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Mineralogical and physico-chemical study of four soils from different cereal regions of Morocco

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Abstract

The aim of this work is to investigate four samples of agricultural cereal soil, collected in four regions of Morocco: Tadla-Azilal, Chaouia-Ouardigha, Rabat-Sale and Meknes-Tafilalet. Mineralogical composition was determined by X-ray Fluorescence analysis (FX). Thermal analysis, Infrared spectroscopy (IR) and X-ray diffraction (XRD) analysis were performed to characterize the studied soils. The results, of the FX analysis, showed that the most abundant major components are silica, alumina, iron oxide, calcium oxide, magnesium oxide and the organic component. The XRD patterns confirm that the soil from Tadla-Azilal region consists of Quartz, Calcite, Illite and Kaolinite. The soil sample of Khouribga consists of Quartz, Calcite and Dolomite. The soil sample from Rabat-Salé-Zemmour consists of Quartz and Mica. The soil sample Meknes-Tafilalet consists of Quartz and Muscovite. The results of IR and thermal analysis confirm the mineralogical phases identified by XRD and lay in evidence the existence of organic matter in the four soil samples.

Keywords: Sol, Muscovite, Dolomite, Illite, Kaolinite, Infrared Spectroscopy, Fluorescence

Introduction

Agriculture is a powerful instrument leading to growth, the overcoming of poverty and the reinforcing of food security. Since the Earth Summit was held in Rio in 1992, it has been agreed upon that the agriculture program in service of development is inseparable from the environmental program. To this end, perennial agriculture must mainly be linked to a better management of natural resources, particularly agricultural soils. The majority of these soils are contaminated with pesticides **[1]** and organic pollutants **[2],** the reduction of the environmental impact of which requires the understanding of the processes they are subject to in the soils, mainly the retention **[3]**, transformation, and transfer processes **[4]**. Understanding the retention and pollutant transfer phenomena in the soil calls for the precise knowledge of the chemical composition and the mineralogical structure of the soil's clay minerals. The structural chemical complexity of the clay minerals requires the use of sharp analysis methods **[5]**, such as X-ray fluorescence and diffraction, infrared spectroscopy **[6]**, thermal analysis, atomic absorption spectrophotometry **[7]**, electronic microscopy. The objective of this work is to characterize four cereal soil samples in Morocco, using the analysis methods mentioned above.

2. Materials and methods

2.1.Studied Materials

The four samples are those of cereal soils that have been taken in four agricultural regions in Morocco (Figure 1). These samples were taken from untreated parcels, using a probe that was vertically inserted to a constant depth of 20 cm. At the delivery of the sample, the large clumps are smashed and dried in ambient air, inside a dust-free room. Once dried, rocks and plant debris are removed and the aggregates are crushed using a mortar. The samples are strained with the help of a 2 mm wide riddle and preserved in ambient temperature in plastic containers. The conservation period, from taking the sample to analyzing it must not exceed 6 months **[8]**.

2.2. Experimental techniques

The chemical analysis by X-Ray fluorescence was conducted using wavelength dispersion Spectrometer (Type Axios). The analyzed samples were prepared following the pellet method.

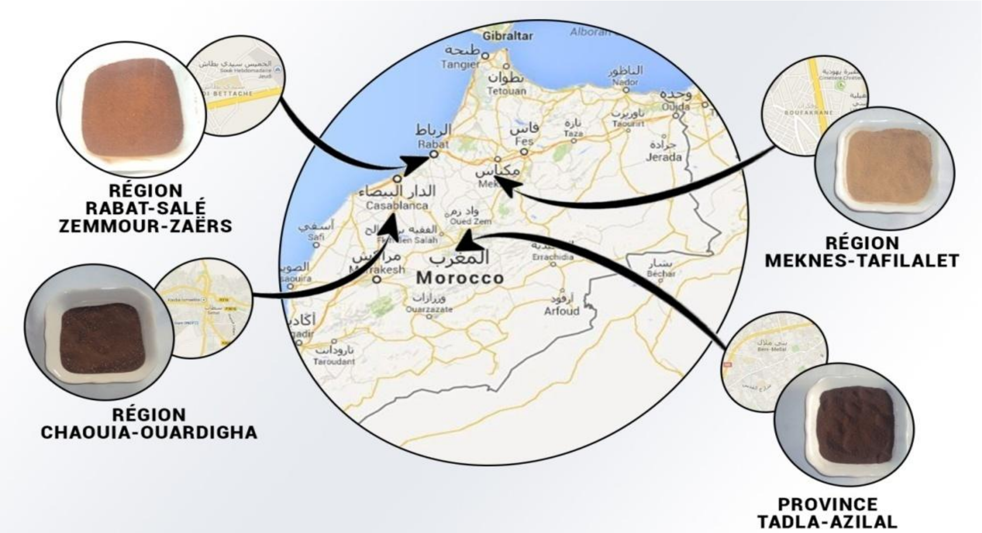

Figure1: Topographic map of collection sites of soil samples: Sample 1: region Tadla –Azilal, Sample 2: region chaouia-ouardigha, Sample: 3 region Rabat-Salé, Sample 4: region Meknes-Tafilalt

