



## Physico-Chemical and Mineralogical Characterization of some Clays from Coastal Sedimentary Basin of Benin used in Ceramic

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### Abstract

Three sites of Benin's clays from Gbédji-Kotovi, Massi-Sèhouè and Zogbodomèy were characterized in this study. Physico-chemical and mineralogical analysis were performed by X-Rays Diffraction, chemical analysis, thermal analyses ATD/ATG, infrared IR, specific surface area and granulometry. Density of clayey particles, capacity of cationic exchange (C.C.E.) and exchangeable bases were also done. It comes out from these analyses that clays of Zogbodomèy are essentially kaolinitic while those of Gbédji-kotovi and of Massi-Sèhouè are with smectitic predominance. By its composition the sample of Zogbodomèy is constituted by a natural mixture of the elements necessary for the production of ceramic (bricks, tiles, pottery etc). The two others series of samples from Gbédji-kotovi and Massi-Sèhouè will require some kaolinite and sand additions because of their strong proportion in smectite. Thus, they would be more useful in agronomy and environmental protection

**Keywords:** Clay, X-ray, granulometry, mineralogical structure, BENIN.

### Introduction

According to their structural compositions and their properties, minerals clays are employed for various applications and specific uses<sup>1-6</sup>. The clays used in ceramic industry must show certain characteristics specific to each application.

For instance, to product good enamel, they must contain a small rate of smectite to guarantee a good rheological stability, and to have a relatively low content of iron and potassium in order to obtain a white color after cooking<sup>7</sup>.

Besides, clays for bricks and tiles must answer some criteria of composition in: Mineral clayey ensuring the plasticity and the cohesion of the paste before cooking and the ceramic bonding at high temperature, a kaolinite-illite mixture with a little smectite being most favorable; quartzous sand serving as grease-remover allowing to reduce the drying and cooking withdrawal and to facilitate the water flow of shaping; colouring elements also serving as melting, such as Fe<sub>2</sub>O<sub>3</sub>, TiO<sub>2</sub>, MnO<sub>2</sub><sup>8</sup>.

In Benin, minerals clays used in ceramic activities are often taken in the coastal sedimentary basin. The geological reserves of these clays are estimated at 5.157.600 tons in Gbédji-Kotovi, 1.530.000 tons in Massi and 10 000.000 tons in Zogbodomèy<sup>9</sup>. The characteristics of these clays were not well

study except some rare chemical analyses and x-rays diffraction analysis<sup>9</sup>. This reveals that a good knowledge of these characteristics (compositions and properties) will improve the output and the quality of the finished products.

It is the objective in this study which aims to the determination of the physico- chemical characteristics and mineralogical by four methods (the diffraction of x-rays, chemical analysis and the thermic analyzes ATD/ATG and the infrared IR) supplemented by measurement of the density, of capacity of cationic exchange and of granulometry of these clays.

### Material and Methods

**Materials:** Located at south-west of Benin between the meridians 1°40' E and 2°45' E and the parallels 6°15' N and 7°30' N, the basin where the samples were took belongs to the basin of Gulf Guinea (figure-1). On the geomorphological level this basin includes two zones (figure-2). A zone of 7 plateau limited by the valleys of the principal rivers (Ouémé, Sô-ava, Couffo and the Mono) and the depression of Lama. They are the plateau of Aplahoué, Abomey, Zagnanado and Kétou and those of Comé, Allada and Saketé. A zone of low plain constituting a margino-littoral field occupied by marshy depressions, lagoons (lagoon of Porto-Novo, coastal lagoon), sand cords and lakes (Ahémé lake, Nokoué lake). On the geological level, this basin is of cretaceous age to current. It

contains gritty, sandy, argillaceous and calcareous formations<sup>10,11</sup>.

The studied materials come from Gbedji-Kotovi (GK), Massi-Sèhouè (MS) and Zogbodomey (ZY). These localities are represented on figure-2. The first prospected site GK is located between 2°00' and 2°02' East longitude and 6°40' and 6°42' North latitude. Ten (10) holes of 1m of diameter and 5m of maximum depth are dug there with the mesh of 100m. Overall, the clay are black with by places of the tasks rusts. The second site MS is between 2°13'E and 2°16'E, between 6°57'N and 6°59'N in the depression of Lama. Ten (10) holes to the mesh of 100 m with a maximum depth of 5m for the majority and sometimes 7m were explored there. The clay of this site is in general of beige color. At the 3<sup>rd</sup> site ZY, it is located between 2°06' E and 2°08' E and between 7°04' N and 7°06' N. 6 holes in bulk, of maximum depth of 7m were done. In general clay appears only after lateritic layer from 2 to 3m. It is initially white with red bands (zone of transition), then white with yellow passages and of the red tasks. The exact geographical coordinates of each hole were raised using a system of positioning by portable satellite of type G.P.S (Global Positioning System).

**Methods:** Before the preliminary analyses, the samples were grinded in a coarse way in agate mortar and sieved through 2mm mesh sieve. The fraction obtained is subjected to a series of physico-chemical analyses, namely the density, cationic exchange capacity, the exchangeable bases, specific surface and granulometry. Then the argillaceous fraction lower than 2 µm is obtained by purification and sedimentation. This fine fraction, dried and finely crushed allowed to prepare oriented pastes on natural trial and having undergone specific treatments (Ethylene glycol, Hydrazine, heating during 4 hours at 490°C). Crude clay and these oriented pastes were subjected to x-rays diffraction. The diffractograms were recorded using a Philips diffractometer equipped with a generator PW 1800 with graphite monochromator, using the radiation of cobalt and functioning under 40 kV, 40 mA. They were acquired by data APD and were treated by the software X' PERT and IDENTIFY and X' PERT High Score. The results obtained by DRX (diffraction at X-Ray) are supplemented by the elementary chemical analyses using an atomic spectrophotometer of emission by coupling inductive plasma (I.C.P./AES) Jobin Yvon of the mark Ultima C V5 which makes it possible to have the proportion of chemical elements constitutive of clay material. The curves of DTA (differential thermic analysis) were recorded by differential calorimetry with sweeping of argon with apparatus TG-DTA 92 SETERAM. The reference is calcined alumina. The two powders (sample and reference) are packed in identical platinum crucibles. They are then heated from the ambient temperature to 1100°C at the speed of 10°C/mn. Measurements are made here on the crude or total samples grinded with granulometry 100 µm. Measurements of GTA (Gravimetric thermic analysis) are taken simultaneously with the same apparatus and the same thermal cycle as that of DTA. The granulometry analysis was

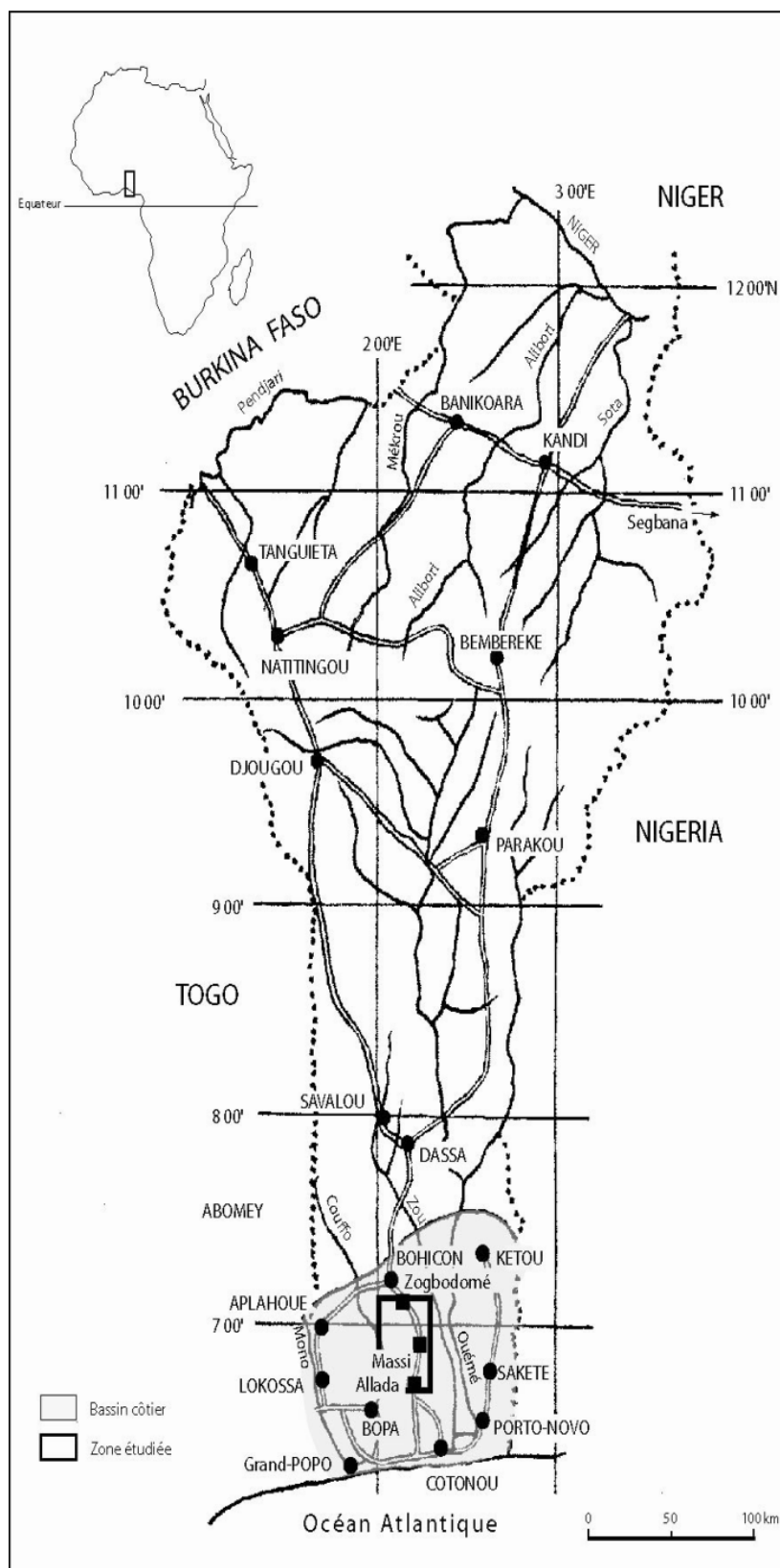
carried out on the fine particles of diameter lower than 500 µm using a laser particle-measurement instrument MALVERN of the type MATERSIZER. Specific surfaces were given starting from the analysis of the isotherm of adsorption of a gas by the solid by using the method of Brunauer, Emmett and Teller (B.E.T.) Moreover for the infra-red spectroscopy, after a mixture (2% in mass approximately) with of KBr (average IR) or polyethylene (remote IR), the samples, (fine fraction < 2µm) are put in pastilles of diameter of 13 mm and thickness of about 0,4mm. Measurements were carried out in the field of the average infra-red between 400 and 4000 cm<sup>-1</sup> using a spectrometer with Fourier transform of the type PERKIN ELMER (model 1760X), provided with a software of automatic processing data. In the remote infra-red (between 50 and 400 cm-1), the spectra IR were recorded with a spectrometer BONEM D.A. 8 with Fourier transform. As for the calculation of the density it was carried out by pycnometry with the hexachlorure of methane. The principle is based to the measure of the mass of the unit volume of material. The cationic exchange capacity measurements was done on the total rock using the method of Aubert<sup>12</sup>.

