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### RESEARCH ARTICL

#### UV IDENTIFICATION FOR TARFAYA'S OIL SHALE AND ASHING AT LOW TEMPERATURE OF Z<sub>1</sub> LAYER (MOROCCO)

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#### Abstract

In order to elucidate our knowledge of oil shale, this work has been initiated. Morocco has large oil shale reserves, the most important deposits of which are in Timahdit, Tarfaya and Tangiers .As oil shale is first-round energy materials that can be used to further valorize these resources, we are interested in the research and development of oil shale-based materials capable of retaining pollutants present in wastewater. In this study, we discuss the role that oil shale can play in inhibiting the infiltration of micro pollutants into the water table. The part of this work presents a bibliographical study on the mineralogy, geochemistry and petro chemistry of oil shale. The use of these materials in the field of environmental protection is discussed. Firstly, an experimental identification work was carried out using the spectroscopic apparatus of our establishment to study the Z<sub>1</sub> layer of the Tarfaya deposit in its raw state and in the screen solubilized with chloroform. The Z<sub>1</sub> layer has a percentage of organic matter of 12.3% and mineral matter of 29.4% for a heating rate of 21°C/min (A. Attaoui:1999). Then, within the framework of a clean use of the material as an absorbent or depolluting (He.G.Liang et al:2019, S.Gamoudi et al :2019) we carried out the ashing at low temperature of the oil shale, which consists in carrying out combustions on this shale, more precisely on the organic part and not altering the mineral part. In this context, we carried out this incineration on the oil shale of Tarfaya (Z<sub>1</sub>) at temperatures ranging from ambient to 227°C. The samples were then subjected to HCl acid attacks, and the remaining part was measured and the quantity of the constituents sensitive to this acid attack was evaluated. Pure calcite was taken as a reference and the PH-meter was used to analyses the phenomenon.

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#### Introduction:-

Oil shale ( pyroschists, kerobituminous) are fine-grained sedimentary rocks containing enough organic matter, kerogen, to provide oil and gas fuel (X.Tang et al:2016, H.Gud et al:2016) Contrary to their name, these rocks are not necessarily shale (rocks that have a layered appearance).

Oil shale vary considerably from each other in their chemical composition, mineral content, age, type of kerogen and the way they were deposited.

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The kerogen in oil shale can be converted into oil through the chemical process of pyrolysis, i.e. the decomposition of organic matter under the influence of heat. Indeed, the kerogen contained in oil shale is a kind of "unfinished oil" that has not undergone sufficient temperature and pressure conditions to be converted into oil.

Oil shale can also be burned directly as a low-grade fuel for electricity and heating, and can be used as a raw material in chemical industries for further extraction (e.g. sulphur, ammonia, mastic, road bitumen, cement or bricks)(**T.Sun et al: 2010**).

Their name is sometimes confused with other types of unconventional hydrocarbons, notably oil sands and shale gas. Oil shale contains kerogen that must be processed before oil can be obtained, whereas oil sands and shale gas are directly exploitable, containing trapped bitumen and gas respectively.

Oil shale can be converted to hydrocarbons through the chemical process of pyrolysis, burned directly as a low-grade fuel for power generation in the form of electricity, and can be used as a feedstock in the chemical and construction materials industries(**W.Gege et al: 2018**).

Oil shale varies according to their yields in oil production, whether by pyrolysis (Fisher test) or hydro pyrolysis (Hydrotorting test). This variation in sample yields is imperatively linked to the geological formation stage of the oil shale layer, such as the Z3 and Z4 layers of the Tarfaya deposit. The latter two were formed in the secondary era, more precisely in the Upper Cretaceous (**D.Lahmadi: 2015**). The Z4 layer was formed in the Cenomanian geological stage and the Z3 layer in the Turonian, and the climates of these two geological stages were warm climates. In comparison, the temperature of the Turonian (Z3) climate was higher than that of the Cenomanian.



**Figure.1:-** Oil shale.

### 1/ Reserves.

Although oil shale is found in many countries, only 33 countries have economically recoverable deposits. Known deposits, potentially classified as reserves, include the Green River deposit in the US, the Queensland Tertiary deposits in Australia, deposits in Estonia and Jordan, and deposits in China and Russia

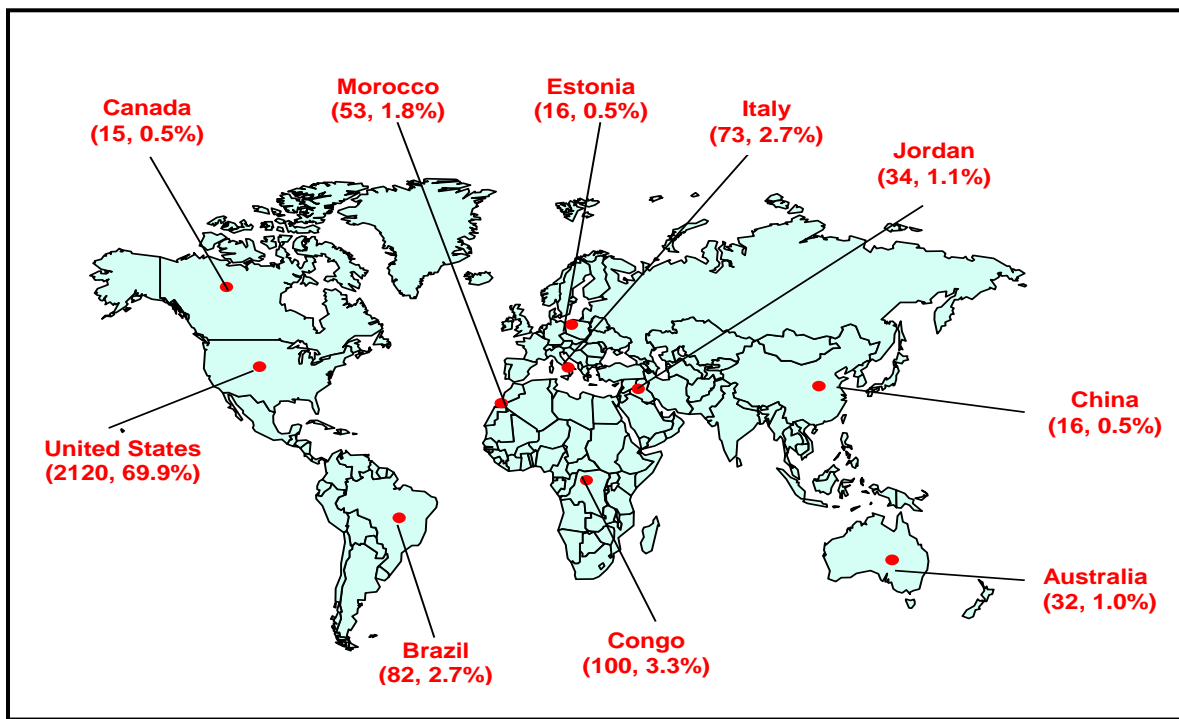


Figure. 2:- World oil shale reserves and their locations.

The oil shale industry, although young and immature, is becoming structured throughout the world:

- Our country has a certain potential in oil shale
- Attractive option and real challenge in terms of investments
- The development of oil shale remains a medium and long term option.

The major challenges to be met to promote the development of oil shale are

- Economic challenge; the volatility of oil prices does not give confidence to investors in these projects, characterized by the size of the investments and the staggered development phases
- Technological challenge, as the treatment processes need to be developed rapidly to reach the industrial phase

### 2/ Solubility by toluene

The Chinese Maoming oil shale was subjected to supercritical fluid extraction with water and toluene separately. The oil shale was also subjected to pyrolysis in an argon atmosphere and Soxhlet extraction with tetrahydrofuran. Oils with similar hydrogen distributions were obtained from SFE (supercritical fluid extraction), pyrolysis (when heated from room temperature to 673 K and cooled immediately, both in SFE and pyrolysis) and also from Soxhlet extraction. Under supercritical conditions, it was found that the polar components were more easily decomposed with water than with toluene. The yield of the non-polar components was not affected by the solvents, water and toluene.