The X-Ray diffraction mineralogical analysis (XRD) was conducted using a powder diffractometer (system XPERT-PRO with Copper anticathode($\lambda K\alpha 1$ = 1,54060 Å, $\lambda K\alpha 2$ = 1,54443 Å) and filter ($\lambda K\beta$ = 1,39225 Å)), linked to a computer which allows the automatic rotation piloting of the goniometer (PW3050/60) in angle interval 2θ set between 3 and 89 ° with a step of 0,067 °. The identification of the phases was carried out using the ASTM files in the data base.

A soil / water solution in mass ratio 50-50 was prepared with distilled water is kept for 24 hours at temperature T=25°C to allow ions to pass into solution. When measuring the pH, the solution is homogenized by a mechanical stirrer.

The Fourier Transform Infrared Spectroscopy IRTF was carried out with the help of the Fourier Transform spectrophotometer VERTIX 70. The studied spectral interval ranges from 4000 to 400 cm^{-1}, with a resolution of 4 cm^{-1}. Sample preparation consists in mixing a few milligrams of material, that have been previously dried at 60°, and ground with KBr. The mixture was prepared in disk form with 13 mm diameter and 1.5 mm thick.

The differential thermal analysis (ATD) and thermogravimetric (ATG) curves of the studied soil samples are obtained using device SDT 2960, equipped with a simultaneous thermal analyzer (coupled ATD-ATG), data acquisition and processing software. 15 mg of each sample is placed inside an alumina crucible and exposed to the temperature rise under nitrogen flux. During the heating of the sample, from 20°C to 900°C with a 10°C/min, the mass loss and the temperature difference are measured continuously.

3. Results and discussion

3.1. Chemical analysis (FX).

Tables 1 and 2, display the results of the elements and components, corresponding to the four studied soil samples.

Table 1 : Chemical analysis of the elements

Element	O	Si	AL	Fe	C	Ca	Mg	K	Ti	Total(%)
Sample1	50,0	22,9	9,36	5,1	3,9	2,9	2,2	1,98	0,44	98,79
Sample2	50,9	23	5,77	2,17	4,73	9,97	1,56	0,67	0,33	99,10
Sample3	51	29,6	9,78	4,45	1,89	0,76	0,76	0,68	0,52	99,44
Sample4	52,2	33,9	7,2	1,77	1,91	0,23	0,49	1	0,43	99,13
The trace elements : Na, P, Cl, S, Ba, Mn, Zr, I, Zn, Rb, Sr, Y, Nb, Pb										

Analysis of the results of Table 1shows that the main elements in the four samples of soil are: Silicon, Oxygen, Aluminum, Iron, Carbon, Calcium, and Magnesium. The contents of the elements Silicon, Aluminum and Iron can be correlated to the quantity of quartz, clay and iron oxide present in the soil. Silicon and Iron come respectvely from the Quartz and Iron oxides, but also enter in the composition of the clay minerals. The Aluminum, mean while, comes exclusively from clays.

Table 2: Chemical analysis of the compounds in the soils

Compound	SiO_2	Al_2O_3	Fe_2O_3	CaO	MgO	K_2O	TiO_2	P_2O_5	P.A.F	Total(%)
Sample1	49,0	17,7	7,26	4,05	3,54	2,39	0,73	0,4	14	99,1
Sample2	49,2	10,9	3,11	14	2,59	0,81	0,55	0,64	17,3	99,1
Sample3	63,3	18,5	6,37	1,05	1,21	0,82	0,86	0,25	6,92	99,3
Sample4	72,6	13,6	2,56	0,32	0,80	1,22	0,70	0,12	6,99	98,9
Trace element : SO3 , Na2O, Nb, Y2O3 , Rb, SrO, ZnO, I, ZrO2, MnO2, BaO, Cl, PbO										

The calcium element can be correlated to the presence of limestone in the soil samples. Indeed, the comparison of its content in different samples can generally find different soil groups previously defined by their composition of limestone. Thus, samples 1, 3 and 4 of weakly limescale soils, have the lowest level of calcium, while the sample 2 of ground limestone present a medium rate of 9.97% of Ca.

