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Spectroscopic Investigation of Macro and Micro Nutrients in Al-Uja Area Soil for Date Palm Trees

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1440/2019

Dedication

I dedicate this effort to the soul of my martyr brother

Raed Mahmud Ahmad Abu Hammad

Asmaa Mahmud Ahmad Abu Hammad

Declaration:

I Certify that this thesis submitted for the degree of Master, is the result of my own research, except where otherwise acknowledged, and that this study has not been submitted for a higher degree to any other university or institution.

Signed:

Asmaa Mahmud Ahmad Abu Hammad

Date: 10 / 4 /2019

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A special thanks for my lovely husband Moath abu Dayah. Thank you for your true love that give me a huge power to continue and thanks for holding my hands when the others left.

Finally:

Fun of Access is fleeting, the Secret is in the Journey

Abstract:

In this study, soil samples from Date Palm farm in Al-Uja area were collected from different four sites. Soil samples were collected from 0-20, 20-40, 40 -60, and 60-80 cm depth of equal 50cm distances from the trunk of the tree.

The main objective of this study was to develop and implement a new methodology for the first time in Palestine that study plant nutrients of soil, by using a spectroscopic techniques and give a better understanding for the relationship between soil and fertilizers based on vibrational mid-Infrared (IR) spectroscopy, fluorescence spectroscopy, fluorescence - Xray spectroscopy, and for macro and micro elements in soils samples mass spectrometer (ICPMS) was used.

The study is divided into two parts, the first one related to investigate the effect of using different types of fertilizers on soil using spectroscopic techniques, this part of study was carried out from real field area where blank and treated samples are collected from different four positions in Al-Uja area and consider as business as usual. The second part was conducted in the lab by using blank samples that were collected from filed and treats them by certain concentration of feed solutions that prepares in lab and then study the relation between these feed solutions and soil by using the same spectroscopic techniques.

For the first part of study, lab analysis for soil samples showed that the soil were sandy loam and loam in texture and the salinity rang were between saline and very saline soils with pH in range 7-8.5 and that was the favorite soil properties for date palm tree.

ICPMS analysis showed that the soil for all position of the study area site were suffered from the lack of micro nutrients, also the macronutrients levels were around the very low range at different depth except the sodium levels were very high in all positions.

The fluorescence analysis showed that the intensities for all positions decreases as the depth increase and that indicated that there was a strong binding between fertilizers and soil as soil depth increasing and in particularly in depth 80 cm.

The FTIR analysis showed a three bands assignment for all of positions and showed the intensity-depth dependents and they exhibiting the difference between fertilizers samples and control ones.

The X-rays analysis shows a powerful data that showed the minerals of soil of the study site for position one (P_1) and four (P_4), it showed that the most minerals were found in depth 60cm for both positions. And shows the most chemical compositions for the study area.

For the second part of study, the relation between fertilizers concentrations and soil were difficult to study because of there a various other variables effect this relation such as pH value variable and the environment variable, the fluorescence showed the intensity concentration dependent for the first two positions of the study site and showed a different relation for the other positions.

The ATR-FTIR analysis were a powerful tools, the spectrum showed the intensity concentration independent. And give a huge band assignments of functional groups peaks in soil.

This present study showed that the spectroscopic techniques were a useful tools for given a better understanding of the relationship between the depth of soil and the interaction between soil and fertilizer

The soil analysis indicates the over salinity of soil farm and this may refer to an increase of the underground level caused by excessive drought situations (high evaporation); and also refer for the using of high salts content water. This high values of salinity make a negative impact on soil such as high concentrations of soluble salts, and high soil pH, and a negative effect of sodium on the plant metabolism.

From results of the four positions on the study area it was clear that the applied fertilizers are not site- specific and not finely tuned to local soil chemical conditions. So it need a specific information on soil nutrients and improving soil fertility using agroforestry techniques.

We recommended also to make a up scaling study for all Date Palm trees areas in order to be soured if this deficiency presents in all sites or not.

For future work it's useful if study the relation between fertilizers and soil through a simulation study based on leaf/soil analysis and date palm requirements using these same spectroscopic techniques.

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List of Abbreviations and Symbols

Abbreviations/symbol	Description
IR	Infrared
NIR	Near Infrared
MIR	Mid Infrared
EMW	Electro Magnetic Wave
UV-VIS	Ultra Violet-Visible
E	Energy
N	Frequency
C	Velocity of light
Λ	Wavelength
H	Plank's constant
E_{tot}	Total Energy
E_{rot}	Rotational Energy
E_{Vib}	Vibrational Energy
E_{ele}	Energy of electron
S_0	Energy ground state
S_n	Energy excited state
A	Absorbance
C	Concentration
T	Transmittance
P^0	Initial light intensity
P	Final light intensity
A	Absorptivity
ε	Molar absorptivity
B	Light path length
IRS	Infrared spectroscopy
K	Force constant
M	Mass
X	Distance
V	Vibrational quantum number
FTIR	Fourier Transform Infrared
ATR	Attenuated Total Reflection
FS	Fluorescence Spectroscopy
ICPMS	Inductively Coupled Plasma-Mass Spectroscopy
XRD	X-ray Diffractometer

XRF	X-ray Fluorescence
F_0	Initial Fluorescence Intensity
F	Final Fluorescence Intensity
K_q	Quenching constant
τ_0	Fluorescence life time
K_{sv}	Stern-Volmer constant
K	Binding constant
L	Quencher concentration
N	North
E	East
No.	Number
P	Position
N_n	Number of sample
D	Depth
B	Blank Sample
D.W	Distilled water
EC	Electrical Conductivity
F	Feed solution
F_0	Blank sample without feed solution
ID.	Identity
Con.	Concentration
Per	Percent
et al.	Other
2^{nd}	Second
M	Molar
mg/L	milligram/Litter
Ppm	Part per million
EC_{SE}	Electrical Conductivity Saturated Extract
ADMC	Air-Dry Moisture Content
µS/cm	micro Siemens/ centimeter
mmhos/cm	milimhos/centimeter
VL	Very Low
L	Low
M	Medium
H	High
VH	Very High
Q	Quartz
C	Calcite
D	Dolomite
K	Kaolinite
Cr	Cristobalite
A	Argonite

Chapter One
Study Description

1.1 Introduction

Chemical composition have various methods to determine in sample of matter, which are basis of analytical chemistry. Most common methods can be ether instrumentals or classical methods. For many years ago of chemistry most of analysis were depends on the classical methods, but in the second half of twentieth century, most of researchers were go to the direction of using the measurements that depends on the physical properties of analyses such as light emission or light absorption, fluorescence, conductivity and mass to charge ratio, which are called instrumentals methods where the spectroscopy depends on the interaction between matter and electromagnetic radiation (Skoog *et al.*, 1998).

In the recent researches there was an increasingly using of spectroscopic techniques especially in agricultural and food industries. The laboratory methods for soil, plant and food analyses have many disadvantages such as they are expensive, time consuming and there is much works required in these methods began with sample collection and end with laboratory work itself also they require a highly skills. All these reasons made these methods not effective enough for the increasing of demand of industry (McCarty and Reeves,2006).

On the other hand, infrared, fluorescence and fluorescence X-ray spectroscopies, ICP- mass spectrometry and many other instruments techniques were used for determining the product composition recently which all have many advantages such as they are rapid, low cost and nondestructive tools. These techniques have been applied in soil science and shows a huge potential for soil analyses especially when large number of samples and analyses are required which appeared more effective and accurate than the digestion for soil organic analyses (Nanni and Demattê,2006).

In this concept, soil is considered to be an important source of food and it is necessary for growth of plant. Therefor plant need a specific amount and type of fertilizers application to improve yield of food and the quality. Soil fertility is one important variable of soil to be showed and sensed various within a field depending on some characteristics such as agronomic changes, soil type and previous management practices. (Hummel *et al.*,1996).

The most important soil nutrients are known as nitrogen, phosphoresce, potassium, carbon, calcium and micronutrients where they plays the most important role in soil fertility. Laboratory analysis were usually used to determine the nutrients content. Hence with use of crop management instrumental techniques becoming a promise strategies that able to increase the production of food as well as reduced the input cost that provides the sustainability of environment. (Kim,2005).

In particular, Date Palm (Phoenix dactylifera L.) is one of the oldest cultivated trees in the world. According to FAO.(FAO,2000) Date fruits consider a major part of the diet of the Palestinian people, especially in the month Ramadan. By consider the daily requirements of macro elements by human 15 dates fruits provided more than 80% of the daily requirement of magnesium, 70% of sulfur, 25% of potassium, 20% of calcium, and a substantial amount that body needed from iron, manganese, copper and zinc (Robinson,1972);(Uvderwood,1971).

Date palm has fertilizer requirements like other cultivated crops. Nutrient element needful for growth of plant and production which absorbed from the soil (not absorbed from the air), i.e.: boron, chlorine, cobalt, copper, iron, magnesium, manganese, molybdenum, nitrogen, phosphorus, potassium, sodium, sulfur and zinc, are all needed at several rates (Date,1990).

Palestinian farmers had adapted the drip irrigation technology during the last century though, water/fertilizer use efficiency still in need for further improvement. Therefore, adapting optimization of using chemical fertilizers according to the available natural nutrients contents (macro and micro) is a promising approach. In 2014, Palestinian farmers applied about 2.6 million tone of supplement NPK fertilizers with a value of 2.3 million USD/a, only for Date palm tree fertilization. The current use of fertilizers is mostly without spatial assessment of soil macro-and micro nutrients. This could be optimized according to the availability of natural soil nutrients, which could have reduced the cost of production (FAO,2000).

Jordan Valley is reasonable suited for cultivation of Date Palm, which is an important cash crop in the area. Fertilizers are used to increase yield, but the available fertilizers are very expensive, thus reducing the profit of farmers. More importantly, it is not even well known which fertilizers types would be most effective on the soil-crop combinations. Currently, most of the fertilizer applied is a blend of macro nutrients such as Nitrogen (N), Phosphorus (P). However, crops require even more Calcium (Ca), Magnesium (Mg) and Sulfur (S) than P. Moreover, NPK blends are inefficient by definition since among these nutrients there exist antagonisms where uptake by the plant is concerned. Furthermore, it may well be that rather than N, P and K, one or more micronutrient (s) is in fact the most limiting factor where date palm yield is concerned (B, Fe, Mn, Mo or Zn)

1.2 Recent Studies

(Bellon Maurel and McBratney,2011), used “Near-Infrared (NIR) and Mid-Infrared (MIR) Spectroscopic Techniques for Assessing the Amount of Carbon Stock in Soils”.

(Mahandrimanana and Joseph,2013), used “X-ray fluorescence to determine the physicochemical properties of three various types of clay soils which showed the variation of composition of the major elements”.

(Zhu *et al.*,2011), used the “X-ray fluorescence for characterizing of soil mineral and elements”.

(Volkan Bilgili *et al.*,2010), used “Near-Infrared (NIR) to predict the soil properties related to four different series of soil”.

(Du *et al.*,2010), used “Mid-infrared (MIR) Spectroscopy for characterizing of Soil Clay”

(Rinnan and Rinnan,2007), used of “near infrared reflectance (NIR) and fluorescence spectroscopy to analysis of microbiological and chemical properties of arctic soil”.

1.3 Research Statement

In this study, soil of Date Palm farm were collected from different four positions in Al-Uja area, samples were collected from 0-20 cm, 20-40 cm, 40 -60 cm, 60-80 cm depth of 50 cm equal distances from the trunk of the tree.

The mean objective of this study was to developing and implementing a new methodology for the first time in Palestine that study plant nutrients of soil, by using a spectroscopic techniques and give a better understanding for the relationship between soil and fertilizers based on vibrational mid-Infrared (IR) spectroscopy, fluorescence spectroscopy, fluorescence - X ray spectroscopy, and for macro and micro elements in soils samples mass spectrometer (ICPMS) was used.

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In addition of this chapter, this study includes four chapters more: chapter two will discuss the theoretical aspects to guide readers to the important ideas of this study. Chapter three includes details of the experimental, procedures, and instruments used. In chapter four the results obtained are presented and discussed. Final chapter contains the conclusions and future work.

Chapter Two:

Theoretical Background

2.1 Soil

Soil is consider the main natural body that covering the earth's surface that support the plant growth with chemical, biological and physical properties. Moreover, it is the natural beds for roads, houses and factories; also it is the natural resource of production for plants and food in order to maintain the human being and animals. Soil is the receivers of municipal, industrial and animal. There is a complex structure for each type of soil which is called soil profile that consists of versus layers began in the regolith part until reached the bedrock part.

The underlying rocks on which the regolith portion is deposited known as bedrock. While all loose materials formed by weathering of bedrock or by transportation actions of wind, ice or water known as regolith and it is display as a huge variation in composition from one place to another. The upper part is different from the lower part because it is rich in highly content of organic matter and minerals due to the presence of plants root and soil organisms and also because there is a horizontal layers that support the growth of higher plants (Buckmann and Brady,1969).

Macronutrients make up the most significant portion of plant's diet, up to 99%. Nitrogen, phosphorus, and potassium are the principal nutrients, and those most likely to be deficient in soils. Although micronutrients are used in much smaller amounts, their presence and availability to plants, even in trace amounts, are essential to plant growth. They are limited in arid sandy soils, muck soils, soils with high pH, and soils intensively cropped and heavily fertilized with macronutrients only. (Buckmann and Brady,1969).

2.1.1. Soil Profiles:

Soil profiles are the vertical sections of soil exposing the layers. Each profile consist of upper layer which is called A-horizon or top soil layer, this layer has a higher concentrations of organic matter content and its color is darker than the layers below. The mid layer is B-horizon or sub soil layer its color consider as glaring color and it is contains a large amount of clay mineral. A topsoil layer and B subsoil horizons both are indicates to the true soils. Third one known as C - horizon which called parent material it can be as thin or thick layer .(Buckmann and Brady,1969).

2.1.2. The Composition of Soil:

Organic matter and mineral matter are the two contents of the solid portion of soil. Mineral matter is formed from parent rock or C-horizon. Living organisms in soils creates the organic matter. In addition water and air are fill up the pore space beside the solid portion.

2.1.3. Soil Types:

According to the composition of soil, soil divided in two categories are: mineral soil and organic soil. Soils that formed moist areas and bogs are containing organic carbon in percentage between 12 to 18 % -around 20 - 30 % organic matters- are known as organic soils. This type of soil consist of living microbes like fungi, living macroorganisms such as earthworms, insects, plant roots, bacteria and remains of dead macrooganisms as well as splits non-living macroorganisms. (Troeh and Thompson,1993).Organic soil are important for providing a high value of crop production such as fresh market vegetable. Also they consider as organic supplements for homes, potted plants and gardens. Therefore, this type of soil submit as an economical significance in localized region.

Mineral soil considered as more important type than organic type of soil that because this type occupies the highest fraction of the total land area. It is formed from sediments and rocks, they are the top and biological part of regolith. Mineral soils consist of around 45% mineral matter, 25% soil air, 25% soil water and 5% organic matter as shown in figure 2.1. (Troeh and Thompson,1993)

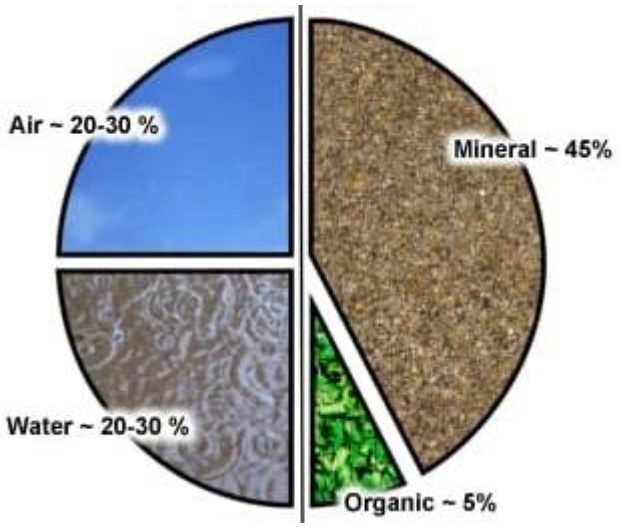

Figure 2.1: Composition of a mineral soil (Troeh and Thompson,1993)

2.1.4. Soil Water:

Soil water and dissolved salt together make the soil solution that essential not only for physiological process of plant but also for maintain the plant growth. It is consider as effective regulator for the temperature of soil and fill within the pores of soil. As plant catch some amount of water by the soil and also consume some amount from solid portion.(Hummel, Gaultney *et al.*,1996)

2.1.5. Soil Air:

Soil air is important for cycle of life for soil, plants and animal and it is filled the pores between liquid particles and solid in soil layers. The distinguished points of soil air from the atmosphere are: First one, soil air which is lying in the pores of soil between the solid parts. Second one, soil moisture content value of soil air overtake that of the atmosphere and

finally, the CO_2 content is higher than the amounts in atmosphere while that of O_2 is lower . The most found gasses in soil air are N_2, O_2 and CO_2.(Hummel, Gaultney *et al.*,1996)

2.1.6. Soil Mineral Content:

Physical and chemical weathering processing formed the mineral content in the soil from rock and these minerals are versus in size and compositions. The range of sizes begin from the size of submicroscopic clay to the size of stones, particles that with diameter more than 76 mm are stones and other particles that have a diameter less than stone size but more than 2 mm are gravels. While mineral particles with diameter less than 2 mm may be clay, silt and sand. Clay particles have size less than 0.002 mm in diameter, Silt particles have size between 0.002 to 0.05 mm and Sand particles have size between 0.05 to 2 mm. Most of minerals in the clay size some example such as motmorillointe, kaolinite and silicate. (Hummel, Gaultney et al.,1996).

