

Full Length Research Paper

Characterization of clays from Tharaka-Nithi County in Kenya for industrial and agricultural applications

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Clay samples from Tharaka-Nithi County in Kenya were characterized by hydrometer, X-ray fluorescence spectroscopy (XRF), atomic absorption spectroscopy (AAS), TGA, scanning electron microscopy (SEM) and powder diffraction (XRD) methods. The F-test and t-test were used to interpret the results. The major oxides present were Al₂O₃, SiO₂ and the minor ones were CaO, TiO₂, MnO, Fe₂O₃, K₂O, MgO and Na₂O. The values of SiO₂ were greater than those of Al₂O₃, indicating that the samples were of clay minerals. The clay minerals with low cation exchange capacity (CEC) were present in the samples. The Atterberg limits showed that the inorganic clays of either low or intermediate plasticity having low contents of organic matter were present in the samples. The analysis further showed the availability of essential elements necessary for plant growth. The TGA analysis indicated that the decomposition of clay samples occurred in four steps. The scanning electron microscope photographs revealed that the samples contained a mixture of minerals of morphologies with crystallinity, high porosity and unstable under the electron beam. The major impurity in the clay is quartz, ranging from 22.6-31.9%. Albite is the most dominant component in the clay minerals contributing to 30.3 to 44.1%. The clay from the study area can be used as agro mineral additive to enhance soil fertility for crop production, a fluxing agent in ceramics and glass applications and also as functional fillers in the paint, plastic, rubber and adhesive industries after beneficiation.

Key words: Scanning electron microscopy, X-ray diffraction, clay minerals, Atterberg limits, atomic absorption spectroscopy (AAS), Fourier transform infrared spectroscopy (FTIR), TGA, quartz.

INTRODUCTION

Clay is a term used to describe either the size of the individual particles present in a deposit (clay size fraction) or specific minerals (clay minerals) of a small size of less than 0.002 mm in dimension (Fabio et al., 2009; Nwosu et al., 2013; Obase et al., 2013; Abuh et al., 2014).

Understanding of the distinction between clay size and clay minerals in the assessment of clay minerals is important because two samples of clay having identical particle size can have very different behaviors based on the clay minerals present (Gray et al., 2013). Clay mineral

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formation in the soil involves slow processes that depend upon the weathering environment, which in turn is mainly controlled by climate and drainage conditions of the landscape (Konta, 2005; Emdadul, 2013). Different clay minerals will exhibit different physical, chemical and mechanical behaviors depending on the structure developed in the course of mineral formation. For instance, in the presence of free water montmorillonite, clay minerals will swell to many times their initial volume as a result of taking water into the layers between the individual unit layers of clay, while kaolins will remain essentially unchanged.

As a result of these substantial differences in the behavior of the various clay mineral types, determining the type and proportion of clay minerals in a particular clay deposit is one of the first and the most important steps necessary in screening a source mineral. The chemical and physical properties of clay minerals are of great importance to industry, agriculture and the environment owing to their abundance, high specific surface area, high layer charge, laminar morphology and chemical reactivity with both neutral and charge species (Murray, 1999; Hoidy et al., 2009). The minor oxides components (impurities) which occur in variable quantities are important as their presence imparts some properties to clay. The presence of iron in the crystal structures of the clay minerals infuses an exceptionally important additional facet into their importance because its oxidation state can be rather easily modified *in situ* and such changes evoke profound differences in the surface chemical and structural behaviour of the clay mineral. Example of clay mineral properties that are greatly affected by changes in iron oxidation state are swelling in water, cation exchange capacity (CEC), cation fixation capacity, surface area, clay-organic interactions, surface pH, reduction potential, ability to transform chlorinated organic compounds and ability to degrade pesticides and thereby alter their toxicity. Clay has a huge potential for the synthesis of clay polymer nanocomposites with superior mechanical and thermal properties. The optimization of adsorption properties, swelling behaviour, colloidal and rheological properties, and the design of new types of organoclays also open prospects of using clay minerals for pollution control and environmental protection. Clay was implicated in the prebiotic synthesis of biomolecules at the very origin of life on earth and has also become indispensable to modern living (Bergaya et al., 2012).

Kaolin clay finds a large market in the ceramics, paper, paint, plastics, pharmaceutical, cosmetics and tooth paste industries. It is also used to prevent insect damage on crops and on apple farms to prevent the sun scalding the fruits and also in radiological dating because it often contains trace amounts of thorium and uranium (Abel et al., 2012). However, the presence of impurities such as siderite, pyrite, quartz and titanium impair the characteristics of kaolin and affects its utility for various end applications depending on the origin and depositional

environment (Borthakur et al., 2003).

Bentonites, because of their fine particle size and expanding lattice characteristics, are used in large amounts for applications such as abider for foundry sands, as a mid constituent for oil and water well drilling, in the construction of special foundations for digging diaphragm walls and bored pipes, as an animal feed supplement and as a pelletizing aid in the production of animal feed pellets. Bentonite is also effective against mycotoxins, is used in environmental protection for water clarification and as an aid to polyelectrolyte and inorganic flocculants and as an ion exchanger for soil improvement. Other uses of this element include: enhancing ceramic paste plasticity as an anti-setting agent in ceramic enamels, improving the efficiency of conversion of pulp in paper, as well as for paper quality, enhancing clarification and protein stabilization in wine making, as a filler in pharmaceuticals, as softener for fabrics in detergents, liquid cleaners and soaps, removal of impurities in oils and as a thickening and/or suspension agent in paints and varnishes (Abel et al., 2012).

Catalysts producing mainly high octane gasoline in petroleum industry have been produced from clays composed of montmorillonite, halloysite and kaolinites. Illite clays are suitable in structural clay industry while clay containing halloysite, montmorillonite, chlorite and hydrobiotite predominantly do not produce structural clay products of good quality. Knowledge of the nature and content of the clay minerals, and the accessory minerals present along with the clay mineral is required for the prediction of the firing behaviour of clays.

A better understanding and control of the stabilization of soil for the construction of roads and airport runways can be achieved only if the mineralogical nature and content of the soil is known. Kaolinite adsorbs only a small amount of plant nutrients; it parts with the nutrients much more readily than montmorillonite or illite, hence from a proper economy of fertilizers, it is expedient that kaolinite soils should be treated with fertilizers in small quantity. In the case of montmorillonite soils, a larger quantity of fertilizer should be added, all at one time. Acid clays release Al and Fe ions on treatment with fertilizers. These ions fix the phosphate nutrients making them unavailable to the plants. Furthermore, phlogopite, Illite and glauconite clays are employed as agro mineral additive to enhance soil fertility for crop production because of their high content of potassium. This calls for the characterization of the clay minerals in various regions in order to establish the types of clay minerals in the region so as to enable the farmers to benefit from these low cost materials in comparison with fertilizers.

Many types of clay in Kenya are predominantly montmorillonite and highly contaminated with quartz (Muriithi et al., 2012). A study carried out in the south of Nairobi city in Kenya showed that the red soils in the study area was mainly kaolinite in composition and polygenetic in origin while the black clays in the study

area was dominated by smectites (Otando, 2004). The study on clay minerals and humus complexes which was carried out for five profiles around the Longonot and Suswa volcanoes in Kenya showed that profiles 1 and 4 contained embryonic halloysite with X-rays amorphous iron oxide and silica whereas profile 5 contained a kaoline mineral, chlorized 2:1 layer silicates, gibbsite and hematite (Wada et al., 1987). Smectite, kaolinite and dehydrated halloysite which contained curved layers were found to be present in the soil samples from volcanic ash in Kenya and Tanzania (Van Der Gaast et al., 1986). The analysis of magnesium-rich clays in the Amboseli basin in Tanzania and Kenya revealed that the carbonate rocks consisted of limestone and dolomite for Tanzania, but only dolomite in Kenya. Sepiolite, dolomite and illite were also found to be available in the samples (Itay et al., 1995). The study on the samples from Pleistocene Alorgesailie in Southern Kenyan Rift consisted mainly of Smectic clays (Deocampo et al., 2010).

Tharaka-Nithi County in Kenya has a number of places with the clay that have not yet been exploited. The characterization of clays for various applications in agriculture, industry and environment is necessary for its utilization and exploitation. The objective of this study was to characterize the clays in Tharaka-Nithi County using different techniques. Results from this study will open ways for further research on its beneficiation with a view to upgrading the properties of the clays in this region to that of the standard commercial clay of various types.

MATERIALS AND METHODS

Sampling techniques

Clay samples were collected from three different sites (Mukunga, Kibao/Mbaraga and Kankoma) in Kithangani Location at depths of 20, 40 and 60 cm. Contaminants such as leaves of trees were removed from samples and then dried at ambient temperatures for 21 days. Thereafter, the samples were finely ground with a gate mortar and then passed through a 2 mm mesh sieve to obtain very fine particles. Air-dried, ground and sieved samples from each specific site and depth was mixed using coning and quartering techniques so as to obtain representative analyte samples.

Reagents

Reagent grade chemicals from Sigma-Aldrich Cheme GmbH, USA were used. All the reagents used conformed to the specifications of the committee on analytical reagents of the American Chemical Society (ACS) where such specifications were available. De-ionized double distilled water was used throughout.