Analysis of minor trace elements shows that sample 1 contains traces of zinc, sample 3 contains traces of lead and other samples do not contain heavy metals.

These results indicate that the most abundant major elements in the four samples are essentially silica, alumina, iron oxide, calcium oxide, magnesium oxide, potassium oxide, and loss on ignition (P.A.F), an indicator of the important presence of organic matter and carbonate of calcium.

Computing the ratios SiO_2/Al_2O_3 and $SiO_2/(Al_2O_3+Fe_2O_3)$ yields value that range respectively from 2,77 to 5,34 and from 1,96 to 4,5, which ascribes these samples as clay minerals **[9]**. The high content in potassium oxide (2,39%) in sample 1 indicates that it's probably rich in Illite.

The presence of organic matter in high quantity in samples 1 and 2 explains their darker color **[10]** (figure1) and the high content in iron oxide in samples 3 and 4 is responsible for the yellow-brown color **[11]**.

The high content in P_2O_5 and calcium oxide CaO in sample 2, compared to other samples, is due to the proximity of the site where the sample was taken, to the Moroccan phosphate region, and allows to predict the augmentation of its base nature.

3.2. pH measurements

The results of measurement of pH of the four soils are shown in Table 3

Table 3: pH and status of the four simple soils

	Sample 1	Sample 2	Sample 3	Sample 4
pH	8,2	8,6	7,4	6,4
Status	basic soil	basic soil	neutral soil	slightly acidic soil

These results demonstrate that samples 1 and 2 are alkaline soils, sample 3 is the neutral ground and sample 4 is acidic soil. High levels of oxides CaO, MgO and K_2O in samples 1 and 2, compared to other samples, confirm alkaline character of these soils.

3.3. Mineralogical analysis XRD.

A mineralogical analysis of the four soil samples was conducted by X-Ray diffraction (DRX) **[12]** aiming to identify the principal constitutive phases of the mineral fraction of the soil. The obtained diffractograms are shown in figure 2 and 3.

The analysis of these spectra shows that the dominant peaks correspond to quartz at (2θ = 20,8°; 26,7°; 29,9°; 36,6°; 50,2°; 60,1°) and Calcite (2θ = 29,5°; 2θ = 39,4°). Other less intense lines show the presence of clay minerals, more precisely the Kaolinite (2θ = 26,6° ; 2θ = 36,6 ; 50,2° ; 60,0°; 68,24°), the Illite (2θ = 26,6° ; 36,6°), the Muscovite (2θ = 26,6°; 36,6°; 39,5°) and the Dolomite (2θ = 30,89°; 59,95°; 50,12°). The less prominent peaks correspond to the Mica (2θ = 19,86° ; 2θ = 34,96°).

The analysis of the diffractograms using the program X'Pert High Score PANalytical **[13]** and the database leads to the identification and quantification of the mineral fraction. The results are displayed in figure 3 and table 3.