2.2 Soil Nutrients

2.2.1. Plant Growth Factors:

Soil is a major operator which provides many plant growth factors. These factors can be as follows: a. sunlight, b. water, c. air, d. mechanical support, e. heat, f. nutrients. The plant growth can be described by principle known as the principle of limiting factors. This principle state that plant growth cannot be more than that allowed by the limiting factors that affect the growth. (Figure 2.2). Any of these factors in lower amount than the other can limits the growth plants. Therefore, when supplying soil nutrient elements, the relationship between all these factors must be considered.(Buckmann and Brady,1969)

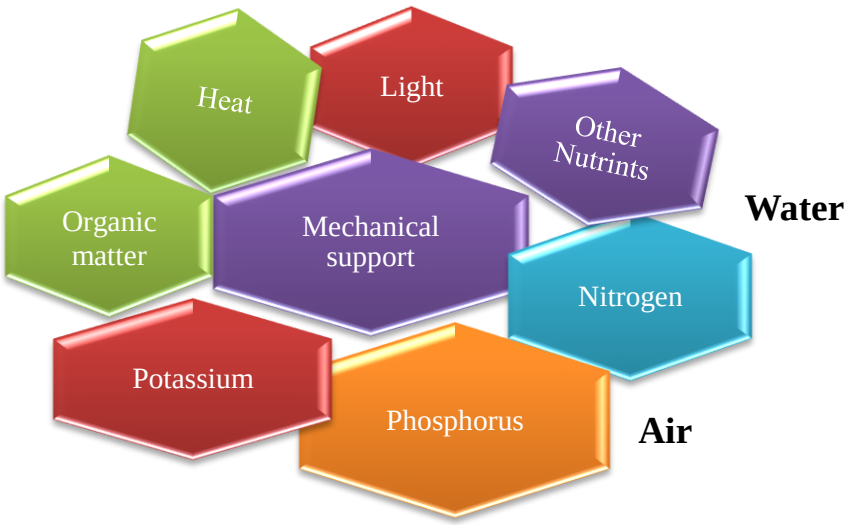

Figure2. 2: Principle. of limiting factors(Buckmann and Brady,1969)

2.2.2. Essential Soil Nutrients:

Table 2.1 shows that from several 17 important elements there are three of them, oxygen, hydrogen and carbon are taken from water and air, while others are taken from the soil. Most taken amount of oxygen and carbon are supplies from air by the process of photosynthesis, and hydrogen taken from soils water, and around 94 to 99.5% of tissue for fresh plant is consist of oxygen, carbon and hydrogen, and around 0.5 to 6% is constituents of soil.

Table 2.1: important nutrients element in soil. (Buckmann and Brady,1969).

Essential used Elements in a large quantities		Essential used elements in a small quantities	
Mostly of air & water	of soil solid	of soil solid	
Carbon	Nitrogen	Iron	Copper
Hydrogen	Phosphorus	Manganese	Zinc
Oxygen	Potassium	Boron	Chlorine
	Calcium	Molybdenum	Cobalt
	Magnesium		
	Sulfur		

Six elements of the fourteen elements that acquired from soil applied in a large quantities and they know as macronutrients. Nitrogen, potassium and phosphorus are define as primary elements from these macronutrients, they applied to soil by the supplements of manure or commercial fertilizers. They also consider as a critical macronutrients as they are he answerable for hinder of plants growth when the soil suffering from theirs lack. (Buckmann and Brady,1969).

Sulfur, magnesium and calcium defined as secondary elements, magnesium and calcium are known as lime elements because they are applied in limestone for acidic soils. The rest of nutrients, such as copper, iron, zinc, manganese boron, chlorine, cobalt and molybdenum that acquired from soil are used in small quantities and they defined as micronutrients. Usually, they are available in most of soil types in low concentrations, whereas this low availability does not consider as big problem as macronutrients lacks.

2.2.3. Macro nutrients: nitrogen, phosphorus and potassium:

Nitrogen

Organic or inorganic fertilizers are used for supplying the required amount of essential elements that needed for crop management. The presence of nitrogen fertilizers for example is an advantage to safety the required level of nitrogen in soil. Organic fertilizers such as sewage sludge, manure and compost piles. Inorganic fertilizers are cheaper than organic forms because they consider as mineral fertilizers, easier to use, more concentrated and more available for plants. (Table2.2). In particular, nitrate fertilizers is the easiest absorption

fertilizer for plants because it is highly solubility in solution. (Hummel, Gaultney *et al.*,1996). Table 2.2 below shows the must nitrogen fertilizers.

Table 2.2: Nitrogen fertilizers (Hummel, Gaultney et al.,1996).

Fertilizer	Chemical form	Percent Nitrogen
Ammonium Sulfate	$(NH_4)_2SO_4$	20.5
Ammonium Nitrate	NH_4NO_3	33.5
Sodium Nitrate	$NaNO_3$	16
Calcium Nitrate	$Ca(NO_3)_2$	15.5
Potassium Nitrate	KNO_3	14
Calcium Cyanamid	$Ca(CN)_2$	18 – 21
Ammonium nitrate sulfate	NH_4NO_3-$(NH_4)_2SO_4$	26
Urea	$CO(NH_2)_2$	46
Ammonium chloride	NH_4Cl	25

- Urea and Ammonium sulfate are the most used fertilizers in Al-Uja area

Nitrogen is used by plant for build a fresh cells with new organic components for their tissues. Compounds such as nucleic acids, amino acids, energy transferring compounds and many enzymes they all having a percentage of nitrogen that exist in the plant tissues. For example, Nitrogen absorption from cereals, caused to improve the plumpness and protein percentage. Moreover, its existence with other nutrients like potassium and phosphorus in a balance manner help to form a deeply green color for plant leaves. When the plant suffering from the lack of nitrogen then the outgrowth will stopped, limit root system and also made its system does not able to absorb sunshine light. .(Aochi and Farmer,2011)

Phosphorus

Phosphorus consider as a portion of nucleoproteins that holds the genetic codes of any living thing, so it handed out to every living cell. Also it is an important factor of genetic materials in the nucleus and in joining with other elements such as carbon and hydrogen has an essential impact for building a complex molecules in the cells. It also play a major rule in transfer, storage and energy release. Phosphorus lack will has negative affect such as slow the ripeness and stunting. (Bautista-Cruz *et al.*,2007)

There is an essential note of applying fertilizers on soil must be consider, which state that there must be a specific distance between the plants root and the fertilizers and it should be as minimum as possible. Generally, there is a localized bands must be used of phosphorus fertilizers around the root of plants in order to minimized any connection with soil. (Hummel, Gaultney *et al.*,1996) .Table 2.3 shows most of the phosphorus fertilizers.

Table 2.3: Phosphorus Fertilizers (Hummel, Gaultney et al.,1996).

Fertilizer	Chemical Form	Phosphorus %	Approximate % of available P_2O_5
Superphosphates metaphosphate	$Ca(H_2PO_4)_2$ and $CaHPO_4$	7 – 22	16 – 50
Ammonium	$NH_4H_2PO_4$	21	48
Phosphate			
Diammonium	$(NH_4)_2HPO_4$	20 – 23	46 – 53
Phosphoric acid	H_3PO_4	24	54
Calcium	Ca3(PO3)2	27 – 28	62 – 63

Potassium

Potassium also very essential for plant especially its job as regulator of osmotic concentration to preserve cells swelling. It has also a major function in transportation and formation of many compounds such as proteins, starch and chlorophyll. In potassium deficiency case, leaves color changes to brown or yellow, brown spots will formed on the leaves. The deficiency of potassium percentage in soil can be amended or improved by using commercial fertilizers that containing the required amounts of potassium. Potash fertilizers are the most fertilizers that used because they are water soluble so it is easy to absorbed from plants.(Table 2.4) (Hummel, Gaultney *et al.*,1996)

Table 2.4: Potash Fertilizers(Hummel, Gaultney et al.,1996).

Fertilizers	Chemical Form	K_2O %	K %
Potassium Chloride	KCl	48 – 60	40 – 50
Potassium Sulfate	K_2SO_4	48 – 50	40 – 42
Potassium Nitrate	KNO_3	44	37

Spectroscopic techniques have been applied in soil science and shows a huge potential for soil analyses especially when large number of samples and analyses are required which appeared more effective and accurate than the laboratory method for soil analyses, in the text below there is a simple description of these techniques.

2.3 Spectroscopy Definitions

Spectroscopy is a science field that study the interaction of matter with electromagnetic radiation.(Skoog *et al.*,2007). Spectroscopy concept based on any interaction of radiated energy as functions of its frequency or wavelength. Data that excluded from spectroscopy are represented as spectrum which is a plot for the interaction statues. (Herrmann and Onkelinx,1986).

Spectroscopy began with Newton's discovery in the 17^{th} century of the nature of light and the basics of color. Fraunhofer in 1800's then made an advances experiment with dispersive spectrometers that made spectroscopy to be precise and quantitative technique. Then, spectroscopy played a major role in physics, astronomy and chemistry. Then the development of spectroscopic instrumentation were concerned for applications of industry in the second half of the 20^{th} century.(figure 2.3)(Brand,1995).

In this respect, this development reach to researchers in different science such as agricultural fields, while low interest were given in the chemical industry. These techniques developed into essential methods in a different application for scientific research such as chemistry, agriculture, environmental analysis and different fields of life sciences(Siesler *et al.*,2002).

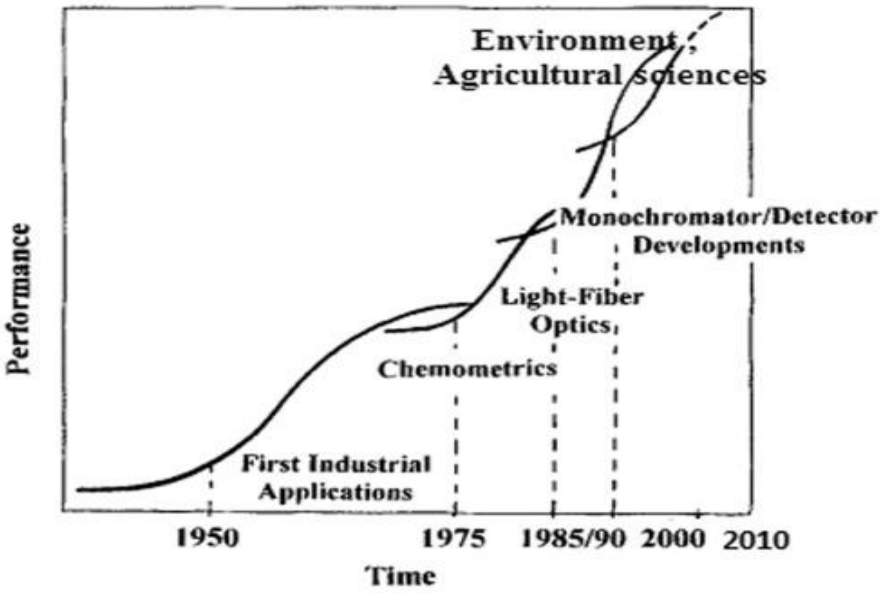

Figure 2.3: Developments of spectroscopic techniques (Siesler, Ozaki et al.,2002)

2.4 Electromagnetic Waves

Electromagnetic waves (EMW) are transverse oscillating waves composed of electric and magnetic fields perpendicular to each other and perpendicular to the direction of propagation as shown in figure 2.4. EMW propagate as sine or cosine waves at the speed of light in vacuum. The electromagnetic spectrum consists of radio waves, microwaves, infrared radiation, visible light, ultraviolet radiation, X-rays and gamma rays as shown in figure 2.5(Stuart,2004).

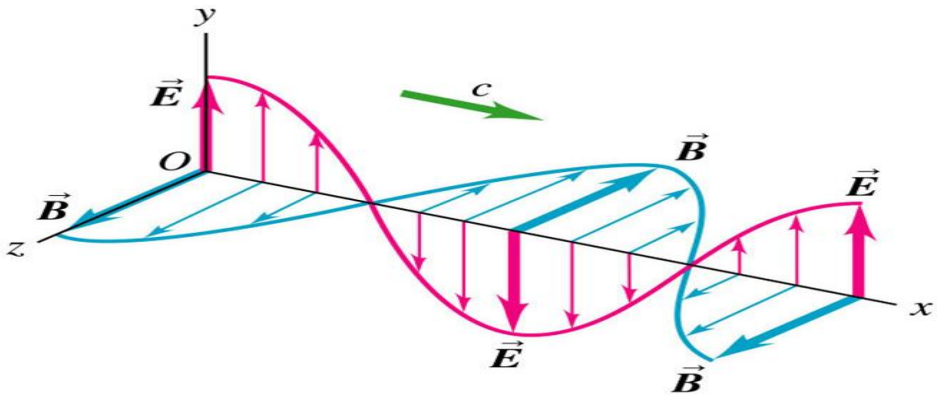

Figure 2.4: electromagnetic wave(Sharma 2007).

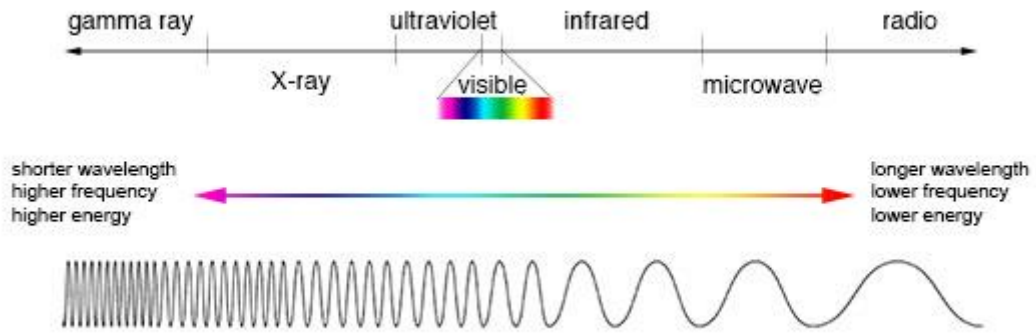

Figure 2.5: Electromagnetic spectrum (NASA's,2014)

Infrared radiation has a wavelength between ≈ (780 nm - 1 mm) in vacuum, can be divided in Near, Mid and Far IR. Our work utilizes region of Near-, Mid-IR from 4000-400 cm^{-1} where vibrational and rotational bands are observed and the UV-VIS region from 10-800 nm (Hollas,2004).

The interaction between incident light electronic field components and the molecules is the main concept of vibrational spectroscopy, the interaction occur when the molecules absorbed the light only if incident light energy (E) is equal to the energy difference (λE) in between the energy levels of molecules vibrational states. (Mohamed *et al.*,2018). The relationship between these concepts can be expressed by Planck–Einstein equation:

$$E = h\nu = \frac{hc}{\lambda} \qquad 2.1$$

Thus $\lambda = c/\nu$,

Where:
ν is the frequency of incident light,
c is the velocity of light,
λ is the wavelength, and
h is Plank's constant

The energy difference is specified by chemical bonds of functional groups in the molecules. The atomic spectra arise from the transition of electron between atomic energy levels, where three types of energy transitions can be presents which are molecular rotation, molecular vibrational, and electronic transition(Workman,1996). Thus the total energy of the molecule can be given by:

$$E_{total} = E_{ele} + E_{vib} + E_{rot} + \cdots \qquad 2.2$$

Where:
E_{rot} is rotational energy due to the molecule rotation about the axes,

E_{vib} is vibrational energy due to the periodic displacement of atoms around their equilibrium positions, and

E_{ele} is related to the energy of the molecule's electrons.

When radiated light (photon) falls on a molecules it may be absorbed, this occur as we said before when the energy of radiation matches the difference in energy levels of the molecule , otherwise it may be either transmitted or scattered. In order to represent the quantized rotational, electronic and vibrational states figure 2.6 showed that transitions between electronic energy states require more energy than transitions between vibrational energy states and rotational states (Clark,1999).

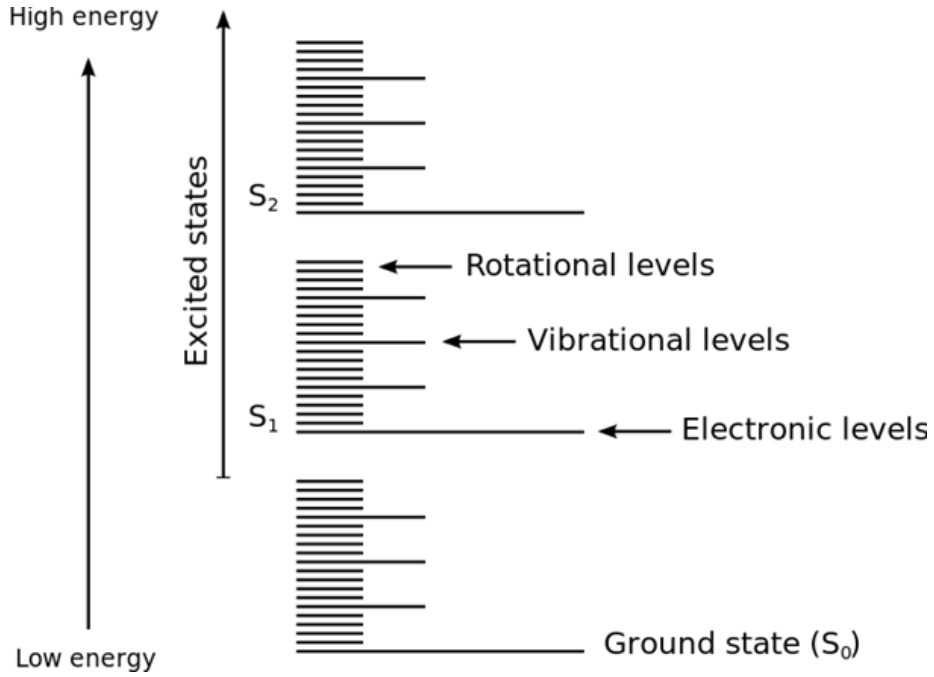

Figure 2.6: Representation of the quantized rotational, electronic and vibrational states.(Levien,1995)

The molecules absorbed amount of light, this absorption consider as a function of the absorber concentration. Beer-Lambert law, describe the relationship between absorbance (A), concentration (c) and transmittance (T), for monochromatic light expressed by:

$$A = \log(1/T) = \log(P_\circ/P) = \varepsilon bc = abc \,, \qquad 2.3$$

Where:
P^o is the intensity of incident light,
P is the intensity after the absorption occur,
a, ε is absorptivity(L/g cm), molar absorptivity(L/mole cm) respectively and
b is the path length of light through the sample.

The molecular absorption coefficient is characterized of each molecule and is dependent on the light's wavelength.