Extraction and analysis of samples

Extraction of individual elements from the collected soil samples was done according to the EPA Method 3050. A. 0.1 g of an air-dried, ground and sieved sample was weighed and transferred to a conical flask. Then 10 ml of 1:1 HNO₃ was added and the slurry mixed and covered with a watch glass. The sample was then

heated to 95°C and refluxed for 15 min without boiling and allowed to cool. Then 5 ml of concentrated HNO₃ was added, the watch glass replaced and refluxing done for 30 min and repeated to ensure complete oxidation. A ribbed watch glass was used to allow the solution to evaporate to 5 ml without boiling, while retaining a cover at the bottom of the beaker. The solution was allowed to cool and then 2 ml of water and 3 ml of 30% H₂O₂ added. The beaker was then covered with a watch glass and returned to the hot plate for warming and to initiate peroxide reaction. The heating continued until effervescence subsided, followed by cooling of the beaker. Care was taken to ensure that losses did not occur. After this, 1 ml of 30% H₂O₂ was continuously added (to a maximum of 10 ml) while warming until effervescence was minimal. Samples prepared for AAS analysis including Ag, Al, Ba, Be, Ca, Cd, Co, Cr, Cu, Fe, K, Mg, Mn, Mo, Na, Ni, Os, Pb, Ti, V and Zn were further treated with 5 ml of HCl and 10 ml of water. The beaker was covered and returned to the hot plate and refluxed for an additional 15 min without boiling. It was cooled and diluted in water to a volume of 100 ml. The particulate matter in the digestate was removed by filtration using Whatmann filter paper No. 41. The samples prepared for furnace analysis included As, Be, Cd, Co, Cr, Fe, Mo, Pb, Se, Ti and V. Each sample was covered with a ribbed watch glass and heated in the acid peroxide digestate as previously described until the volume reduced to about 5 ml. The samples were cooled and diluted with water to 100 ml followed by filtration. A blank reagent was prepared following a similar procedure but without the samples.

Chemical analysis

The measurements were performed using the PG-990 atomic absorption spectrophotometer. For flame and graphite furnace power supply analysis, Analytikjena model CONTRAA 700 was used for all the absorption measurements. The hollow cathode lamps were fitted for specific element that had to be analyzed with its respective wavelength and the slit width was adjusted accordingly. Signal measurement was done in peak area and calibration was in linear mode. The heating program of GF-AAS is drying, pyrolysis, atomization and cleansing (Elarina et al., 2014). Perkin ELMER NIST traceable calibration standards in acid for atomic spectroscopy were used as the stock standards for preparing working standards. All the working standards were prepared. Micropipettes with disposable tips were used for pipetting solutions. Certified reference material-soil solution A for trace metals from high purity standards NIST traceable standards, Charleston SC was used for validating the method. Quality control standard was prepared at the midpoint of calibration for all elements. The quality control check was performed immediately after the end of analysis and was ensured to fall within EPA set limits of 90-110% (Praveen, 2009). The Zaimoglu and Yetimoglu (2011) method was employed in the determination of Atterberg limits.

The infrared spectra were recorded on IRAffinity-1 FTIR spectrophotometer Shimadzu. The KBr pressed-disc technique was used for scanning of the spectra. Samples of 1 mg were dispersed in 200 mg of KBr. These intimate mixtures were then pressed at a very high pressure to obtain the transparent discs which were then placed in the sample compartment. The calibration of this instrument was done using polystyrenes and silicate oxide of thickness 0.05 nm. TG analysis was carried out using Perkin Elmer model TGA 7. Thermal gravity analyzer was used to measure the weight loss of the samples. The samples were heated from 0-1000°C with the heating rate of 10°C min⁻¹ under nitrogen flow rate of 20 ml min⁻¹.

The selected clay samples were characterized by means of morphology, crystal habit, size, electron diffraction and element

Table 1. Chemical composition (%) of clay samples using XRF and AAS.

Sample site	Depth (cm)	XRF							AAS										Conductivity in μS
		Al ₂ O ₃	SiO ₂	CaO	TiO ₂	MnO	Fe ₂ O ₃	K ₂ O	Al ₂ O ₃	SiO ₂	CaO	TiO ₂	MnO	Fe ₂ O ₃	K ₂ O	MgO	Na ₂ O	LoI	
Mukunga	20	28.00	47.00	2.70	1.20	0.27	20.20	1.10	18.62	57.27	3.75	0.99	0.13	8.80	0.68	2.60	2.17	5.86	0.36
	40	-	61.00	3.80	1.80	0.34	31.90	1.20	19.34	57.07	3.37	2.13	0.12	10.20	0.66	2.50	1.99	5.74	0.23
	60	35.00	36.00	0.91	1.30	0.20	26.40	-	30.10	45.76	1.84	1.00	0.13	13.80	0.39	2.30	0.82	14.77	0.22
Kibao/Mbaraga	20	34.00	36.00	1.20	1.50	0.33	27.00	-	30.60	45.72	2.13	1.04	0.14	14.50	0.59	2.30	0.94	13.77	0.26
	40	36.00	34.00	0.97	1.30	0.26	27.40	-	33.80	49.05	1.95	1.06	0.13	14.80	0.57	2.30	0.78	8.79	0.24
	60	27.00	46.00	2.60	1.20	1.20	20.10	0.60	24.50	55.91	3.35	0.90	0.11	10.40	0.65	2.50	1.95	5.73	0.20
Kankoma	20	35.00	39.00	2.50	1.20	0.30	22.50	-	22.20	49.05	5.08	0.85	0.17	11.20	0.34	3.00	2.11	3.26	0.30
	40	37.00	40.00	-	1.20	0.29	21.90	-	25.30	46.01	3.99	0.82	0.15	12.40	0.31	2.60	1.55	4.18	0.27
	60	35.00	37.00	4.00	1.20	0.32	21.40	-	21.18	46.85	4.46	0.84	0.15	12.20	0.31	2.70	1.71	9.05	0.28

distribution by scanning electron microscopy (SEM). The crystalline phases were verified using EDS. In the present investigation, SEM was carried out using a transmission electron microscope JEOL JEM-1210 (120KV, MULTISCAN camera). All the clay samples were analyzed by powder diffraction (XRD). ICRAF whole rock approach method was employed for quantitative analysis. The X-ray diffraction was carried out using Bruker AXS D8 Advance diffractometer using Cu K α radiation. The data were collected between 5 and 60° (2 θ) at the rate of 1 min⁻¹ with a 0.02 scanning step size (Amer et al., 2001). The peaks were recorded and identified by a computer library system.

RESULTS AND DISCUSSION

Results of the chemical composition (in %) of the clay samples tested using XRF and AAS are shown in Table 1. The results of Al₂O₃ were used for comparing these two methods. The F_{tab} for $V_1=7$ and $V_2=7$ is 3.79 and the F_{cal} is 2.06. Since $F_{\text{cal}} < F_{\text{tab}}$, there is no significant difference in the preci-

sion of AAS and XRF, indicating that the standard deviations arise from random error and not the samples analyzed. This validated the use of the t -test. The t_{tab} at 0.95 confidence level for $df_{14} = 2.14$ while the $t_{\text{cal}} = 3.31$, indicating a statistical difference between the two methods. In view of this, the AAS was employed for characterization of the clay samples.

Results of the full assays based on the major and minor compounds and their average concentrations were as follows: Major compounds: Al₂O₃ (33.80–18.62%), SiO₂ (57.27–45.72%) and minor compounds: CaO (5.08–1.84%), TiO (2.13–0.82%), MnO (0.17–0.11%), Fe₂O₃ (14.80–8.80%), K₂O (0.68–0.31%), MgO (3.0–2.3%) and Na₂O (2.17–0.78%). These results revealed that the samples were of clay. Theoretically, the ratio of Al₂O₃: SiO₂ for clay minerals is 1:2. In this study, samples from Mukunga, Kibao/Mbaraga, Kankoma at a depth of 20-40, 60 and 20-60 cm respectively, had a higher amount of SiO₂ than the theoretical

value. This excess could be attributed to the presence of quartz in the samples. On the other hand, SiO₂ concentrations of samples obtained from Mukunga, Kibao/Mbaraga and Kankoma at depths of 60, 20-40 and 40 cm, respectively, were lower than expected. This could be due to the fact that Si is readily leached as compared to Al, and this might have been caused by rainfall and long-term intensive weathering of minerals in the humid warm conditions experienced in the study area. This may have caused the mineral to dissolve and slowly leach away resulting in low levels of silicate in the remnant materials. The red colour of the samples from Mukunga and Kibao/Mbaraga was associated with the presence of hematite (Fe₂O₃). Values of iron III oxides obtained were high and generally increased with depth for samples from all sites with exception of samples from Kibao/Mbaraga and Kankoma at the depth of 60 cm which recorded lower values. This could be due to increased rates of leaching of dissolved iron and

Table 2. Concentration in mg/kg of elements in the clay samples.