## Results and Discussion

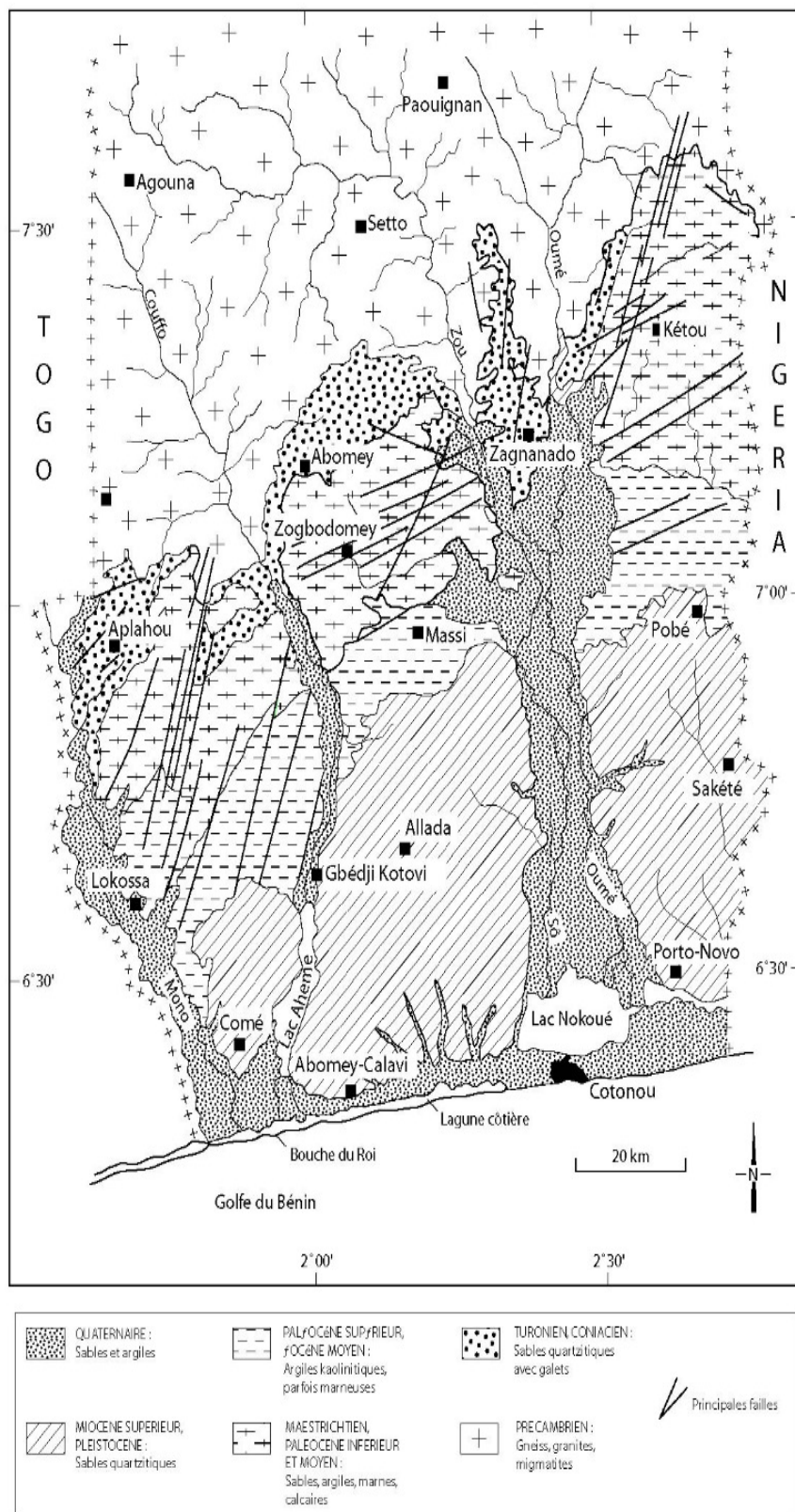
**Physico-Chemical and Granulometric Analysis:** On the average, the values of density, those of the capacity of cationic exchange and those of specific surface area are gathered in table-1. These values are similar for GK and MS. The figures-3a, 3b and 3c show the curves of particles distribution of some samples of the three sites. The curves are bimodal for samples GK, a big mode and a small one between 0,1 and 100µm and trimodal between 000,1et 200µm for samples ZY as in case of the kaolinitic compounds<sup>13</sup>. While with samples MS, its curves are trimodal successively a big mode a small and a smaller one beyond 100µm<sup>14</sup>. The particles of these samples are divided into four, even five great classes as shown it tables 4 Clays (diameter < 2µm) are on average, in a decreasing way, 44,8; 33,1 and 30,4% respectively for samples GK, MS and ZY. The fine silts (2-20µm) are more numerous in samples MS (59,1 %), than samples GK (52,7 %) and ZY (43,6 %). The coarse silts (20-50µm) are more significant in samples ZY (14,5%), than samples MS (3,5%) and GK (1,9%). Fine sands (50-200µm) are in an increasing way 0,6; 4,1 and 11,5% respectively for samples GK, MS and ZY. Finally, only samples MS present a small quantity (0,3 % on average) of coarse sands (0,2-0,5mm) per place.

**Table-1**  
**Cationic Exchange Capacity (CEC), Specific Surface area and Density of samples (GK), (MS) and ZY on average**

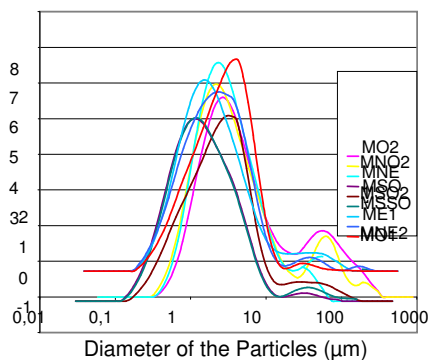
| Samples | CEC in meq/100g | Density | Specific Surface (m <sup>2</sup> /g) |
|---------|-----------------|---------|--------------------------------------|
| GK      | 34,84           | 2,37    | 105,41                               |
| MS      | 37,18           | 2,36    | 100,59                               |
| ZY      | 4,16            | 2,61    | 69,2                                 |



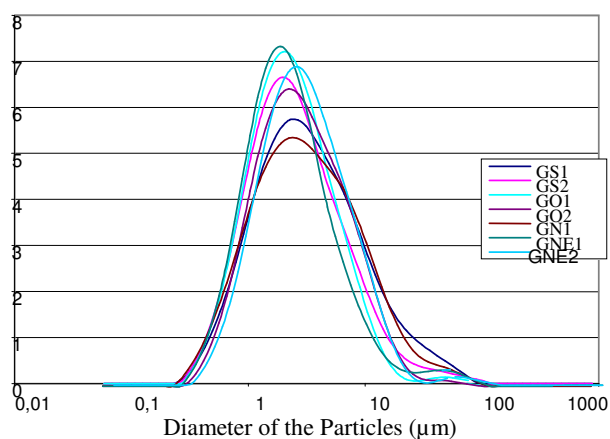
**Figure-1**  
Card of geographical situation of Benin (IHETA et al, 1983)



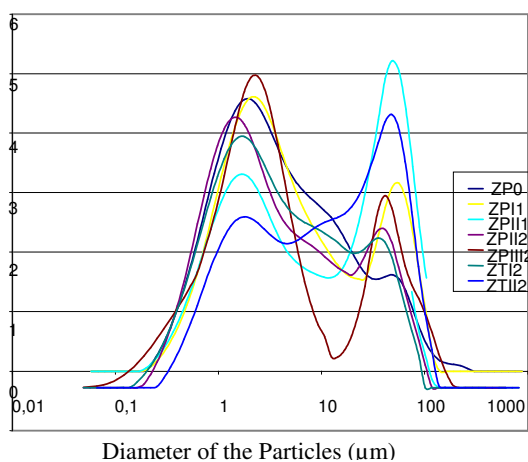
**Figure-2**  
**Geological Card of the coastal basin of the Benin (Slansky, 1962)**



