentonite (Bn), mixed with the following K/Bn mass ratios: 100/0, 90/10, 70/30, 50/50, 30/70, 10/90 and 0/100. Specifically, for this work the bentonite was supplied by Scandinavian Ceramics (Catalog number: 1410-5) in its powdered form, while the Speswhite Kaolinite (CAS number: 1332-58-7) was provided by Imerys. As the mixture clay content is known to be higher than 90%, there was no need to define it testing randomly oriented samples, so that only oriented samples were investigated. These specimens did not undergo any pre-treatment, and the wet mixtures were transferred to glass slides to be afterwards dried and analysed with the X-Rays, by means of three different preparation methods (Moore and Reynolds, 1997), the Glass Slide preparation, here called Drop method (D), the Smear mount preparation (S) and the Vacuum preparation (V). It may be noted that the use of a glass base is limiting, as it gives high amorphous signals if the clay sample is not sufficiently thick (Moore and Reynolds, 1997), and it softens above 300°C, risking to influence the clay orientation and, thus, the XRD pattern.

Regarding the sample preparation, the Drop methodology is the easiest, and most commonly used sample preparation. The sample is prepared by mixing 0.03 g of ground clay sample with 1.5 ml of deionized water. Then it is dropped by the use of a pipette on a glass microscope slide and left to air dry. However, it provides with poorly homogeneous, highly segregated particle samples and small thickness. For all these reasons, samples prepared with this method are more appropriate to perform qualitative analysis. The Smear mount method can be used to determine the constituents of a bulk sample and perform semi-quantitative analysis, and it is performed by placing a few mm³ of dry clay on a microscope slide, and smearing with a micro-spatula the paste created after adding two drops of dispersant solution on the glass slide. This technique is more complicated to perform than D, especially when smectitic clay samples are

prepared, as they tend to stick to the spatula instead of the glass, being moved instead of smeared. According to Moore and Reynolds (1997), the Vacuum method is the most reliable when a quantitative analysis has to be performed. An amount of 0.1 grams of dry clay sample is brought in suspension with 0.30 ml of dispersant prepared as per Moore and Reynolds (1997) and then placed under vacuum in a funnel to deposit onto a paper filter. In these conditions, at the beginning, the flow rates through the non-clogged filter are high and the particles transit through it without any significant particle segregation. After a sample thick enough is deposited on the filter, in order to avoid air to be drawn through the cake, the vacuum flask is brought to room pressure. Afterwards, the excess of water in the funnel is removed and the 0.45 µm filter paper is removed and placed face down on a glass substrate. It is important that no air bubbles are formed during the process. Pollastro (1982) originally recommended the use of a roller in order to ensure the sample sticks on the glass. However, Moore and Reynolds (1997) suggest to perform the operation without rollers as the rolling procedure can produce a particle orientation. For this work, the filter was gently laid over the glass by means of a micro-spatula, without applying any pressure. When the filter-sample-glass package is ready, it is left for 4 minutes in contact with the air, and then the filter is removed. It is important to highlight that if the filter is removed too soon the sample does not transfer on the glass while, if it is removed too late, the filter becomes too brittle, making it impossible to remove. In order to perform this sample preparation, Moore and Reynolds (1997) recommend the use of the Millipore® apparatus as the authors consider it the best they have found in commerce.

Regardless of the sample preparation method utilized, in order to check the preparation process quality, several samples using the same K/Bn percentage were tested, and no appreciable difference in the final minerals content measurement could be detected.