Considerable attention is being paid to the use of water as a supercritical fluid extraction (SFE) of organic matter from fossil fuels. Authors (G.V.Deshpande et al: 1984) found that supercritical water acts not only as a solvent but also as a reagent in the conversion of coal to gases and liquids. Similarly, other authors (T.J. Houser et al: 1986) found that supercritical water (SC) is actively involved in the decomposition of organic compounds. Compared to the considerable amount of work done on coal EFS, only a small amount of work has been done on oil shale EFS. Similarly, other authors (K.Z.Qui et al: 1984, Y.Zhu: 1982) studied the EFS of Chinese oil shale with toluene. The Standard Oil Company has patented a process for recovering upgraded hydrocarbons from oil shale with SC water and with a mixture of SC water, hydrogen and catalysts. McKay et al (G.W.Gardner et al: 1983,

**J.F.Mckayet al: 1983)** studied the ESF of the Green River oil shale with water and a mixture of water and various organic solvents, and found a mixture of water and methanol effective for extraction.

### **3/ Low temperature ashing.**

Low temperature ashing (LTA) has been used to extract minerals from coal (**A.R.Shirazi et al: 1993**). The problem is that the calcination temperature could not be measured, and therefore the calcination processes could not be controlled. The calcination temperature in the present study was measured by thermographs, which indicate the highest temperature reached during calcination. Some of the disadvantages of LTA were shown to be due to the calcination temperature being too high (150-300°C). It has also been confirmed that the mineral materials, especially sulphide, generally oxidize and some are lost as SO<sub>2</sub>. To solve these problems, a new method has been developed, very low temperature ashing (VLTA), to preserve and extract mineral matter from coal without loss or damage to the initial phases. It has been shown that to obtain an in situ ash, the ashing temperature should not exceed 60-70°C, regardless of the coal quality. To lower the calcination temperature, oxygen was diluted with helium to reduce the reaction rate. To reach this very low temperature, the calcination atmosphere (oxygen/helium ratio) has to be adjusted for the coal type and sulphur composition (**A.R.Shirazi et al: 1993**)

For various applications, it is necessary to study the isolated state of minerals found in coal, e.g. clay, sulphide and carbonate minerals, in a group, which means that most of the coal must be removed. It should be checked that none of the minerals have been lost or changed in composition or phase during sample preparation. Low temperature ashing (LTA) has been used to study the occurrence of different sulphide minerals in coal. It is obviously not possible to use high-temperature calcination in the presence of high concentrations of oxygen, as the sulphide then oxidizes rapidly and there is a significant risk of losing the initial phases. LTA has been a relatively good solution for separating the mineral content from the carbon matrix in coal. However, LTA does not oxidize a coal sample completely, and there is no temperature measurement or control, either in surface area or in number of samples. The temperature of the calcination of a coal sample in this process (LTA) is a function of the sample calorific value, the concentration of oxygen in the calcination atmosphere (gas flow rate) and the intensity of ash reduction of the LTA. The calcination temperature in the LTA cannot be determined by conventional temperature measurement, for example with a thermocouple. As there are reasons to believe that the temperature could be quite high, especially above the surface of the sample, methods to measure the calcination temperature have been investigated (**A.R.Shirazi et al: 1993**).

The aim of this study was to oxidize coal samples as much as possible, without any oxidation of the sulphide minerals. When a coal sample has been incinerated in this way, the analytical work with the minerals will be simplified and improved, especially for minerals that occur at low concentration. Very low temperature ashing (VLTA) is a process in which the temperature (calcination process) can be controlled for various samples of different calorific value of coal. In summary, this study shows that the type of coal still plays a major and necessary role for low temperature ashing. At 100% oxygen (LTA), high quality coals oxidize faster and more easily than low quality coals. This relationship is reversed in the process under consideration (VLTA), which means that the low quality coal can be oxidized less quickly than the other. This can be explained by the surface factor.

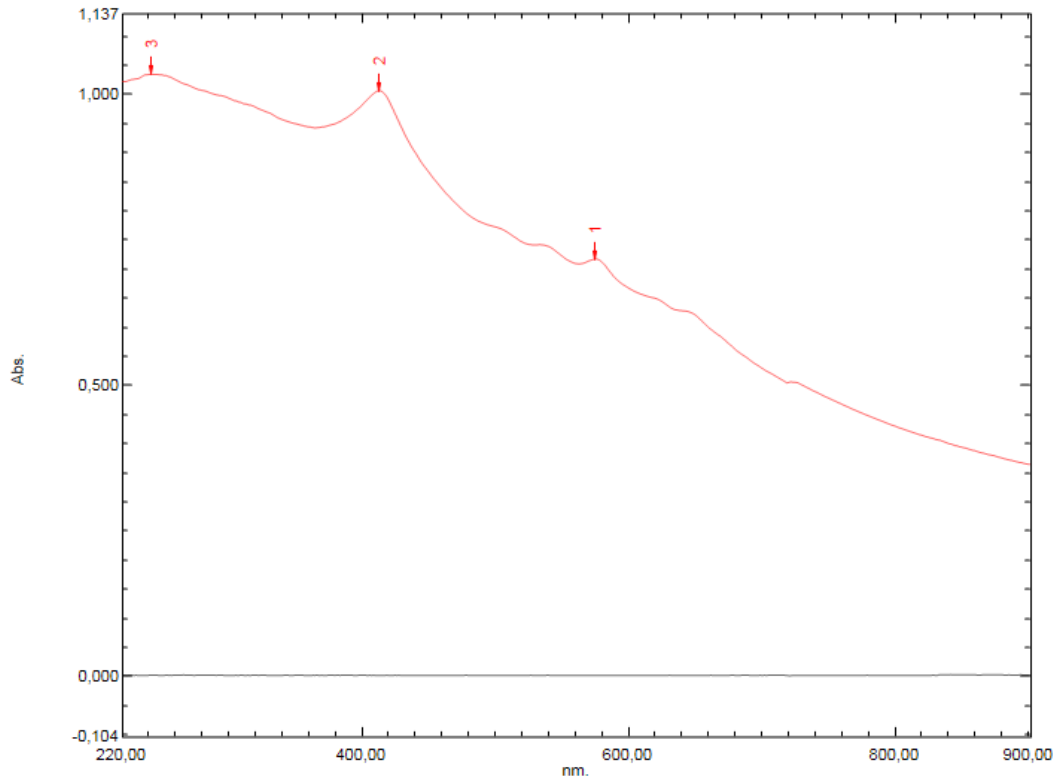
There is no complete oxidation of the samples in either the LTA or VLTA processes. In VLTA the total oxidation is lower than in LTA, but some carbon atoms are left in the ash in both methods. Selective oxidation in VLTA starts at the beginning of the calcination process at a temperature of 60-70°C. This means that if there is no sulphur lost at the beginning of the ash reduction process, there will be any loss over a long period of ash reduction. However, after a sufficient time the selective oxidation ceases and the sulphur is depleted, so the oxidation process must be stopped (**A.R.Shirazi et al: 1993**).

### **4/Experimental part**

The experimental part is based on spectroscopic analyses, a new spectrometer from our institution was used to analyze samples in the solid state, and another old spectrometer apparatus uses solvents to get the liquid phase. The choice of chloroform was important as this strong solvent has often been used in the case of oil shale.

#### **4.1 Results and Discussion for layer Z1:**

a- The following figure 1 represents the spectrum of the Z1 layer of Tarfaya oil shale in its raw state.



**Figure. 3:-** UV and visible spectrum of the oil shale sample from the Z1 layer of the Tarfaya deposit in its raw state.