When absorption of radiated light at a certain wavelength occur by molecule, the electrons excites from ground state to higher energy states, but when the relaxation occurs from higher vibrational states to the lower vibrational state of the excited electronic state, the electrons return back to their ground state by emitting a photon. This is called as fluorescence emission (Figure 2.7) (Karoui *et al.*,2003)

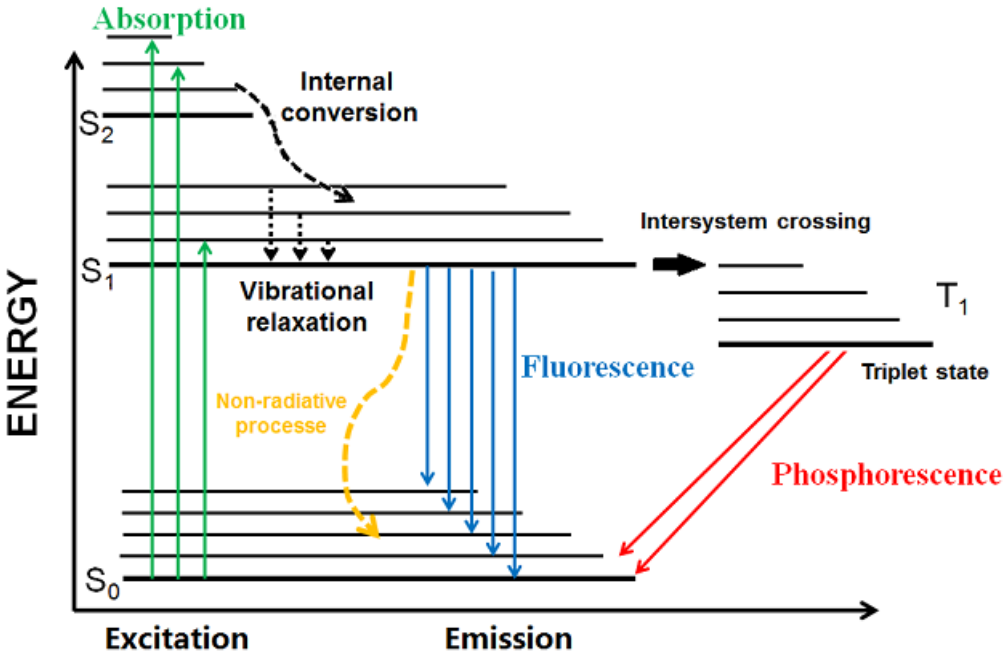

Figure 2.7: Fluorescence emission (Institut de Biologie Structurale,2018)

2.4.1. Infrared Spectroscopy (IRS):

Infrared spectroscopy is a method that study the interaction between sample of matter under investigation and electromagnetic energy in the infrared range of 0.8-1000 µm. This range divided into four regions, labeled near-, mid-, thermal- and far infrared, respectively as shown in figure 2.8. When IR radiation absorbed by a molecule at the same frequencies of its own molecular vibration, it caused an increase of the amplitude of the vibrations at these

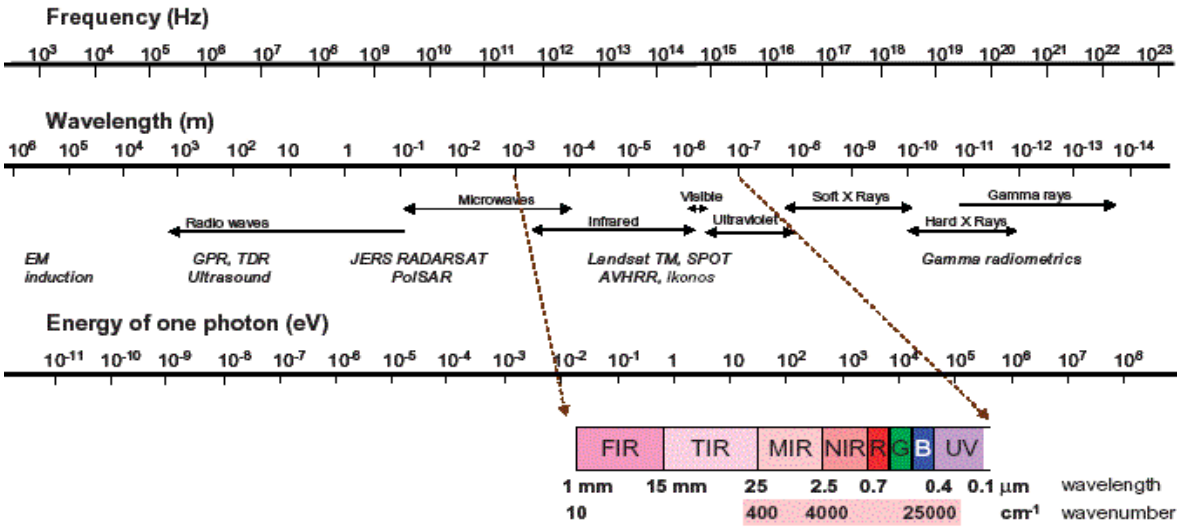

Figure 2.8: The IR -range in EM spectrum (Viscarra Rossel et al.,2006)

frequencies. Each frequency represented by a given amount of energy and specific molecular motion such as stretching, contracting or bending of chemical bonds(figure 2.9) (Du,2008).

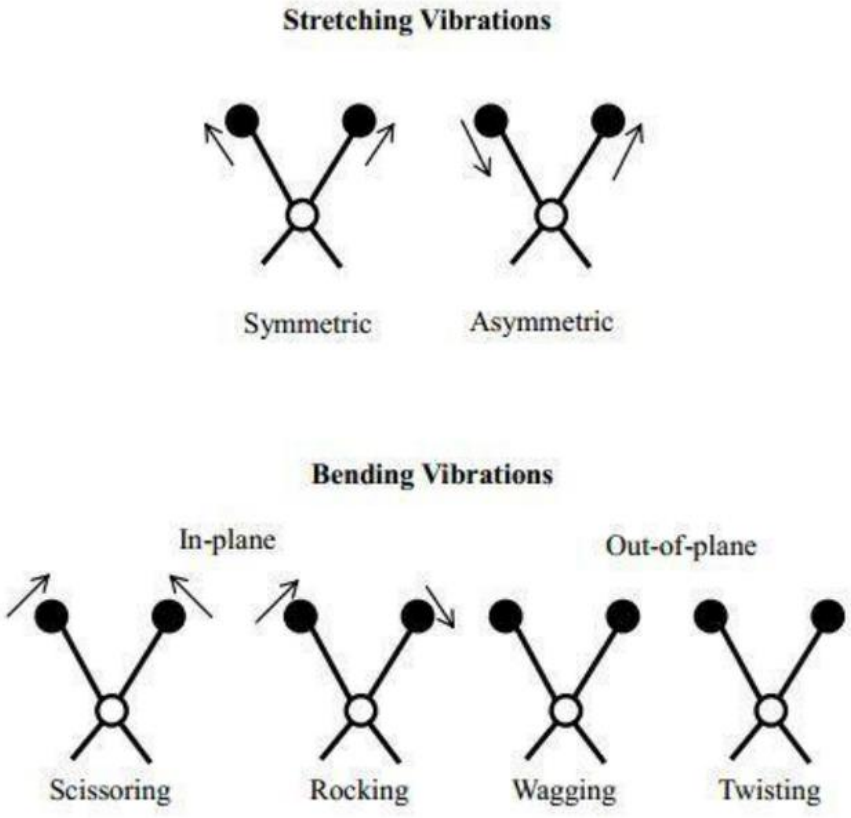

Figure 2.9: Types of molecular vibrations(Skoog, Crouch et al.,2007)

The IR spectrum can reveal the kind of that motion of molecules and bonds or in other words the functional groups that are present in the molecules and as a result it can provides a unique finger print of compounds. Also many functional groups have specific IR absorption bands that do not change for various compounds (Linker,2011). The net change in dipole moment of a molecules is conceder to be the main variable that the adsorption of infrared radiation depends on, as a consequence of molecules vibrational motion. In fact, atoms do not have a fixed position in a molecules but instead continuously fluctuation because of a various types of vibrational motions that being about the bonds in the molecule. (Skoog, Holler *et al.*, 1998).

When a change in dipole moment made the vibrations accompanied, the energy that transfer from radiation to molecule will be observed and force the molecule to exited to a higher energy level. And this transmission energy can be measured as a spectrum, which is a plot of energy that reflectance or absorption versus wavelength or wavenumber (the inverse of wavelength). All the molecules expect symmetric molecules such as H_2, C_2 or O_2 can absorb IR radiation and they are called infrared active, but symmetric molecules have a vibration that do not haunt by a dipole moment so they considered to be infrared inactive. (Xie,2003).

The vibrational motion of two atoms can be presented by the movements of two spheres that are connected by a spring, the stiffness of spring represented by the strength of bond and the masses of the spheres represent the atoms masses. If one mass is disturbed along the spring axis, then a low of simple harmonic oscillation is that the vibration obeyed or in other words Hook's law (Wetzel,1983).

The vibration's frequency can be calculated as:

$$v = \frac{1}{2\pi} \times \left(\frac{k}{\mu}\right)^{1/2} \qquad 2.4$$

Thus:

$$\mu = \frac{m_1 \times m_2}{m_1 + m_2} \qquad 2.5$$

$$v = \frac{1}{2\pi} \times \sqrt{\frac{k \times (m_1 + m_2)}{m_1 \times m_2}} \qquad 2.6$$

Where:

v is vibrational frequency,
k is force constant,
μ is reduced mass, and
m_1 and m_2 are the mass of atoms, 1 and 2 respectively.

The potential energy of simple harmonic oscillation can be calculated from:

$$E = \frac{1}{2} \times k \times x^2 \qquad 2.7$$

Where x is the intermolecular distance.

In fact, the harmonic equation do not enough to explain the behavior of atoms. That because the energy is not transfers continuously, but in discrete values of packets called quanta. (Osborne and edited by Meyers,1986).

The packets of energy consider as discrete energy levels, which defined by whole numbers 0, 1, 2..,then the potential energy can be written as:

$$E = \left(\mathrm{v} + \frac{1}{2}\right) \times \frac{h}{2\pi} \times \sqrt{\frac{k}{\mu}} \qquad 2.8$$

Where:
h is Plank's constant,
v is vibrational quantum number.

Not the same as harmonic oscillation equation in which the vibration can be any value of potential energy, quantum mechanical equation can take only these certain packets of energies.

Substituting equation 2.4 into2.8, the energy equation will be:

$$\mathrm{E} = \left(\mathrm{v} + \frac{1}{2}\right) \times h \times v \qquad 2.9$$

The net transition energy between two energy levels can be calculated from equation 2.9,

$$\mathrm{v} = 0, \quad \mathrm{E} = \frac{1}{2} \times h \times v \qquad 2.10a,$$

$$\mathrm{v} = 1, \quad \mathrm{E} = \frac{3}{2} \times h \times v \qquad 2.10b,$$

$$\Delta E = \left(\frac{3}{2} \times h \times v\right) - \left(\frac{1}{2} \times h \times v\right) = \mathrm{h} \times v \qquad 2.10c$$

All molecules remain at zero energy level at room temperature. Fundamental transition ($\Delta \mathrm{v} = \pm 1$) is the possible transition from 0 to 1 in any one of the vibrational state ($\mathrm{v}_1, \mathrm{v}_2, \mathrm{v}_3, \ldots$) (Skoog, Crouch *et al.*,2007). This type of transition is allowed in HO due to the selection rule of quantum theory, which state that the only place that can the transition takes is in a unit change in the vibrational quantum number ($\Delta \mathrm{v} = \pm 1$).

When the chemical bond in a molecule extend a stretching vibration, the bond may be break if the vibrational energy level reaches the dissociation energy that is required to dissociate two atoms repelling each other. In this particular case, the transition that happened from energy level 0 to 2, 0 to 3, 0 to 4 etc. are observed and considered as first, second, third, etc. overtones. Where the overtones have two, three, four, etc. times the fundamental, but have much weaker intensities than the fundamental bonds. The vibration of higher energy levels can be illustrated by the anharmonic oscillation. (figure2.10).

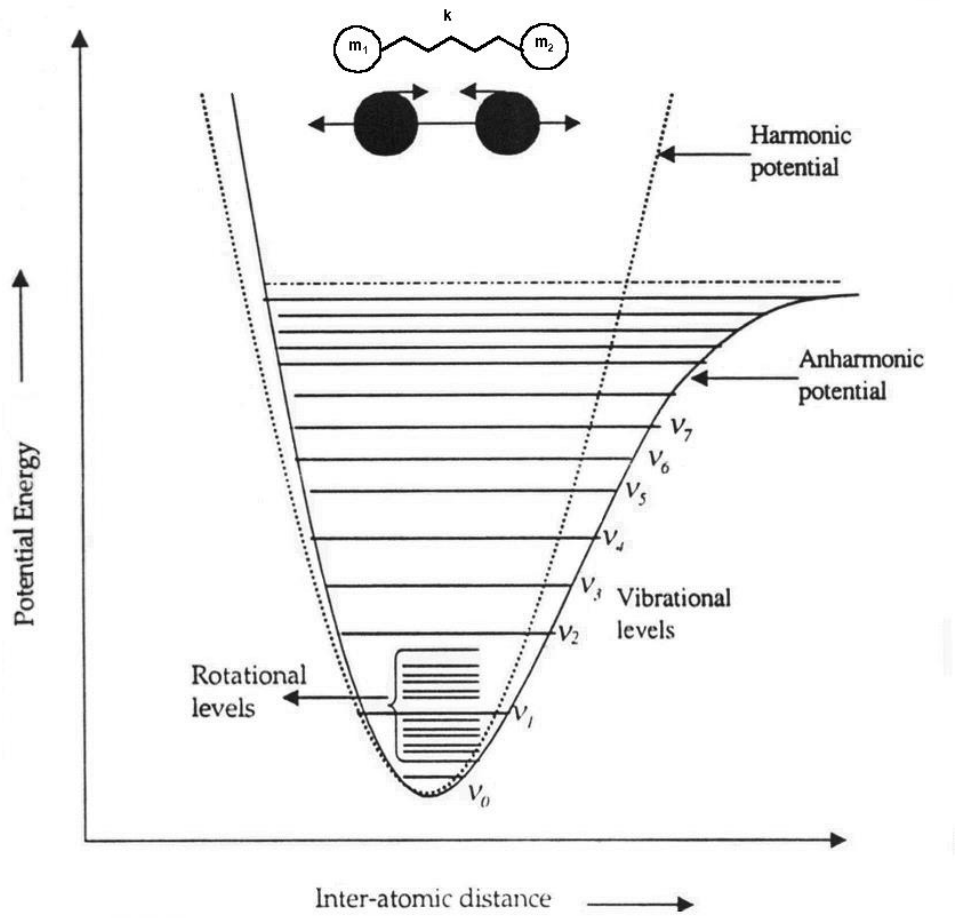

Figure 2.10: Potential energy of harmonic and anharmonic oscillation. (Ozdemir,1999)

As shown in figure 2.10, the molecules do not return back to the equilibrium and that because of the dissociation at higher energy levels. In addition to overtones lines, the combination of bands can be also observed as the result of simultaneous of the two modes of vibrations by a photon. This can be happen when two bonds absorbed energy rather than one, then the combination bands frequency can be the sum or difference of two fundamental frequencies. (Herrmann and Onkelinx,1986).

For an ideal harmonic oscillation the selection rules state that the transition between more than one vibrational state are not allowed and only fundamental vibration is allowed, but this transition do appear as a result of anharmonic oscillation (Herrmann and Onkelinx,1986). In the near IR region most of absorption bands observed are overtones and combination of fundamental vibrational bands in the mod IR region. The responsible bonds for this type of absorption bands, are that strong bonds having the lightest atom like hydrogen and a heavier atom such as carbon, oxygen or nitrogen (C-H, N-H, O-H).

2.4.2. Fourier Transform Infrared Spectrometer (FTIRS):

Fourier Transform Infrared spectrometer in nowadays consider as common laboratory method because of its ability to provide quantitative information in an accurate and rapid fashion. IR spectrum is obtains in typical FTIR by collecting interferogram of signals, this interferogram contains all IR frequencies then by applies the Fourier Transform gets the output spectrum. Interferometer is the most essential part of FTIR which used to splits the incident beams into two beams. (Griffiths and Haseth,1986).

The principle method of FTIR based on the interference that presences between two radiation beams. Figure 2.12 shows the Michelson interferometer which is the main part of FTIR, when the incident light come from the strikes beam splitter, then some of light transmitted to removal mirror and other is reflected to a stationary mirror before both beams are recombined again on the detector where they interfere each other. However, both light paths returning from both mirrors are not in phase, thus they interfere constructively and destructively to produce interferogram. The optical system in an FTIR spectrometer consist of the interferometer requires two mirrors, an infrared light source, an infrared detector, and a beam splitter. (Figure2.11). (McCarty and Reeves,2006)

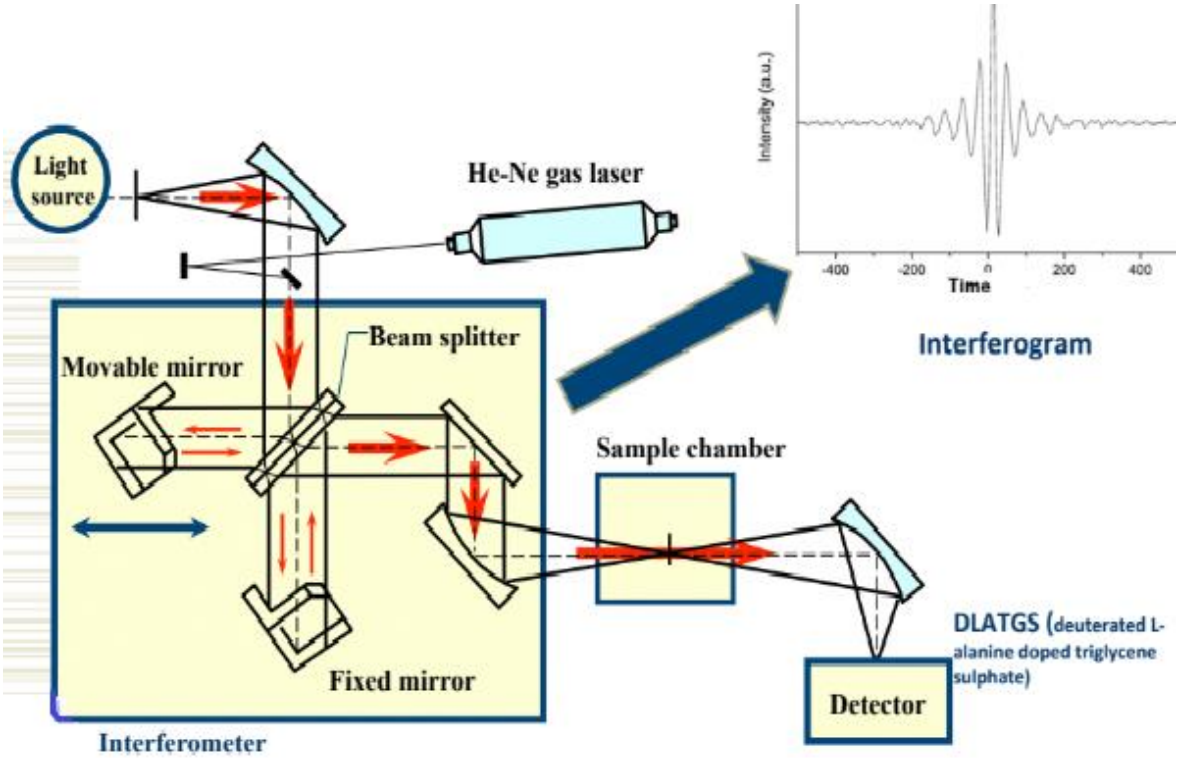

Figure 2.11: FT-IR spectrometer layout and basic components. (McCarty and Reeves,2006)

Clearly, this technique is applicable only to samples that do not absorb all the incoming IR energy and are sufficiently transparent in this spectral range. For highly absorbent samples, such as soils, it is necessary to prepare a pellet that embeds the soil sample in a transparent matrix, most usually KBr. The pellet preparation involves grounding 2-3 mg of soil with ~1 g of KBr using a mortar and pestle and using a hydraulic press and die to create a thin, IR transparent disk (figure 2.12).