After preparing the clay particle sample following one of the previously explained methods, this was inserted into the X-Ray machine to be tested. For this work, the XRD X'Pert PRO MPD equipment was used, using 0.004 radians Soller slits, a 4° Divergence slit opening used with an Automatic Divergence slit correction, a 10mm beam mask, an Anti-scatter slit of 2°, and a Nickel Kβ filter. The different slit and masks were chosen to fulfil the recommendation of the XRD equipment provider, and those of Moore and Reynolds (1997). The air dried samples were tested in the 4-60° 2θ interval with a step of 0.05°/sec and a duration of 125 sec. Afterwards, the sample was put face up in a desiccator, filled with ethylene glycol, avoiding contact with the liquid. The container was then left in the oven at 60° for at least 8 hours to allow the organic compound to evaporate and saturate the clay expandable layer, swelling them. Once the samples were taken off from the oven, they were left in the desiccator at room temperature and were tested up to 15°, up to 60° and again up to 20° with a step of 0.05°/sec and a duration of 125 sec. This operation is done in order to guarantee that the ethylene glycol is not evaporated from the surface of the sample during the high angle test and that the registered diffraction pattern is representative of the sample while it still has the expandable layers swelled.

For the analysis of the obtained diffraction patterns four different Single Reflection approaches were used: the Mineral Intensity Factor (MIF), the method proposed by Bjørnslev, that based on the curves fitting, and that based on the absorption coefficients. The MIF method is based on the assumption that every mineral has a unique mineral intensity factor called MIF value associated to a specific XRD reflection. Therefore, once the intensity and the mass of a reference material present in the mixture are known, by knowing the intensity of the investigated material, it is possible to calculate its mass, using the following formula (Moore and Reynolds, 1997)

$$\text{MIF} = \left(\frac{I_x}{I_s}\right) \left(\frac{W_s}{W_x}\right) \quad (1)$$

Where I_x is the intensity of the clay mineral X in the analysed mixture, I_s is the intensity of the standard material added to the mixture, W_x is the mass% of the clay mineral and W_s is the mass% of the standard material. Practically, the sample is mixed with a low absorption compound having a structure similar to that of the clay minerals in order to avoid influencing the preferred oriented structure of the sample, and which XRD reflection does not overlap with the clay diffraction peaks. For this work, ZnO nanoparticles were used as a standard reference material. As no pure illite was used for this study, it was not possible to obtain its MIF value directly. This was obtained by assuming an illite content of 5% for the 100/0 kaolinite sample. As the utilized kaolinite is not a pure mineral, a recursive iteration system had to be used in order to define the mass percentage of the clay. Therefore, for this work W_x is not a unique value. $W_{\text{kaolinite}}$ is assumed to be equal to a reasonable value in order to obtain a reference $\text{MIF}_{\text{kaolinite}}$ value. The same operation is performed in order to find $\text{MIF}_{\text{illite}}$ and MIF_{ZnO} . Using these MIF values, the % of the Kaolinite, Illite and ZnO contained in the mixture are found. Therefore, the new W_x are found, that are used to produce new MIF values. The iteration is repeated until convergence is achieved. The MIF values obtained for the different minerals, for each of the three preparation samples, are presented in the first section of Table 1.

Professor O. Bjørnslev (Awadalkarim and Fabricius, 2014) performed a series of XRD tests on smeared samples of monominerals and known mixtures of them obtaining a set of correction factors to be applied to the (001) clay minerals reflection intensity for the Air-dried and 550°C step, and to the peaks area for the ethylene-glycolated samples. These values are shown in the second column of the second section of Table 1. As the values were obtained only for the smeared samples, only one set of data is available. Finally, for this work, this approach is referred as approach B.

Knowing the chemical composition of the commercial bentonite used, and due to the fact that the illite and kaolinite chemical structures do not vary significantly in nature, it was possible to calculate the characteristic mass absorption coefficients (a_{ch}) of the 3 clay minerals. This is defined as (Moore and Reynolds, 1997)