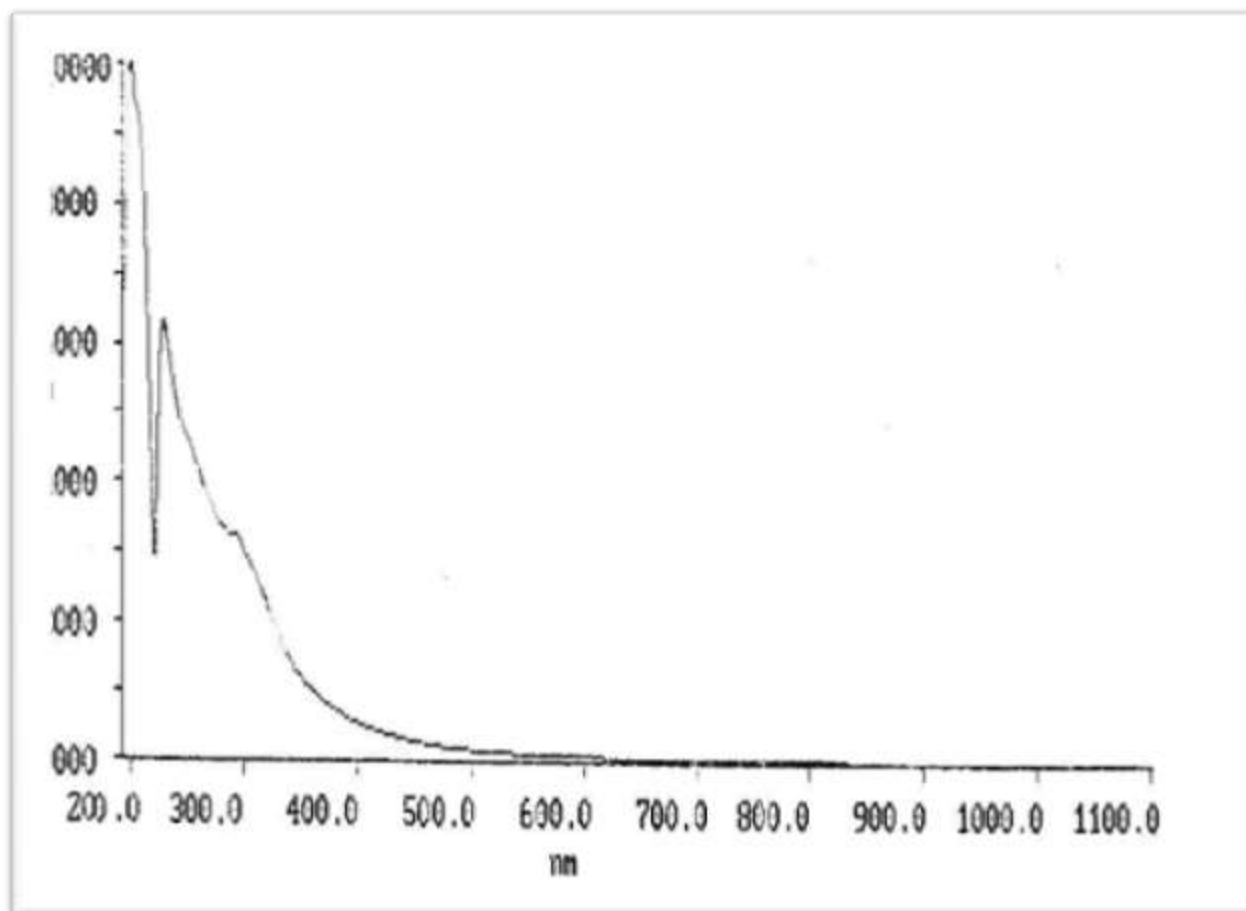
We observe three distinct peaks: a peak 1 in the UV range, a peak 2 in the visible range and another peak 3 also in the visible range. The characteristics of the three peaks are given in the following table:

Z1	Absorbance	L of waves
Peak 1	1,03	245nm
Peak 2	1	420 nm
Peak 3	0,72	620 nm

By calculating the identification energies knowing Planck's constant, the speed of light and the wavelength of the peak, we obtain the following table:

Peak	Identification energy (J)
Peak	$8,1 \cdot 10^{-19}$
Peak	$4,7 \cdot 10^{-19}$
Peak	$3,2 \cdot 10^{-19}$

b- We previously solubilized 2g of the Z1 layer in  $50\text{cm}^3$  of a chloroform solution ( $0,17\text{mol/l}$ ), heated to a temperature of  $97^\circ\text{C}$  with constant stirring, then filtered and  $3\text{cm}^3$  were passed to the liquid phase spectroscopic apparatus to obtain the following spectrum:



**Figure.4:-** spectrum of Tarfaya Z1 oil shale solubilized with chloroform.

Figure 4 includes two peaks, one at 200nm and the other at 240 nm, the absorbance of the peaks are respectively  $A=1$  and  $A=0.64$ . Using the Beer Lambert law knowing the cell constant  $\epsilon l = 5.04$  Al/mol (calibrated by methylene blue), we arrive at the following concentrations of soluble products in following table:

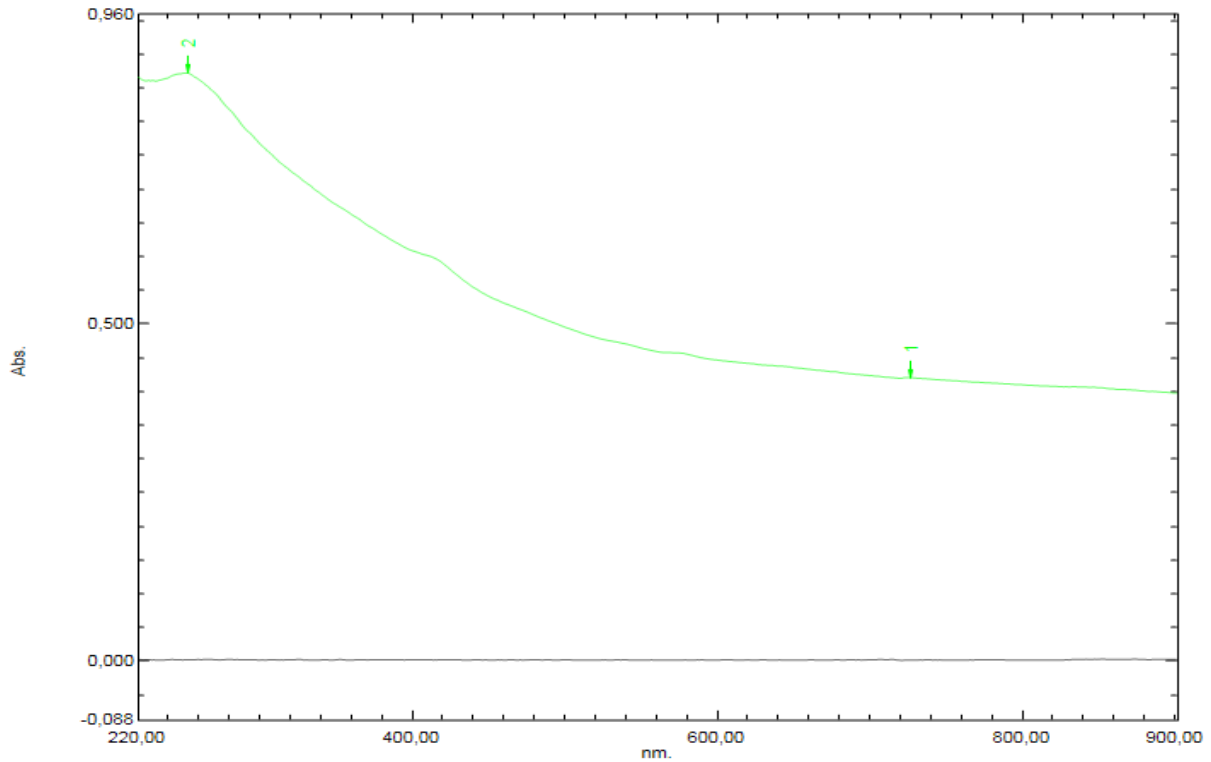
Peak	Concentration mol/L
Peak 1	0,20
Peak 2	0,13

We interpret that a chloroform is a strong polar solvent (A.F.Muhamad et al: 2011, A.AitLahcen et al: 2008) with the ability to crack light organic matter (visible) which decomposes into methane hence the disappearance of the two peaks 2 and 3 (crude spectrum), whereas peak 1 (crude) which represents high molecular weight hydrocarbons (C7 and above) splits into two peaks (chloroform test). This new peak multiplicity shows the appearance of two kinds of high molecular weight hydrocarbon products as well.