Site	Depth (cm)	Na	Ca	K	Mg	Fe	Mn	Zn	Cu	Cr	Pb	Al	Sb	Co	Cd
Mukunga	20	586	1020	3050	1141	86100	370	23	24	114	10	14960	-	3	ND
	40	495	1012	2170	1132	87700	335	19	15	113	4	15510	-	ND	ND
	60	450	512	632	1109	79800	426	13	28	114	8	23160	-	1	ND
Kibao/ Mbaraga	20	277	718	1070	1000	86000	440	20	27	135	8	32610	-	1	ND
	40	438	547	1042	1112	106700	515	18	29	147	ND	3430	-	2	ND
	60	232	932	3050	1130	62000	362	18	ND	137	4	18430	-	ND	ND
Kankoma	20	277	1410	544	1211	73200	358	14	49	139	2	22810	-	ND	ND
	40	532	1093	357	1131	71400	366	8	77	125	ND	17240	-	ND	ND
	60	306	1224	466	1148	82000	421	14	63	133	ND	18710	-	ND	ND

high permeability. Further investigations are needed to establish whether there are sufficient ore reserves in the area to warrant a mining operation.

The loss of ignition value ranged between 14.77-3.26%, revealing that clay samples analyzed had low carbonaceous but higher mineral matter. The conductivity of the samples ranged between 0.36-0.20 μS . This was observed to be low and could be partly attributed to high levels of quartz in the samples. Low values of electric conductivity indicate high clay mineral dominance in the samples bearing high CEC, such as Smectite. Therefore, minerals with low CEC such as kaolinite may have been available in the samples.

The results of metals present in the samples in mg/kg have been summarized in Table 2. The analysis showed the presence of the following elements; Na (586-232), Ca (1410-512), K (3050-357), Mg (1148-1000), Fe (106,700-62,000), Mn (515-538), Zn (23-8), Cu (77-below detection limit), Cr (147-113), Pb (10 - below detection limit), Al (32,610-3,430) and Co (3-below detection limit). From these results, the major elements present in the samples were Al and Fe. This is in agreement with the results obtained from the full assay. The levels of Cd in the samples were below detection limits. The samples from Mukunga, Kibao/Mbaraga and Angoma at depths of 40, 60 and (20, 40, 60 cm) respectively had their Co levels below the detection limit of the instruments used. It is evident from these results that clay minerals present in the analyzed samples were; Na, Ca, K, Mg and Fe while the impurities present were; Mn, Zn, Cu, Cr, Pb and Co. These results further revealed, the presence of essential elements necessary for plant growth like K, Ca, Fe, Zn, Cu in the samples hence Agricultural activities can be carried out in this region with the help of irrigation. The presence of potassium in the clay samples suggested that, the clay from this region can be utilized as agro mineral additive for enhancing soil fertility for crop production.

Table 3 shows the properties of sampled clay textures.

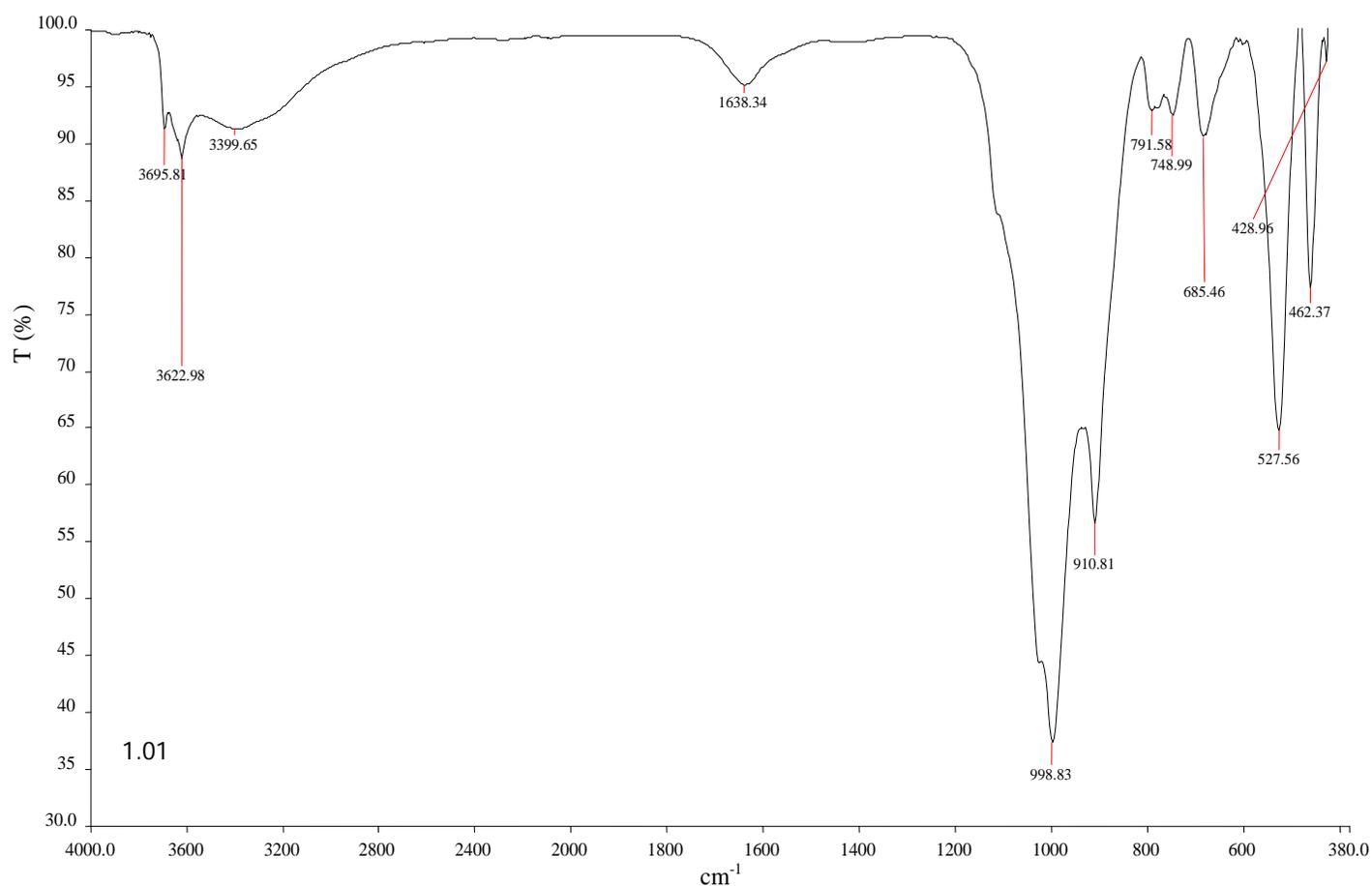
The percentage ranges of Atterberg limits were as follows: liquid limits (41.60-28%), plastic index (25.0-11.60%), linear shrinkage (10.0-5.70%), clay (44-20%), silt (20.0-10.0%), sand (66-31%) and gravel (6.0-0.0%). These results show that samples from Mukunga and Kibao/Mbaraga at the depths of 20-40 and 60 cm, respectively, were inorganic clays of low plasticity while the rest of the samples were of intermediate plasticity. All the samples tested had low compressibility and a low value of shrinkage limit. Shrinkage limit value is an important criterion for assessing and preventing excessive cracking of clay linearly in the reservoir embankment or canal. The high permeability obtained in this study indicated that soil percolation is high, increasing the chances of compacting of the soil during dry conditions.

The low gravel values indicated that the samples had a small amount of organic matter but a large amount of inorganic materials. The values of texture and fine earth in all the samples tested revealed that they were basically clayey sand except the sample collected at the 40 cm depth from Kankoma, which was sandy clay.

Figures 1-6 show the FTIR spectra of the clay samples. They range from 380.0 to 4000 cm^{-1} . The peaks at position 462.37, 527.56, 428.96, 685.46, 748.99, 791.58, 910.81, 998.83 cm^{-1} lie within the mid infrared region (1200-400 cm^{-1}). The peak at 685.46 is unique to the crystalline materials. The bands at 998.83 appear due to the silicon-oxygen stretching to vibrations and the tetrahedral-tetrahedral ions vibrations affected the band at 791.58 cm^{-1} for silicate; the tetrahedral dimensions are generally considered to be little affected by pressure and temperature (Bhaskar et al., 2008). The absorption band at 685.46 cm^{-1} arises due to the octahedral site symmetry. The tetrahedral site symmetry is stronger than that of octahedral site symmetry. Therefore, for any structural change, the damage occurs faster in octahedral symmetry than in tetrahedral site symmetry. The intensity of the bands due to the vibrations of these two

Table 3. Properties of sampled clay textures.