$$a_{\text{ch}} = \left(\frac{\mu}{\rho}\right) * \text{wt}\% \quad (2)$$

Where μ/ρ is the mass absorption coefficient and has a tabulated set of values that depend on the intensity of the X-Ray wave used, and wt% is the atomic weight percentage of each of the elements composing the clay mineral (Moore and Reynolds, 1997). The empirical chemical composition of the bentonite used for this work is $(\text{Al}_2\text{O}_3)_1(\text{SiO}_2)_4(\text{H}_2\text{O})_9$, therefore it has characteristic $a_{\text{ch}}=31.8$. Pure kaolinite has a calculated $a_{\text{ch}}=29.8$, obtained from its chemical formulation $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ while $a_{\text{ch}}=41.2$ was obtained from a well crystallized illite having the following empirical formula $\text{K}_{0.6}(\text{H}_3\text{O})_{0.4}\text{Al}_{1.3}\text{Mg}_{0.3}\text{Fe}^{2+}_{0.1}\text{Si}_{3.5}\text{O}_{10}(\text{OH})_2$. The ratios of a_{ch} obtained for the different minerals, to that obtained for kaolinite is used as a correction factor, to amplify the area detected and calculate the percentage based on the obtained modified areas. These correction coefficients are shown in the third column of the second section of Table 1. The absorption coefficients do not depend on the sample preparation method, thus only one set of data are provided. For this work, this approach is referred to as approach AC.

As the samples masses were known, it was possible to fit half of their 100% diffractogram to fit the 50/50 values. However, the simple overlap of the two curves was not sufficient to fit the

100% curve. Therefore, the kaolinite curve was fixed, while the values of the pure bentonite curve were amplified of a certain correction factor that are therefore used for the quantification. As the only illite available in the sample is that present in the kaolinite, its correction factor was set equal to 1, as shown in the third section of Table 1. For this work, this approach is referred to as approach CF.

All the values presented in Table 1, refer to the 12.3 (Smectite), 10 (Illite) and 7.2 (Kaolinite) Å d spacing. The XRD patterns were analysed using Origin. The peaks characteristics were interpreted using “Peak analyser” function (Analysis, Peaks and Baseline, Peak Analyser, Open dialog) with its function “Fit Peaks” (PRO). First, the baseline was manually defined and removed. This operation was the most sensitive to the operator experience, as the clay samples frequently contain amorphous materials, which background curve must be removed. Then, the representative peaks were determined, and the pattern was fitted with a series of Pseudo Voigt curves. The main output obtained are the peak centre, its maximum height, and its area. The quantification was performed on the pattern obtained after treating the samples with ethylene glycol, in order to avoid any overlapping of the illite and the smectite peak. The area values were multiplied to the correction factors of Table 1, and the percentage of the modified areas over the sum of them, was recorded as the mass% value of the sample.

Table 1 – Correction coefficients applied to the areas of the different minerals, according to the different sample preparation and quantification methods.

	<i>MIF D method</i>	<i>MIF S method</i>	<i>MIF V method</i>
Kaolinite	0.41	0.59	0.94
Smectite	0.18	0.16	0.28
Illite	0.13	0.42	1.35
ZnO	0.55	0.59	0.51
	<i>Approach B</i>		<i>Approach AC</i>
Kaolinite	1.00		1.00
Smectite	1.15		1.07
Illite	3.00		1.38
	<i>Approach CF</i>		
	<i>D method</i>	<i>S method</i>	<i>V method</i>
Kaolinite	1.00	1.00	1.00
Smectite	1.69	1.04	2.11
Illite	1.00	1.00	1.00

3 RESULTS AND DISCUSSION

Before looking at the quantitative results, a qualitative analysis of the sample preparation influence on the XRD diffractogram is performed. Figure 1 shows the diffraction patterns of a 100% kaolinite and a 100% bentonite pattern. The peak marked with Sm is that characteristic for the Smectitic soils, that with I for the Illite and that marked with K is the characteristic Kaolinite peak. It may be noted that no overlap of the main peaks is present, simplifying the peaks recognition. Moreover, it should be highlighted that, as discussed in the methodology section, the kaolinite utilized is not pure, as the illite peak is present at 8.7°. Figure 2 shows the diffraction patterns obtained by testing a mixture of 50% kaolinite and 50% smectite samples, prepared with the Drop, the Smear mount and the Vacuum method. It may be noted that the Drop method shows a considerably larger area

for the smectite peak, and a smaller for the kaolinite, while the Illite peak is completely embedded in the smectite peak. The Smear mount shows a similar distribution for the kaolinite and the illite peak, but a lower peak intensity for the smectitic sample. The shape of a mineral curve, is generally used to determine its crystallization state, so that a wider curve indicates the presence of a diffraction planes far from the main one, and thus, a lower crystallization level (Moore and Reynolds, 1997). According to this definition, the investigated kaolinite shows a high degree of crystallization, regardless of the sample preparation.