Figure 2.12: KBr pellet technique. (Mohamed, Saleh et al.,2018)

This spectroscopic technique has advantages over some of the conventional techniques of soil analysis in that they are rapid, timely and less expensive, hence are more efficient when a large number of analyses and samples are required (McCarty *et al.*,2002)

2.4.3. Attenuated Total Reflection (ATR) – FTIR spectroscopy:

Over the previous years, Attenuated Total Reflection (ATR) has become one of the most technique in infrared spectroscopy. ATR spectroscopy measured the change that happened on a totally internally IR beams when the interaction is happened between sample and incident light. (Odlare *et al.*,2005).

Attenuated total reflection is producing in specific wavelengths corresponding to the vibrational frequency. The main advantages of ATRS is refer to its ability to study the samples with avoiding problems resulting by water absorbance from samples in IR region. ATR crystal induces an evanescent field penetrating the first µm of the sample which can remain open at the upper side and can be studied under physiological conditions, i.e., in presence of solution. (Odlare, Svensson *et al.*,2005).

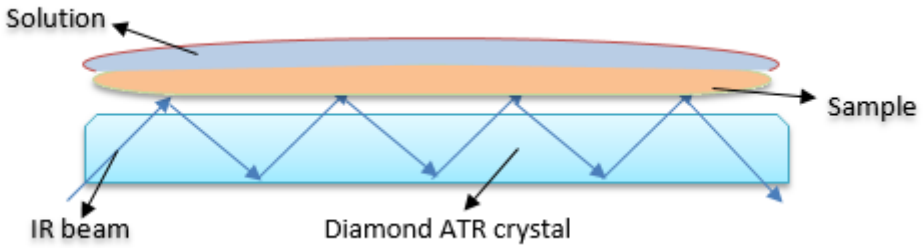

Figure 2.13: Schematic representation of ATR Principle

ATR principle shown in fig.2.13, with this accessory IR incident light propagate through a crystal, usually is made of diamond, with high refractive index which allows the radiation reflected within the ATR element one or several times. The sample is pressed into intimate contact with the crystals top surface, then IR radiation enters the crystal and reflected through it and penetrated a finite amount into sample and then in the end of the crystal the beam light back to normal path of spectrometer.

2.4.4. Spectroscopic Instrumentations Techniques:

In this study research, the main used spectroscopic technique instrumentation is FTIR in the Bruker IFS 66/S spectrophotometer model which is the most instrumentation that used from the researcher for data analysis. Other spectroscopic instrumentation that are mentioned in the table 2.5 that give a summary about the models of instrumentation that used to get the results of this study and shows the references of methods for measurements and a references of each one in studies published for soil analysis uses.

Table 2.5: Synopsis for instrumentations techniques that used in this study research.

Instrumentation	Model No.	Method reference	References
Fluorescence spectroscopy (FS)	NanoDrop ND3300	NanoDrop 3300 Fluorospectrometer, User's Manual (Manual,2008)	(Zsolnay *et al.*,1999) (Rinnan and Rinnan,2007) (Milori *et al.*,2006)
Inductively coupled plasma-mass spectrometry (ICP-MS)	Agilent Technologies 7500	(Agilent Technologies,2005)	(Balcaen *et al.*,2015) (Jaber *et al.*,2009) (Olesik John,1996) (Profrock and Prange,2012)
X-ray spectroscopy : X-ray Diffractometer (XRD) X-Ray Fluorescence (XRF)	XRF -1800 Sequential X-Ray Fluorescence , Shimadzu XRD-7000 MAXIMA	(Bernick *et al.*,1995)	(Bertsch *et al.*,1994) (dos Anjos *et al.*,2000) (Revenko Anatoly,2002)
ATR-FTIR spectroscopy	Thermo Fisher Scientific ATR-FTIR spectroscopy	(Schuttlefield and Grassian,2008)	(Schuttlefield and Grassian,2008)

Spectroscopic techniques have many advantages such as they do not need a costly and time-consuming sample processing also they do not used any harmful materials of environment like for example chemical extracts. The application of spectroscopic techniques versus between the agricultural products analysis, food product analyses, polymers and wool analyses, biomedical, process analysis and pharmaceutical. In addition, the applications in cereals products, meat, fruit, dairy products and milk, fish and vegetable confectionery. (Valdes *et al.*,1997)

Infrared spectroscopy, in particular, consider as more accurate than traditional method of soil analysis and more straightforward. ((Reeves *et al.*,2001)). For example, McCauley et al. (1993) suggested that "infrared spectroscopy may be more accurate than dichromate digestions for analysis of soil organic carbon" (McCauley *et al.*,1993). Precisely, FTIR spectroscopy used in soil applications for the identification of specific functional groups or chemical compounds of soil molecules. ((Johnston and Aochi,1996); (Haberhauer and Gerzabek,2001))

Fluorescence spectroscopy with compared to FTIR spectroscopy is the greater sensitivity achieved for samples that because the zero background of fluorescence signals and this advantage make it able to work at low concentrations. Furthermore, FS used in soil application for study the molecules electronic structure and for quantitative measurements

because of its sensitivity for fluorescent compounds in soil molecules. (Herrmann and Onkelinx,1986).

The FS quantitative measurements depends on fluorescence quenching which can be defined as a bimolecular process that reduces the fluorescence intensity without changing the fluorescence emission spectrum; it can result from transient excited-state interactions (collisional quenching) or from formation of non-fluorescent ground-state species. Decrease of fluorescence intensity by interaction of the excited state of the fluorophores with its surroundings is known as quenching and is relatively rare. Quenching can occur in several mechanisms, collisional quenching occurs when exited state fluorophores are deactivated upon contact with some other molecule in sample, which is called quencher. Dynamic quenching and static quenching are the two types of quenching can they distinguished by different ways. (Turro, 1991).

Stern-Volmer equation can described the quenching mechanism which state that:

$$\frac{F_0}{F} = 1 + K_q \tau_0 \ (L) = 1 + K_{sv} \ (L) \qquad 2.11$$

Where:

F_0 is fluorescence intensity in the absence of quencher,
F is fluorescence intensity in the presence of quencher,
K_q is quenching constant
τ_0 is fluorescence lifetime without quencher
K_{sv} is Stern-Volmer constant for fluorophoreor sensitivity to a quencher
L is the quencher concentration

With Quenching the decrease in intensity is given by modified Stern-Volmer equation for binding constant:

$$\frac{1}{F_0 - F} = \frac{1}{F_0 KL} + \frac{1}{F_0} \qquad 2.12$$

Where:

F_0 is fluorescence intensity in the absence of quencher,
F is fluorescence intensity in the presence of quencher,
K is binding constant,
L is the quencher concentration.

The quenching constant indicates the sensitivity of the fluorophores to the quencher. There are a wide variety of molecules that acts as a collisional quencher such as oxygen, halogen, amines, and electron deficient molecules like acrylamide (Turro,1991).

X-ray Spectroscopy was used in soil applications to identify primary soil minerals such as feldspars, quartz and secondary soil minerals such as clays, silicates, aluminosilicates (Revenko Anatoly,2002)

ICPMS is an alternative technique in soil application used for measure soil nutrients elements, such as, Al, Li, B, Na, Mg, , Fe, Sr, Ba, TI, Pb, Bi, K, Cr, Mn, Co, Ni, Cu, Zn, Mo. (Olesik John,1996)

Chapter Three:

Experimental method

3.1 Site and sampling

Site

Soil samples were collected from a study area on the farm of Date Palm tree cultivation in Jordan Valley. The study will be carried out on about 7 years old date palm cultivars grown under condition of Al-Uja area (figure3.1). By considering part of the cultivated land as experimental site and another part as controlled site. The study area was in Saleh Njowm farm for Date Palm Tree cultivation (0735292 N, 3537655 E), 23 soil samples will collected from four different position in the farm: (P_1 from line No.2, P_2 from line No.14, P_3 form line No.21,P_4 from line No.29) (figure 3.2).

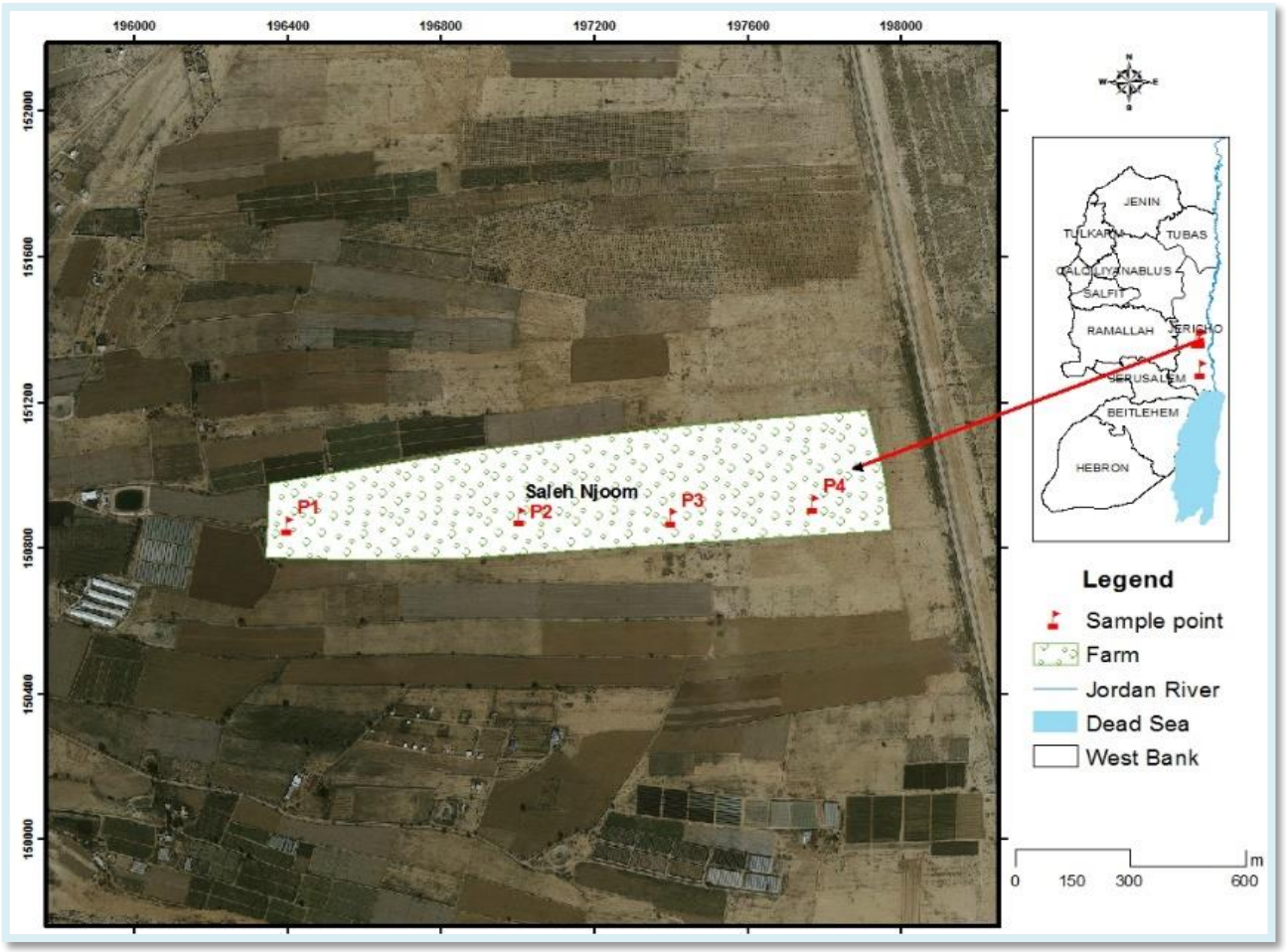

Figure 3.1: Map of Saleh Njoom farm for Date Palm Tree cultivation in Al-Uja

Figure 3.2: Lines of positions in Saleh Njoom farm for Date Palm Tree cultivation in Al-Uja.

Saleh Njowm farm for Date Palm Tree cultivation depends on drip irrigation system from 100m depth well water of EC value equal to 5.5 mS/cm in summer and 3.5 mS/cm in winter sessions, pH equal to 7.07, and with concentrations 500.76 mg/L, 85.83 mg/L, 100 mg/L, 409 mg/L for K, Na, Ca and Mg macronutrients of water respectively.

Sampling

From each line around 4 treated soil sample 20cm to 80 cm depth from the earth surface were collected, and a control sample were collected from each line in depth from 0-20 cm and 20-40cm. Soil treated samples with fertilizers addition were collected from 0-20 cm, 20-40 cm, 40-60 cm and 60-80 cm depth of equal 50cm distances from the trunk of the tree in Oct-Nov as one sample represented each depth from both sites. Table (3.1 and 3.2)

Table 3. 1: Treated soil samples

No.	Sample ID	Position	Line No.	Depth	Orientations
1	$N1D20P_1$	Position 1 (P_1)	Line No.2	0-20	X= 0735292 Y=3537655 Z= -280
2	$N2D40P_1$			20-40	
3	$N3D60P_1$			40-60	
4	$N4D80P_1$			60-80	
5	$N5D20P_2$	Position 2 (P_2)	Line No.14	0-20	X= 0735898 Y=3537692 Z= -290
6	$N6D40P_2$			20-40	
7	$N7D60P_2$			40-60	
8	$N8D80P_2$			60-80	
9	$N9D20P_3$	Position 3 (P_3)	Line No.21	0-20	X= 0736292 Y=3537696 Z= -285
10	$N10D40P_3$			20-40	
11	$N11D60P_3$			40-60	
12	$N12D80P_3$			60-80	
13	$N13D20P_4$	Position 4 (P_4)	Line No.29	0-20	X= 0736662 Y=3537742 Z= -295
14	$N14D40P_4$			20-40	
15	$N15D60P_4$			40-60	

N: Number of treated sample with fertilizers, D: Depth of sample, P: position of sample.

Table 3. 2: Control soil samples (without fertilizers)

No.	Sample ID	Position	Line No.	Depth	Orientations
16	$B1D20P_1$	Positon1 (P_1)	Line No.2	0-20	X= 0735292 Y=3537655 Z= -280
17	$B1D40P_1$			20-40	
18	$B2D20P_2$	Position 2 (P_2)	Line No.14	0-20	X= 0735898 Y=3537692 Z= -290
19	$B2D40P_2$			20-40	
20	$B3D20P_3$	Position 3 (P_3)	Line No.21	0-20	X= 0736292 Y=3537696 Z= -285
21	$B3D40P_3$			20-40	
22	$B4D20P_4$	Position4 (P_4)	Line No.29	0-20	X= 0736662 Y=3537742 Z= -295
23	$B4D40P_4$			20-40	

B: Blank samples without fertilizers treated, D: Depth of sample, P: Position of sample.

3.2 Lab methods analyses

In order to measure the electrical conductivity , pH values, macro elements for control samples, micro and macro elements for all samples and soil texture, soil samples were dried at room temperature and passed through a 2 mm sieve (figure 3.3) .With a 1:5 soil/water ratio soil extraction suspension was prepared where 25mL D.W was added to 5gm of soil from each sample and shacked to mix for one hour, then it is used to measure soil pH with a glass electrode pH meter (McLean,1982), and electrical conductivity (EC) by using a conductivity meter(Janzen,1993).

The soil electrical conductivity EC (1:5) is useful measure for assessing salinity but because the 1:5 soil: water ratio dilutes, EC (1:5) doesn't accurately measure the concentration of soluble salts in a solution likely to be encountered by a plant root. For this reason the EC of a saturated extract (EC_{SE}) is a better measurement for predicting plant response. Conventional laboratory methods for determining EC_{SE} are impractical in a commercial laboratory so mathematical relationships involving EC (1:5) and other soil parameters such as clay content, air-dry moisture content (ADMC) and chloride have been found to be a practical substitute for direct measurement. (Troeh and Thompson,1993) The equation for converting EC (1:5) to EC_{SE} is:

EC_{SE} (µS/m) = EC (1:5) (µS/m) x Conversion Factor 3.1

Figure 3.3: Soil samples dried at room temperature.

Eight different analytes were determined potassium, Na, Mg, Ca, Fe, Mn, Zn and Cu were determined and measured using ICPMS spectrometry by using the same soil extraction 1:5 soil/water. Standards were prepared for a range of concentrations encompassing expected sample concentrations. A minimum of 5mL of standard or sample was used for each run after Filtering samples with a 0.45 µm filter was added a 4. 2% by volume of super pure nitric acid (HNO3) to samples and standards.

Determination of Nitrogen for control samples by Digestion method for soil, while 1g of dry soil dried at 105°C, transferred into the digestion tube and added about 2g catalyst

mixture and 10mL concentrated sulfuric acid, then the tube rack placed in the block-digester and slowly increase temperature to about 380°C and continue heating for 2 hours, then the tube cooled to 50-60°C. Then the digest transferred into the distillation tube and added a 25mL boric acid 4% with 50mL distilled water and 50mL NaOH 35% and started distillation for 5 minutes. Then 5 drop of indicator solution was added and finally the distillate was titration with standardized sulfuric acid (H_2SO_4) solution.

Determination of exchangeable phosphorus in control samples by Oslen method for soil, while 5g of soil added to 50mL 0.5M sodium bicarbonate solution the the solution filtered by using No.40 filter paper. Then a series of standard solution from the diluted stock solution was prepared as follows: Dilute 1,2,3,4 and 5mL. These solution contained 2,4,6,8 and 10 ppm P, respectively. By taking 2mL from each standard and proceed as for the samples and added a 10mL 0.5 $NaHCO_3$ solution with 0.5mL P-nitro phenol; and added a 1mL sulfuric acid 5N until reach the pH 5.0 and added the acid to all unknown. Then by adding 8mL mixed reagent to all standard and samples and use spectrophotometer to read the absorbance at 720nm wavelength. After use a calibration curve for standard we can read the P concentration in the unknown samples.

Determination of exchangeable potassium in control samples by added 50mL ammonium acetate solution to 5g of dry soil and shake for 30 minutes on shaker then transfer the solution to centrifuge tube and spin at 2400 rpm for 10 min then used the flame photometer to measure the sample (soil extract) in order to take the emission reading and then used the calibration curve to read the K concentration for unknown samples.

Determination of soil texture by hydrometer method. In this method the soil particles are dispersed with a sodium metaphosphate (calgon) and then agitated. After dispersion, the amount of each particle group (sand, silt, clay) are determined by using a hydrometer. The hydrometer measures the amount of particles in suspension. The principal of Stokes law, which states that particles will fall out of suspension at different rates over time, based on particle size, is used to determine the amount of each particle size present in a soil. The amount of each particle fraction, sand, silt and clay, determines the soil texture.