**Figure-3a**  
**Particles size distribution in samples MS**



**Figure-3b**  
**Particles size distribution in samples GK**



**Figure-3c**  
**Particles size distribution in samples ZY**

**Mineralogical and Chemical Analysis:** The figures-4a, 4b and 4c show the diffractograms from the crude or total fractions of the samples. On these diffractograms, it is observed that the major crystalline phases contained in all the samples are

kaolinite (k) (7,14Å; 3,56Å), quartz (q) (3,33Å; 1,81Å; 4,26Å), smectite ((S): (Ca, Mg) (Al, Fe)<sub>2</sub> (Si, Al)O<sub>10</sub> (OH)<sub>2</sub> (14-15 Å) and some traces of anatase phase (A) (3,52Å; 1,89Å). Feldspar traces are also noted ((Na, K, Ca) (Al, Fe, Si)<sub>4</sub> O<sub>8</sub> (3,18-3,33Å;

4,02-4,25Å) for the samples GK and goethite (G)  $\alpha$ -FeOOH (4,18 Å; 2,49Å) for the samples ZY. The samples resulting from the same site present same minerals thus showing the homogeneity of each site. The figures-5a, 5b and 5c give the results of the diffractograms of the fine fractions from representative samples of each site after various specific treatments (normal, Ethylène-glycol, Hydrazine, heating at 490°C during 4h). These treatments make it possible to put forward detected minerals.

The results of the chemical analysis are gathered in tables 3.a, 3.b and 3c. Quantitatively the samples contain all mainly oxides  $\text{SiO}_2$  (45,4-63,8%) and  $\text{Al}_2\text{O}_3$  (13,9-23,1%), followed by small quantity of  $\text{Fe}_2\text{O}_3$  (6-11%),  $\text{TiO}_2$  (0,9-1,5%) and according to each site of  $\text{Na}_2\text{O}$ , of  $\text{P}_2\text{O}_5$  of  $\text{MgO}$  de  $\text{CaO}$  and  $\text{K}_2\text{O}$  in variable quantity. Other components (Sr, Ba, Pb, Zn, V, Cu, Ni, Cr) also appear in traces.

**Thermic and Infrared Analyses<sup>2</sup>:** The thermograms of samples GK, MS and ZY are represented respectively in figures 6a, 6b and 6c. The figures-7a, 7b and 7c show the thermogravimetric curves of these same samples. The shape of the curves obtained are those of argillaceous minerals detected by x-rays and their resemblance in each site confirm well their homogeneity.

The curves IR are gathered on the figures 8a; 8b; 8c and 8d. The spectra (medium IR) characterize clayey minerals like the thermic curves, and to be alike of a site another.. What led us to make the remote infra-red only on one representative sample of each site to knowing GNE1 MNO1 and ZTI2

**3-4 Quantitative Semi-Composition of the total samples:** By combination of results of the analysis with the X-ray, the chemical analysis<sup>15</sup> and in addition to the results of CEC by the method QuantArg2<sup>16</sup> one obtains the quantitative semi-composition of the table-4.

**Discussion:** The definition of clay starting from the particle which has a diameter lower than  $2\mu\text{m}$  must be taken with reserve. Indeed, certain clayey particles have a size higher than  $2\mu\text{m}$  while certain mineral particles associated to clays (feldspar, quartz, goethite etc.) have a size lower than  $2\mu\text{m}$ . This is why it is thought that the argillaceous minerals start to be present starting from the fine silts<sup>1</sup>.

The samples of the three sites contain essentially clay and silt (more than 70%) with more clay for GK (44,8%) more fine silt for MS 59,1% and a enough balanced texture for ZY with apart clay and fine silt, has 14,5% of coarse silts and 11,5% fine sand (table-2).

On the figures-5a, 5b, 5c, it is noticed that the smectite, under the normal conditions of moisture is presented at the basal distance d (001) at 14-15Å (to saturation Ca or Mg) (samples

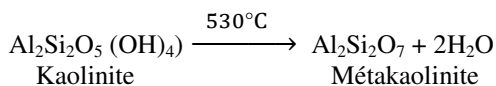
GNE1N, MNO1N, ZTI2N) whereas it inflates and is to 17-18 Å (GNE1G, MNO1G, ZTI2G) with glycol saturation. After heating at 490°C the smectite becomes anhydrous and its basal distance is approximately of 10 Å (GNE1C, MNO1C, ZTI2C)<sup>17</sup>. The basal distance (d001) of kaolinite is approximately 7,15Å (GNE1N, MNO1N, ZTI2N). Treated with hydrazine, the peak of kaolinite moves to 10Å (GNE1H, MNO1H, ZTI2H). In addition, kaolinite is destroyed by heating at 490°C (GNE1C, MNO1C, ZTI2C) and does not inflate with saturation with ethylene glycol (GNE1G, MNO1G, ZTI2G). It is necessary to note the presence of illite traces in samples GNE1 and ZTI2 at 10 Å.

These results confirm well the presence of minerals identified in the total samples and the normal fractions of these samples. The chemical analysis translates the results of the analysis by X-rays diffraction. They show that the samples contain all, a quantity of ( $\text{SiO}_2 + \text{Al}_2\text{O}_3$  ranging between 67 and 81%). They are thus primarily silico-aluminous minerals with prevalence of  $\text{SiO}_2$ . The relatively significant rate of  $\text{SiO}_2$  is probably due to the presence of a significant quantity of free silica (quartz, amorphous silica) detected with the X-ray, especially in the materials of ZY which totalize 39% of quartz on average. All the samples count too, small quantities of  $\text{TiO}_2$  indicating the presence of anatase on average of 1,30 % also detected by X-rays diffraction. Only the samples GK totalize an appreciable quantity of ( $\text{K}_2\text{O} + \text{Na}_2\text{O}$ ) equalizes to 1,5%, suggesting the presence of feldspar detectable too by X-ray diffraction. The average content of ( $\text{MgO} + \text{CaO}$ ) is 2,8 % of samples GK and MS, and show the probable presence of smectites saturated to Mg and Ca. This saturation is checked with DTA. In addition, the content of  $\text{Fe}_2\text{O}_3$  of GK (8%) of MS (6,7%) and ZY (8,7%) on average suggests the presence of goethite found in samples ZY or structural iron in the smectites of the three sites.

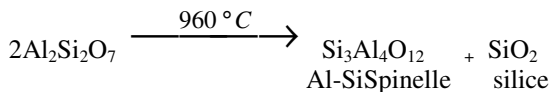
Furthermore, the thermograms analysis of the total part of the samples GK (Figure-6a) showed that the curves are almost the same. This certifies the homogeneity attested by the X-ray. It was observed four phenomena characterizing generally clays of the smectite type<sup>17-19</sup>. Three endothermic peaks follow-ups of an exothermic peak. A first intense accident which are spread out between 0 and 200°C to 300°C correspond at the departure of water slightly linked (water of hydration and zeolitic water). This peak presents an splitting between 170 and 200°C which confirms the presence of the  $\text{Mg}^{2+}$  ions and  $\text{Ca}^{2+}$  contained in the smectite losing its water of hydration<sup>20</sup>. A second endothermic effect which appears towards 500-550°C, indicates the loss of the radicals structural hydroxyls (dehydroxylation) in the form of composition water<sup>18</sup>. This departure of the OH at this low temperature is allotted to minerals of tetrahedral substitutions of beidellite type, nontronite and mixed beidellite<sup>21</sup> whereas true montmorillonites are characterized by a thermal accident between 600 and 700°C<sup>18,19,22,23</sup>. Besides it should be necessary to signalize that the observed temperature of this endothermy in the majority of clays is a data which characterizes them.

Another endothermic accident very widened (right before the exothermic peak) towards 845-860 °C approximately, sometimes non-existent in the case of a beidellite or nontronite like here on our curves, corresponds to the loss of the last hydroxyl traces<sup>18,19,24</sup>. Finally, the exothermic reaction, which is towards 850 -950°C has a round form. Moreover, these samples present an exothermic hump around 384°C and an endothermic derivative towards 428°C which respectively announce the presence of the organic matter and of kaolinite contained in these materials<sup>25</sup>. Organic matter no detectable by the X-ray but detected by hydrogen peroxide 30% and the kaolinite 17% detected by X-ray. For samples MS (Figure 6-b), the thermograms obtained are identical between them (those of MNO1 and MN1 are practically confused) and almost comparable with those of GK. With the only difference that the exothermic hump relating to the organic matter towards 356°C here, is less marked than the cases of GK as well as the drift around 428°C for kaolinite, safe for MEI towards 424°C which is the richest in kaolinite. At last a small hook towards (579-582°C) corresponds to the transition from phase of quartz according to the following reaction<sup>27</sup>:

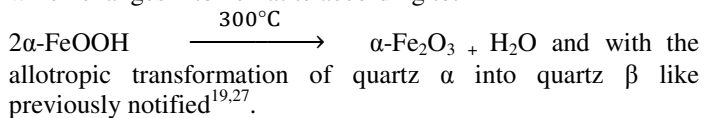
$\alpha\text{-quartz} \xrightarrow{580^{\circ}\text{C}} \beta\text{-quartz}$ . Figure-6c is relative to the curves of ZY. Three fundamental phenomena are also detected there but with the following nuances: Compared to the curves of the preceding sites, the intensity of the first endothermic peak (77-94°C) stripped to the profit of the 2<sup>nd</sup> peak which has increased and is in the neighbourhoods of 529°C. When with the 3rd exothermic accident, it is acuter and is at a temperature higher (955-970°C). All this show the prevalent nature of kaolinite in these samples. If the accident always corresponds at the beginning of hygroscopic or zeolitic water and cannot appear in certain kaolinites. The 2<sup>nd</sup> the departure of structural hydroxyls following by the decomposition of the octahedral layer announces here<sup>28</sup>. Kaolinite loses then its water of composition to form the metakaolinite according to the diagram<sup>8</sup>:



The 3<sup>rd</sup> indicates the transformation of the metakaolinite into a spinel aluminium-silicon and following amorphous silica:



In addition to these traditional accidents, two other endothermic peaks appear in the neighbourhoods of 300 et 580°C allotted to the deshydroxylation of the goethite detected by the X-ray which changes into hematite according to:



When one analyzes the thermogravimetric curves of the samples of GK Figure-7a it is noticed that they are curves with two inflections characteristic of the smectites<sup>8</sup>. Between 20 and 200°C a first hygroscopic and significant zeolitic water departure of about 6 to 9% in loss of mass is followed of a soft slope instead of a stage. This slope, approximately 1,5% of loss of mass, is due to the combustion of the amorphous substances in occurrence of the organic matter. Finally a last reduction in mass of order 4 to 7 % approximately, occurring between 400 with 650°C and follow-up of a stage, correspond at the departure of water of composition. All these losses of mass correspond to accidents of the differential thermal analysis. On the whole the reduction is about 11,5 with 18,5%. These results confirms the phenomena obtained with DTA and shows that the exothermic transformation announced towards 900°C occurs without variation of mass. Figure 14 relating to site MS presents thermogravimetric curves similar to those of GK. The thermogravimetric curves obtained for samples ZY are represented on Figure-15. From 0 to 250°C a loss of mass of 1,5-2,5% announced the departure of the adsorbed water followed by a 2nd light loss approximately of 0,8% correspondent to the deshydroxylation of the goethite transformation into hematite appears. To finish a significant reduction in mass of order 4 to 7 % approximately, ranging between 400 with 650°C following the elimination of the structural hydroxides, the whole followed by a stage. All these results go in the same direction as those observed with DTA. Here also the exothermic reaction occurs towards 900°C without variation of mass.

The results of the physic-chemical analysis (table-1) come to confirm those of the mineralogical analysis. It is noticed whereas clays of the three sites have overall average cationic exchange capacities lower than those their majority clay components. 34,85 meq/100g for the GK ; 37,18 for MS et 4,17 for the ZY against 80-150 for the smectites and 5-15 for kaolinites<sup>12</sup>. These low values would be explained by the fact that in the method used, measurements are done on the total samples which contains in our case a considerable quantity of quartz unable to exchange cations<sup>29</sup>. 27% on average for the GK, 36% for the MS and up to 71% for the ZY. In addition, kaolinites are not very exchanging cations what explain the low value of 4,17 meq/100g of samples ZY which contain more kaolinite than GK and MS.

The density gives an idea of the prevalent species in samples. Thus the samples GK (density =2,36) and MS (density = 2,37) are smectitic (2,08 - 2,35) whereas those of ZY (dmoy=2,61) are kaolinitic (d=2,40 - 2,64) and /or quartzous (d=2,65).

It is noticed too that GNE1 and MNO1, which are more smectitic than ZTI2 have a greater specific surface (100,59 against 69,20 m<sup>2</sup>/g for ZTI2). Moreover ZTI2 contains more kaolinite, a little smectite and a little goethite which has raised his specific surface (69,2 m<sup>2</sup>/g) than a normal kaolinite (10-30 m<sup>2</sup>/g)<sup>15,28</sup>

**Table-2**  
**Granulometric compositions of different samples GK, ZY and MS**

| <b>Nature Samples</b> | <b>Clay (&lt;2µm)</b> | <b>Fine silts (2-20µm)</b> | <b>Coarse silts (20-50µm)</b> | <b>Fine sand (50-200µm)</b> | <b>Coarse sand (0,2-0,5mm)</b> | <b>Total</b> |
|-----------------------|-----------------------|----------------------------|-------------------------------|-----------------------------|--------------------------------|--------------|
| GS1                   | 36,4                  | 58,0                       | 4,8                           | 0,8                         | 0,0                            | 100,0        |
| GS2                   | 45,4                  | 51,7                       | 2,2                           | 0,7                         | 0,0                            | 100,0        |
| GO1                   | 47,3                  | 51,8                       | 0,6                           | 0,3                         | 0,0                            | 100,0        |
| GO2                   | 38,5                  | 60,0                       | 1,3                           | 0,3                         | 0,0                            | 100,0        |
| GN1                   | 36,9                  | 58,3                       | 3,8                           | 1,0                         | 0,0                            | 100,0        |
| GNE1                  | 48,9                  | 48,2                       | 1,9                           | 1,0                         | 0,0                            | 100,0        |
| GNE2                  | 44,8                  | 54,1                       | 0,7                           | 0,5                         | 0,0                            | 100,0        |
| GN2                   | 45,1                  | 53,9                       | 0,7                           | 0,4                         | 0,0                            | 100,0        |
| GC1                   | 43,8                  | 56,2                       | 0,0                           | 0,0                         | 0,0                            | 100,0        |
| GNN1                  | 48,4                  | 48,9                       | 2,4                           | 0,4                         | 0,0                            | 100,0        |
| GNN2                  | 52,0                  | 44,5                       | 2,7                           | 0,8                         | 0,0                            | 100,0        |
| GNO2                  | 50,4                  | 46,7                       | 2,3                           | 0,6                         | 0,0                            | 100,0        |
| GSO1                  | 26,3                  | 57,7                       | 12,0                          | 3,9                         | 0,0                            | 100,0        |
| GSO2                  | 26,4                  | 65,4                       | 7,9                           | 0,2                         | 0,0                            | 100,0        |
| Average               | 44,8                  | 52,7                       | 1,9                           | 0,6                         | 0,0                            | 100,0        |
| MNO2                  | 26,6                  | 51,7                       | 8,8                           | 11,8                        | 1,0                            | 100,0        |
| MO2                   | 35,7                  | 50,0                       | 5,3                           | 8,3                         | 0,8                            | 100,0        |
| MSO1                  | 35,5                  | 54,6                       | 5,4                           | 4,4                         | 0,0                            | 100,0        |
| MSO2                  | 41,7                  | 55,8                       | 1,2                           | 1,3                         | 0,0                            | 100,0        |
| MSSO                  | 23,0                  | 68,2                       | 3,7                           | 4,7                         | 0,4                            | 100,0        |
| ME1                   | 40,4                  | 55,2                       | 1,4                           | 2,7                         | 0,2                            | 100,0        |
| MNE1                  | 37,8                  | 54,8                       | 3,5                           | 3,8                         | 0,0                            | 100,0        |
| MNE2                  | 33,6                  | 62,4                       | 1,6                           | 1,9                         | 0,5                            | 100,0        |
| MNOI                  | 31,4                  | 64,8                       | 3,2                           | 0,7                         | 0,0                            | 100,0        |
| MO1                   | 25,1                  | 73,0                       | 1,1                           | 0,8                         | 0,0                            | 100,0        |
| Average               | 33,1                  | 59,1                       | 3,5                           | 4,0                         | 0,3                            | 100,0        |
| ZP0                   | 36,6                  | 47,6                       | 9,8                           | 5,8                         | 0,0                            | 99,9         |

| Nature Samples | Clay (<2µm) | Fine silts (2-20µm) | Coarse silts (20-50µm) | Fine sand (50-200µm) | Coarse sand (0,2-0,5mm) | Total |
|----------------|-------------|---------------------|------------------------|----------------------|-------------------------|-------|
| ZPI2           | 27,6        | 56,0                | 10,5                   | 5,9                  | 0,0                     | 100,0 |
| ZPI1           | 31,7        | 44,0                | 13,1                   | 11,2                 | 0,0                     | 100,3 |
| ZPII1          | 27,6        | 30,6                | 23,4                   | 18,5                 | 0,0                     | 100,0 |
| ZPII2          | 33,9        | 42,4                | 12,8                   | 10,8                 | 0,0                     | 100,0 |
| ZPIII2         | 31,2        | 42,6                | 9,6                    | 16,3                 | 0,0                     | 99,7  |
| ZTI2           | 31,1        | 46,1                | 13,8                   | 9,0                  | 0,0                     | 100,0 |
| ZTII2          | 23,4        | 39,0                | 22,9                   | 14,6                 | 0,0                     | 100,0 |
| Average        | 30,4        | 43,6                | 14,5                   | 11,5                 | 0,0                     | 100,0 |