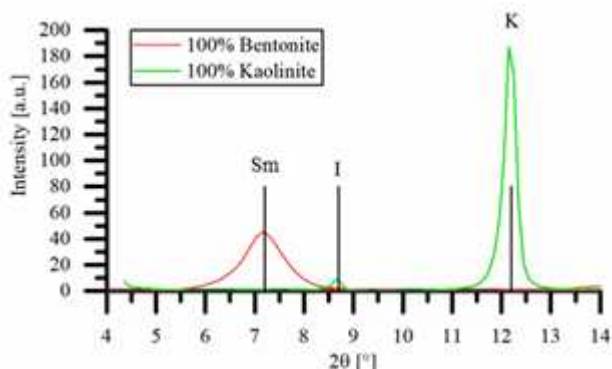


Figure 1- XRD patterns of the 100% bentonite and 100% kaolinite samples, prepared using the Vacuum method.

However, the bentonite seems to change in crystallinity, being more amorphous for the Drop samples. As the temperatures and pressures applied during the sample preparation did not allow for any crystallization of the sample, the presence of a wider smectitic peak corresponds to a lower degree of orientation of the particles, probably linked to the segregation process occurring during the drying procedure of the sample.

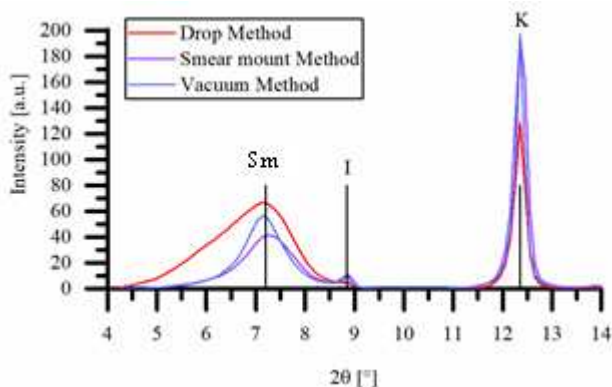


Figure 2- XRD patterns of the 50% and 50% bentonite samples, prepared using the Drop, the Smear mount and the Vacuum method.

The mass percentage of the clay minerals contained in each investigated mixture was known, therefore it was possible to calculate the error as the difference between the value expected based on the percentage of pure mineral mixed in the tested sample and that measured. The 100% mixtures were excluded from the calculation. To ease the discussion, the data obtained from the 7 different mixtures prepared with 3 sample preparation and analysed with 4 different approaches, are plotted in terms of average error and standard deviation. A different colour is used for each sample preparation method, a symbol for each analysis approach, and the error bar indicates the standard deviation.

Figure 3 shows the average of the absolute value of the error calculated on the different mixtures, for all the minerals, on a single sample preparation and analysis method. The need for averaging the absolute values of the error, is due to the fact that the difference between the expected and the measured mass

percentage included positive and negative values, and therefore, averaging the pure numbers would have mistakenly led to an error close to 0. According to Moore and Reynolds (1997) a good quantification method should provide with an accuracy of $\pm 10\%$ for minerals having a concentration greater than 20% and an accuracy of $\pm 20\%$ for the others in order to be considered representative. Focusing on the Smear preparation, the CF preparation shows the lowest standard deviation and a low average error, making it the most repeatable and thus reliable of the set. The high error observed for MIF is supposedly linked to the disturbance of the ZnO micro-powders in the clay particles orientation. It can be noted that despite the B approach was developed for Smear samples, it shows the highest average error. However, it must be stressed that the set of parameters were obtained with a different XRD setup, so that the analysis results are not optimized for the setup used by the authors, leading to a greater error. Focusing on the Vacuum method (see Figure 3b), it may be noted that the MIF and the B approach show both the highest average and standard deviation. On the other hand, the CF and the AC approaches both show an average error of 2% and a standard deviation smaller than the unity, leading to a maximum estimated error of 2%.