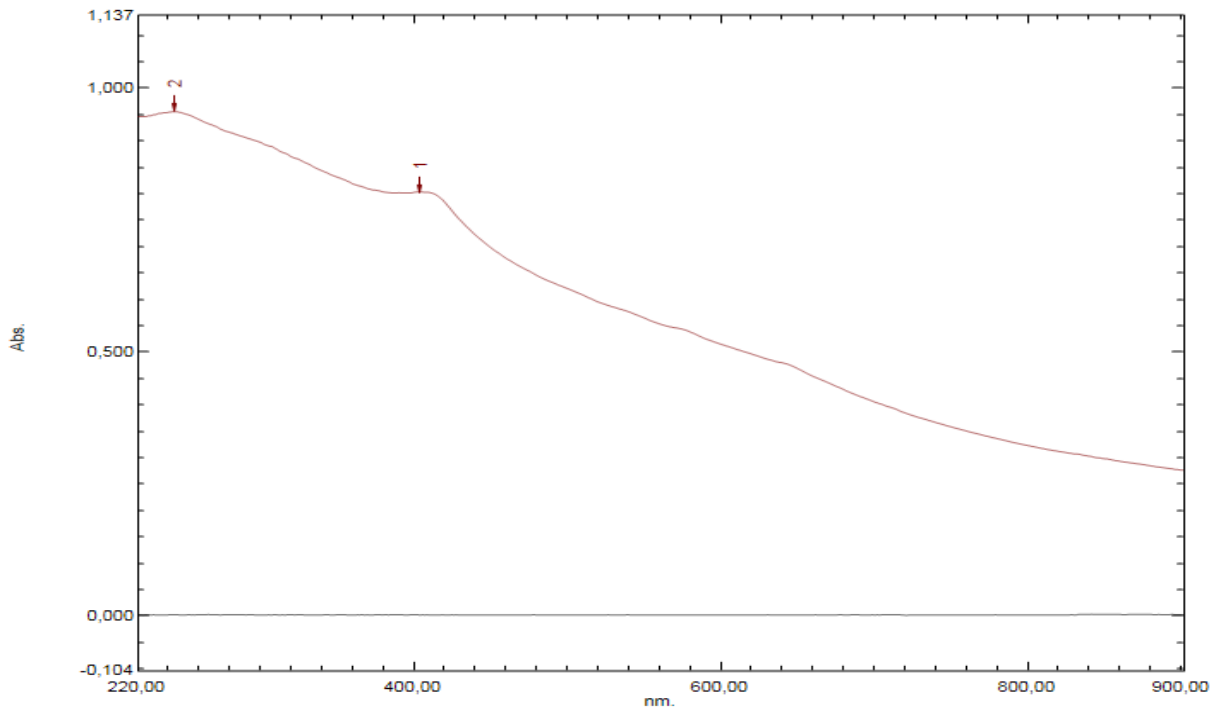
oil shale vary considerably from each other, both in their chemical composition, mineral content, age, type of kerogen and the way they were deposited. The experimental part gave us information on the action of chloroform as a solvent causing the cracking of material to disappear peak 2 or peak 3 (crude), while the heavy hydrocarbon material representing peak 1 (crude) UV was transformed into two others of varying concentrations (Beer Lambert).

**4.2 Solid state spectroscopy (layers 3, 4)**

Two samples of oil shale from the Tarfaya deposit belonging to layers Z3 and Z4 were analyzed in the raw state; the spectroscopic apparatus being (Shimizu 3600 UV-Visible-nir) the mass of the samples is around 2g. The spectra of this analysis are as follows:



**Figure 5:- Z3 layer of Tarfaya oil shale.**



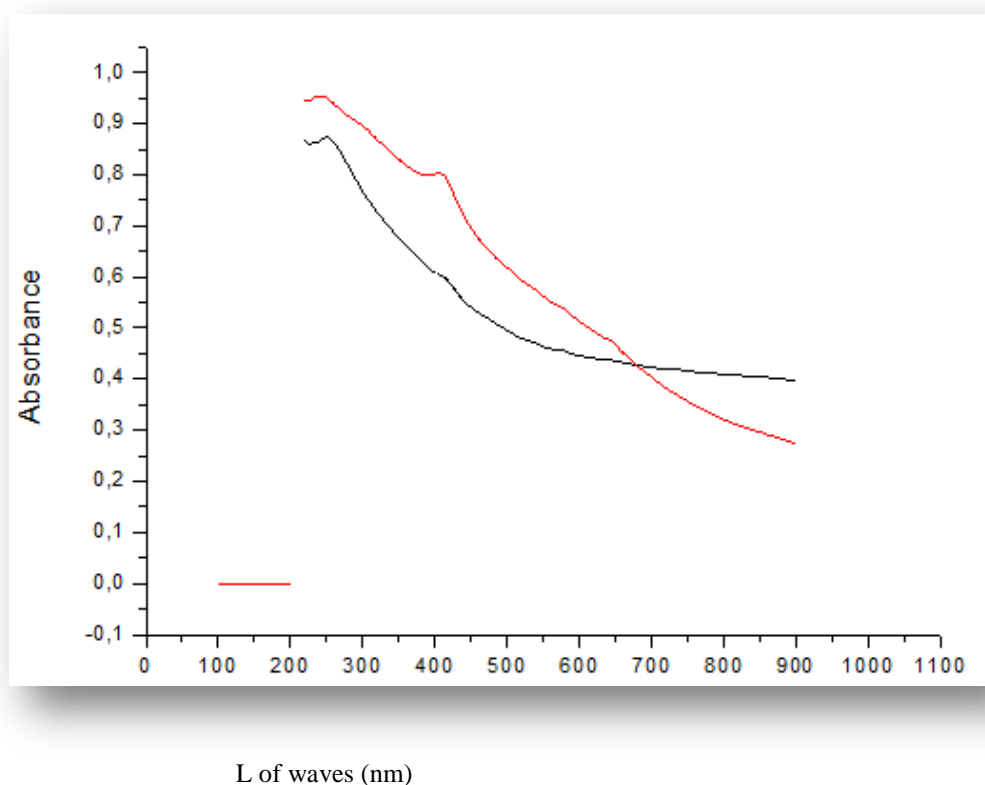
**Figure 6:- Z4 layer of Tarfaya oil shale.**

In the following tables we have the peaks identified according to the wavelength considered and according to the absorbance for the first and second band respectively:

layer	L of waves	Absorbance
Z3	251 nm	0,85
Z4	243 nm	0,95

Layer	L of waves	Absorbance
Z3	412 nm	0,6
Z4	411 nm	0,81

The same curves as before, this time represented by the OGRIGINE software in the same figure are as follows.

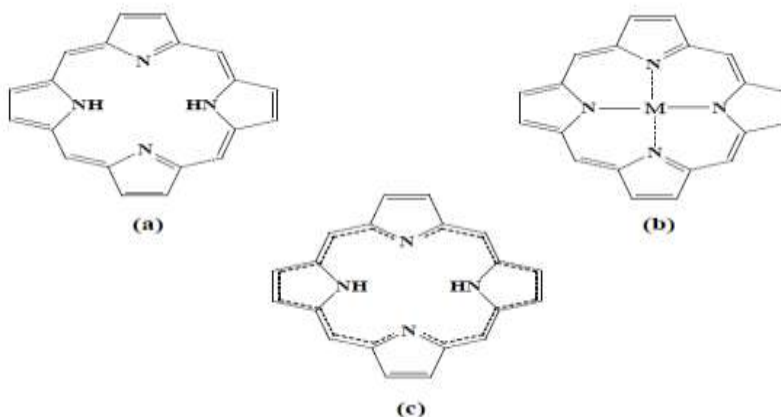


**Figure 7:-** The intersection of the spectra of two layers Z3 ----- and Z4 ----- curves made by the original software.

An intersection of the two curves is identified at a wavelength of 680nm, and this region in the spectroscopy corresponds to the visible range [400nm-800nm]. The compounds identified in this visible range are porphyrins which are conjugated cyclic macromolecules consisting of four pyrrolic rings (C<sub>4</sub>H<sub>5</sub>N). These macromolecules play the role of either dibases or diacids depending on the pH and can then undergo metallization. They are redox, thermal or photochemical agents.