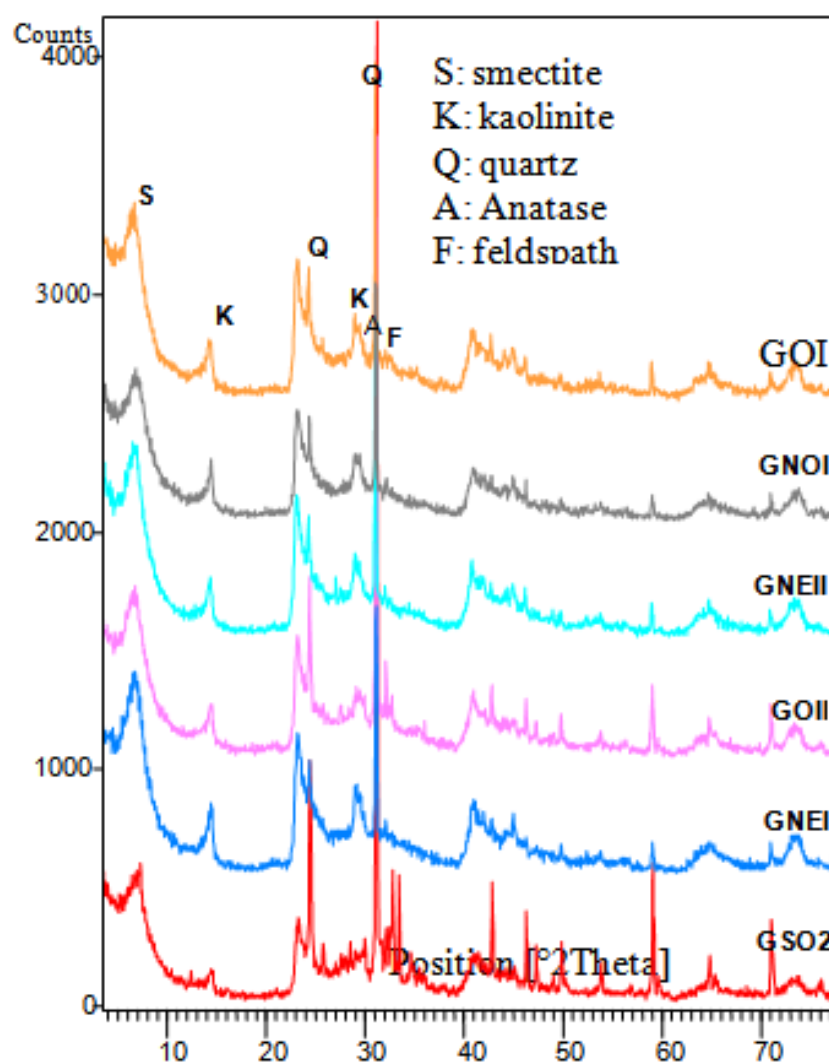
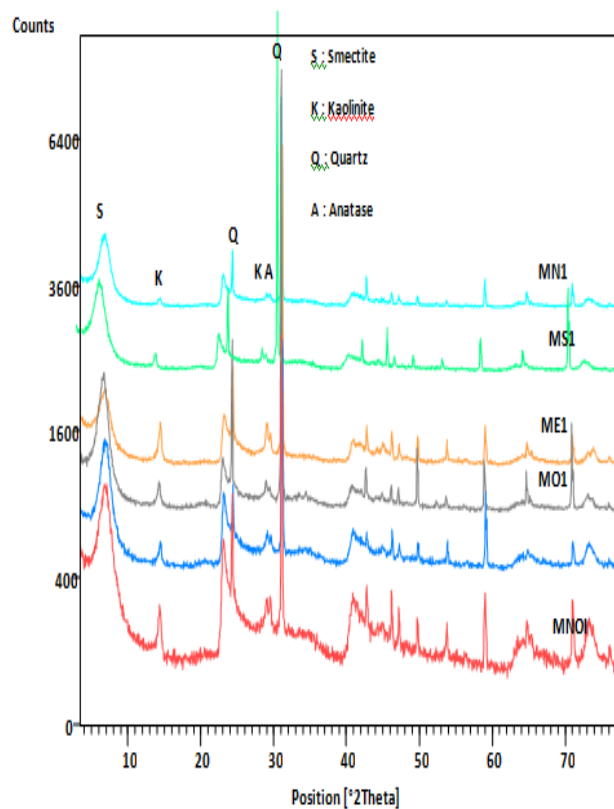
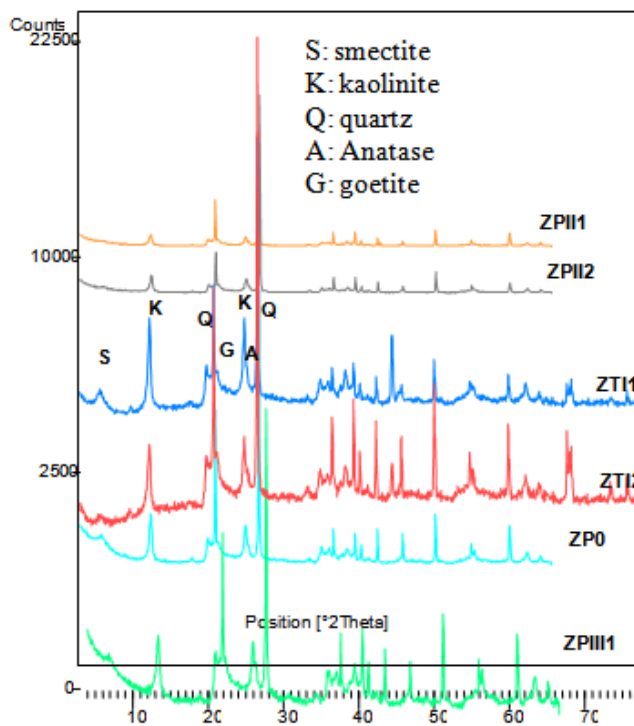


Figure-4a  
Diffractograms of samples GK



**Figure-4b**  
**Diffractograms of samples MS**



**Figure-4c**  
**Diffractograms of samples ZK**

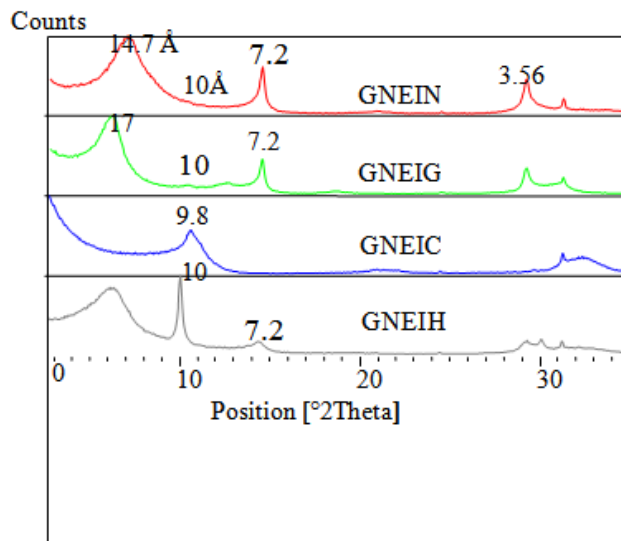


Figure-5a

Diffractograms of samples GK after treatment. GNE1N: normal; GNE1C: heated at 490°C; GNE1G: With glycol; GNE1H: with hydrazine

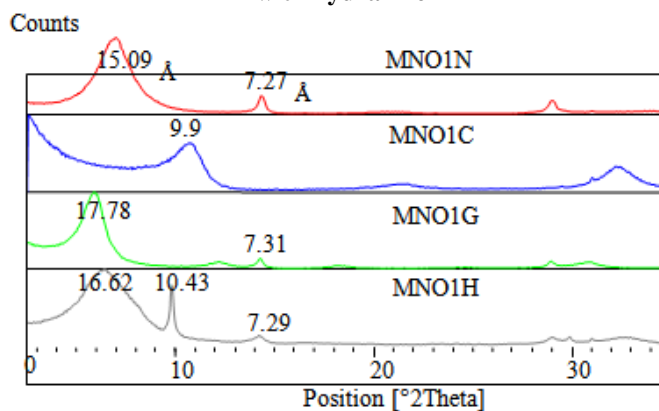


Figure-5b

Diffractograms of samples MS after treatment MNO1N : normal ; MNO1C : heated at 490°C ; MNO1G : with glycol ; MNO1H : with hydrazine

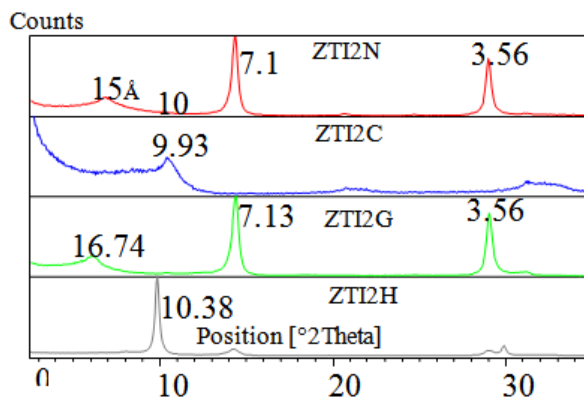


Figure-5c

Diffractograms of ZY after treatment ZTI2N : normal ; ZTI2C : heated at 490°C ; ZTI2G : with glycol ; ZTI2H : with hydrazine