Sample site	Depth (cm)	Atterberg limits (%)				Texture, fine earth (%)			
		LL	PL	PI	SL	Clay	Silt	Sand	Gravel
Mukunga	20	28.00	14.00	14.00	6.42	25.00	20.00	55.00	0.00
	40	29.10	16.00	13.10	6.00	30.00	10.00	59.00	1.00
	60	39.60	24.20	15.40	7.90	44.00	20.00	31.00	5.00
Kibao/ Mbaraga	20	41.00	15.00	25.00	10.00	36.00	19.00	41.00	4.00
	40	41.60	23.60	18.00	8.60	42.00	18.00	36.00	4.00
	60	29.20	15.10	14.10	7.10	31.00	13.00	55.00	1.00
Kankoma	20	35.00	19.00	16.00	7.90	33.00	13.00	48.00	6.00
	40	30.90	19.30	11.60	5.70	31.00	16.00	52.00	1.00
	60	31.20	18.80	12.10	5.70	20.00	13.00	66.00	1.00

**Figure 1.** FT-IR Spectra of representative clayey soil sample from Mukunga site at the depth of 20 cm.

symmetries provides direct information on the crystallinity. The symmetrical bending vibrations of Si-O group obtained at 685.46 cm^{-1} is a diagnostic peak in determining the short range parameter of the quartz. The

absorption bands located at $530\text{-}460$ and $1000\text{-}900\text{ cm}^{-1}$ involve atomic motions within the SiO_4 tetrahedral. The former frequencies represent asymmetric and symmetric Si-O bending vibrations, whereas the latter represent

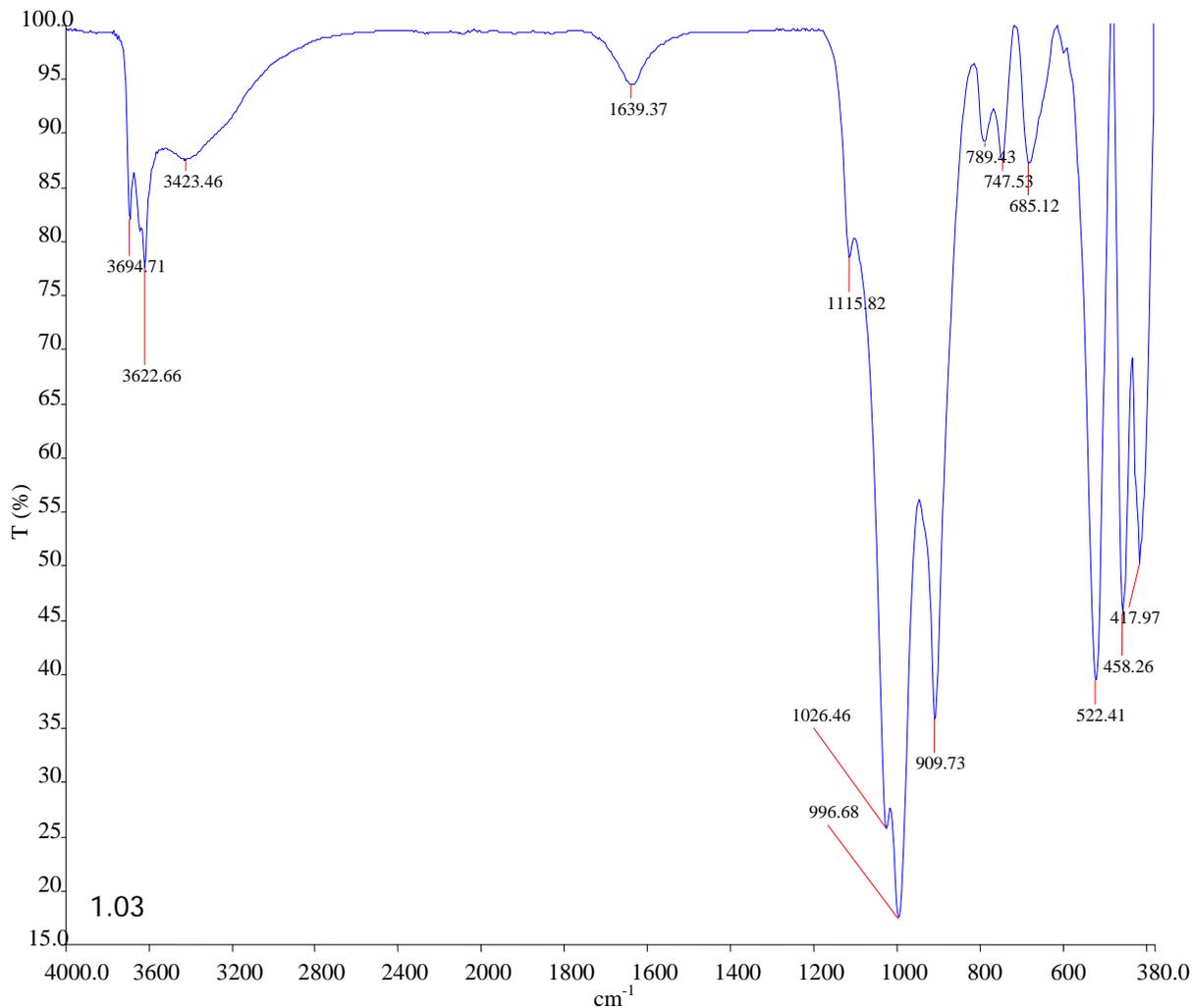


Figure 2. FT-IR spectra of representative clayey soil sample from Mukunga site at the depth of 60 cm.

asymmetric Si-O stretching vibrations (Bhaskar et al., 2008).

A shoulder at 369.81 cm^{-1} and sharp band at 3622 cm^{-1} are related to hydroxyl (Al-OH) group stretching vibrations in the aluminosilicate layers of the clay. These bands, which form doublets, are characteristic of the kaolin group. The doublet at 791.58 cm^{-1} arose from Si-O vibrations in the quartz and aluminosilicate layers. The band at 910.81 cm^{-1} is assigned to Al-OH aluminosilicate. Another band at 685.46 cm^{-1} could be attributed to a vibration of the hydroxyl groups perpendicular to the plane of the layers or to the vibration of the octahedral ions. Both bands at 527.56 and 462.37 cm^{-1} were attributed to Si-O-R³⁺ (R=Al, Fe) vibrations (Naidja et al., 2001). The strong and broad band at 3399.65 cm^{-1} is due to the stretching vibrations of H-bonded OH in aliphatic polyols (Naidja et al., 2001). The band at 1638.34 cm^{-1} in the spectrum of clay suggests the possibility of water of hydration in the clay. The vibrations observed at 910.81

cm^{-1} indicated the possibility of the presence of hematite. A representative of FTIR spectrum is shown in Figure 1.

The thermal decomposition is shown in Figures 7 and 8 in terms of weight loss as a function of temperature. This figure indicates that the decomposition of clay occurred in four parts. The first part involves the loss of free water, which is the water between particles and adsorbed on the external of the crystals. This first part occurs below 200°C . The second part occurs between the temperature range of 200 to 500°C and this corresponds to the region where the organic substance evolves. The third range between the temperature range of 500 and 800°C involves the loss of structural water. The fourth region between 800 and 1000°C is the region where the organic carbon reacts with inorganic oxygen to give a combustion reaction. This finding agrees with the work of previous researchers (Wisam et al., 2009).

The morphological aspects of the clay mineral powder samples are outlined in Figure 9. The scanning electron