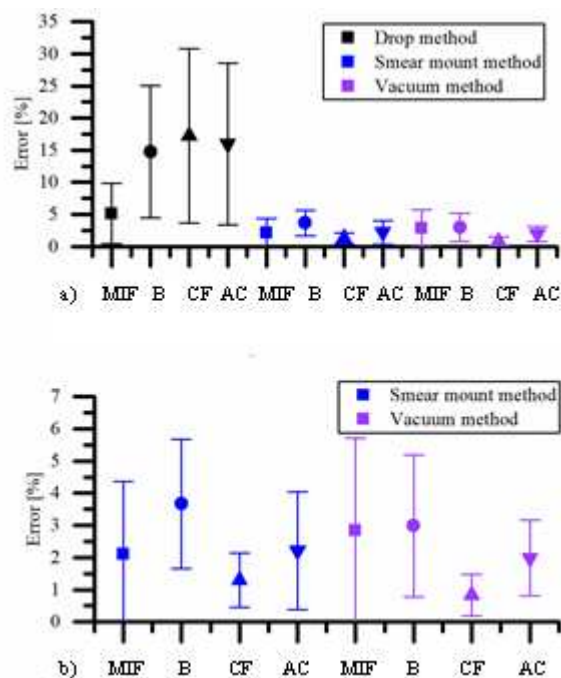


Figure 3 – Average error calculated for the different sample preparation methods (a), while the Drop method is excluded in (b).

Figure 4 shows the error observed for the kaolinite calculation. As observed for Figure 3.a, the Drop method shows the highest error average and standard deviation, so that the kaolinite value is consistently underestimated, reaching a maximum of 35% error for the CF approach. This is in accordance with the segregation effect expected when using the Drop method. As the kaolinite particles show a higher specific gravity and particle size than that of bentonite, they tend to sediment faster, laying on the bottom of the sample, with the smectitic particles covering them. When the soil is tested, the uppermost layer of bentonite scatters and absorbs the X-Rays, so that the radiation is weakened when it reaches the kaolinite strata. Moreover, the diffracted rays are absorbed from the bentonite layer, and the received signal is consistently reduced. It is therefore reasonable that the kaolinite content is strongly underestimated when the samples are prepared using the Drop method. The MIF, on the other hand, seems to correctly forecast the kaolinite content. As the density of ZnO is twice that of

bentonite, it is reasonable to assume that its particles were covered with smectite. Therefore, it diffracted a signal that was filtered by the bentonite as the kaolinite did, so that the detected intensity is reduced for both the signals. Moving to Figure 4.b, a negligible set of errors are observed for both the Smear and the Vacuum method. With exception of the Smear AC, the kaolinite content is consistently slightly overestimated, especially for the MIF and the B approach of the Vacuum method. Moreover, the error bar is consistently showing values smaller than 2%, suggesting a good repeatability of the results. It may be noted that the CF and the AC approaches applied to the Vacuum methods, show an average error of 0, with an error bar of $\pm 1\%$, ensuring a good quality set of results for the characterization of the kaolinite.

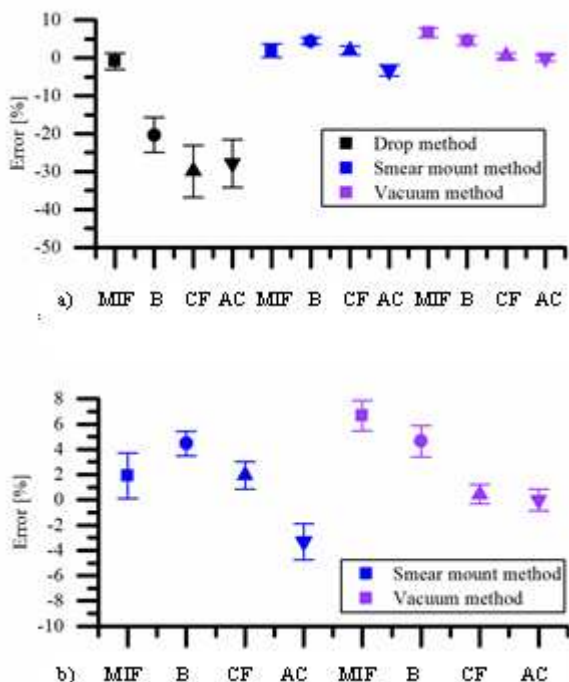


Figure 4 - Average error calculated for kaolinite, in the different sample preparation methods (a), while the Drop method is excluded in (b).