**Table-3a**  
**Chemical composition of samples of Zogbodomey**

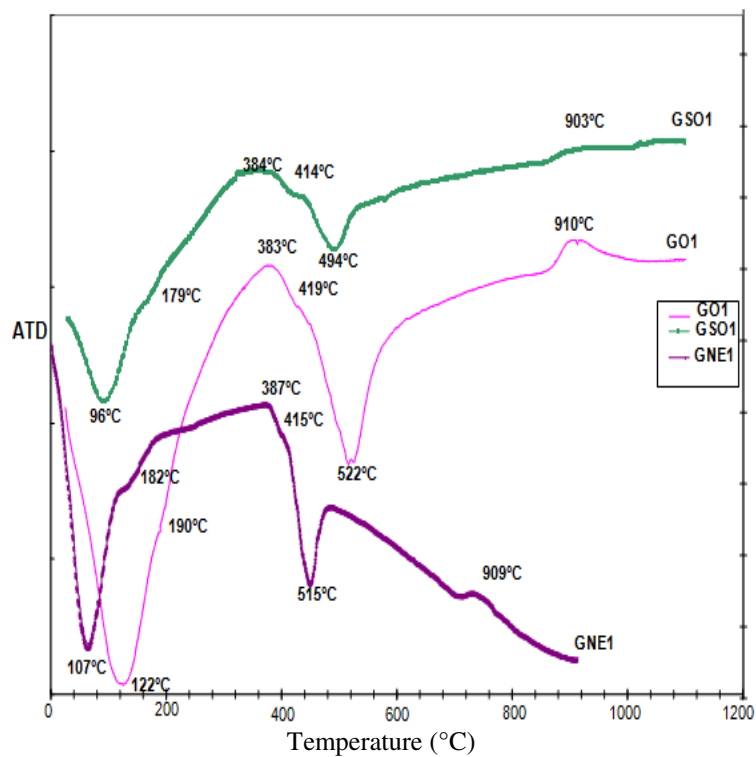
| Oxide Sample | SiO <sub>2</sub> (%) | TiO <sub>2</sub> (%) | Al <sub>2</sub> O <sub>3</sub> (%) | Fe <sub>2</sub> O <sub>3</sub> (%) | MgO (%) | CaO (%) | Na <sub>2</sub> O (%) | K <sub>2</sub> O (%) | P <sub>2</sub> O <sub>5</sub> (%) | H <sub>2</sub> O+ (%) | H <sub>2</sub> O- (%) | Sr (ppm) | Ba (ppm) | Pb (ppm) | Zn (ppm) | V (ppm) | Cu (ppm) |
|--------------|----------------------|----------------------|------------------------------------|------------------------------------|---------|---------|-----------------------|----------------------|-----------------------------------|-----------------------|-----------------------|----------|----------|----------|----------|---------|----------|
| ZP0          | 62,35                | 1,42                 | 17,64                              | 7,47                               | 0,38    | 0,19    | 0,02                  | 0,34                 | 0,09                              | 8,13                  | 1,17                  | 108      | 74       | 67       | 17       | 194     | 184      |
| ZPI1         | 56,6                 | 1,37                 | 23,1                               | 6,99                               | 0,40    | 0,15    | 0,01                  | 0,33                 | 0,11                              | 9,28                  | 1,51                  | 145      | 96       | 58       | 15       | 211     | 148      |
| ZPII1        | 63,84                | 1,31                 | 16,84                              | 8,53                               | 0,26    | 0,12    | 0,01                  | 0,19                 | 0,11                              | 7,67                  | 0,71                  | 128      | 88       | 43       | 17       | 196     | 178      |
| ZPII2        | 62,58                | 1,5                  | 17,36                              | 9,03                               | 0,26    | 0,12    | 0,01                  | 0,14                 | 0,11                              | 7,9                   | 0,65                  | 127      | 79       | 41       | 16       | 184     | 187      |
| ZTI2         | 52,67                | 1,46                 | 21,07                              | 11,25                              | 0,45    | 0,3     | 0,06                  | 0,27                 | 0,05                              | 10,02                 | 1,42                  | 105      | 80       | 59       | 17       | 201     | 423      |

**Table 3b**  
**Chemical composition of samples of GBEDJI- KOTOVI**

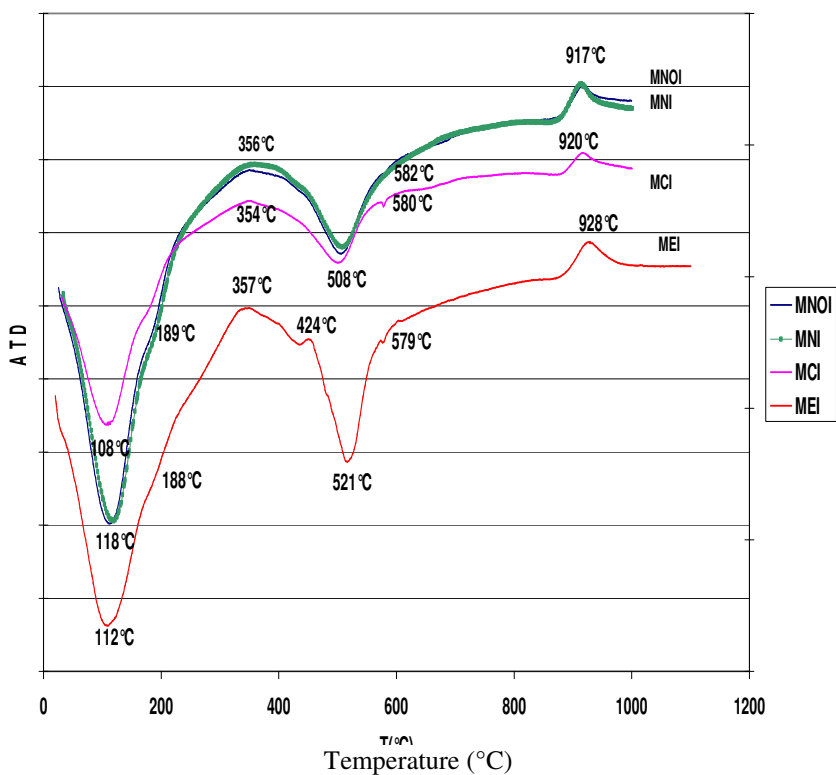
|      |       |      |       |      |      |      |      |      |      |       |      |     |    |    |    |     |     |
|------|-------|------|-------|------|------|------|------|------|------|-------|------|-----|----|----|----|-----|-----|
| GO1  | 47,31 | 1,24 | 21,94 | 8,34 | 1,64 | 1,16 | 0,23 | 0,71 | 0,11 | 12,32 | 4,9  | 590 | 95 | 91 | 44 | 205 | 109 |
| GO2  | 52,45 | 1,35 | 18,79 | 7,68 | 1,69 | 1,18 | 0,39 | 1,17 | 0,12 | 10,15 | 4,05 | 933 | 84 | 97 | 43 | 190 | 111 |
| GSO1 | 57,24 | 1,2  | 16,53 | 7,45 | 1,45 | 1,31 | 0,46 | 1,14 | 0,18 | 9,48  | 3,19 | 774 | 72 | 77 | 29 | 163 | 96  |
| GSO2 | 59,1  | 1,25 | 16,14 | 6,86 | 1,36 | 1,41 | 0,79 | 1,49 | 0,12 | 7,95  | 3,33 | 730 | 78 | 71 | 30 | 154 | 106 |
| GN1  | 45,41 | 1,16 | 21,17 | 8,13 | 1,6  | 1,31 | 0,08 | 0,61 | 0,13 | 14,07 | 5,55 | 450 | 93 | 99 | 43 | 198 | 107 |
| GC1  | 48,59 | 1,38 | 20,06 | 8,44 | 1,69 | 0,96 | 0,32 | 1,13 | 0,17 | 10,82 | 5,09 | 589 | 88 | 99 | 42 | 200 | 115 |
| GNE1 | 45,58 | 1,34 | 21,13 | 9,61 | 1,72 | 0,87 | 0,48 | 1,34 | 0,2  | 14,31 | 5,48 | 533 | 90 | 84 | 40 | 121 | 144 |

**Table-3c**  
**Chemical composition of samples of MASSI-SEHOUE**

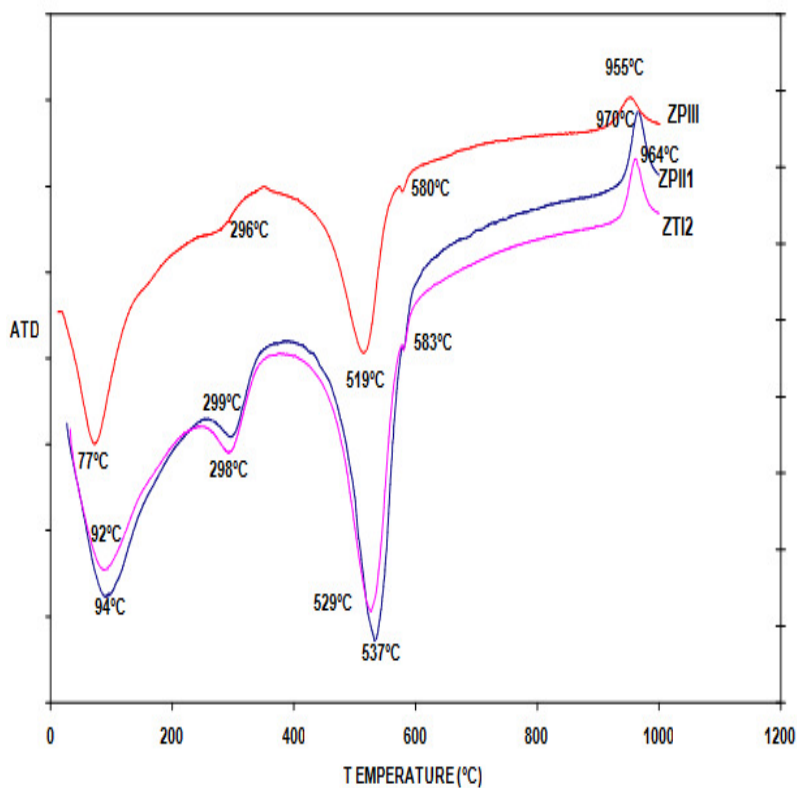
|      |       |      |       |      |      |      |      |      |      |       |      |     |    |    |    |     |     |
|------|-------|------|-------|------|------|------|------|------|------|-------|------|-----|----|----|----|-----|-----|
| MNO1 | 54,84 | 1,09 | 16,75 | 7,11 | 1,51 | 1,1  | 0,01 | 0,01 | 0,07 | 9,57  | 6,84 | 107 | 81 | 73 | 11 | 196 | 177 |
| MNO2 | 54,91 | 1,06 | 16,6  | 6,81 | 1,75 | 1,19 | 0,05 | 0,04 | 0,07 | 9,68  | 6,78 | 309 | 79 | 82 | 11 | 204 | 167 |
| MO1  | 56,12 | 0,89 | 13,86 | 5,92 | 1,68 | 3,75 | 0,25 | 0,08 | 0,06 | 9,85  | 6,14 | 229 | 64 | 70 | 12 | 182 | 132 |
| MO2  | 56,92 | 1,12 | 15,3  | 7,1  | 1,49 | 1,13 | 0,01 | 0,07 | 0,07 | 9,82  | 5,76 | 137 | 78 | 81 | 13 | 198 | 172 |
| MN1  | 56,49 | 1,01 | 15,24 | 6,54 | 1,45 | 0,98 | 0,07 | 0,03 | 0,06 | 9,27  | 5,42 | 387 | 82 | 72 | 11 | 192 | 154 |
| MS   | 57,33 | 0,99 | 14,46 | 6,8  | 1,48 | 1,11 | 0,06 | 0,05 | 0,08 | 8,55  | 6,33 | 63  | 76 | 74 | 10 | 204 | 158 |
| MNE1 | 54,25 | 1,03 | 18,36 | 7,2  | 1,51 | 0,78 | 0,09 | 0,02 | 0,08 | 11,9  | 5,25 | 251 | 91 | 63 | 9  | 115 | 333 |
| MNE2 | 53,37 | 1,07 | 18,83 | 6,78 | 1,68 | 0,9  | 0,17 | 0,07 | 0,06 | 10,75 | 5,17 | 226 | 91 | 71 | 10 | 110 | 208 |
| ME1  | 56,87 | 1,33 | 17,45 | 6,71 | 1,3  | 0,68 | 0,31 | 0,1  | 0,08 | 10,49 | 3,72 | 166 | 94 | 66 | 18 | 166 | 223 |
| ME2  | 60,27 | 1,06 | 14,76 | 6,5  | 1,7  | 1,06 | 0,21 | 0,03 | 0,06 | 9,26  | 4,28 | 289 | 85 | 69 | 17 | 112 | 187 |
| MT2  | 55,64 | 0,95 | 14,87 | 6,24 | 1,59 | 1,18 | 0,05 | 0,02 | 0,06 | 9,28  | 6,19 | 208 | 75 | 73 | 14 | 138 | 162 |