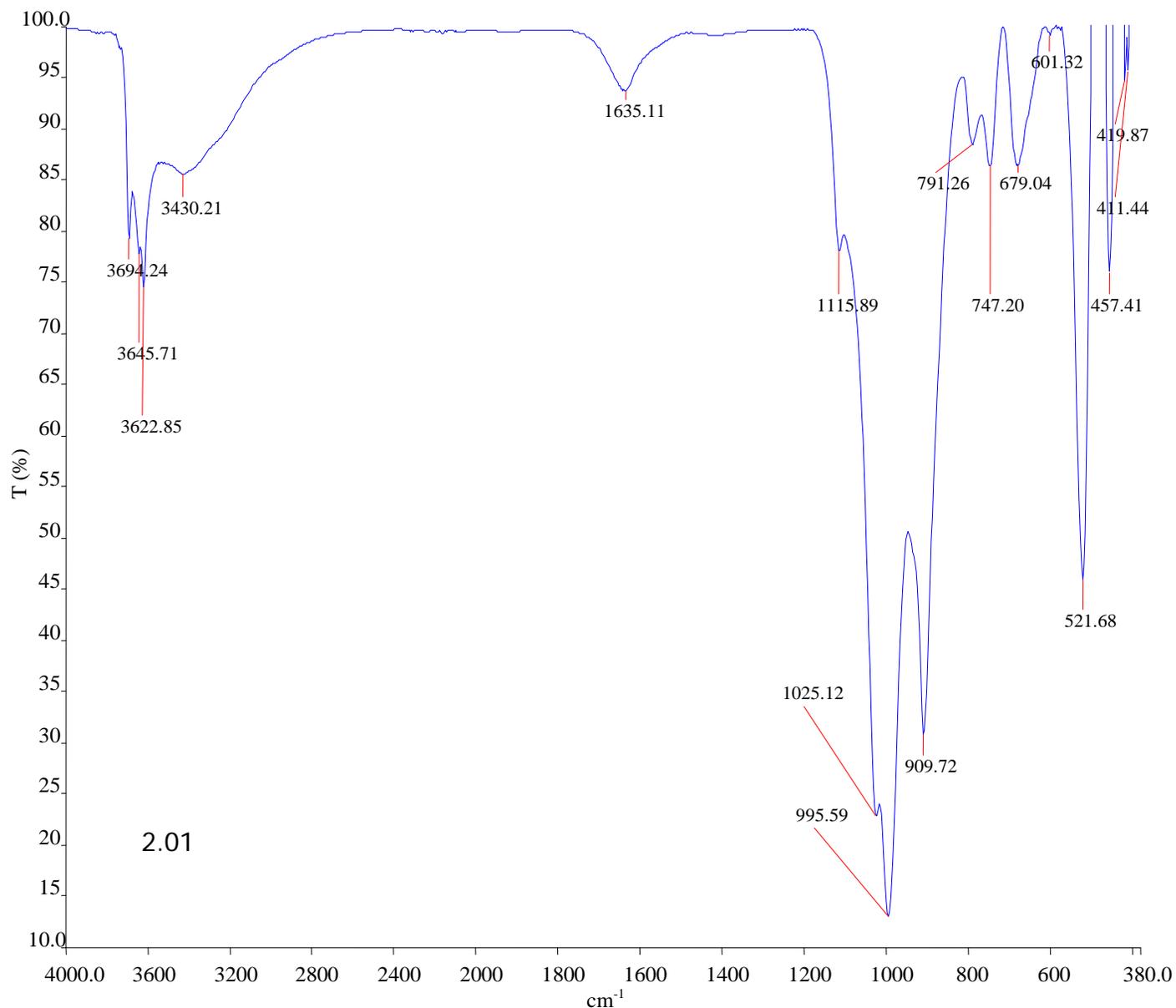


Figure 3. FT-IR spectra of representative clayey soil sample from Kibao/Mbaraga site at the depth of 20 cm.

micrographs show the typical irregular shapes of the particles of different sizes. The pseudo-hexagonal plates with angular edges suggest that, the samples contained clay minerals with crystallinity (Mohsen and El-Maghraby, 2010). The presence of small particles with broken edge in Figure 4 could contribute to increase in the total surface charge hence absorption of impurities. The SEM shows a sample composed entirely of well-rounded quartz with small oval depression fringed by clay. The depressions indicated mild compaction and pressure solution has occurred at points of contact. Pre solved quartz has, locally, re-precipitated near points of contact, forming euhedral overgrowths. The presence of iron oxide has

been shown by appearance of very bright sections. A representative SEM spectrum is shown in Figure 9.

XRD pattern for the clay collected is presented in Figures 10. The XRD pattern of the clay shows peaks at d (Å) = 3.3084, 2.26661, 2.14302, 1.54533 which revealed the presence of quartz. The peaks corresponding to position d (Å) = 4.18846, 3.53620, 4.36585, 2.26661, 1.68219, 1.54533 showed that kaolinite mineral is available in the sample. The strongest reflection was observed at 3.30384, which was more intense than the peaks observed corresponding to kaolinite which indicated the quantity of the quartz in the sample was greater than that of kaolinite. The peak of Illite at

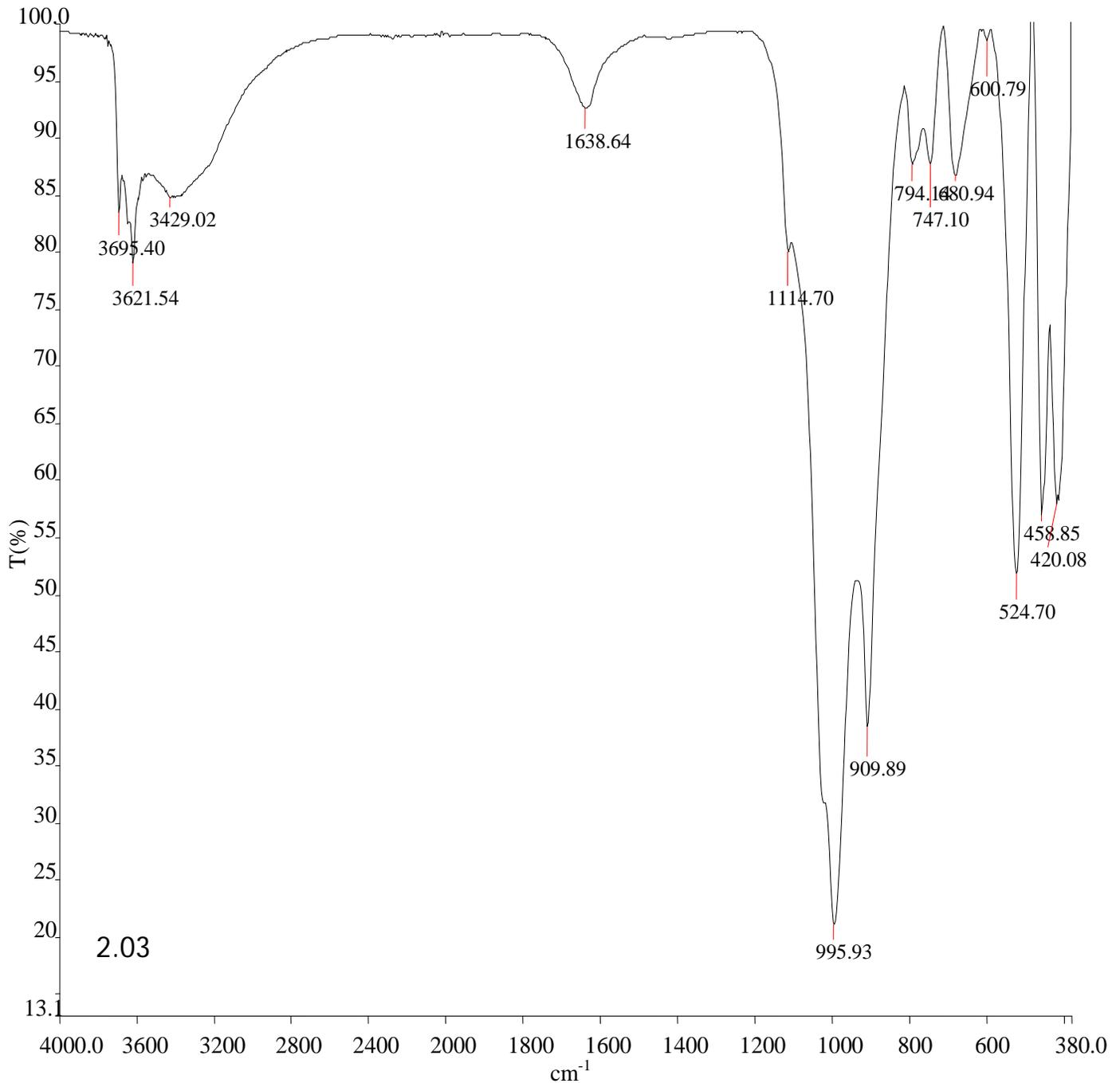


Figure 4. FT-IR spectra of representative clayey soil sample from Kibao/Mbaragaa Site at the depth of 60 cm.

3.32 to 3.35 could not be established with certainty because of the principal reflection of quartz (3.3084 Å) which occurs at almost the same position. The peak at position d (Å) = 3.17378 showed the presence of Albite and it's the most intense peak which revealed that, it is the most abundant clay mineral present in the sample. The bands at 2.67579, 1.68219 revealed the presence of hematite in the clay sample.

The peak at position d (Å) = 3.10070 indicated the presence of Hornblende. The bands corresponding to the position 2.03721, 1.77657 showed Diopside mineral was present in the sample. In similar manner, Figure 11 showed the presence of Albite, Hematite, Hornblende, Magnetite, Nacrite and Quartz while Figure 12 reveals the presence of Albite, Clinocllore, Diopside and Quartz.