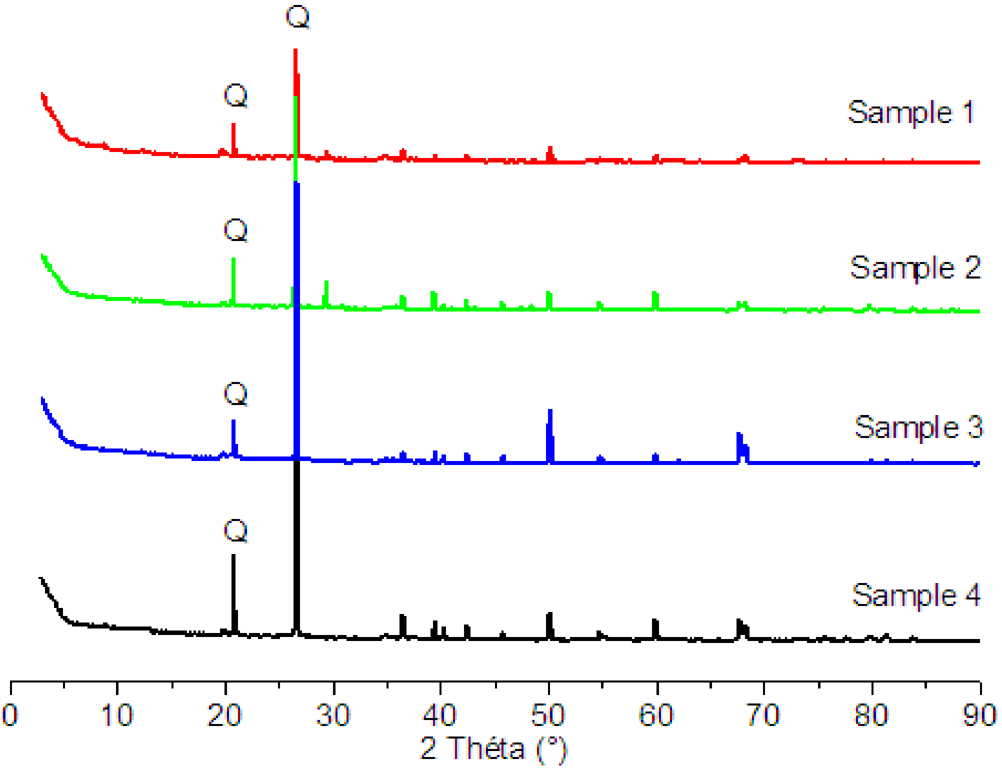

Figure 2: X-Ray patterns of the four soil samples; Q: quartz
Intensity (arb.units)=f(2Theta (deg))

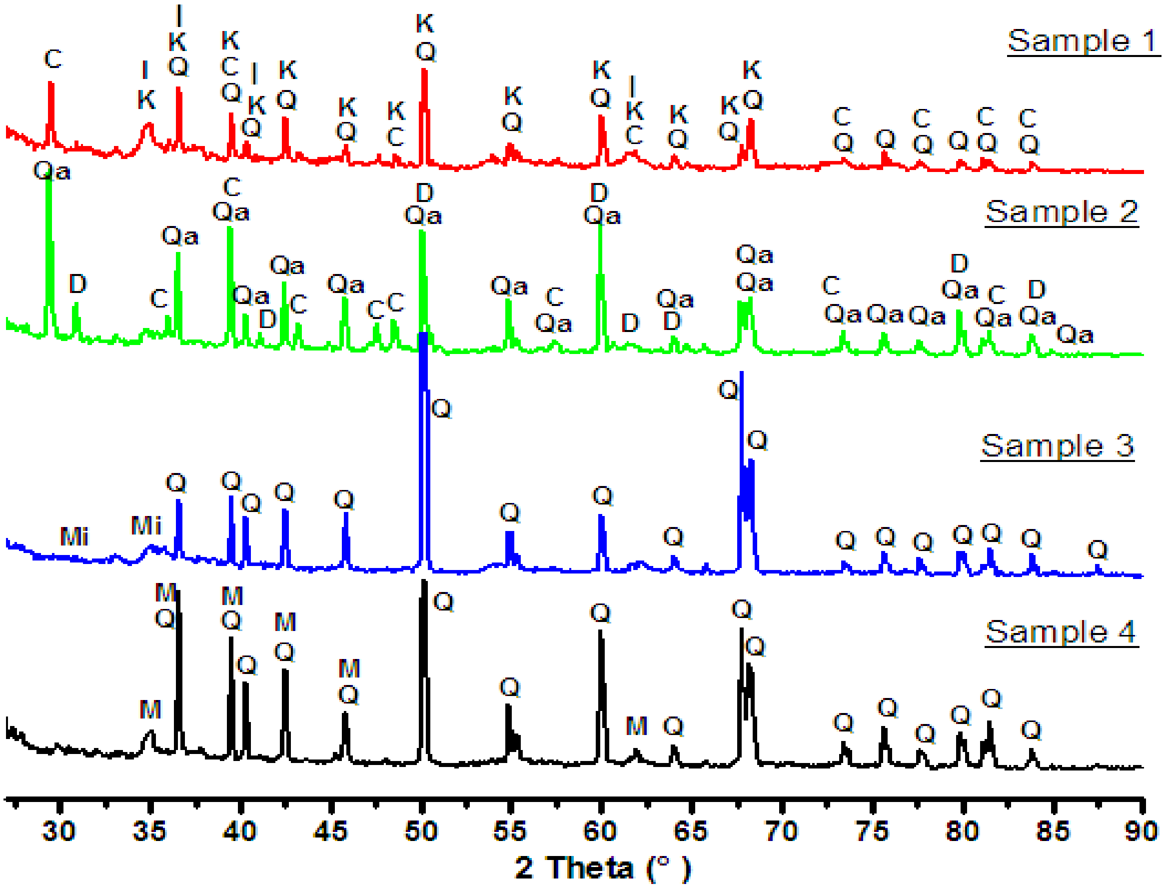

Figure 3: Diffractograms of X-Ray diffraction of the four soil samples
Q: Quartz: C: Calcite, K: Kaolinite, I: Illite , Mi: Mica , D: Dolomite, , Qa: Quartz alpha, M: Muscovite
Intensity (arb.units)=f(2Theta (deg))