The average error and the associated standard distribution for the smectite mineral is presented in Figure 5. As expected, the samples prepared with the Drop method, consistently show an overestimation of the bentonite content, due to the segregation effect already observed. In this case, however, also the MIF shows a significant average error. This is because the MIF value is proportional to the minerals detected intensities, and those are a function of the original X-Ray intensity (as per the Bouguer-Lambert law). If the original ray of the reference material is filtered by the bentonite, this leads to a lowering of the output detected intensity, and therefore to an overestimation of the MIF value, as expressed in Eq. (1), with consequent overestimation of the bentonite content. Moving to Figure 5.b, the Smear and the Vacuum method show also in this case a low set of average errors, with a consistent underestimation of the smectite. In this case, the Vacuum prepared samples analysed with the AC approach, averagely underestimates the smectitic content of 2%, while the CF shows results comparable to those observed in Figure 4.b.

Finally, Figure 6 illustrates the error observed for the Illite content. As the only Illite present in the sample is that contained in the kaolinite, which is expected to be less than 5%, small average errors and standard deviations are observed for all the sample preparations and the quantification approaches, except for the Drop prepared samples, analysed using the B approach.

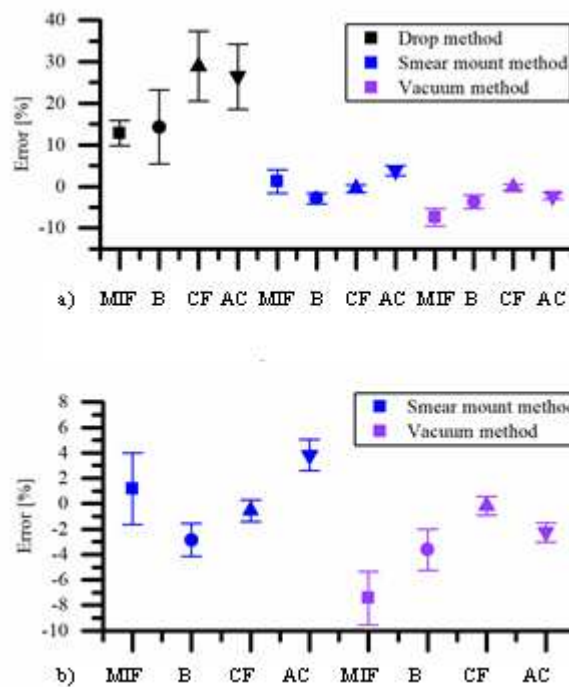


Figure 5 - Average error calculated for smectite, in the different sample preparation methods (a), while the Drop method is excluded in (b).

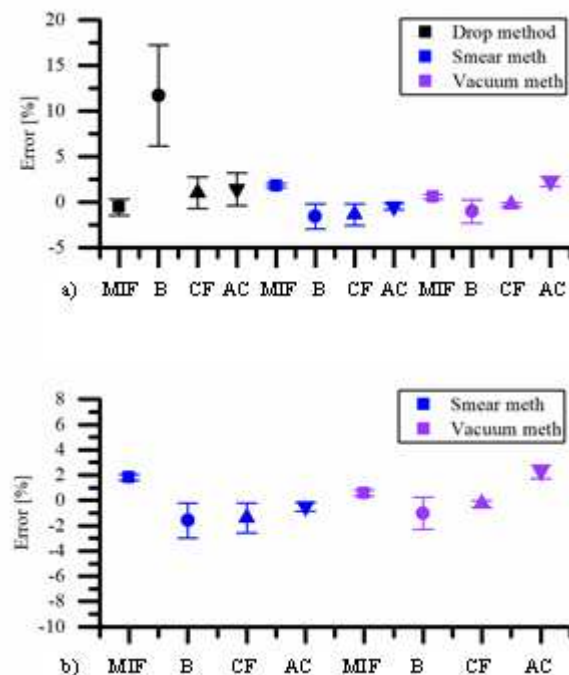


Figure 6 - Average error calculated for illite, in the different sample preparation methods (a), while the Drop method is excluded in (b).