The X-ray diffraction quantitative results are Summa-

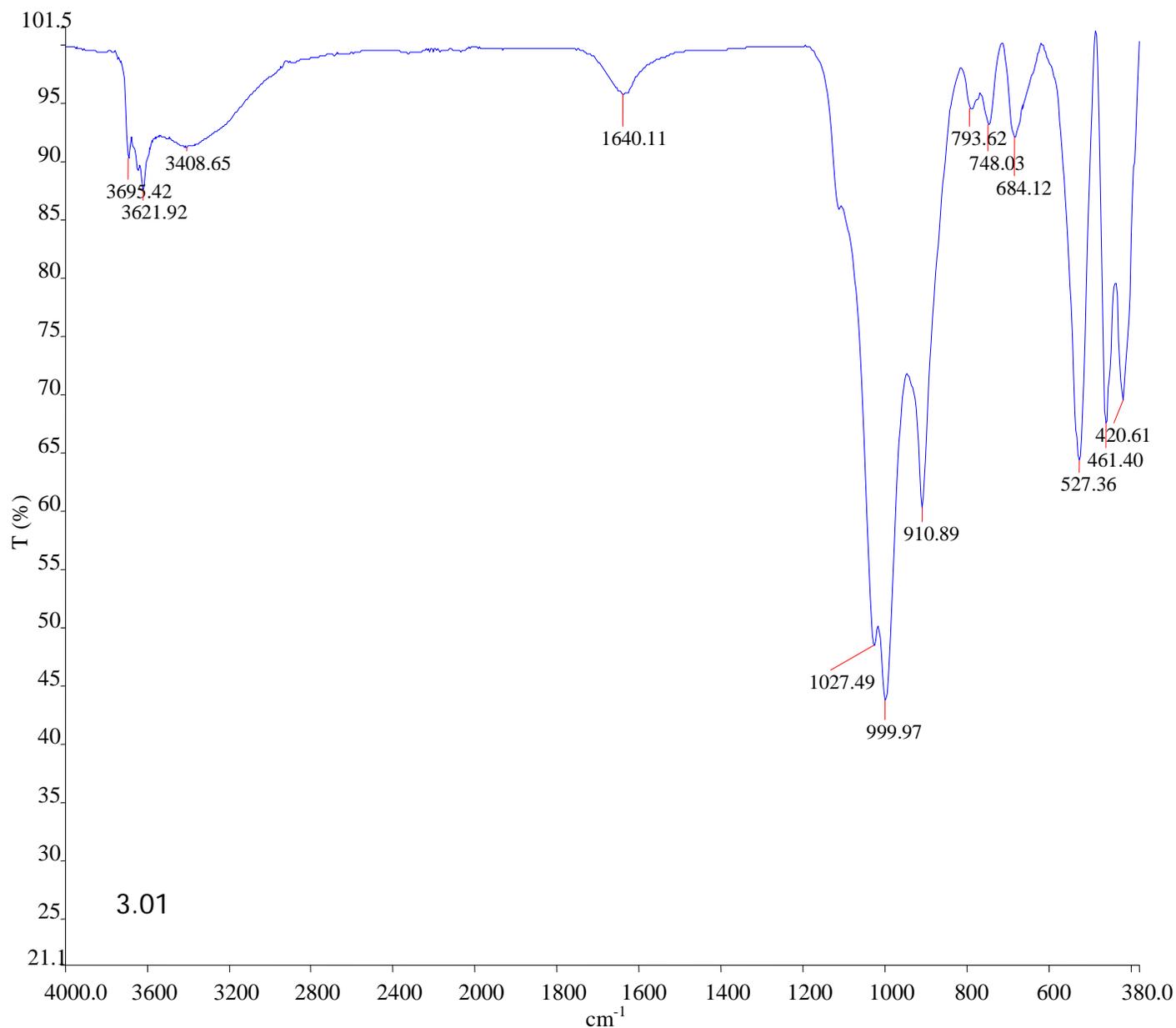


Figure 5. FT-IR spectra of representative clayey soil sample from Kibao/Mbaraga site at the depth of 20 cm.

rized in Table 4. The major clay mineral in the study region is Albite with ranges of 33.1-44.1%. Other clay mineral present in the other sites in minor quantities are as follows: Mukunga: Diopside (4.9%), Hematite (2.8%), Hornblende (10.1%), Kaolinite (6.2%); Kibao/Mbaraga: Hematite (6.0%), Hornblende (14.8%), Magnetite (3.5%), Kaolinite (6.2%); Nacrite (16.6%); Kankoma: Chlinochlore (7.1%), Diopside (10.2%), Hornblende (2.7%). The percentage of quartz in the samples ranged between 31.9–22.6% which was less than the amount of Albite found. Results of XRD further showed that the beneficiation of clay samples in the region is necessary in

order to eliminate impurities present to an extent to which the Albite mineral present can be used as a fluxing agent in ceramics and glass applications, and also as functional fillers in the paint, plastic, rubber and adhesive industries.

The pH of samples from Mukunga, Kibao/Mbaraga and Kankoma sites were 6.27, 6.46 and 6.67, respectively (Table 4). These values were higher than the pH range of 5.5-6.0, which is considered to be optimum for growth of crops. It can be lowered by application of acidic fertilizers and irrigation using a lot of water in order to enhance leaching of basic cations. The soils contain high amounts of calcium, magnesium and potassium, which contributed

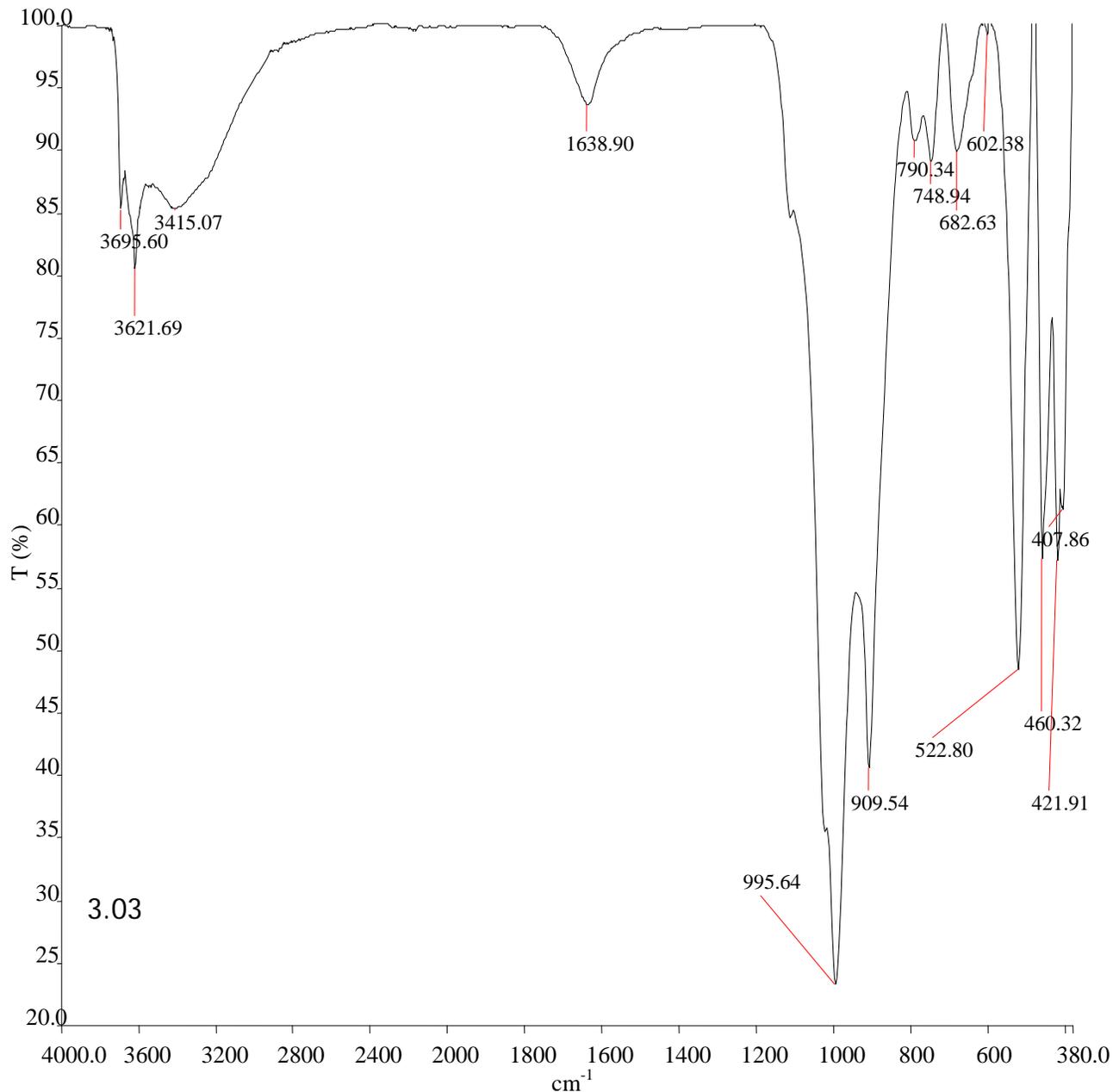


Figure 6. FT-IR spectra of representative clayey soil sample from Kankoma site at the depth of 60 cm.

to alkalinity whereas high levels of aluminum in the sample contributed the acidity, thus leading to the soil being slightly acidic. With proper management, these soils can be used for crop production.