Porphyrin constitutes the core of chlorophyll type a being a porphyrin of metal base (Mg) with different substituents (structure b).

Porphyrin is a substance which, together with iron, forms the hem of hemoglobin.



1) Calculation of the identification energies of the compounds according to the wavelengths of the observed peaks.

We calculated the identification energies of the compounds that appear according to the peaks of the UV spectrum using the wave law including Planck's constant, the celerity of light and the wavelengths, we found:

For the Z3 layer we have:

$$E_1 = \frac{6,63 \times 10^{-34} \times 3 \times 10^8}{251 \times 10^{-9}} = 7,9 \times 10^{-19} \text{ J} = 4,94 \text{ eV} \text{ peak 1}$$

$$E_2 = \frac{6,63 \times 10^{-34} \times 3 \times 10^8}{412 \times 10^{-9}} = 4,8 \times 10^{-19} \text{ J} = 3,0 \text{ eV} \text{ peak 2}$$

For the Z4 layer we have:

$$E_1 = \frac{6,63 \times 10^{-34} \times 3 \times 10^8}{243 \times 10^{-9}} = 8,2 \times 10^{-19} \text{ J} = 5,1 \text{ eV} \text{ peak 1}$$

$$E_2 = \frac{6,63 \times 10^{-34} \times 3 \times 10^8}{411 \times 10^{-9}} = 4,8 \times 10^{-19} \text{ J} = 3,0 \text{ eV} \text{ peak 2}$$

For the intersection of the two curves Z3 and Z4:

$$E_{1,2} = \frac{6,63 \times 10^{-34} \times 3 \times 10^8}{680 \times 10^{-9}} = 3 \times 10^{-19} \text{ J} = 1,9 \text{ eV}$$

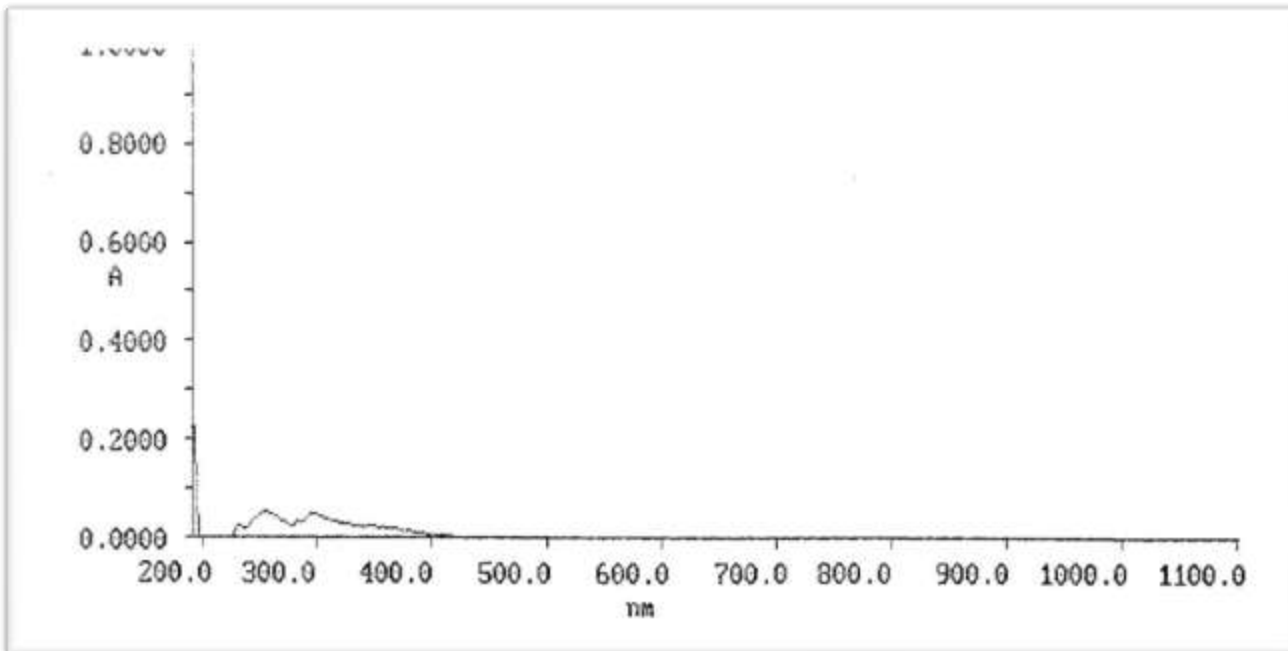
The position of the peaks and their energy are very closely related to the type of layer or more precisely to the history and geological stage of its formation.

In the introduction we mentioned the difference in climate of the geological stage of formation of the said layer. These two layers were formed in the secondary era (Upper Cretaceous) (D.Lahmadi: 2015), the Z4 layer was formed in the Cenomanian stage which had a warm climate and the Z3 layer was formed in the Turonian stage which had a warmer climate. So the different reactivity is quite remarkable, the identification energy of peak 1 for Z3 is lower than that of Z4, similarly the wavelength for the second peak for Z3 is higher than that of Z4. All these experimental assumptions further confirm the higher reactivity of the Z3 layer compared to Z4. In summary for this paragraph the experimentally obtained spectrum for the samples Z3 and Z4 in the raw state showed us the presence of peaks that means the presence of two kinds of hydrocarbon compounds, some of them identify with the UV range, the others identify with the visible range. It should be noted that the characteristics of these peaks follow

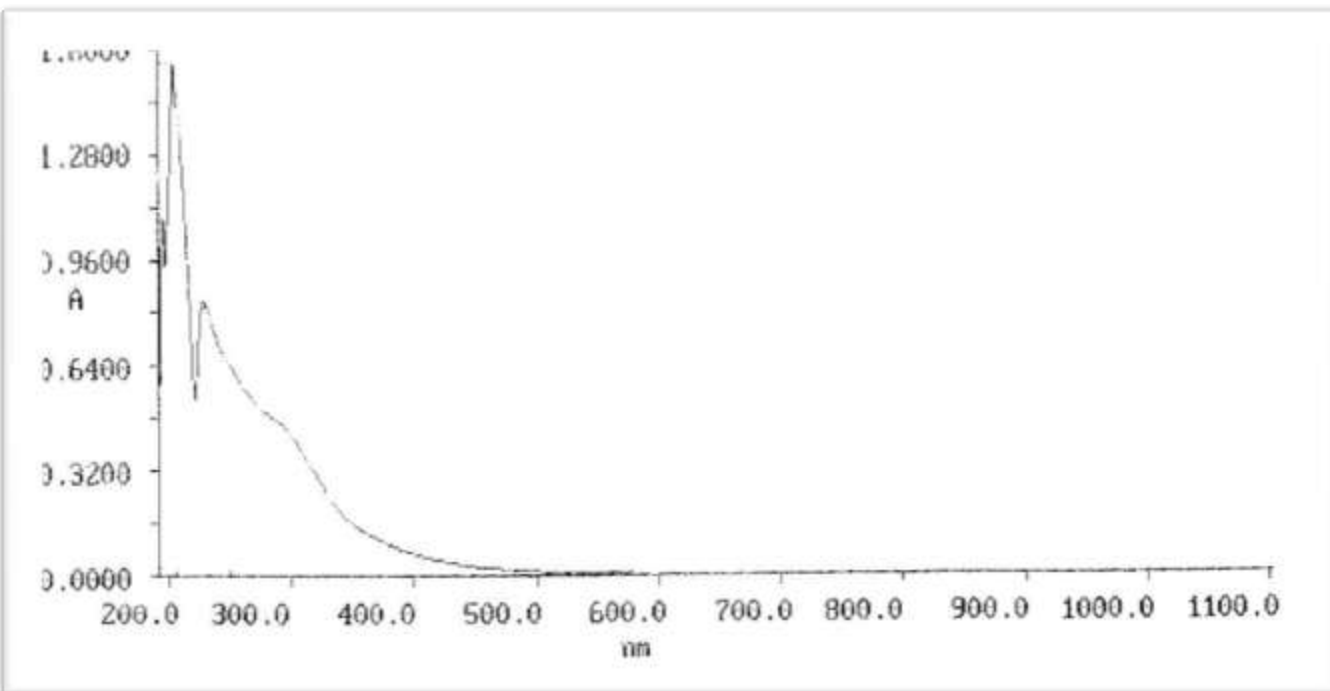
values the reactivity of the layer whether in energy or in wavelength, which postulates for the Z3 layer which was found to be the most reactive.