3.3 Preparation of transparent IR disk

In order to measure the soil samples on FTIR spectrophotometer was essential to prepare IR disk, each 1mg of soil samples was added to 100 mg of KBr using a mortar and pestle. (Figure 3.4) And then a mechanical pressed technique that shown in figure 3.5 was used to compress the powder in order to get a transparent IR disk. Three disks were prepared for each sample in order to measure an average spectra foe each one sample. (Figure 3.6)

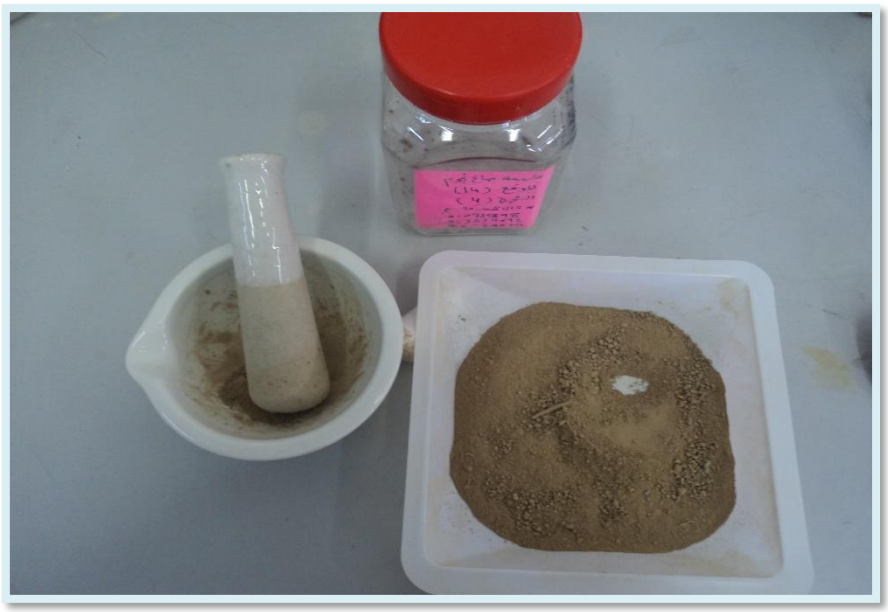

Figure 3. 4:1mg of soil samples was added to 100 mg of KBr using a mortar and pestle

Figure 3.5: Mechanical pressed technique and KBr.

Figure 3.6: Transparent IR disk samples

3.4 Control Experiment

Control experiment was carried out in water and environmental lab in al-Quds University in order to make a simple simulation of that of field with soil and nutrition's fertilizers addition, the reason of this experiment was to make a big understanding of the relation between fertilizers concentration addition and soil. This experiment was based on laboratory preparation of different concentrations of fertilizers, which called liquid feed solutions. Control soil samples No.16, 18, 20 and 22 were used in this experiment using florescence and ATR-FTIR spectroscopes. By deciding which fertilizers are to be used as nitrogen, phosphorus and potassium sources Urea, potassium nitrate and phosphoric acid have been chosen respectively for this experiment. (Table 3.3)

Table 3. 3: Control experiment soil samples with different concentration of fertilizers.

Sample ID	No. of feed solution	Fertilizers total Con.	K Con.	P Con.	N Con.
$B1D20P_1$	F0P1	Blank	550.22 mg/L	49.37 mg/L	0.308 %
	F1P1	380 mg/L	156 mg/L	30 mg/L	200 mg/L
	F2P1	270 mg/L	100 mg/L	20 mg/L	150 mg/L
	F3P1	160 mg/L	50 mg/L	10 m/L	100 mg/L
	F4P1	85 mg/L	30 mg/L	5 mg/L	50 mg/L
	F5P1	32 mg/L	10 mg/L	2 mg/L	20 mg/L
$B1D20P_2$	F0P2	Blank	471.78 mg/L	35.30 mg/L	0.266 %
	F1P2	380 mg/L	156 mg/L	30 mg/L	200 mg/L
	F2P2	270 mg/L	100 mg/L	20 mg/L	150 mg/L
	F3P2	160 mg/L	50 mg/L	10 m/L	100 mg/L
	F4P2	85 mg/L	30 mg/L	5 mg/L	50 mg/L
	F5P2	32 mg/L	10 mg/L	2 mg/L	20 mg/L
$B1D20P_3$	F0P3	Blank	469.59 mg/L	29.49 mg/L	0.210 %
	F1P3	380 mg/L	156 mg/L	30 mg/L	200 mg/L
	F2P3	270 mg/L	100 mg/L	20 mg/L	150 mg/L
	F3P3	160 mg/L	50 mg/L	10 m/L	100 mg/L
	F4P3	85 mg/L	30 mg/L	5 mg/L	50 mg/L
	F5P3	32 mg/L	10 mg/L	2 mg/L	20 mg/L
$B1D20P_4$	F0P4	Blank	579 mg/L	14.81 mg/L	0.245 %
	F1P4	380 mg/L	156 mg/L	30 mg/L	200 mg/L
	F2P4	270 mg/L	100 mg/L	20 mg/L	150 mg/L
	F3P4	160 mg/L	50 mg/L	10 m/L	100 mg/L
	F4P4	85 mg/L	30 mg/L	5 mg/L	50 mg/L
	F5P4	32 mg/L	10 mg/L	2 mg/L	20 mg/L

F0: Blank samples without feed solutions, F_N: samples with feed solutions, P: position *1 per (%) = 10000mg/L.

Each control samples of depth 20 cm from the four positions was used in this experiment and 5 ml from different concentration were added into 10 gm of soil samples. Then dried at room temperature for three days to led the added water equilibrate in the soil. (Figure 3.7)

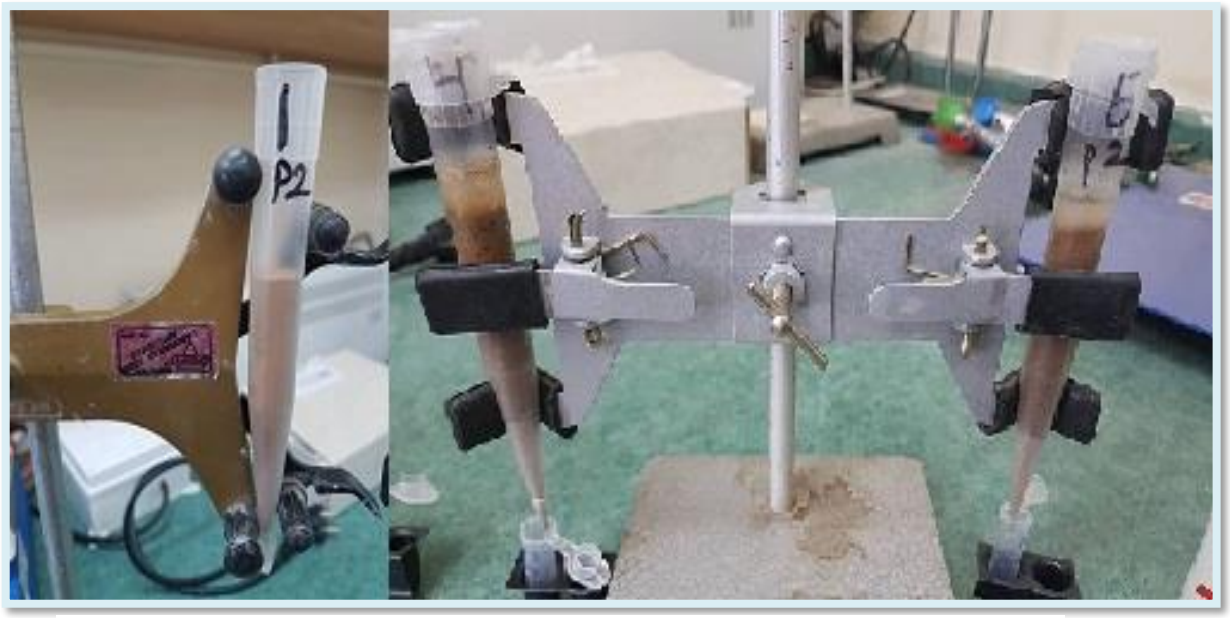

Figure 3.7: Control Experiment design

Preparation of liquid feed solution:

F1 feed solution with concentration 380 mg/L (0.0045M): is prepared from the following solvents:

- 312.7 mg Urea $CO(NH_2)_2$
- 404.1 mg Potassium nitrate (KNO_3)
- 73.2 ml Phosphoric acid (H_3PO_4)

F2 feed solution with concentration 270 mg/L (0.0032M): is prepared from the following solvents:

- 248 mg Urea {$CO(NH_2)_2$}
- 259 mg Potassium nitrate (KNO_3)
- 49 ml Phosphoric acid (H_3PO_4)

F3 feed solution with concentration 160 mg/L (0.0019M): is prepared from the following solvents:

- 178.26 mg Urea {$CO(NH_2)_2$}
- 129.53 mg Potassium nitrate (KNO_3)
- 24.38 ml Phosphoric acid (H_3PO_4)

F4 feed solution with concentration 85 mg/L (0.0010M): is prepared from the following solvents:

- 85.217 mg Urea {$CO(NH_2)_2$}
- 78 mg Potassium nitrate (KNO_3)
- 12.18 ml Phosphoric acid (H_3PO_4)

F5 feed solution with concentration 32 mg/L (0.00038M): is prepared from the following solvents:

- 35.65 mg Urea $\{CO(NH_2)_2\}$
- 25.90 mg Potassium nitrate (KNO_3)
- 4.87 ml Phosphoric acid (H_3PO_4)

3.5 Instruments that used in this study

1. FT-IR Spectrometer:

The FT-IR measurements were obtained on a Bruker IFS 66/S spectrophotometer.

2. ATR-FTIR Spectrometer:

The ATR measurements were obtained on Thermo Fisher Scientific ATR-FTIR spectroscopy

3. Fluorospectrometer:

The Fluorescence measurements were performed by a NanoDrop ND-3300 Fluoros-pectrophotometer.

4. ICPMS

The ICPMS measurements were taken by using ICP-MS Agilent Technologies 7500.

5. X-ray spectroscopy

XRF -1800 Sequential X-Ray Fluorescence. Shimadzu, Japan, Rhodium Target

X-Ray diffractometer, Shimadzu XRD-7000 MAXIMA

3.6 Data processing

Data Software's programing analysis

All the data that measured were analyst by using OPUS software, OriginPro 2015 and OMNIC software

3.6.1. Averaging:

The Averaging command in optic User (OPUS) software generates a new spectrum from a set of original spectra of the same type. The intensities of this new spectrum are calculated by averaging the intensities of the original spectra

Averaging means to calculate the arithmetic mean of $\bar{y}$ identity values included in n original spectra $\bar{y}=\frac{\sum_{i=1}^{n} y_i}{n}$

3.6.2. Baseline Correction:

To recognize the baseline; this is done by selecting a point from spectral points on the spectrum. Then adding or subtracting intensity value from the point or points to correct the baseline offset. Baseline correction task is used to bring the minimum point to zero. This is done by using Optic User Software (OPUS) and successfully removes most baseline offsets. (Figure 3.8).

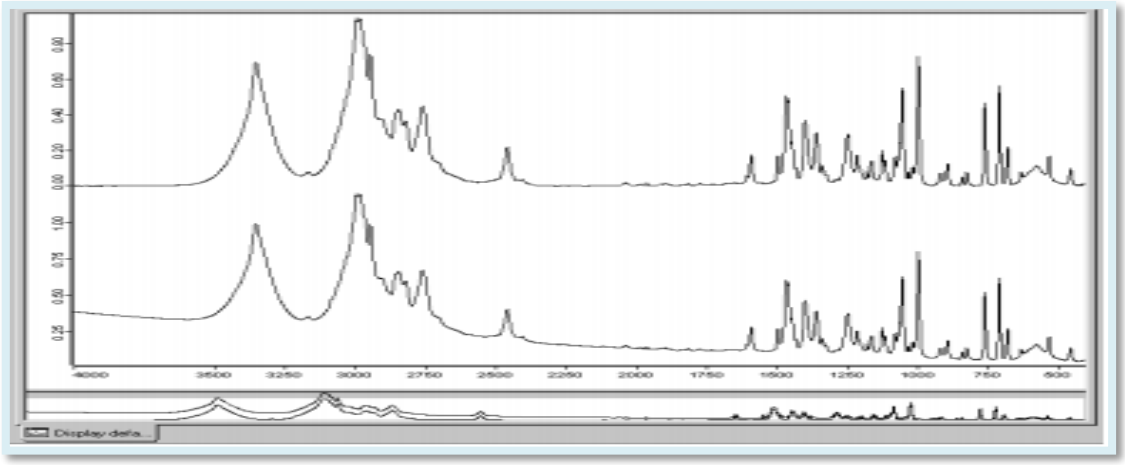

Figure 3.8: Shows an example of a baseline correction: the second spectrum is the original, whereas the first one is baseline corrected. (BRUKER OPTIK, 2004)

3.6.3. Smooth:

The Smooth command allows to smooth spectra by using Optic User Software (OPUS). The smoothing is based on the Savitzky-Golay algorithm. Possible values for smoothing points are between 5 and 25. Smoothing reduces noise but also distorts signal intensities.

3.6.4. Peak Analysis:

OriginPro 2015 64Bit provides several tools for peak analysis. With these tools, we can define and subtract baselines, find peaks, integrate peaks, and fit peaks. For specific in this study OriginPro 2015 64Bit was used for local extreme maximum and 2nd derivative for peak peaking analysis. There is 6 methods for finding peaks: 1. Local Maximum 2.Window Search 3.First Derivative 4. Second Derivative (for hidden peaks) 5. Residual after 1st Derivative (for hidden peaks) 6. Fourier Self Deconvolution.

Peak finding that is based on local extrema (maximum or minimum). The steps are as follows:

1. For every point on the input curve, Origin checks whether it is the extrema among all the points in the range, which centers in this point and has a length which is equal to the value of the Local Points variable. If it is, this point will be marked as the center of a candidate peak.

2. For every candidate peak, Origin further checks whether it meets the constraints specified in the Filter option. If this is true, this candidate peak will be considered a real peak and will be outputted in the result.

Peak finding that is based on Second Derivative Method of the data is capable of detecting local extrema in the raw data, which corresponds to peak positions of both ordinary and hi dden peaks. (figure 3.9)

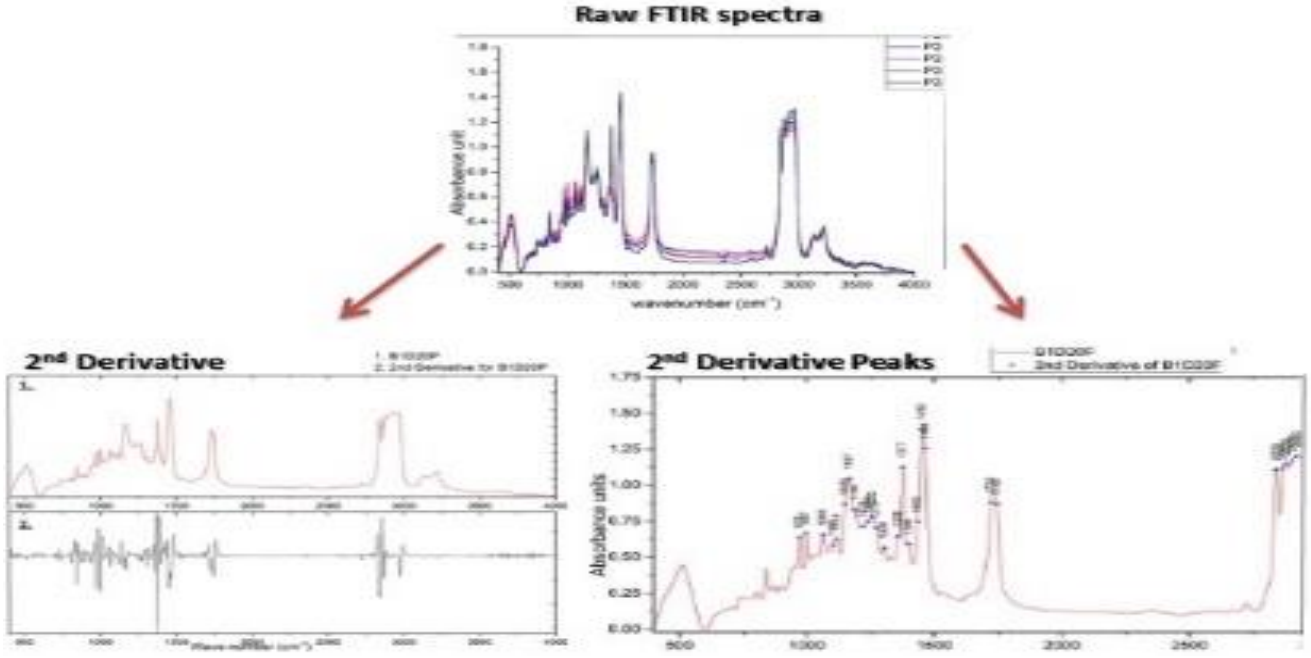

Figure 3.9: Visual effect of different pre-processing steps on a set of FTIR spectra. Common pre-processing sequences of 2nd derivative followed by finding spectra peaks using OriginPro 2015.

3.6.5. OMNIC software analysis:

OMNIC software is an advanced software package for ATR-FTIR spectroscopy that let to perform a wide range of tasks for collecting infrared spectra to preforming quantitative analysis. Figure 3.9 shows the visual pre-processing steps on ATR-FTIR spectra.