Conclusions

The applications of XRF method provided a quick multi element soil analysis. The results from XRF and a full

assay analysis revealed information on the main contents of the soil, which were as follows: Al, Fe and Si. The differences in the results of these two methods might have been due to the presence of water which could not be removed during drying time. The water content influences the XRF intensity. The samples were mainly inorganic clay of either low plasticity (Mukunga and Kibao/Mbaraga) or intermediate plasticity (Kankoma). They were generally clayed sand, consisting of the quartz, minerals of crystalline in nature with low cation

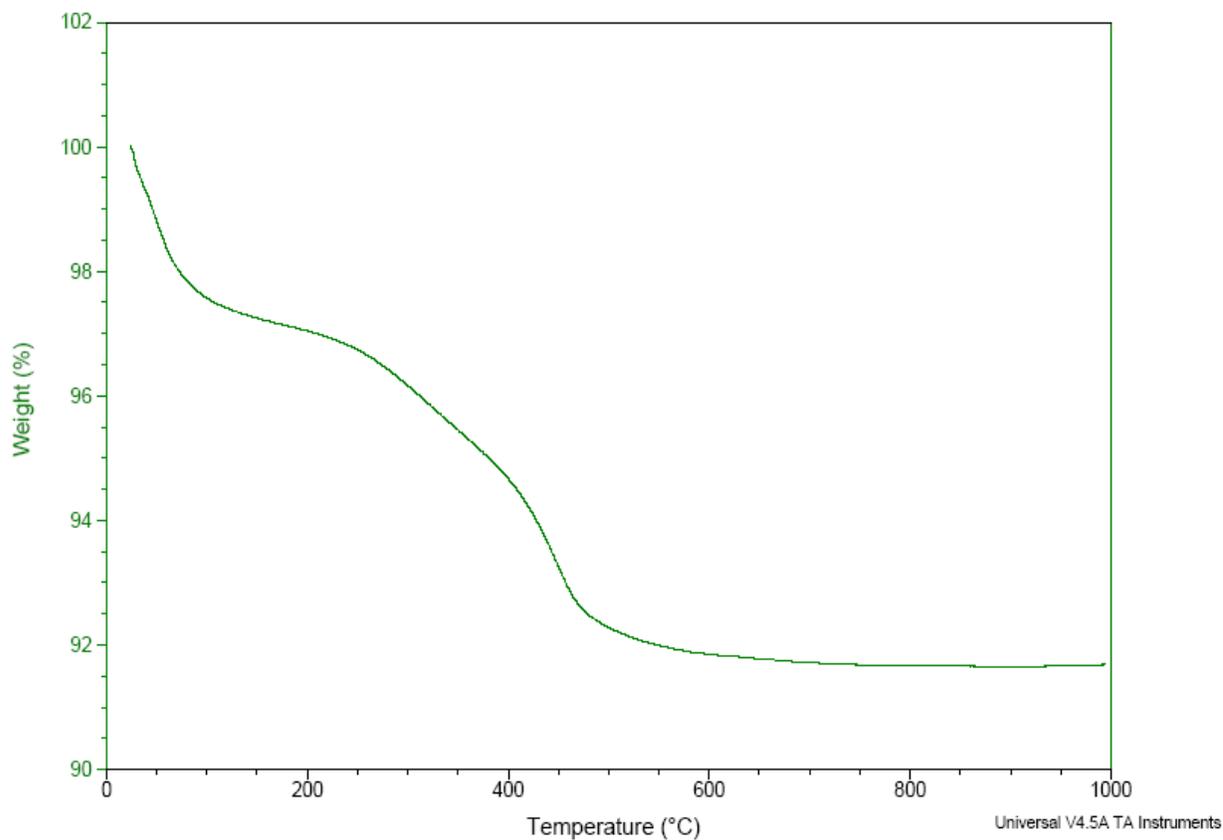


Figure 7. TGA measurements of clayey soil sample from Mukunga site.

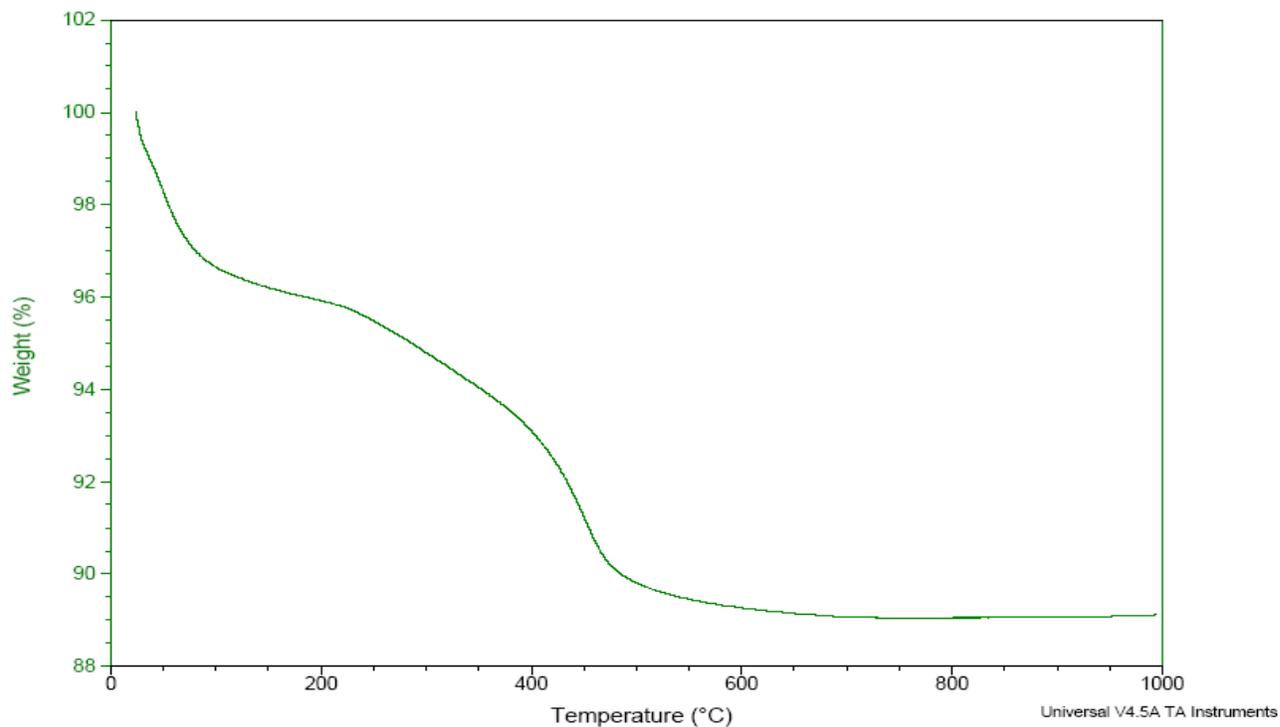


Figure 8. TGA measurements of representative clayey soil sample/Mbaraga site.

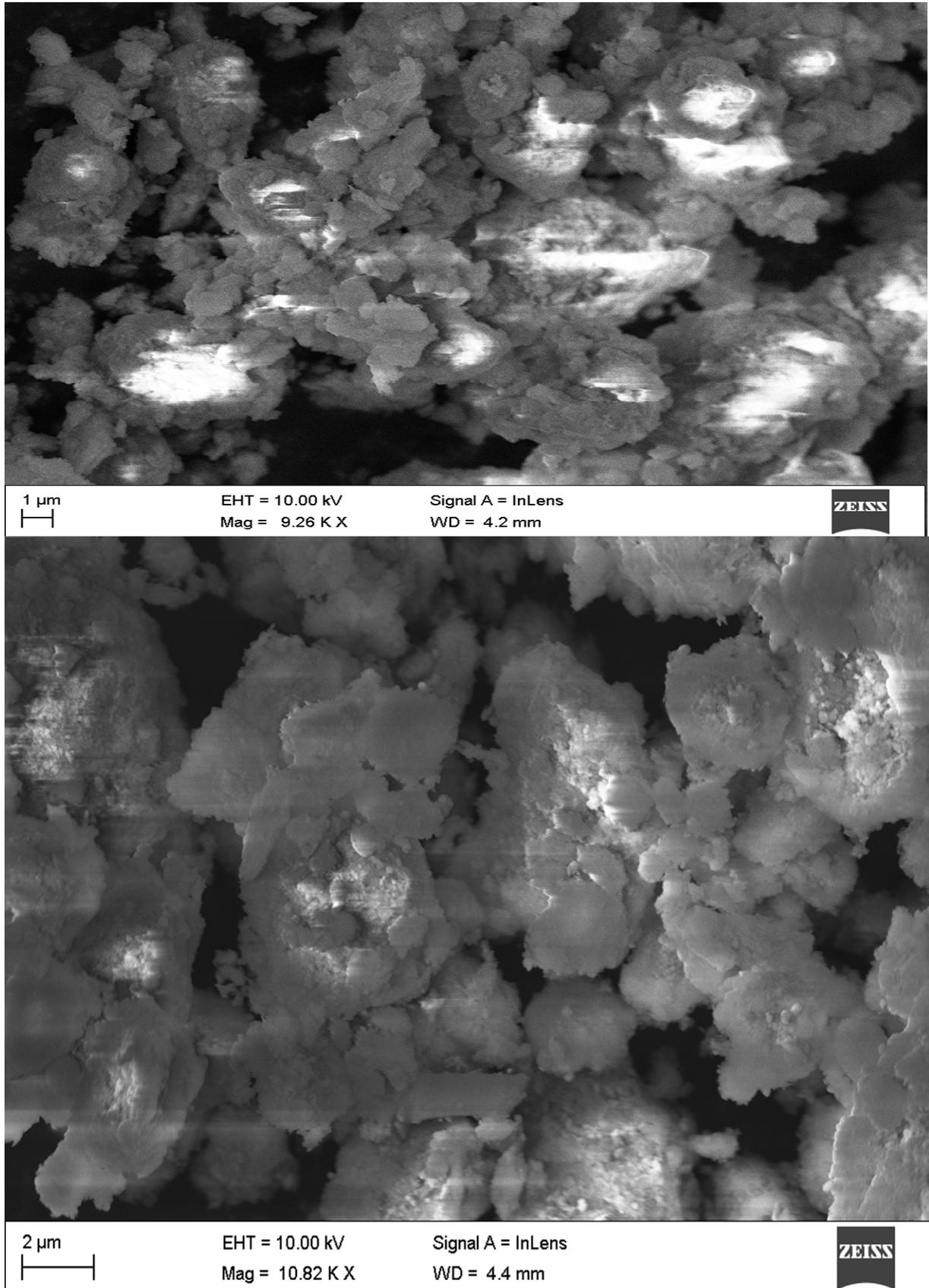


Figure 9. SEM photomicrographs of representative clayey soil sample from Kankoma site.