#### 4.3 UV spectroscopy of oil shale samples solubilized with chloroform.

We solubilized 2g of the Tarfaya oil shale samples with a 50 cm<sup>3</sup> solution of chloroform (0.17mol/l); permanent stirring was used with heating to around 97°C. The absorption spectra can be found in



**Figure 8:-** UV spectrum of the solute after filtration of one gram of Tarfaya shale (Z3) solubilized in 50 cm<sup>3</sup> of chloroform (M=0.17 mole/l) at a temperature of 97°C.



**Figure 9:-** UV spectrum of the solute after filtration of one gram of Tarfaya shale (Z4) solubilized in 50 cm<sup>3</sup> of chloroform (M=0.17 mole/l) at a temperature of 97°C.

The absorption spectra of the two samples show three distinct peaks at different absorption intensities and wavelengths, we gather these characteristics in the following table:

Echantillons	Z3		Z4	
	Ab	WL (nm)	Ab	WL(nm)
Peak 1	0,22	180	1,56	200
Peak2	0,05	255	0,84	225
Peak3	0,04	298	0,46	295

Characteristics of the UV peaks of the Z3 and Z4 layers solubilised in chloroform (97°C)

According to the wavelengths of the previous peaks we observe a very significant decrease for the Z4 layer showing that the spectroscopic energies ( $E=hc/\lambda$ ) have become high, these observations inform us about the quality of the resulting material after treatment of the Z4 layer with chloroform.

This resulting organic matter became different in quality and quantity. In a previous work (S.Hafid et al: 2008) calibrated the spectroscopic apparatus of use in liquid phase (chloroform for the shales) by solution of methylene blue they were able to reach the constant of cell  $\epsilon I$  according to the law of Beer Lambert ( $A= \epsilon I C$ ). The value of the latter by BM calibration is found to be equal to 5.04 l/mol/cm, so we can calculate the concentrations of the material found for each peak. We have compiled these concentrations in the following table:

Sample	Z3 C(mol/l)	Z4 C(mol/l)
Peak 1	0,044	0,310
Peak 2	0,010	0,167
Peak 3	0,008	0,091

### Interpretation

The overall organic matter was measured by true thermogravimetry and has a mass percentage for a heating rate of  $\theta=21^\circ\text{C}/\text{min}$ , we have 16.4% for Z3 and 14.4% for Z4. In the following section we will draw up a table including the quantitative ratio for each quality of material identified by the given techniques, this ratio will be of the kind Z3/Z4 :  
Interprétation Thermogravimétri spectro in raw state spectro solubility with  $\text{CHCl}_3$

Technic	Thermogravimetry	Spectro in raw state		Spectro solubility with $\text{CHCl}_3$		
		Peak 1	Peak 2	Peak 1	Peak 2	Peak 3
$\neq$ peak	stage in the decomposition of organic matter					
Z3/Z4 report	1,14	0,88	0,74	0,14	0,06	0,09

The amount of total organic matter is higher for Z3 than Z4, this was found by thermogravimetry in several tests and with several heating rates. When we move on to the amount of molecular weight material detected by UV spectroscopy for the raw samples, we notice a slight decrease for the Z3 layer than for the Z4 layer, this is true for both the 245nm and 410nm peak.

This time when the oil shale is solubilised with chloroform, we observe that the absorption peak around 410nm has completely disappeared, which shows that the material at this position is completely decomposed by the chloroform, usually in the form of gas. The crude identification peak at around 245nm has split into three peaks (chloroform) whose wavelengths are significantly higher for Z3 than for Z4, which again proves the high reactivity for this layer (Z3), Indeed the Z3 layer was formed in the Upper Cretaceous at the Turonian geological stage which was the hottest stage in the Upper Cretaceous quantity, when solubilized with chloroform we notice a rather high difference, the Z4 layer has a quantity of this high molecular weight heavy material more than ten times compared to the Z3 layer The Z3 layer, which had a higher percentage of total organic matter (thermogravimetry), has little high molecular weight organic matter, whereas this heavy matter is concentrated in the Z4 layer. This can only be explained by the phenomenon of in situ pyrolysis occurring in this geological stage of the secondary era (Upper Cretaceous), which is the Turonian.

We note that the first peak (raw) had a slightly higher identification energy (211nm) becoming higher (200nm) for the Z4 layer, this shows that chloroform makes the material even denser hence the property of chloroform to cause polymerisations of the material as well as the appearance of hydrocarbons of even higher molecular weight.

**5. Isothermal combustion of oil shale (Z1) at different temperatures (low temperatures to realized ashing as reaction).**

Seven 1g samples of the same product (Z1 layer) were treated at different temperatures in a sand bath where they underwent isothermal combustion. Every 10 min the temperature was taken.

**5.1 Acid attack (HCl) of calcite at room temperature**

Acid etching is often used for compounds that release CO<sub>2</sub> in gasometry. A 0.3 g sample of calcite is etched with 50 cm<sup>3</sup> of HCl (0.0474N), then filtered and 10 cm<sup>3</sup> of the filtrate is dosed with NaOH (0.0274N) to work out how much was consumed during the etching process (back-dosing). This part of the determination is done by PH-meter (Tacussel with Orion electrode).

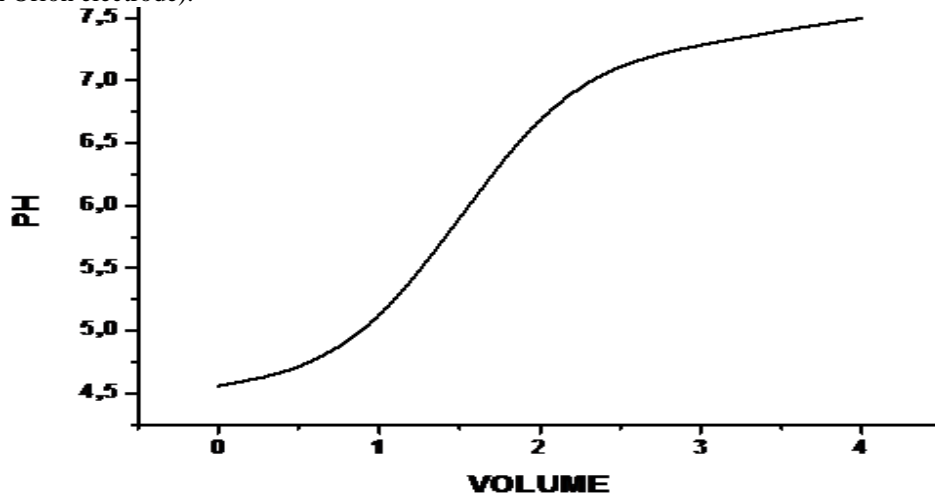


Figure. 10:- dosage of acid attack of calcite at room temperature.

**5.2 Acid attack of oil shale layers in the raw state.**

The same conditions were used for the study of oil shale layers in the raw state, the dosages that were made are represented in the following figure.

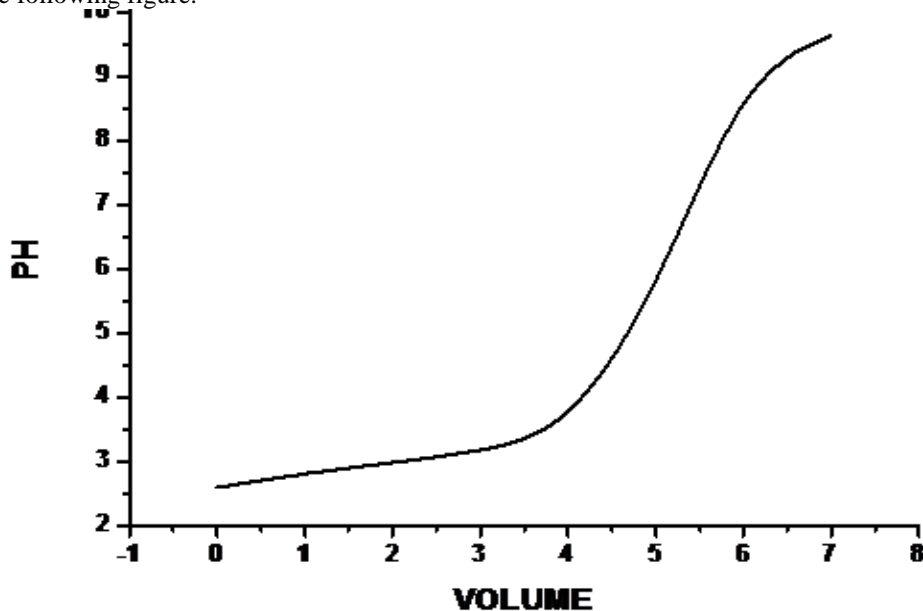


Figure 11:- HCl by NaOH dosage curve from acid attack of raw oil shale layers (Z1).