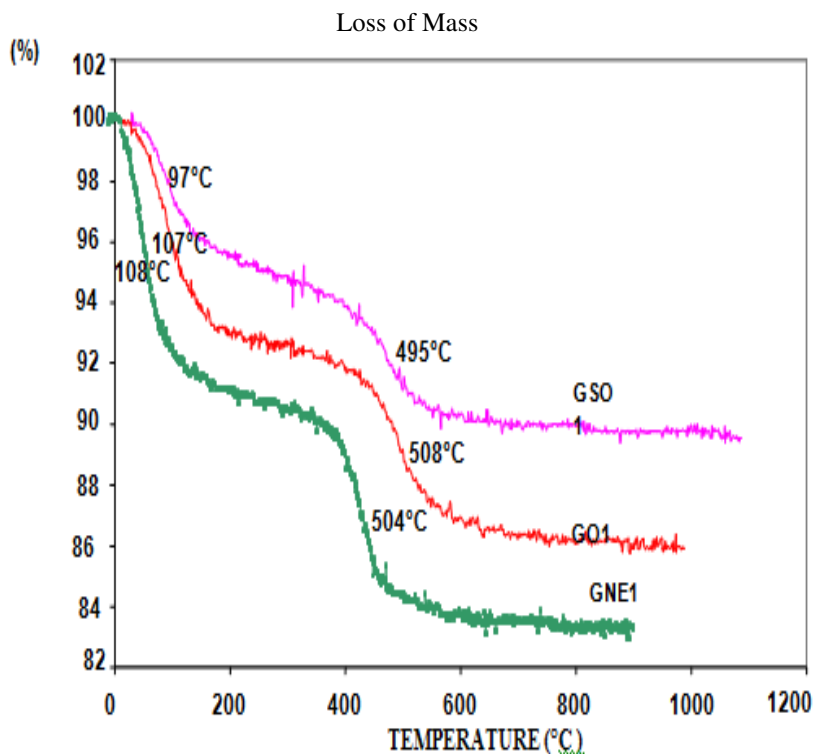
**Figure-6a**  
**Thermograms of samples GK**



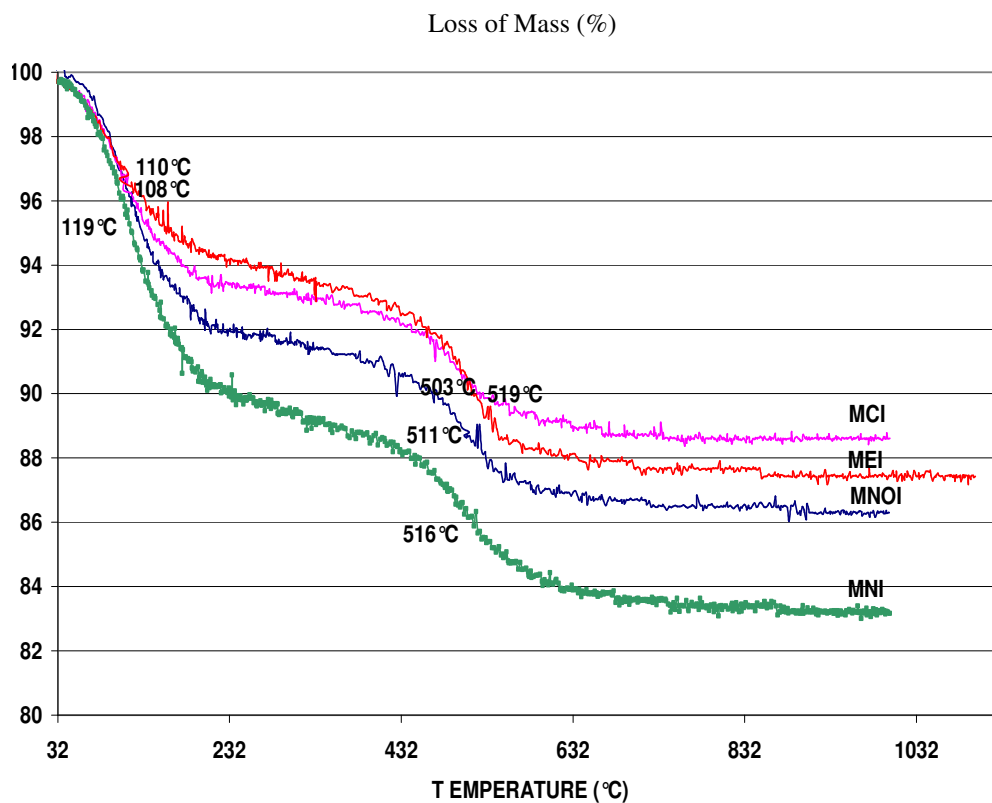
**Figure-6b**  
**Thermograms of samples MS**



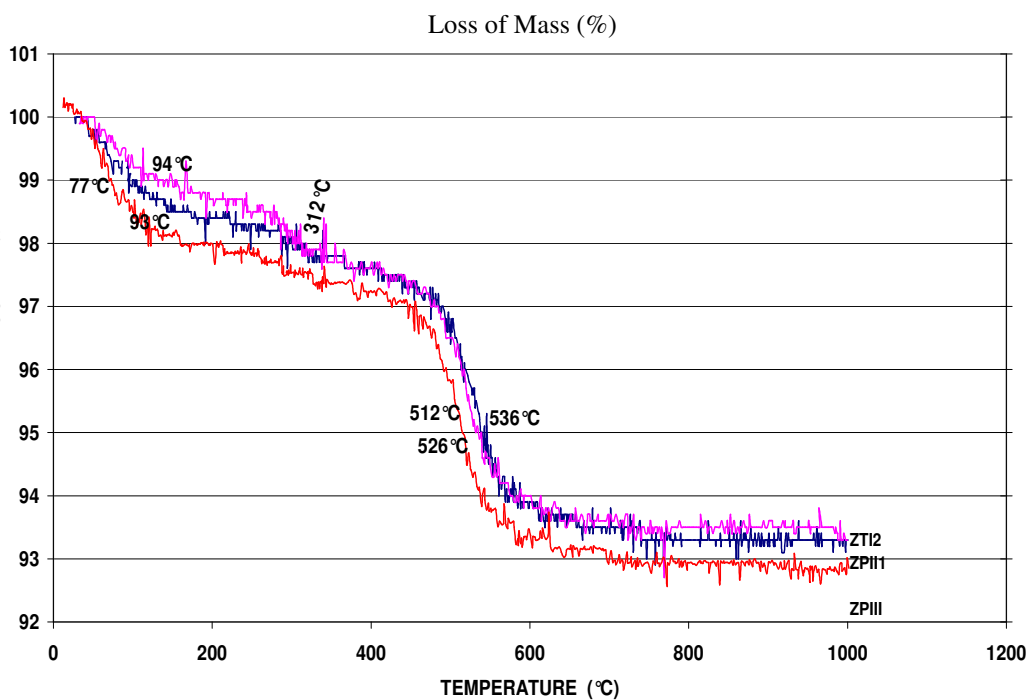
**Figure-6c**  
**Thermograms of samples ZY**