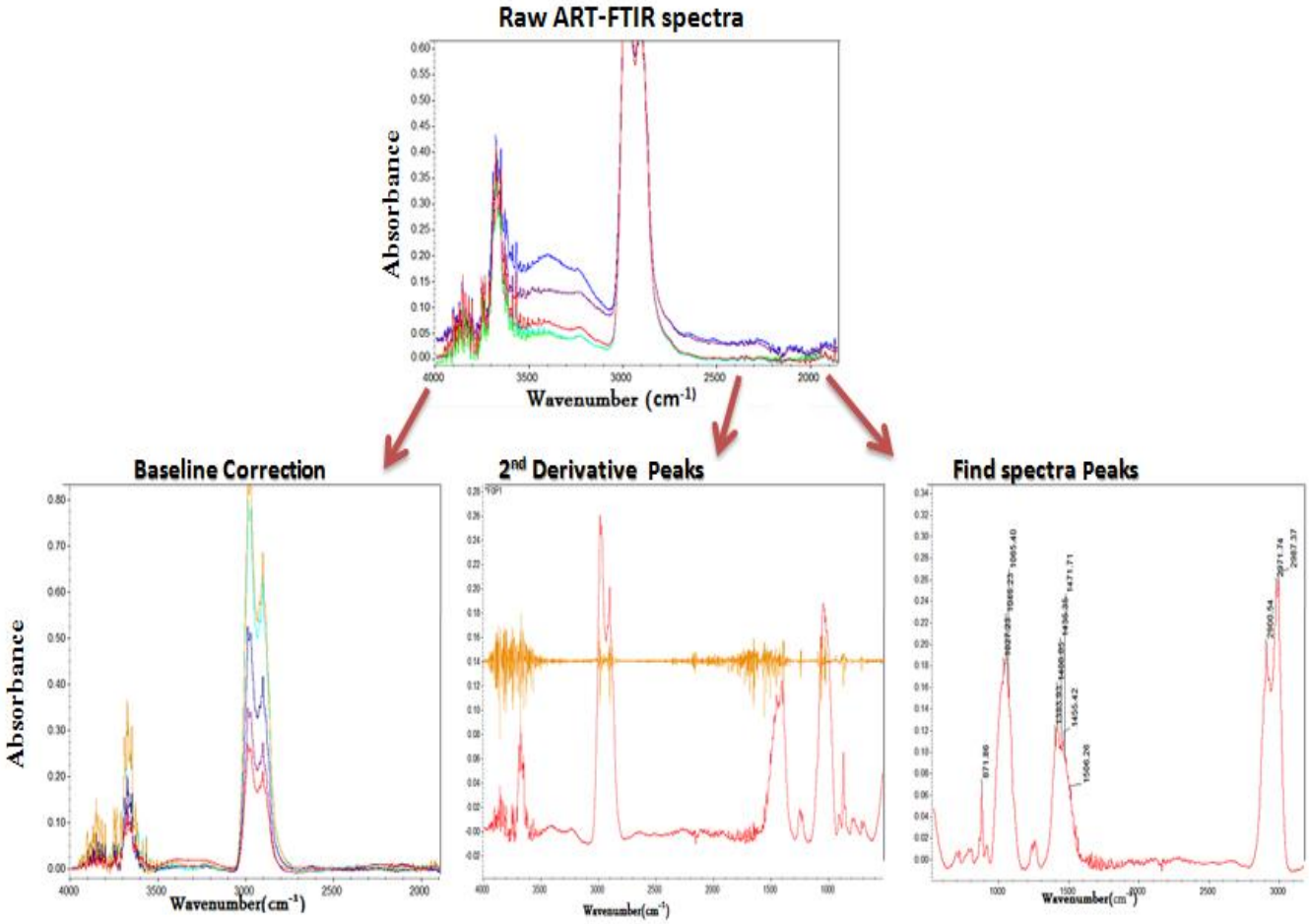

Figure 3.10: Visual effect of pre-processing steps on a set of ATR-FTIR spectra. Common pre-processing of rubber band baseline correction followed by finding 2nd derivative and spectra peaks using OMNIC software

Chapter Four:

Results and Discussion

This chapter includes the main results, analysis and discussions of different positions data. In the first section, spectrophotometric results for position one (P_1) samples are discussed and analyzed. The next section deals with spectrophotometric results for position two (P_2) samples. The third section about spectrophotometric results for position three (P_3) samples. In the fourth section, spectrophotometric results for position four (P_4) samples and data analysis are given and in the final we have an X-ray analysis for position one (P_1) and postion four (P_4) and in the last section we have the analysis for control experiment and finally the conclusion for all study results.

4.1 Position One (P_1) Results and Discussion

4.1.1. Chemical analysis of P_1 soil samples:

According to the tentative values of the soil characterization and available nutrient concentration by (Hummel, Gaultney *et al.*,1996) ,(Kalra,1971) data presented in Table (1) indicate that the soil was sandy loam in texture.

Table 4. 1: EC., pH and soil type texture of Position one (P_1) soil samples.

Sample ID / Soil Tests	B1D20P_1	B1D40P1	N1D20P_1	N2D40P_1	N3D60P_1	N4D80P_1	Soil type: **Sandy Loam** Of texture:
Depth (cm)	0-20	20-40	0-20	20-40	40-60	60-80	Sand % 56.00
EC. (1:5) (µS/cm)	509	565	1311	577	675	923	Silt % 30.04
Convert EC.(1:5) to EC_{SE} by multiplied of factor then divided by 1000 for mmhos/cm							
$EC._{SE}$ (mmhos/cm)	5.45	6.04	14.03	6.17	7.22	9.88	Clay % 13.96
pH (1:5)	7.00	7.54	7.81	8.12	8.35	8.22	
Nitrogen (%)	0.308	0.280					
Phosphorus (ppm)	49.37	43.56					
Potassium (ppm)	550.2	474.91					

Using equation 3.1 for converting EC (1:5) to EC_{SE} where the Conversion Factor is derived from clay content, in this case for sandy loam with 13% clay content the factor = 10.7 ,

According to the values that showed in table 4.1, values of soil EC and pH indicated that the soil of position No.1 is saline soils, which have an electrical conductivity EC of their saturated extract higher than 4 mmhos/cm at 25C° and pH less than 8.5. (Kalra,1971)

Saline soil is usually as result of high evaporation, using of high salt content water irrigation and very poor drainage system. However saline soil is common in date plantations. (Hummel, Gaultney *et al.*,1996).

Data also showed that control samples suffers from excessive range of phosphorus and high value of potassium and medium amount of nitrogen, a high availability of nutrient in the soil dose not necessary mean that the plant can extract enough of that nutrient to meet its need. This means that the nutrients in the soil are imbalanced and this will made the plant cannot absorbed its needed amount. According of rating values shown in table A.1(a) in Appendix A (Adjei-Nsiah et al.,2007).

4.1.2. ICPMS analysis of P_1 soil samples:

Macro elements such as potassium(K^+), sodium(Na^+), magnesium(Mg^{2+}) and calcium(Ca^{2+}) were determined and measured using ICPMS spectrometry by using soil extracting 1:5 soil/water ratio for position one soil samples. Table 4.2 shows data soil analysis of the soil samples. The tentative rating values of soil fertility status presented in appendix A (Table A.1 (b))

Table 4. 2: Extractable macroelements soil data analysis of position one samples

Sample ID / Analysis	B1D20P1	B1D40P1	N1D20P_1	N2D40P_1	N3D60P_1	N4D80P_1
Depth(cm)	0-20	20-40	0-20	20-40	40-60	60-80
Extractable Macroelements (mg/100g)						
K^+	26.7 M	26.9 M	16.9 L	6.6 VL	7.1 VL	8.8 VL
Na^+	9.9 VL	9.9VL	66.8 VH	36.9 H	48.8 H	68.9 H
Mg^{2+}	3.4 VL	4.3 VL	11.3 L	2.8 VL	2.6 VL	3.0 VL
Ca^{2+}	3.1 VL	2.8 VL	3.6 VL	1.5 VL	1.8 VL	1.6 VL

B: Blank sample, N: Number of treated sample, D: Depth of sample, P: Position of sample, VL= Very low, L=Low, M=Medium, H=High, VH= Very High (Ankerman and Large,1974)

Table 4.2 presented data of macroelement for position one (P_1) samples, tables showed that the control samples were contained a very low amount of macro elements except potassium that was in a medium range, and also it showed that the treated samples with fertilizers application in the field from the farmer have higher amount of macronutrients than control sample -that without fertilizers application- and data indicate that the most higher concentration was in depth 20 cm which in the surface of field soil but it still in low range except sodium concentration. The highest Na^+ concentration expected to be as a result of evaporation of excess of irrigated water. (Figure 4.1)

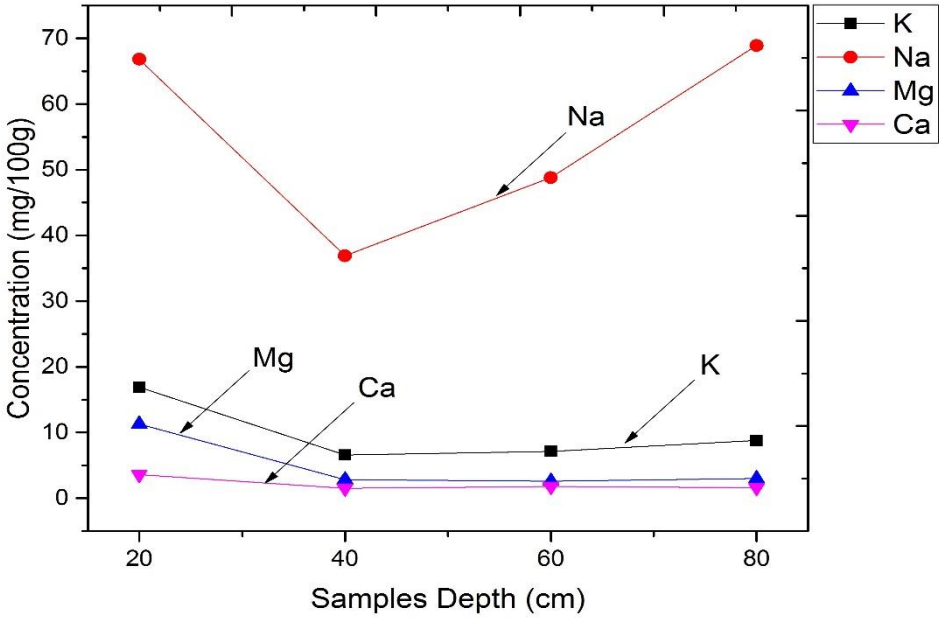

Figure 4.1: Extractable macro elements soil of position one (P_1) treated samples

Microelements such as Iron(Fe^{3+}), Manganese(Mn^{2+}), Copper(Cu^{2+}) and Zinc(Zn^{2+}) were also measured by using ICPMS spectrometry for the same soil extracting 1:5 soil/water ratio for position one soil samples. Table 4.3 shows data soil analysis of the soil samples.

Table 4. 3: Extractable microelements soil data analysis of position one samples

Sample ID / Analysis	B1D20P1	B1D40P1	N1D20P_1	N2D40P_1	N3D60P_1	N4D80P_1
Depth(cm)	0-20	20-40	0-20	20-40	40-60	60-80
Extractable Microelements (ppm)						
Fe^{3+}	3.73 VL	3.8VL	3.88 VL	2.81 VL	2.52 VL	2.59 VL
Mn^{2+}	0.05 VL	0.07VL	0.10 VL	0.19 VL	0.017 VL	0.019 VL
Cu^{2+}	0.12 VL	0.85 L	0.09 VL	0.08 VL	0.11 VL	0.051 VL
Zn^{2+}	0.54 L	0.47L	0.62 L	0.39 VL	0.35 VL	0.71 L

B: Blank sample, N: Number of treated sample, D: Depth of sample, P: Position of sample, VL= Very low, L=Low, M=Medium, H=High, VH= Very High (Ankerman and Large,1974)

Table 4.3 presented data of microelement for position one samples, tables showed that all samples depth contained a very low amount of microelements. There were no different between 20cm and 40cm control samples, data indicate that the soil of position one (P_1) was very poor and this may be because of that there is a general believed between farmers that date palm tree does not need microelements fertilizers addition.

4.1.3. Fluorescence analysis of P_1 samples :

NanoDrop ND-3300 Fluoros-pectrophotometer was used for study the relation between soil samples and added fertilizers from farmer in the field at different depths. Figure 4.2 shows fluorescence of soil samples were quenched in a depth dependent. Fluorescence spectrum exhibiting the peak maximum at 450 and the intensity decreases as the depth increased. The peak positions shows little or no change at all.

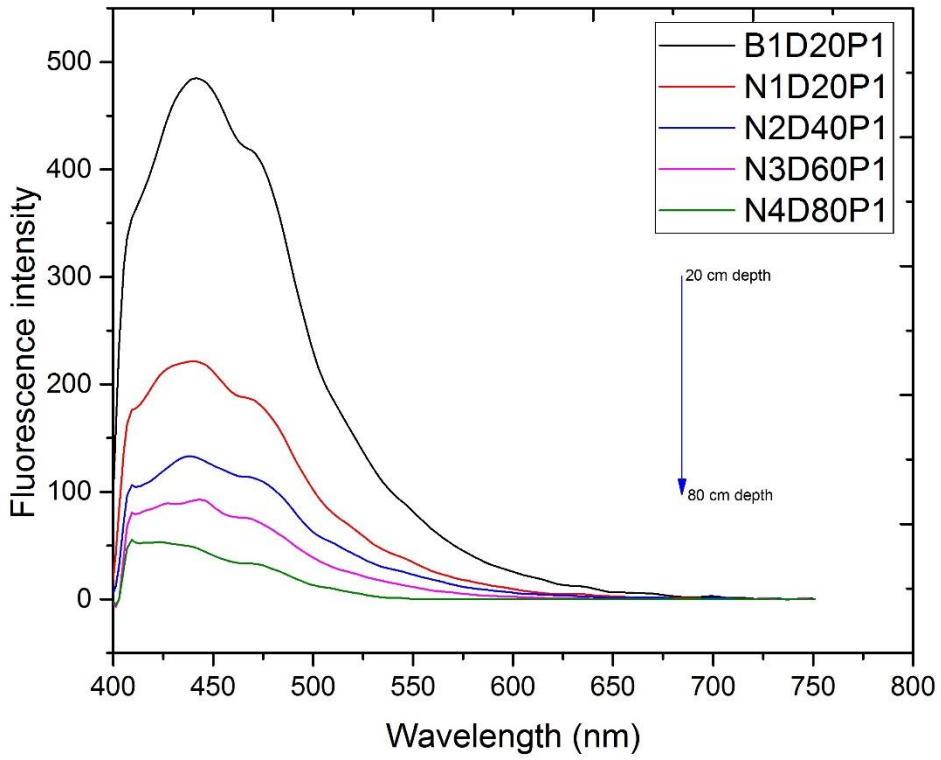

Figure 4.2: fluorescence spectra of P_1 soil's samples at increasing depths

As mentioned before, quenching can occur in several mechanisms, collisional quenching occurs when exited state fluorophores are deactivated upon contact with some other molecule in sample, which is called quencher, and then form a complex molecules which caused the intensity reduction because this quensher prevent the absorption of light to happen. Which in other word mean that there was an interaction between soils and such quencher may be fertilizers or oxides or other variables presents in soil at different depths and strong interaction on the longest depth 80 cm.

4.1.4. FTIR analysis of P_1 samples:

The soil mid infrared spectrum 400-4000cm^{-1} is divides in to three regions and the nature of group frequency can determined by the region in which it is located. These regions are: fingerprint region (650-1500 cm^{-1}), Triple-bond stretching region (1500-2500 cm^{-1}) and fundamental vibration region (2500-4000 cm^{-1}). Figure 4.3 shows the FTIR spectra of position one samples.

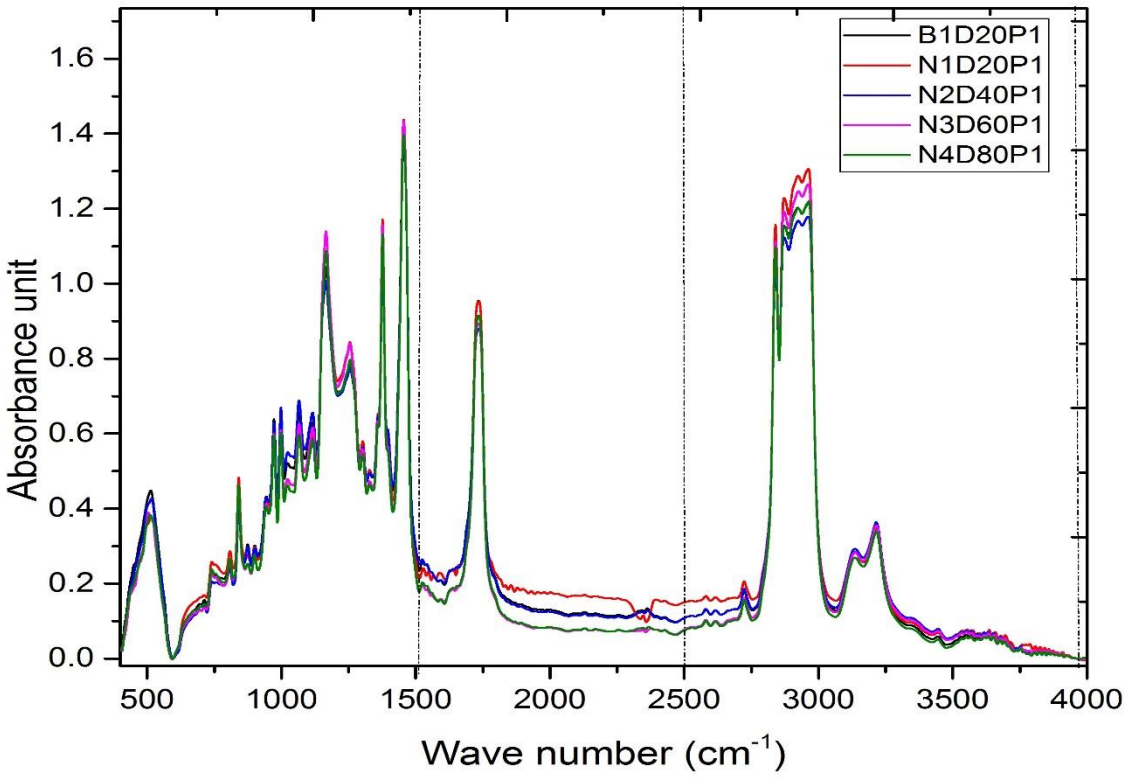

Figure 4.3: FTIR spectra of position one samples (400-4000 cm-1).

As assumed that each band in IR region spectrum can assigned to a specific deformation of molecular vibration, the stretching or bending of bonds, the movements of group of atoms, many vibrations vary by hundreds of wavenumbers, and these most bending or skeletal vibrations, which absorb in finger print region. Principal bands in 1500-2500 cm^{-1} region are as a result of C=C and C=O stretching. The last fundamental region is due to O−H, C−H and N−H stretching.

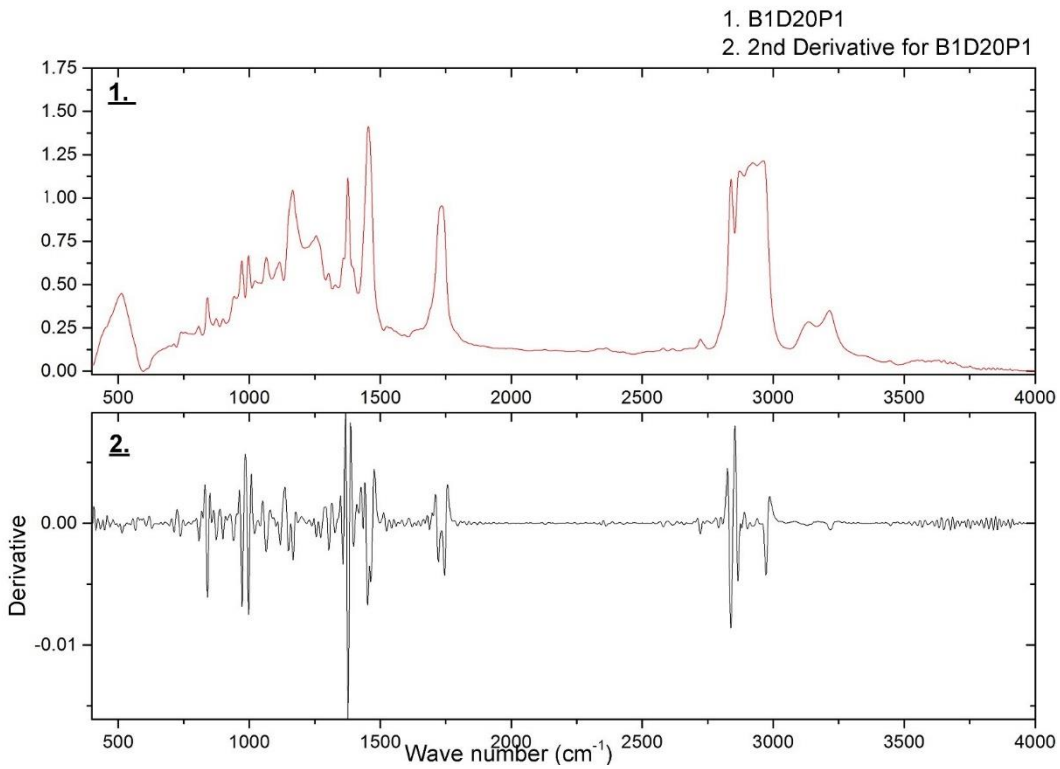

Figure 4.4: 2nd derivation peak analysis for position one control sample (B1D20P1).