**5.3 Acid attack of oil shale samples at different combustion temperatures.**

Acid attack is often used for the case of compounds releasing CO<sub>2</sub> in gasometry. Samples having undergone combustion at different temperatures were subjected to this acid etching, 0.3 g of sample is etched by 50 cm<sup>3</sup> of HCl (0.0474N) then a filtration is made and 10 cm<sup>3</sup> of the filtrate is dosed with NaOH (0.062N) to conceive the quantity which was consumed during this etching (back determination). This part of the determination is done by PH meter (Tacussel with Orion electrode).

The following curves represent the back-assay (NaOH) of this acid attack for shale samples that have been burnt at different temperatures.

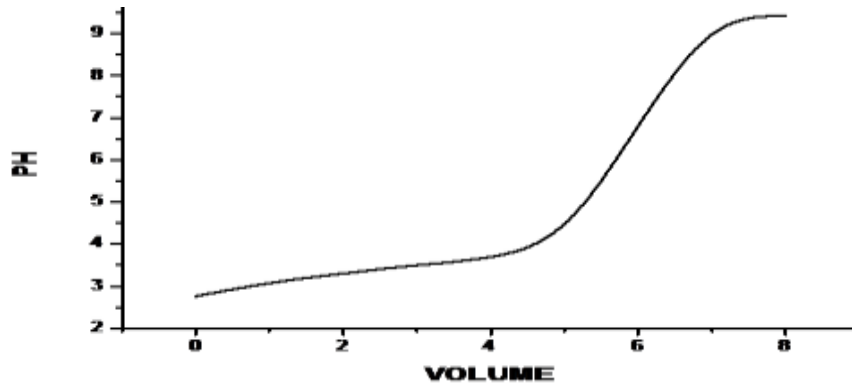


Figure 12:- Curve for the dosage of HCl by NaOH from the acid attack of oil shale sample (Z1) at 59°C.

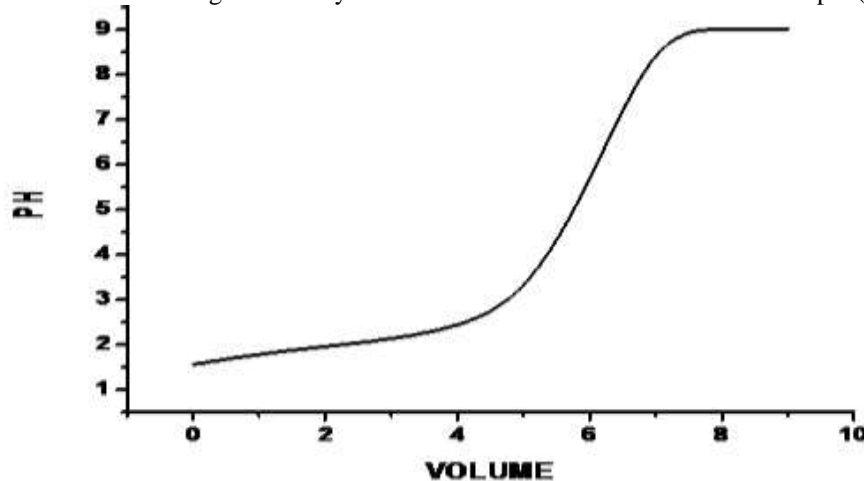


Figure.13:- Curve for the dosage of HCl by NaOH from the acid attack of oil shale sample (Z1) at 82°C.

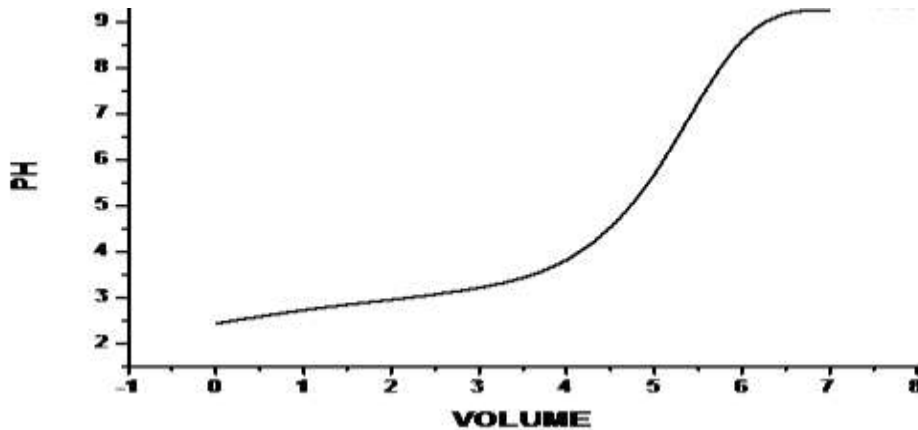


Figure 14:- Curve for the dosage of HCl by NaOH from the acid attack of oil shale sample (Z1) at 90°C.

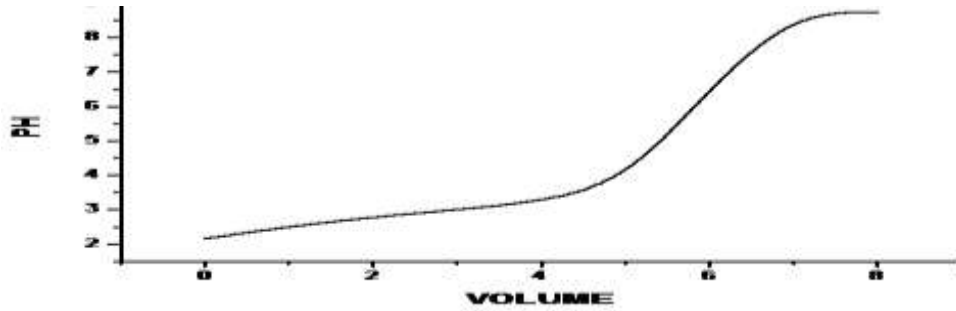


Figure 15:- Curve for the dosage of HCl by NaOH from the acid attack of oil shale sample (Z1) at 116°C.\

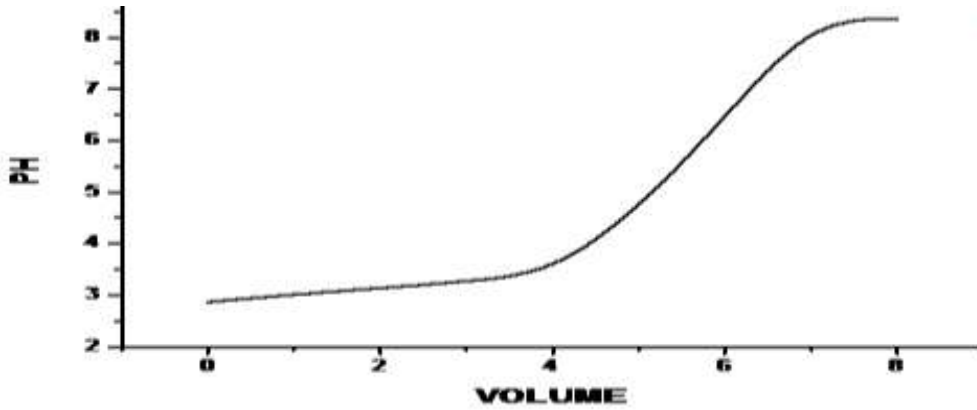


Figure 16:- Curve for the dosage of HCl by NaOH from the acid attack of oil shale sample (Z1) at 148°C.