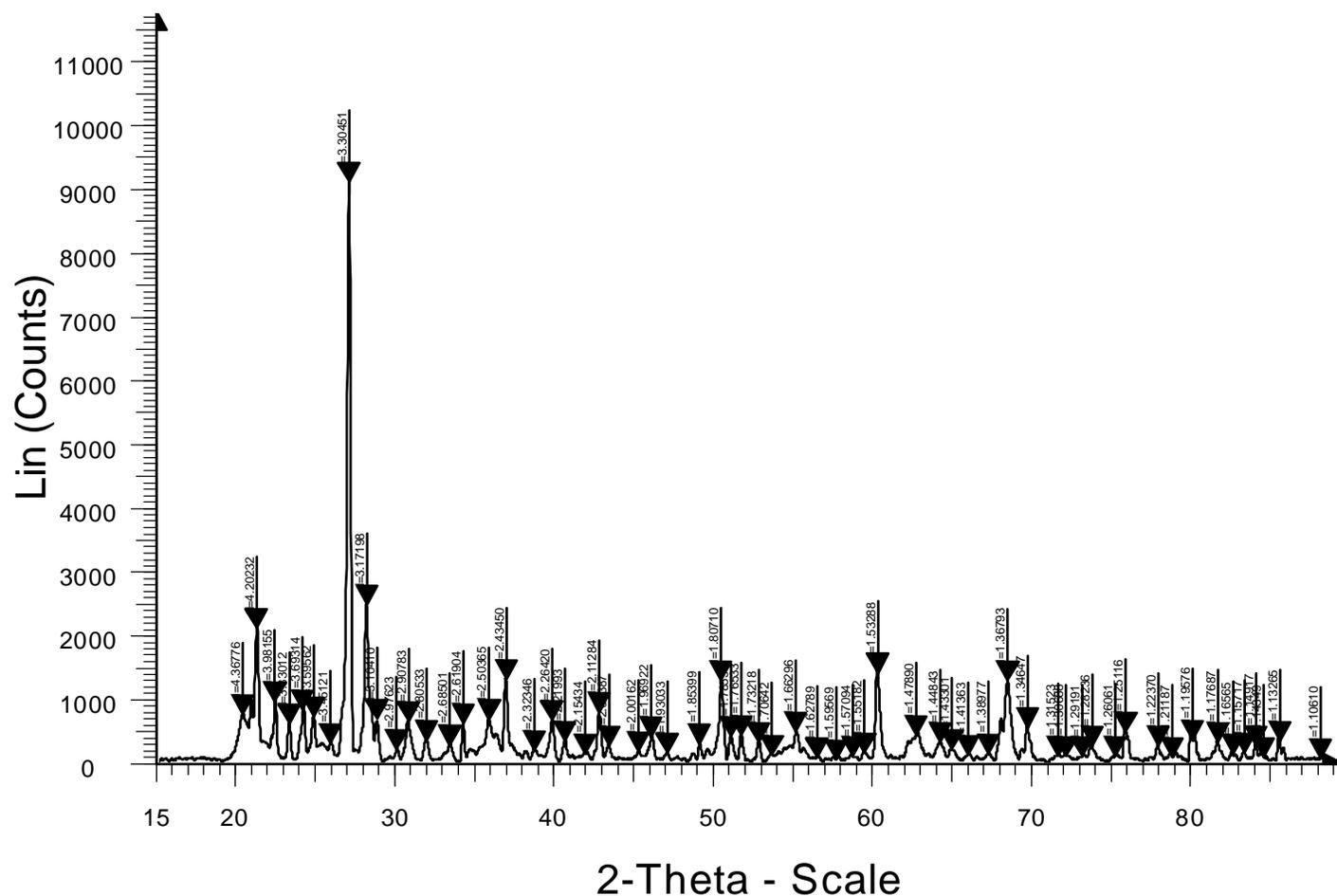


Figure 10. XRD spectra of representative clayey soil sample from Mukunga site.

exchange and high permeability. TGA curves for these samples showed four step degradation which corresponded to water desorption, dehydration, followed by decomposition of the organic matter and the dehydroxylation of the clay minerals. The morphological aspects of the clay minerals showed that clay samples were composed of a mixture of mineral particles of different morphologies having crystallinity, high porosity and unstable under the electron beam.

The results of the study further showed that, the soil in the study area consists of essential elements necessary for plant growth. The high content of potassium in the samples analyzed, revealed that, they can be used as agro mineral additive to enhance soil fertility for crop production. The soil in the study area does not contain Kaolinite in a reasonable amount hence a large quantity of fertilizer must be added all at one time. The specification analysis of elements in soil from the study area needs to be carried out in order to establish the concentration of elements available for plant intake. The results of XRD showed that the sampled clay minerals consist mainly of Albite with impurities like quartz, Fe_2O_3 , etc which will

affect its utility for various end applications. The clay minerals from the area of the study can be applied as a fluxing agent in ceramics and glass applications and also as functional fillers in the paint, plastic, rubber and adhesive industries after beneficiation. The high percentages of iron obtained indicated the possibility of the region having sufficient iron ore reserves. The results also provided information for further studies concerning clay related material like in the field of geology and archaeology.

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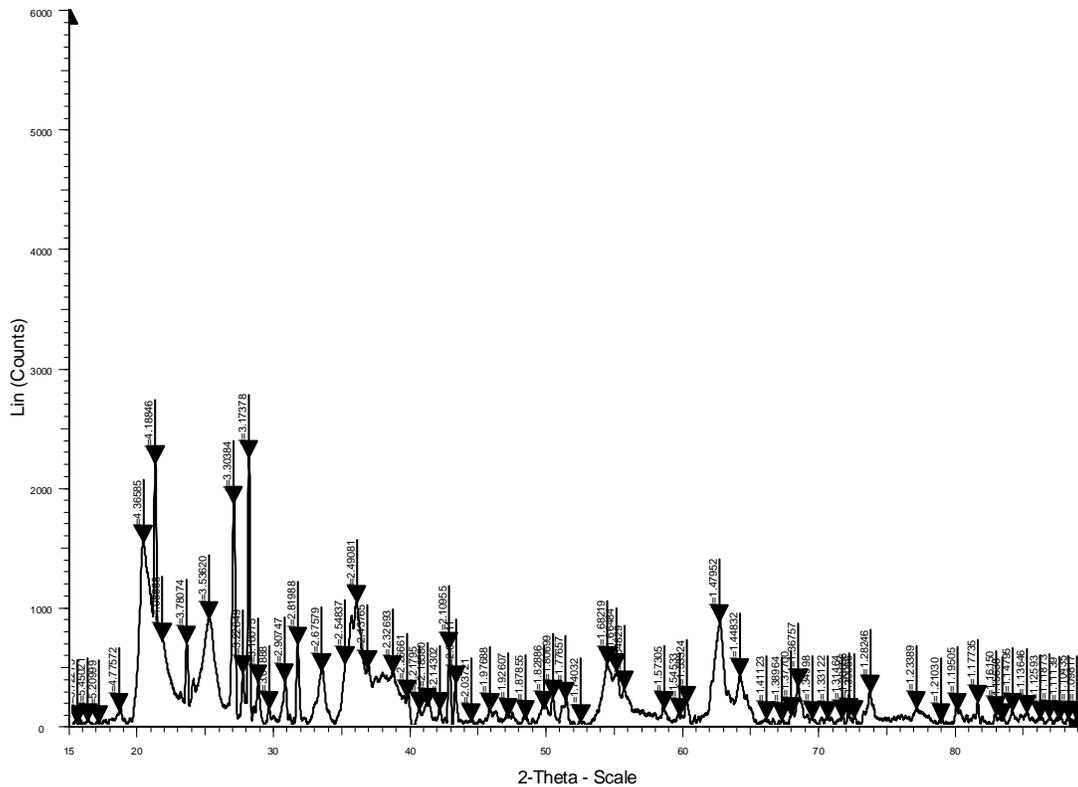


Table 4. Quantitative analysis of clay samples using XRD.

Site	Depth (cm)	Albite	Clinochlore	Diopside	Hermatite	Hornblende	Kaolinite	Magnetite	Microline	Nacrite	Quartz	pH
Mukungu	40	44.1	-	4.9	2.8	10.1	6.2	-	-	-	31.9	6.27
Kibao/ Mbaraga	40	30.3	-	-	6	14.8	-	3.5	-	16.6	28.8	6.46
Kankoma	40	33.1	7.1	10.2	-	2.7	-	-	-	-	22.6	6.67

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Conflict of interest

The authors did not declare any conflict of interest.

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