By 2nd derivation peak analysis of using OriginPro 2015 (figure 4.4) and according to (Calderón *et al.*,2011b, Demyan *et al.*,2012) the Assignments of the main bands observed in the MIR spectra of soil shown in table 4.4.

2nd derivation peak analysis for position one soil samples are shown, and 2nd derivative assignments of the main bands observed in the FTIR spectra of all samples are shown in Appendix B.

Table 4. 4: Band assignments in the FTIR spectra of soil (Calderón et al.,2011b, Demyan et al.,2012)

Band Regions (cm^{-1})	Functional group or chemical ponds	Peak position (cm^{-1})
2500-4000	O-H stretches	3700-3600
	C-H stretches	3000-2850
	N-H stretches	3400-3300
2000-2500	C≡C stretches	2300-2050
	C≡N stretches	2300-2200
1500-2500	C=C stretches	Around 1650
	C=O stretches	18030-1650

After scan the spectrum from left to right and use the peaks ranges in table 4.4 to quickly determine whether certain important functional groups are present or absent in soil samples at different depths, table 4.5 showed the observable peaks in the all soil samples, as showed in spectrum plot, there is no significant peaks between 2000 and 2500 cm^{-1} which means the sample does not contain any C≡C, C≡N bonds, also the there is no O-H bond between 3600-3700 and that may be because the samples where dried at room temperature.

As a notation IR spectrum is not a democracy and not all peaks are created equal, some peaks are useful and other are useless, thus table 4.5 shows the diagnostically useful peaks.

Table 4.5: 2nd derivative assignments of the main bands observed in the FTIR spectra for organic compounds of soil samples

Max. peak observed (cm^{-1})	$B1D20P_1$ peak intensity	$N1D20P_1$ peak intensity	$N2D40P_1$ peak intensity	$N3D60P_1$ peak intensity	$N4D80P_1$ peak intensity	peak Mean value	Functional group
Around 3300	-	-	-	-	-	3300	N-H weak stretching
2879.20	1.15	1.22	1.11	1.18	1.15	2898	C-H stretching
2971.76	1.16	1.22	1.12	1.19	1.16		
2838.70	1.11	1.16	1.06	1.11	1.10		
2902.34	1.17	1.25	1.13	1.20	1.17		
1722.12	0.88	0.88	0.90	0.83	0.84	1738	C=O stretching
1745.26	0.87	0.87	0.88	0.81	0.83		

B: Blank sample, N: Number of treated sample, D: Depth of sample, P: Position of sample.

Many functional groups have multiple peaks in MIR and tracking down as many peaks as possible for them raises the probability of correct interpretation, and table 4.5 shows these secondary beaks. Each IR spectrum can give a useful information from peaks position, intensities, widths and shapes of each peak, for present study, all these variable keeps constant with no change except the peaks intensity, there was a difference between soil samples at different depths in peaks intensities and that what table 4.5 showed.

As shift in peak position usually means the hybridization state or electron distribution in the molecular bond has changed, the change in the peak intensity usually means a change in the amount (per unit volume) of the functional group associated with the molecular bond. Table 4.5 showed that the most intense band in the spectrum was at depth 20 cm soil samples at 2922 cm^{-1} and it is due to stretching of the C-H bond and the lower intense band of the same stretching bond was at depth 40 cm soil sample.

The weaker band in the spectrum was for small amount size peak near 3300 cm^{-1} which is indicating there are a N-H bonds in the samples. The highest intense C=O stretching was at 40 cm depth while the lower intense was at 60 cm depth. Finger print region has a small change in the peaks intensities however this region have difficulty interpretation.

4.2 Position Two (P_2) Results and Discussion

4.2.1. Chemical analysis of P_2 samples:

According to the tentative values of the soil characterization and available nutrient concentration by (Hummel, Gaultney *et al.*,1996) ,(Kalra,1971) data presented in Table 4.6 indicate that the soil was loam in texture.

Table 4. 6: EC., pH and soil texture of Position two (P_2) soil samples

Sample ID / Soil Tests	$B2D20P_2$	$B2D40P_2$	$N5D20P_2$	$N6D40P_2$	$N7D60P_2$	$N8D80P_2$	Soil Type: **Loam** Of texture:
Depth (cm)	0-20	20-40	0-20	20-40	40-60	60-80	Sand % 49.88
EC. (1:5) (µS/cm)	568	533	4130	4710	1898	2260	Silt % 32.48
Convert EC.(1:5) to EC_{SE} by multiplied of factor then divided by 1000 for mmhos/cm							Clay % 17.64
$EC._{SE}$ (mmhos/cm)	5.05	4.74	36.75	41.92	16.89	20.11	
pH (1:5)	8.04	8.14	6.97	7.27	7.76	7.78	
Nitrogen (%)	0.266	0.210					
Phosphorus (ppm)	35.30	29.49					
Potassium (ppm)	471.78	469.6					

B: Blank sample, N: Number of treated sample, D: Depth of sample, P: Position of sample.

The Conversion Factor is derived from clay content, in this case for loam with around 20% clay content the factor = 8.9 ,

According to the values that showed in table 4.6, values of soil EC and pH indicated that the soil of position two (P_2)is very strongly saline soils except the control samples, samples have an electrical conductivity EC of their saturated extract is extremely higher than 16 mmhos/cm at 25C° and pH less than 8.5 and this mean that this position has grate heat and much evaporation where the water evaporates quickly and salts are left on the top of soil and this is noticed in depth of 20-40 cm. as a result this salinity values affect negatively on the Date palm yield, (Kalra,1971) also data showed that control samples has high range of phosphorus and high value of potassium and medium amount of nitrogen (Adjei-Nsiah, Kuyper *et al.*,2007).

4.2.2. ICPMS analysis of P_2 samples:

Macro elements of soil extracting 1:5 soil/water ratio for position two soil samples. Table 4.7 shows data soil analysis of the soil samples.

Table 4. 7: Extractable macroelements soil data analysis of position two (P_2) samples

Sample ID / Analysis	$B2D20P_2$	$B2D40P_2$	$N5D20P_2$	$N6D40P_2$	$N7D60P_2$	$N8D80P_2$
Depth(cm)	0-20	20-40	0-20	20-40	40-60	60-80
Extractable Macroelements (mg/100g)						
K^+	12.2 VL	12.0VL	28.7 M	29.8 M	14.8 L	14.4 L
Na^+	29.8 M	29.9M	183.6 VH	239.8 VH	125.3 VH	143.8 VH
Mg^{2+}	3.3 VL	3.06VL	48.8 M	52.5 M	10.7 VL	13.5 L
Ca^{2+}	2.6 VL	2.9VL	17.3 VL	16.1 VL	3.2 VL	4.1 VL

B: Blank sample, N: Number of treated sample, D: Depth of sample, P: Position of sample, VL= Very low, L=Low, M=Medium, H=High, VH= Very High (Ankerman and Large,1974)

Table 4.7 showed that the control sample contained a very low amount of macro elements except sodium that was in a medium range, and also it showed that the samples with fertilizers application in the field from the farmer have higher amount of macronutrients than control sample. Sodium concentration were in very high concentration in treated soil sample which may indicate that may be there is no absorption of sodium from Date palm tank and that because of high salinity of soil. Potassium and magnesium were in medium range at the surface depth and low range between 60 and 80 cm, finally calcium were in very low range at all depth and that indicate that soil suffers from the lack of calcium. (Figure 4.5)

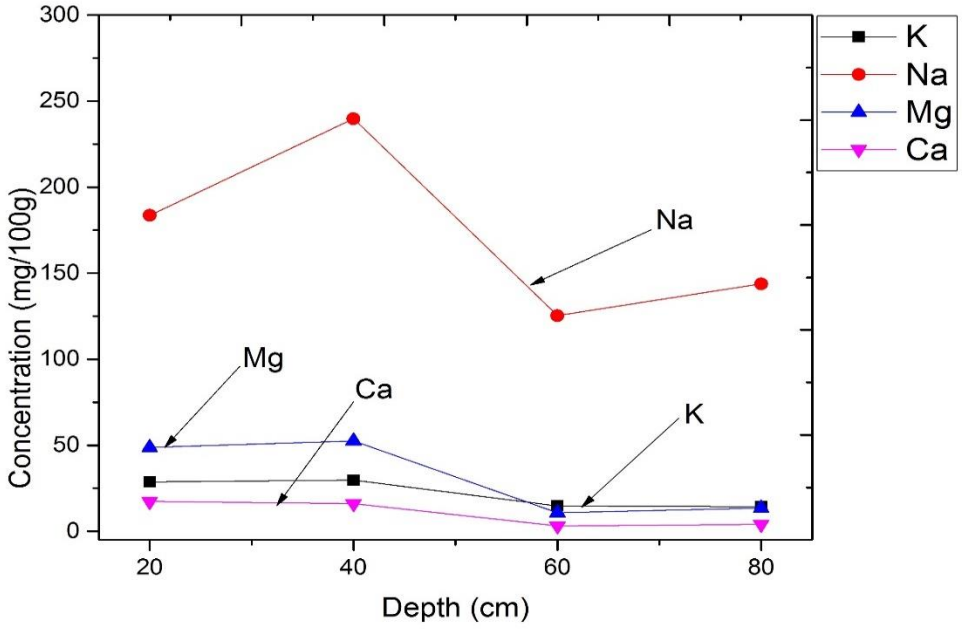

Figure 4.5: Extractable macroelements soil of position two (P_2) treated samples

Microelements for the same soil extracting 1:5 soil/water ratio for position two soil samples. Table 4.8 shows data soil analysis of the soil samples. Table 4.8 presented data of microelement for position two samples, tables showed that all samples depth contained a very low amount of microelements except treated samples at depth 20 and 40 which contain a medium and very high amount of Fe and Zn respectively. Data indicate that the soil of position two also was very nutrition poor.

Table 4. 8: Extractable microelements soil data analysis of position two (P_2) samples

Sample ID / Analysis	$B2D20P_2$	$B2D40P_2$	$N5D20P_2$	$N6D40P_2$	$N7D60P_2$	$N8D80P_2$
Depth(cm)	0-20	20-40	0-20	20-40	40-60	60-80
Extractable Microelements (ppm)						
Fe^{3+}	2.81 VL	3.6 VL	13.4 M	13.3 M	3.2 VL	4.04 VL
Mn^{2+}	0.024 VL	0.094 VL	0.11 VL	0.051 VL	0.014 VL	0.053 VL
Cu^{2+}	0.084 VL	0.026VL	0.217 VL	0.086 VL	0.11 VL	0.114 VL
Zn^{2+}	0.68 L	0.65L	2.59 VH	2.92 VH	0.56 L	0.53 L

B: Blank sample, N: Number of treated sample, D: Depth of sample, P: Position of sample, VL= Very low, L=Low, M=Medium, H=High, VH= Very High (Ankerman and Large,1974)

4.2.3. Fluorescence analysis of P_2 samples:

Figure 4.6 shows fluorescence of soil samples were quenched in a depth dependent except 20cm fertilizers soil. The peak positions shows little or no change at all, fluorescence spectrum exhibiting the peak maximum at 450 and the intensity decreases as the depth increased. The intensity of soil at maximum started at depth 20 cm then it is begin to quenched until depth 80 cm as strong interaction.

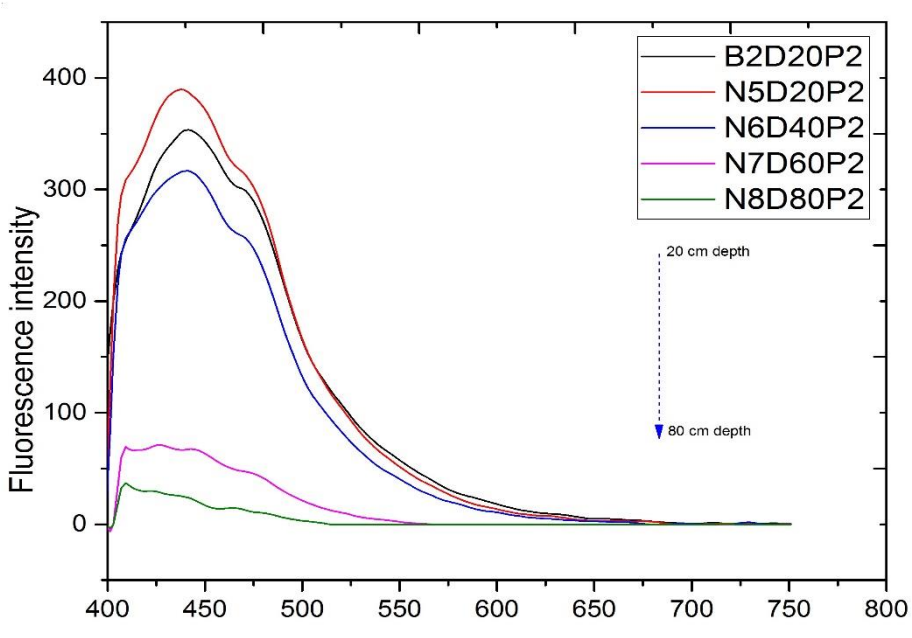

Figure 4.6: Fluorescence spectra of soil's samples at increasing depths.

4.2.4. FTIR analysis of P_2 samples:

Figure 4.7 shows the FTIR spectra of position two soil samples in IR region 400-4000cm^{-1} and figure 4.8 present the 2nd derivative of position two (P_2) control soil samples.

2nd derivation beak analysis for position two (P_2) soil samples, and 2nd derivative assignments of the main bands observed in the FTIR spectra of all samples are shown in appendix C

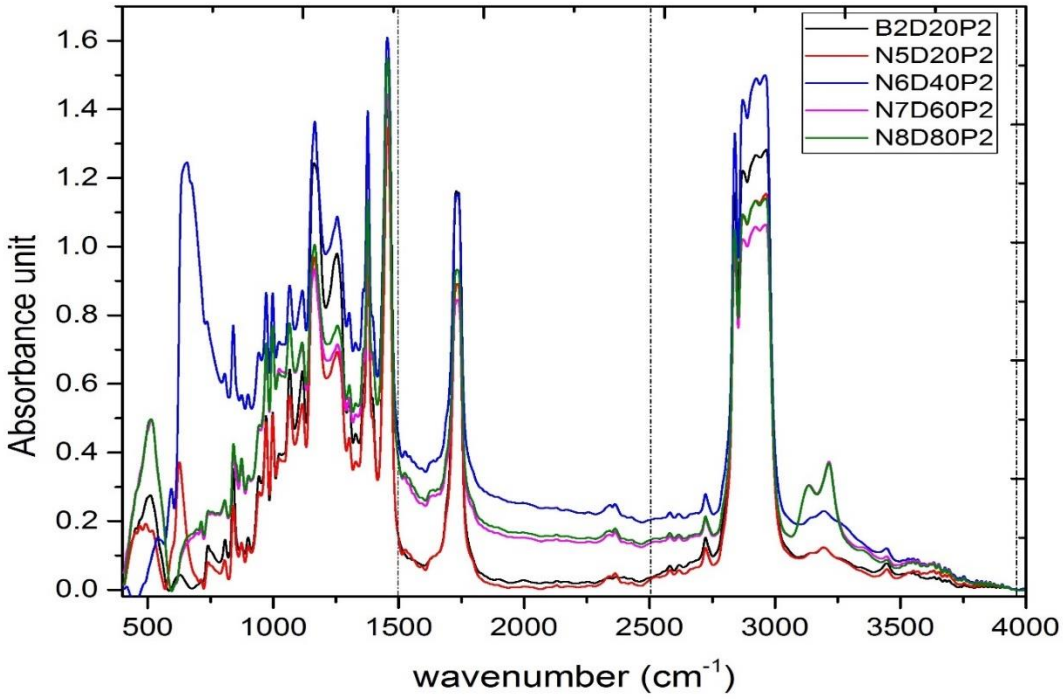

Figure 4.7: FTIR spectra of position two samples (400-4000 cm-1)

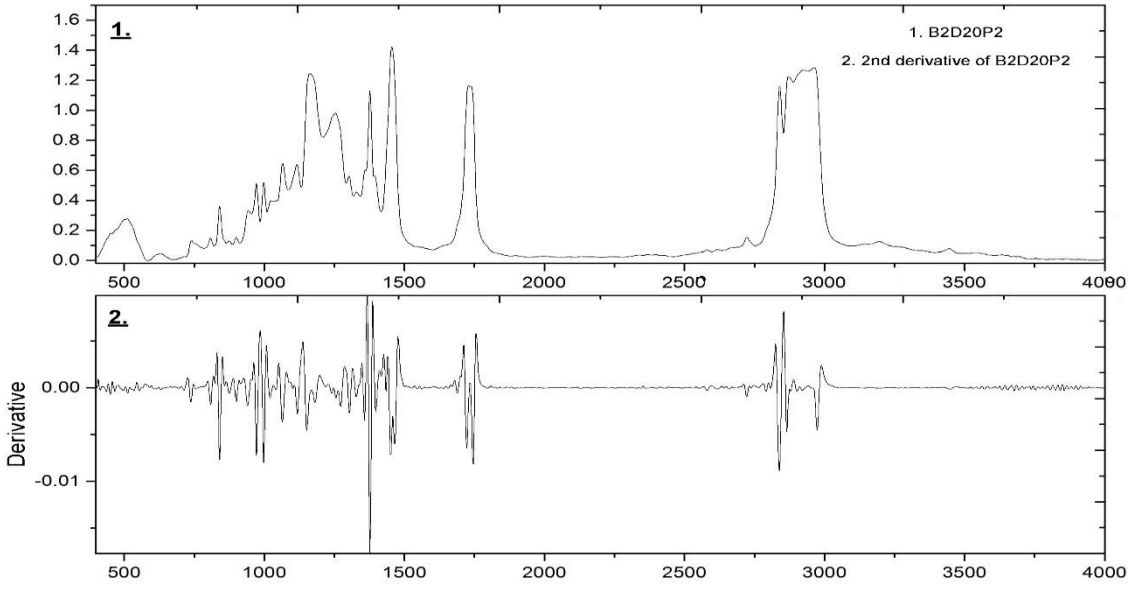

Figure 4.8: 2nd derivation peak analysis for position two control sample (B2D20P2).