Table 4: Phase identification of soil samples

	Quartz	Calcite	Kaolinite	Illite	Muscovite	Dolomite	Mica	KCl	Totale (%)
Sample1	41,6	19,9	9,72	15,27	0	0	0	13,43	99,92
Sample2	46,28	36	0	0	0	17,71	0	0	99,90
Sample3	71	0	0	0	0	0	28,9	0	99,90
Sample4	75,4	0	0	0	24,59	0	0	0	99,99

The analysis of the data, present in the table 4, shows that the mineral fraction of the soil samples is mainly composed of three phases: quartz, calcite and clay minerals (Kaolinite, Illite, Muscovite, and Dolomite). Samples 1 and 2 are ranged of respectively 41,6% and 46,2% of Quartz, 36% and 19,9% of calcite, and 25% and 17,7% of clay minerals, while samples 3 and 4 are ranged of respectively 71% and 75,4% of Quartz, and 28,9% and 24,5% of clay minerals.

3.4. IR spectroscopy analysis

This technique is to improve the characterization by X-ray diffraction in the case of poorly crystalline material. The infrared spectra of the four samples are shown in figure 3.

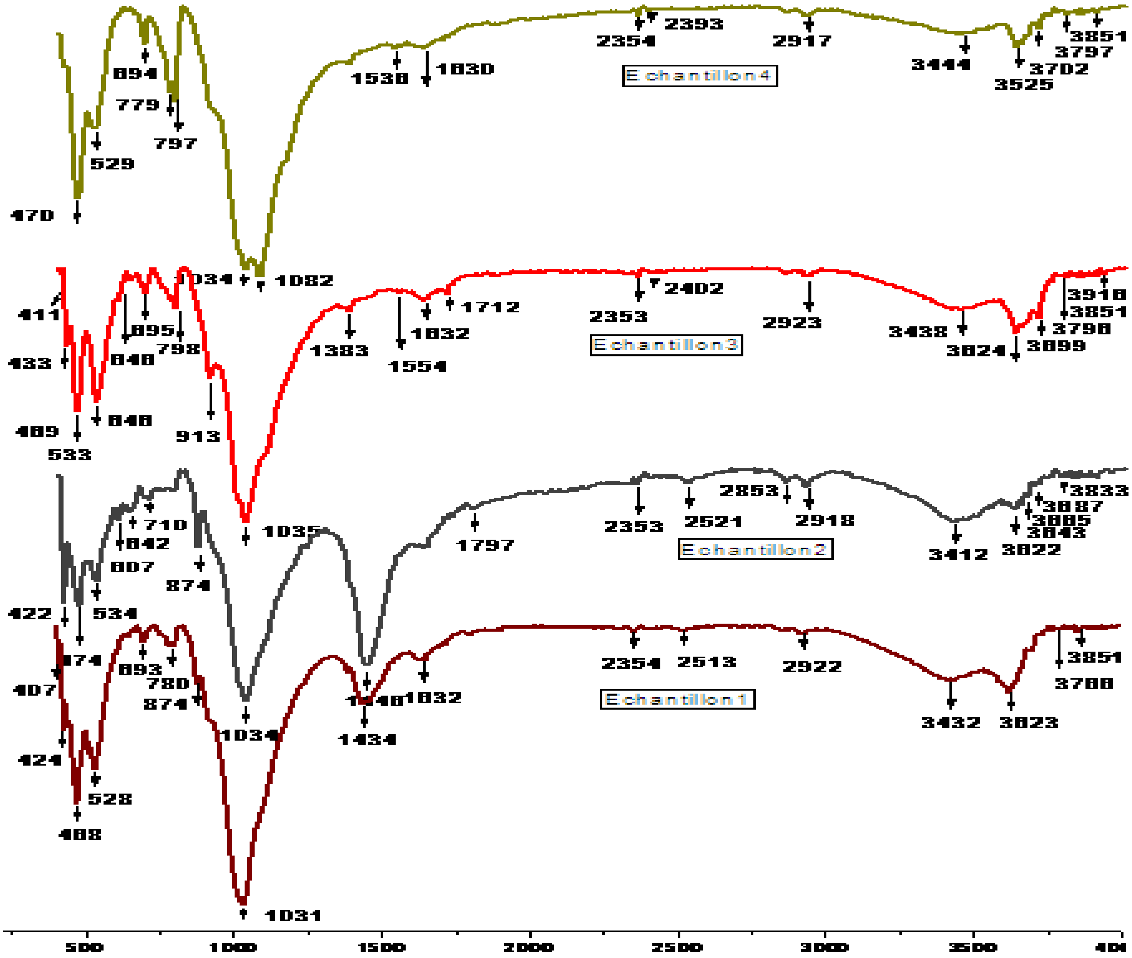

Figure 4: Infrared spectra of soil samples Transmittance(%)]=f(Wavenumber (cm^{-1}))