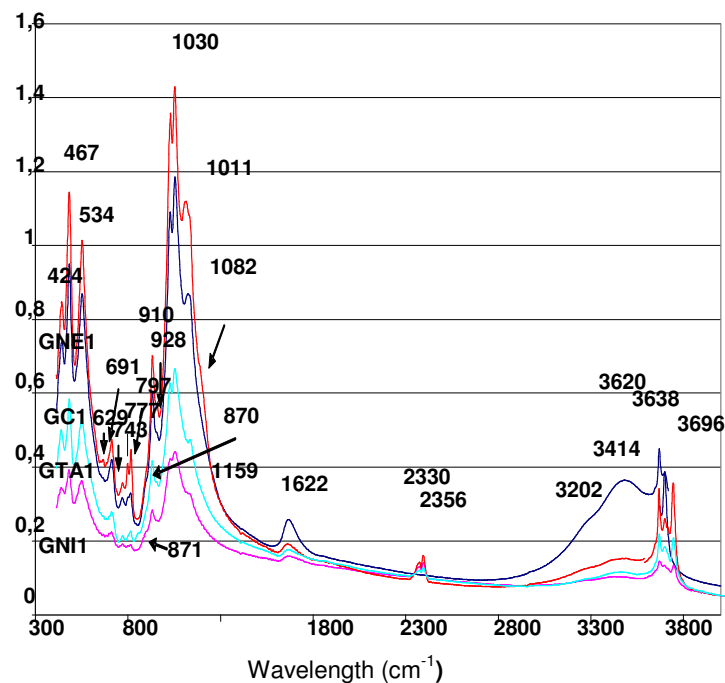
**Figure-7a**  
**Thermogravimetric curves of samples GK**



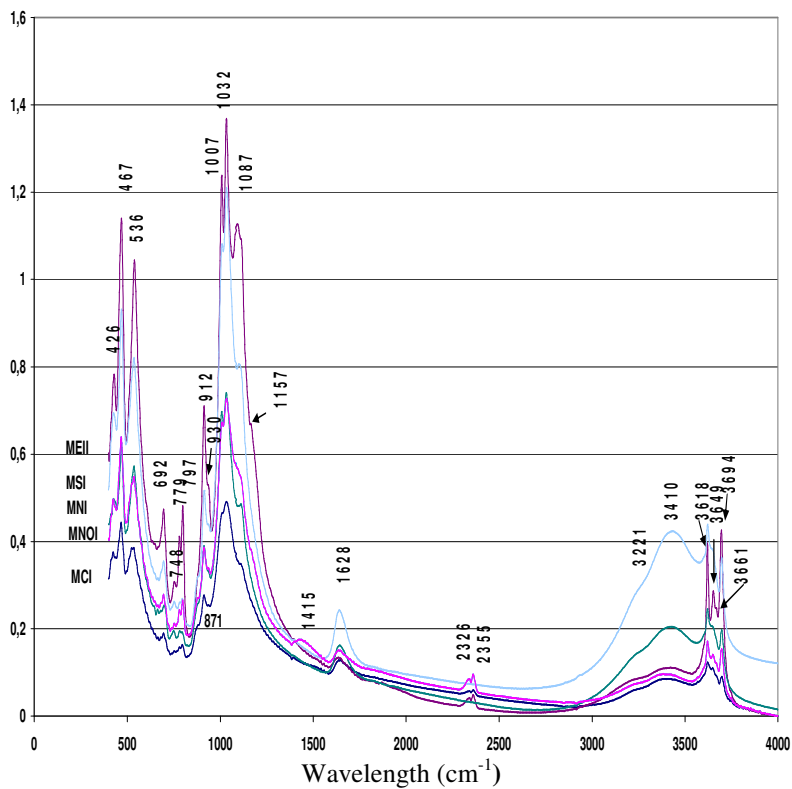
**Figure-7b**  
**Thermogravimetric curves of samples MS**



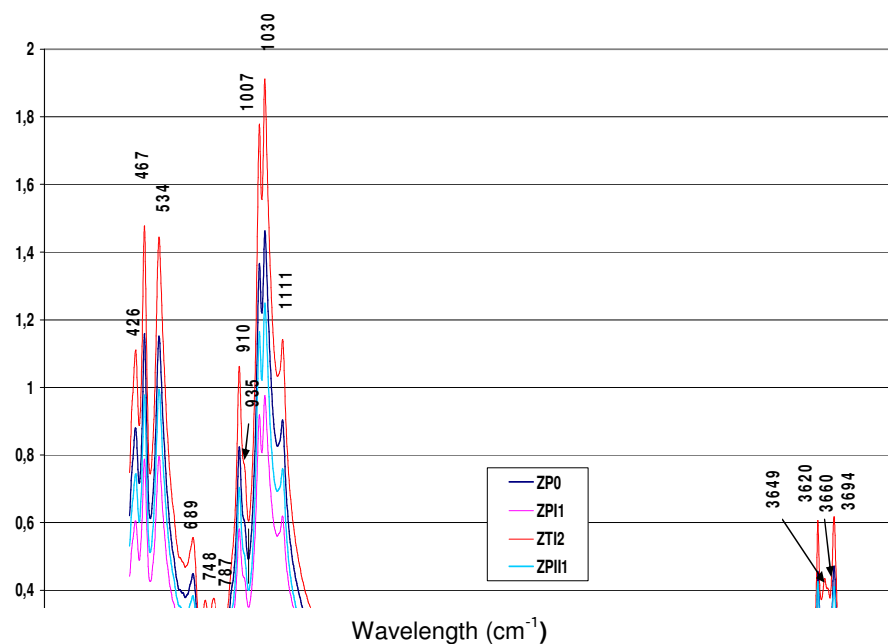
**Figure-7c**  
**Thermogravimetric curves of samples ZY**



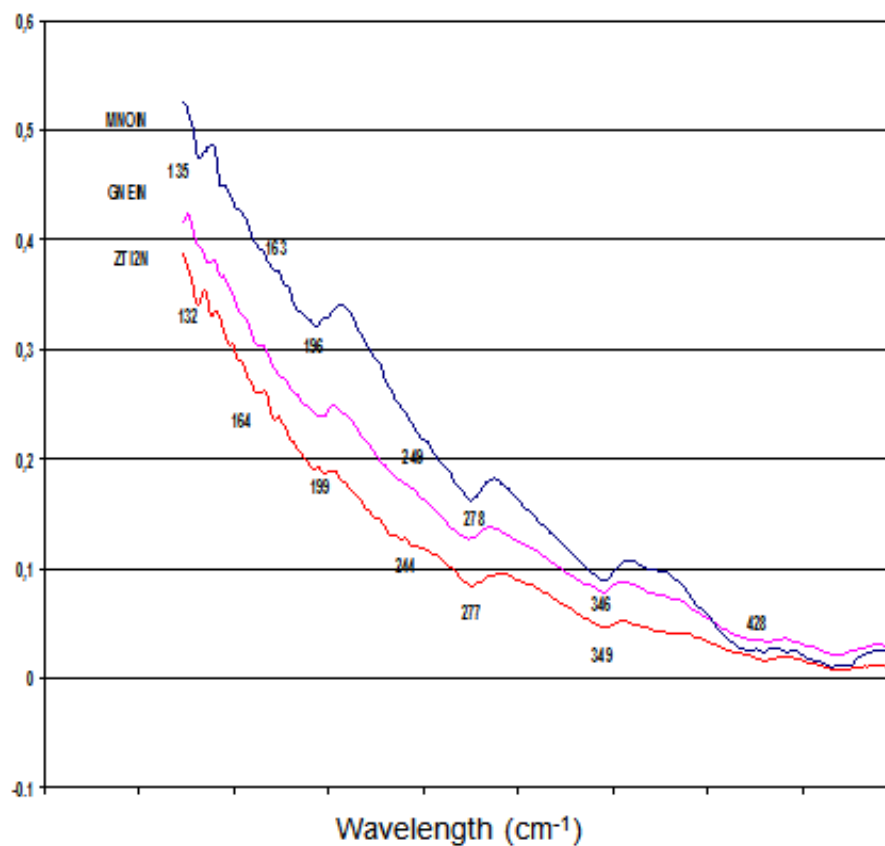
**Figure-8a**  
**Spectra Infra-red of samples GK**



**Figure-8b**  
**Spectra Infra-red of samples MS**



**Figure-8c**  
**Spectra Infra-red of samples ZY**



**Figure-8d**  
**Spectra Infra-red of samples GNE1N, MNO1N and ZTI2N between 50 and 450 $\text{cm}^{-1}$**

**Table-4**  
**Quantitative semi- composition of samples GK, ZY and MS**

| Samples | Smectite | Kaolinite | Illite | Quartz | Goethite | Albite | Orthoclase | Anathase |
|---------|----------|-----------|--------|--------|----------|--------|------------|----------|
| ZY      | 5        | 40        | 4      | 39     | 10       | -      | -          | 2        |
| GK      | 53       | 17        | 11     | 13     | —        | 2      | 3          | 1        |
| MS      | 59       | 12        | -      | 28     | -        | -      | -          | 1        |

## Conclusion

The combination of several methods of physico-chemical and mineralogical analysis have shown that the clays of the three sites contain mainly kaolinite, smectite and quartz in variable proportion. They are primarily silty-argillaceous (more than clay 70% + silt). Taking into consideration results of analysis and above mentioned criterion, clays of the three sites are appropriate for the discounted use. By its composition the samples of Zogbodomey constitutes a natural mixture of the necessary elements with the condition to remove slightly iron.. The two other sectors, because of their strong proportion of smectite, will require some kaolinite and sand grease-remover. Tests laboratories and geotechnics tests will confirm that these clays are ready to provide raw materials of quality for production of bricks, tiles, confined, hollow block. Elsewhere, the layers of Gbédji-kotovi and Massi-Sèhouè because of their strong proportion in smectite would be more useful in agronomy and environmental protection.

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