As already mentioned, as this was developed for Smear, and thus non segregated, samples, it is reasonable that its application to a different sample preparation leads to an error that is more than twice the mass % of the mineral contained in the pure kaolinite mixture. It therefore appears, that no matter which quantification method is used, Smear mounted and Vacuum prepared samples provide a set of reliable, repeatable mineral composition results. However, in order to obtain representative multiplication coefficients for the MIF and the CF approach, it is

necessary that the pure materials contained in the investigated mixture are available, and it has already been discussed that this is rarely possible for natural clays. Moreover, the B approach was developed in a way similar to that exposed for the CF approach, showing the same problems. The AC approach, however, provides values that are only dependent on the chemical formulation of the minerals. The characteristic absorption coefficient of a series of minerals belonging to the smectite family, calculated using Equation (2), are shown in Table 2. These include the dioctahedral aluminium based smectites (Beidellite, Bentonite, Montmorillonite), trioctahedral magnesium (Saponite, Stevensite) and sodium based (Hectorite) smectites. It may be noted that no major variation in the correction coefficient is observed. The only exception is observed for the iron based smectites, such as the Nontronite, for which a much higher coefficient of correction is observed. It can therefore be expected that the AC approach correctly represents the mass percentage of the different clay minerals contained in a naturally sedimented soil, when no Fe based smectites are present in the sample. In order to detect whether this is the case, XRF tests should be performed on < 20µm clay powder samples.

Table 2 – Characteristic absorption coefficient of a series of smectitic minerals, and their normalization over the kaolinite value.

	$a_{ch,smec}$	$a_{ch,smec}/a_{ch,Kaolinite}$
Bentonite	31.79	1.07
Montmorillonite	33.01	1.11
Beidellite	31.55	1.06
Saponite	30.85	1.04
Stevensite	31.07	1.04
Hectorite	31.15	1.05
Nontronite	91.73	3.08

4 CONCLUSIONS

The quantification of the mineralogy of natural clays, is still an unresolved problem due to technical problems such as the difficulties in the determination of the single minerals chemical formula, the absence of well crystallized structures and the need to readapt the amplification factors to the used equipment. Several steps forward have been done in the last decades, so that several quantification methods have been developed, together with a set of sample preparation methods. For this study, the influence of 3 different sample preparation methods, applied to 7 bentonite and kaolinite mixtures, having different ratios, and analysed with 4 different approaches were investigated. It emerged that the Drop sample preparation method consistently gives higher error and standard deviations. This effect is due to the sample segregation that happens during the preparation process, which finally leads to an overestimation of the smectitic content and to an underestimation of the kaolinite content.

On the contrary, the Smear mounted and the Vacuum prepared samples show a good repeatability, together with a low measured error, with a minimum obtained when they are analysed using the CF approach. It must therefore be concluded that, when the pure materials are available, it is recommended to utilize the CF approach. However, for natural soils, this is rarely the case. The AC approach showed high repeatability, together with a low average error, even though the factors obtained for this study referred to the bentonite, while other types of smectites can be found in natural deposits. Nevertheless, it has been observed that the amplification factor obtained for different, common types of smectite minerals, does not vary more than 0.08, when non Fe-smectitic samples are investigated.

Furthermore, using X-Ray Fluorescence tests on natural soils it is possible to make an accurate guess on the clay particles mineralogy and therefore to calculate with low error a series of representative a_{ch} values that can be used for the approach. For all these reasons, the AC approach is expected to give good results also for the mineralogy analysis of natural clays.

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