The analysis of these spectra is used to take the following points:

- Quartz observed by XRD for the four samples is reflected by the shoulder measure data frequency of 1031 cm^{-1} (1034 cm^{-1}) **[14]** and by a group of stretching vibrations of the Si-O bond at 914 cm^{-1}**[15].**
- The first line will appear around the frequency 3622 cm^{-1} for the four samples corresponding to stretching vibrations of the OH groups of the water content, the second band, which lies environ 1632 cm-1

corresponds to H de formation vibrations OH due to adsorbed water molecules between the layers. The comparison of band intensities requires a high degree of hydration of the sample1 **[17]**.

- The calcite observed by XRD for samples1 and 2 is demonstrated by the presence of a first band of the stretching vibration of C-O bond around the frequency of 1448 cm^{-1}(1434 cm^{-1}) and a second frequency band to 874 cm^{-1}. Note that the bands of the sample1are more intense than those seen in sample 2, which proves the high calcite content for sample 1 **[16]**.
- Bands appearing around 3623, 3432 and 1632 cm^{-1} revealed the presence of Illite and Kaolinite in the sample1. Bands appearing around 470, 530 and 797 cm^{-1} for Sample 4 showed the presence of muscovite.
- The bands appearing around 2922, 1538, 1797 and 3442 cm^{-1} for the four samples characterize humic substances **[18]**.

3.5. Thermal analysis

The thermograms recorded for samples soil are shown in figure 5, 6,7 and 8.
The nature of the peaks and the associated loss in mass for the four samples is shown in Table5.

Table 5: Nature of peaks and loss mass (Pm) of samples

Sample	Nature peak	T(°C)	Pm (%)	Attribution
1	Endothermic	70	9,7	Departure of adsorbed water
	Exothermic	370	1,5	Combustion of the organic material and the crystallization of amorphous organic material.
	Endothermic	500	3,7	Deshydroxilation of the Kaolinite
	Endothermic	700	2,8	Déshydroxilation of the Illite
2	Endothermic	70	2,6	Departure of adsorbed water
	Endothermic	450	3,6	Deshydroxilation the loss of structural water
	Endothermic	578	0,8	Transformation Quartz α → β
	Endothermic	756	9,6	Decomposition of the dolomite
3	Endothermic	70	2,1	Departure of adsorbed water
	Exothermic	260	0,7	Presence of Mica
	Exothermic	370	0,9	Combustion of the organic material and the crystallization of amorphous organic material.
	Endothermic	454	1,5	Déshydroxilation the loss of structural water
	Endothermic	580	0,5	Transformation Quartz α → β
4	Endothermic	70	0,3	Departure of adsorbed water
	Endothermic	280	1,2	Water structure
	Exothermic	370	1,1	Combustion of the organic material and the crystallization of amorphous organic material.
	Endothermic	422	1,3	Deshydroxilation the loss of structural water
	Endothermic	570	0,8	Transformation Quartz α → β

Thermal analysis of the sample 1 shows the presence of two endothermic peaks at 500 and 700°C, assigned to the decomposition respective of Kaolinite and Illite. The exothermic peak observed at 370°C is due to breakdown of organic matter. The alpha quartz and dolomite in sample 2 are confirmed by the recorded of the two endothermic peaks at respectively alpha quartz 578 and 756°C. The sample 3 showed the presence of Mica (exothermic peak at 260°C), quartz (endothermic peak at 580°C) and organic matter (exothermic peak at 370°C). The sample 4 thermogram shows the presence of quartz (endothermic peak at 570°C) and organic matter decomposition (exothermic peak at 370°C). We observe an endothermic peak for the four samples at 70°C.This peak is attributed to the removal of water on the particle surfaces and/or dehydration of interlayer’s cations. The mass loss associated to sample 1 is about 9.7% greater than the other samples due to the higher absorption capacity for water.