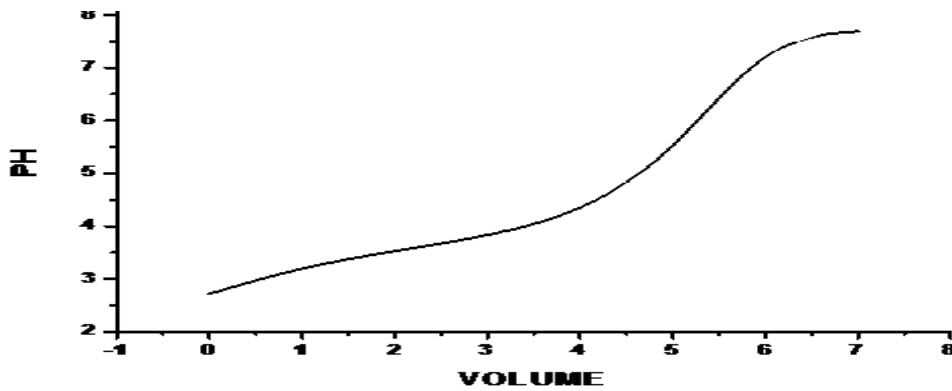


Figure 17:- Curve for the dosage of HCl by NaOH from the acid attack of oil shale sample (Z1) at 169°C.

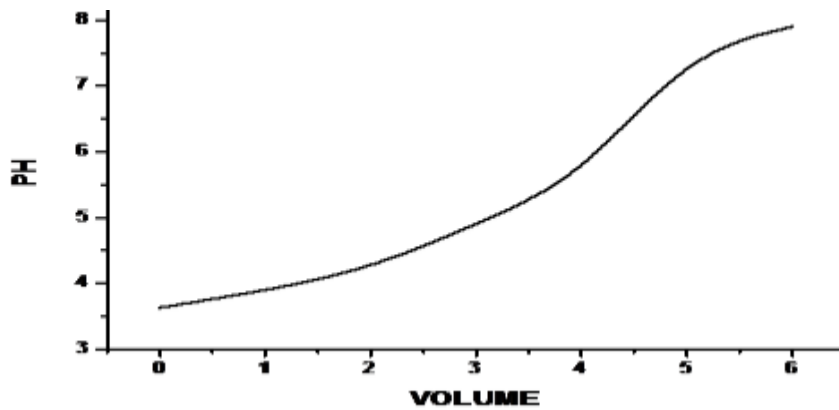


Figure 18:- Curve for the dosage of HCl by NaOH from the acid attack of oil shale sample (Z1) at 227°C.

	Volume of dosage (ml)	PH	Volume of dosage for acid for attack
HCL alone	17.3	6.8	—————→
Raw layer Z1	5.2	6.4	12.1
Layer Z1 at température 59°C	5.9	6.6	11.4
Layer Z1 at température 82°C	6	5.7	11.3
Layer Z1 at température 90°C	5.1	6.2	12.2
Layer Z1 at température 116°C	5.8	6	11.5
Layer Z1 at température 148°C	5.6	6	11.7
Layer Z1 at température 169°C	5.3	5.9	12
Layer Z1 at température 227°C	4.3	5.8	13
Calcite	5.9	1.5	11.4

**Table. 1:-** Dosage volumes and dosage of attack volumes for different oil shale samples.

### Interpretation.

The evolution of the concentration of the compounds for the Tarfaya oil shale sensitive to acid attack is carried out in four distinct ways according to the temperature range considered: between the ambient and 82°C, then between 82°C and 90°C, then between 90°C and 116°C and finally between 116°C and 227°C. We summarized these four ways by symbolizing the concentration of the compounds, given that the latter are proportional to the attack volumes (see previous table) by a as follows

- Ambient -59°C-82°C:  $a_1 > a_2 > a_3$
- 82°C - 90°C:  $a_3 < a_4$
- 90°C - 116°C:  $a_4 > a_5$
- 116°C -148°C - 169°C - 227°C:  $a_5 < a_6 < a_7 < a_8$

We interpret this variation in the way that between ambient and 82°C we notice that the thermal phenomenon prevails over the decomposition under area.

- Ambient - 59°C - 82°C we have the effect of thermal activity.
- 82°C - 90°C decomposition of light organic matter and water.
- 90°C -116°C we have thermal activity
- 116°C - 148°C - 169°C - 227°C: Finally we have the decomposition of organic matter (aromatics, aliphatic)

Two qualities of decomposition under air (combustion with departure of CO<sub>2</sub>) have been identified: a first one results from the combustion of light organic matter and the departure of water between 82°C - 90°C, a second one between 116°C - 148°C - 169°C - 227°C and which is interpreted by the combustion of light hydrocarbons in C<sub>3</sub>, C<sub>4</sub>, C<sub>5</sub> as well as the cyclic ones (aromatics included)

### Conclusion:-

Oil shale vary considerably from one another, they vary in their chemical composition, mineral content, age, type of kerogen and the way they were sediment. The experimental part(Z1) informed us about the action of chloroform as a solvent causing the cracking of material until disappearance with the departure of gas such as CH<sub>4</sub>, peak 2 or peak 3 (crude), while the material formed of heavy hydrocarbon representing peak 1 (crude) UV was transformed into two others of variable concentrations (Beer Lambert)

For the two layers of the Tarfaya oil shale deposit, the Z4 layer at depth is followed by the Z3 layer. The experimental part is carried out by two spectroscopic apparatuses, one operating in the solid state and the other in the liquid state, The compiled remarks obviously showed following the UV spectroscopic analysis in the raw state of the two layers Z3 and Z4 of Tarfaya oil shale that these two layers present the first peak in the UV domain (251nm)

for Z3 and (243nm) for Z4 and the second peak respectively for Z3 and Z4 (412nm) and (411nm) being in the visible. The position of the first peak in the wavelength axis which is proportional to the identification energy shows us that the latter is relatively lower for Z3 than for Z4; the reactivity of the Z3 layer cannot be interpreted only by the climate difference of the surrounding geological era (Upper Cretaceous)

The study of the solubilisation of oil shale (Z3, Z4) in chloroform revealed various changes in the spectra due to the effect of this solvent, firstly the disappearance of the peak at 410nm. Thermo gravimetric analysis (Z3/Z4) and spectroscopy in the crude state as well as in the solubilized state showed the massive character of Z4 compared to Z3. The existence of this heavy material is the consequence of the phenomenon of in-situ pyrolysis favored more in the warmest climate (Turonian of the secondary era).

We have noted two properties of chloroform as a solvent, firstly it makes light compounds (high wavelength) disappear by cracking material in the form of gas, secondly the high molecular weight material undergoes polymerization as well as the appearance of hydrocarbons of even higher molecular weight.

Ashing at low temperatures being the main reaction also, in order to use the material as an absorbent or depolluting, of this study followed by an acid attack (HCl) and dosage by pH-meter. The compound to be studied is the Tarfaya oil shale (Z1), and there are four ways in which the reaction evolves according to the chosen temperature range (ambient - 227°C)

1/ Ambient - 59°C - 82°C we have the effect of thermal activity.

2/ 82°C - 90°C decomposition of light organic matter and water.

3/ 90°C - 116°C we have thermal activity

4/ 116°C - 148°C - 169°C - 227°C: Finally we have the decomposition of organic matter (aromatics, aliphatic)

Two qualities of decomposition under air (combustion with departure of CO<sub>2</sub>) have been identified: a first one results from the combustion of light organic matter and the departure of water between 82°C - 90°C, a second one between 116°C - 148°C - 169°C - 227°C and which is interpreted by the combustion of light hydrocarbons in C3, C4, C5 as well as the cyclic ones (aromatic included).

Thus a competition between the thermal effect and the combustion of two qualities of oil shale compounds as well as the departure of water occurs during ashing in the selected temperature range (ambient - 227°C), the combustion prevails in two clearly distinct temperature ranges [82°C-90°C] and [116°C - 227°C].

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