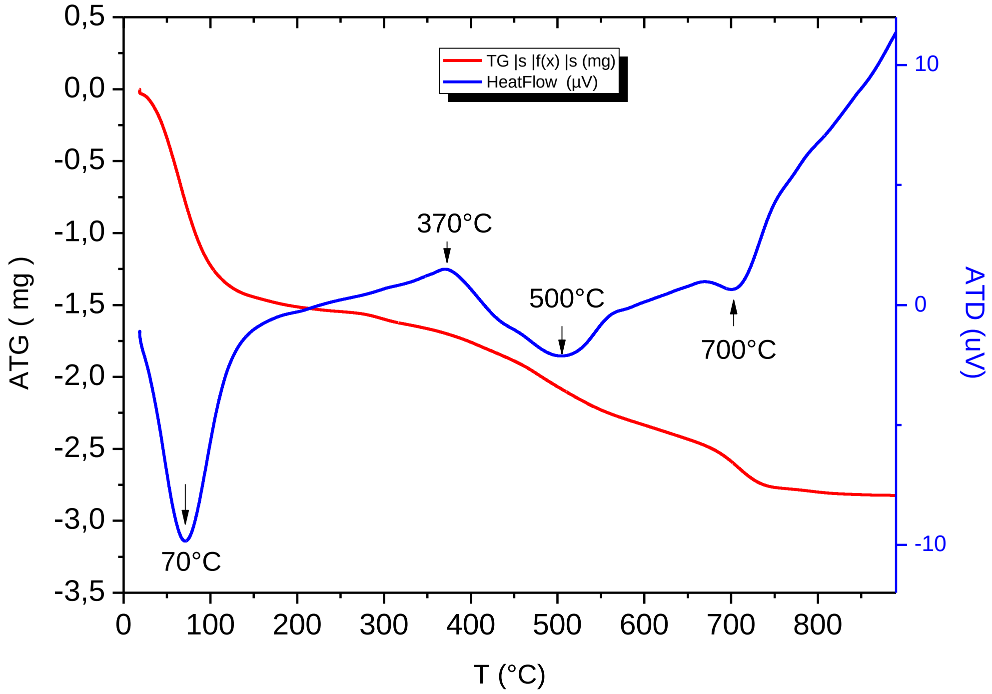

Figure 5: ATD/ATG curve of sample1

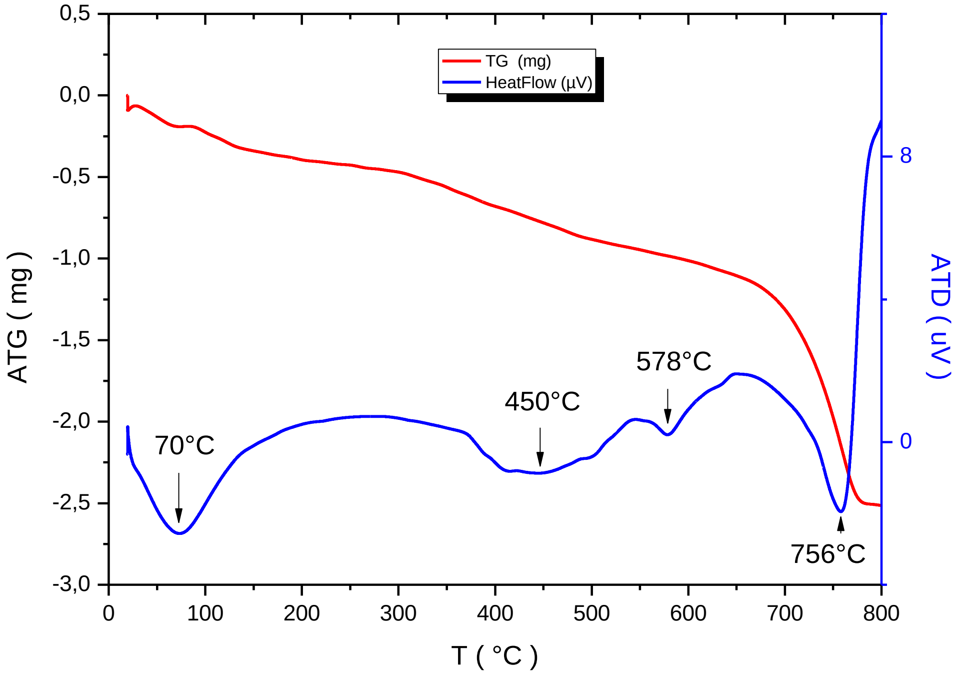

Figure 6: ATD/ATG curve of sample2

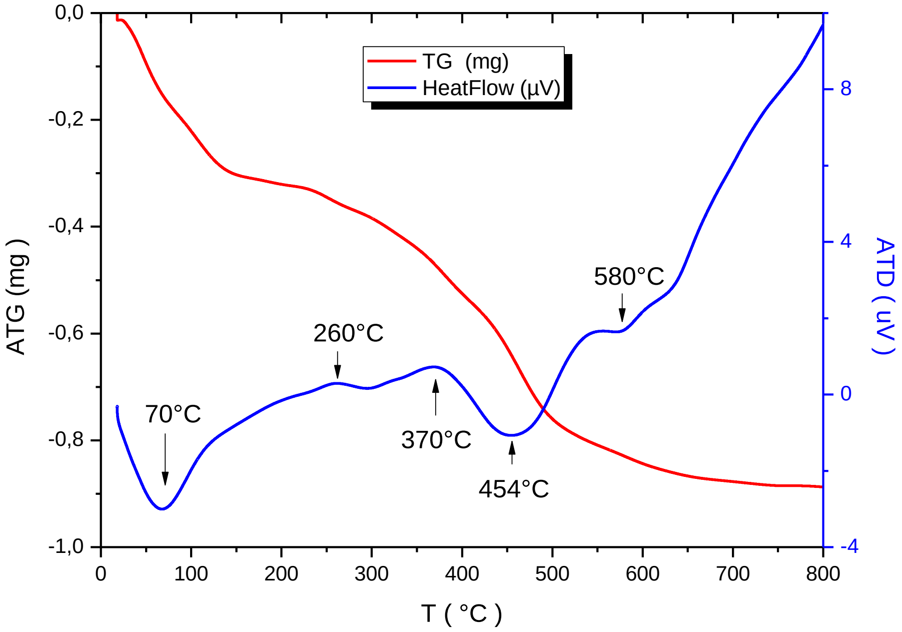

Figure 7: ATD/ATG curve of sample3

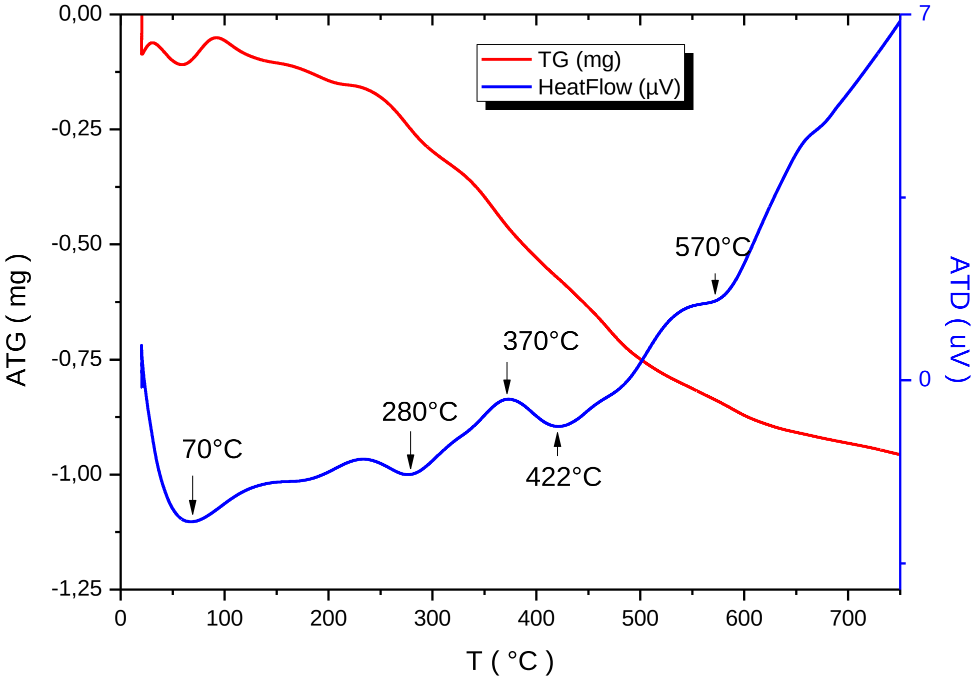

Figure 8: ATD/ATG curve of sample4

Conclusion

Various additional analyzes were performed to characterize four samples of agricultural soil grains. They showed a great variability in terms of physico-chemical and mineralogical composition. The soil sample Tadla-Azilal consists of Quartz, Calcite, Illite and Kaolinite, sample soil Khouribga consists of quartz, calcite and dolomite, sample soil Rabat Salé consists of Quartz and Mica and the soil sample Meknes-Tafilalet consists of quartz, muscovite and humic substances which also belong in the other samples. These samples are clay minerals, both soils Tadla-Azilal and Khouribga are alkaline soils, soil sample Rabat is neutral and the one from Meknes slightly acidic. This variability leads us to expect different affinities for various pesticides.

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