Table 4.9 showed the result of observable peaks in the all soil samples, as showed in spectrum plot, as position one samples there is no significant peaks between 2000 and 2500 cm^{-1} which means the sample does not contain any C≡C, C≡N bonds, also the there is no O-H bond between 3600-3700.

Table 4. 9: 2nd derivative assignments of the main bands observed in the FTIR spectra for organic compounds of soil samples

Sample ID	B2D20P2	N5D20P2	N6D40P2	N7D60P2	N8D80P2	Functional group
peak (1) (cm-1)	2965.9	2964.0	2960.1	2962.1	2962.1	C-H stretching
peak intensity	1.28	1.15	1.49	1.06	1.14	
peak (2) (cm-1)	2923.5	2923.5	2925.5	2921.6	2921.6	
peak intensity	1.27	1.13	1.49	1.06	1.13	
peak (3) (cm-1)	2871.5	2871.5	2871.5	2871.5	2871.5	
peak intensity	1.22	1.09	1.43	1.02	1.09	
peak (4) (cm-1)	2838.7	2840.6	2840.6	2840.6	2838.7	
peak intensity	1.16	1.03	1.33	0.98	1.05	
peak (5) (cm-1)	1739.4	1731.8	1733.7	1733.7	1733.7	C=O stretching
peak intensity	1.16	0.89	1.15	0.84	0.93	

B: Blank sample, N: Number of treated sample, D: Depth of sample, P: Position of sample.

As assumed that many functional groups have multiple peaks in MIR and tracking down as many peaks as possible for them raises the probability of correct interpretation, table 4.9 showed the secondary beaks. For present study peaks position and intensities both were changed, there was a difference between soil samples at different depths in peaks intensities and peak positions. Table 4.9 showed that peak no. (1) at 2966 cm^{-1} of control sample was shifted to lower wavelength by max. 4 wavenumber of fertilizer samples and this called blue shift. And for peak no. (2) and peak no.(4) there was a small change shifted between control and fertilizers sample by max. 2 wavenumber, while peak (3) does not change in peak position. Peak (5) showed also a large shift to lower wavenumber from control samples to fertilizer samples by max. 7 wavenumber and this also called blue shift.

Most intense band in the spectrum was at depth 40 cm at all peaks positions and it is due to stretching of the C-H bond and the lower intense band was at depth 60 cm soil sample, the highest intense C=O stretching was at 20 cm control sample while the lower intense was at 60 cm depth. Which may be the reason of this behavior is the low amount of macro and micro elements at these depths.

4.3 Position three (P_3) Results and Discussion

4.3.1. Chemical analysis of P_3 samples:

According to the tentative values of the soil characterization and available nutrient concentration by (Hummel, Gaultney *et al.*,1996) ,(Kalra,1971) data presented in Table (4.10) indicate that the soil was loam in texture.

Table 4. 10: EC., pH and soil texture of Position three (P_3) soil samples.

Sample ID / Soil Tests	B3D20 P_3	B3D40 P_3	N9D20P_3	N10D40P_3	N11D60P_3	N12D80P_3	Soil type: **Loam** Of texture:
Depth (cm)	0-20	20-40	0-20	20-40	40-60	60-80	Sand % 48.68
EC. (1:5) (µS/cm)	5120	4220	987	848	999	2140	Silt % 34.40
Convert EC.(1:5) to EC_{SE} by multiplied of factor then divided by 1000 for mmhos/cm							Clay % 16.92
$EC._{SE}$ (mmhos/cm)	45.6	37.5	8.8	7.5	8.9	19.046	
pH (1:5)	7.8	7.7	8.5	8.5	8.5	8.2	
Nitrogen (%)	0.210						
Phosphorus (ppm)	29.49						
Potassium (ppm)	469.5						

B: Blank sample, N: Number of treated sample, D: Depth of sample, P: Position of sample.
The Conversion Factor is derived from clay content, in this case for loam with around 20% clay content the factor = 8.9 ,

According to the values that showed in table 4.10, values of soil EC and pH indicated that the soil is very saline soils for control samples, with electrical conductivity EC_{SE} is extremely higher than 16 mmhos/cm at 25C° and pH less than 8.5 this may be because of the accumulation of salts due to evaporation.

The other samples with fertilizers application have saline soils, which have an electrical conductivity EC of their saturated extract higher than 4 mmhos/cm at 25C° and pH less than 8.5. (Kalra,1971) Data also showed that control sample has high range of phosphorus and high value of potassium and medium amount of nitrogen also can be interpreted by highly concentrated water irrigation. (Adjei-Nsiah, Kuyper *et al.*,2007).

4.3.2. ICPMS analysis of P_3 samples:

Macro elements of soil extracting 1:5 soil/water ratio for position three (P_3) soil samples. Table 4.11 shows data soil analysis of the soil samples.

Table 4. 11: Extractable macroelements soil data analysis of position three samples.

Sample ID / Analysis	$B3D20P_3$	$B3D40P_3$	$N9D20P_3$	$N10D40P_3$	$N11D60P_3$	$N12D80P_3$
Depth(cm)	0-20	20-40	0-20	20-40	40-60	60-80
Extractable Macroelements (mg/100g)						
K^+	32.5 H	31.5H	13.02 L	12.1 L	11.9 L	19.84 L
Na^+	205.3 VH	175.8 VH	65.95 VH	62.4 VH	73.5 VH	159.4 VH
Mg^{2+}	62.9 M	36.87M	4.8 VL	3.7 VL	3.34 VL	11.94 L
Ca^{2+}	23.6 VL	11.8 VL	1.8 VL	1.7 VL	1.44 VL	3.6 VL

B: Blank sample, N: Number of treated sample, D: Depth of sample, P: Position of sample, VL= Very low, L=Low, M=Medium, H=High, VH= Very High (Ankerman and Large,1974)

Table 4.11 presented data of macroelement for position three (P_3) samples, tables showed that the treated samples were contained a range of low amount of macro elements. While it showed that the control samples have higher amount of macronutrients except calcium. Calcium were in very low range at all depth and that indicate that soil suffers from the lack of calcium as previous positions. (Figure 4.9)

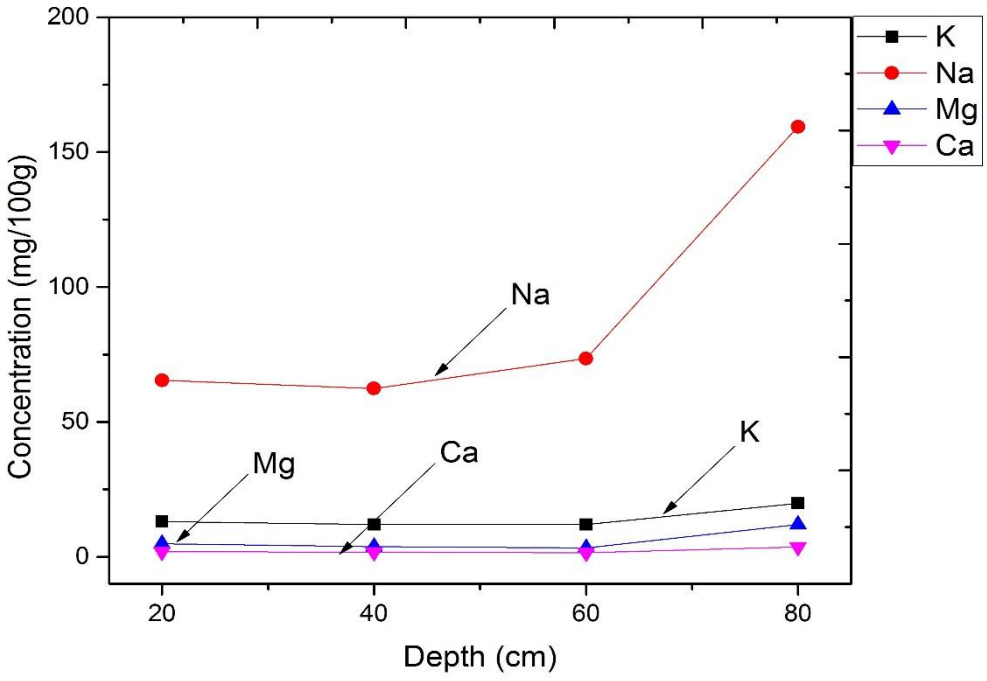

Figure 4.9: Extractable macroelements soil of position three (P_3) treated samples.

Microelements for the same soil extracting 1:5 soil/water ratio for position three soil samples. Table 4.12 shows data soil analysis of the soil samples. Table 4.12 presented data of microelement for position three samples, tables showed that all samples depth contained a very low amount of microelements except control samples which contains a medium and high amount of Iron. Data indicate that the soil of position three also was very nutrition poor. The lack of Iron, Manganese and Zinc causing the death of palms within period of 5-7 years because of a disease of broken leaves.

Table 4. 12: Extractable microelements soil data analysis of position three samples

Sample ID / Analysis	$B2D20P_3$	$B2D40P_3$	$N9D20P_3$	$N10D40P_3$	$N11D60P_3$	$N12D80P_3$
Depth(cm)	0-20	20-40	0-20	20-40	40-60	60-80
Extractable Microelements (ppm)						
Fe^{3+}	19.9 H	11.5 M	3.1 VL	3.03 VL	2.6 VL	4.4 VL
Mn^{2+}	0.08 VL	0.04 VL	0.02 VL	0.06 VL	0.02 VL	0.04 VL
Cu^{2+}	0.06 VL	0.06 VL	0.06 VL	0.09 VL	0.04 VL	0.06 VL
Zn^{2+}	0.8 L	0.7 L	0.99 L	0.8 L	0.8 L	0.93 L

B: Blank sample, N: Number of treated sample, D: Depth of sample, P: Position of sample, VL= Very low, L=Low, M=Medium, H=High, VH= Very High (Ankerman and Large,1974)

4.3.3. Fluorescence analysis of P_3 samples:

Figure 4.10 showed fluorescence spectra of soil samples of position three (P_3) were quenched in a depth dependent. The peak positions shows little or no change at all, fluorescence spectrum exhibiting the peak maximum at 450 and the intensity decreases as the depth increase. The intensity of soil at maximum started at depth 20 cm then it is begin to quenched until depth 80 cm as strong interaction.

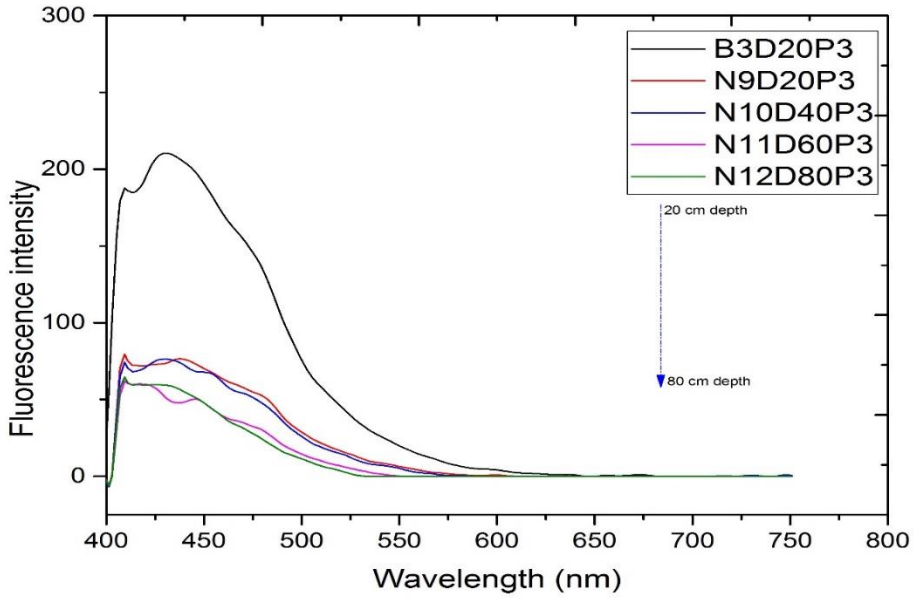

Figure 4.10: Fluorescence spectra of soil's samples at increasing depths.

4.3.4. FTIR analysis:

Figure 4.11 show the FTIR spectra of position three soil samples in IR region 400-4000cm^{-1}

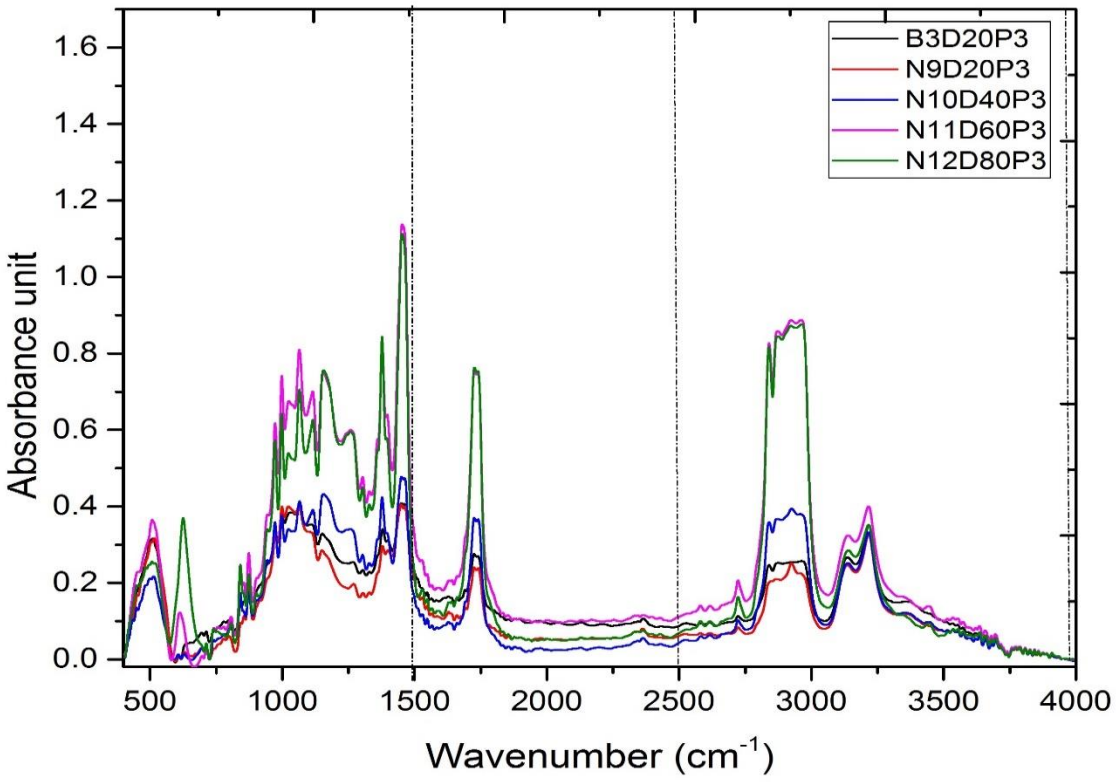

Figure 4.12: FTIR spectra of position three samples (P_3) (400-4000 cm-1)

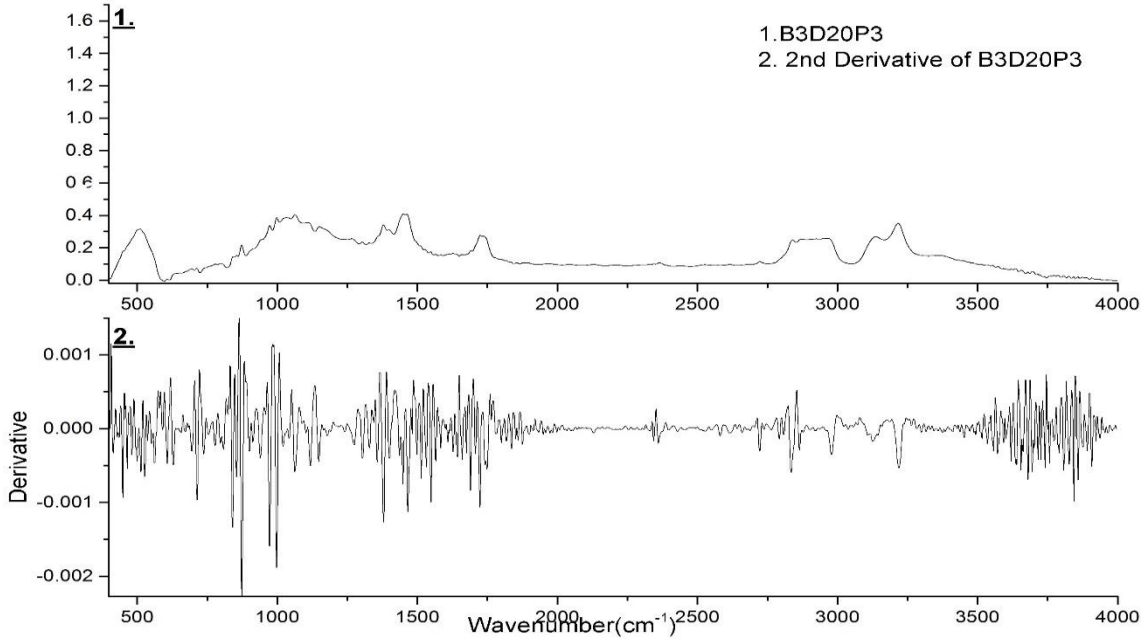

Figure 4.11: shows the 2nd derivative of position three control soil sample (B3D20P3).

2^{nd} derivation beak analysis for position three soil samples, and 2^{nd} derivative assignments of the main bands observed in the FTIR spectra of all samples are shown in appendix D.

Table 4. 13: 2nd derivative assignments of the main bands observed in the FTIR spectra for organic compounds of soil samples.

Sample ID	$B3D20P_3$	$N9D20P_3$	$N10D40P_3$	$N11D60P_3$	$N12D80P_3$	Functional group
peak (1) (cm-1)	2875.3	N.D.	2877.3	2877.3	2877.3	C-H stretching
peak intensity	0.25	N.D.	0.37	0.86	0.84	
peak (2) (cm-1)	2925.5	2923.5	2923.5	2919.7	2919.7	
peak intensity	0.25	0.25	0.39	0.88	0.87	
peak (3) (cm-1)	2964	N.D	2977.3	2875.6	2875.6	
peak intensity	0.26	N.D	0.36	0.84	0.83	
peak (4) (cm-1)	1739.5	N.D.	1747.2	1745.3	1745.3	C=O stretching
peak intensity	0.27	N.D	0.34	0.720	0.723	

Table 4. 13showed the observable peaks in the all soil samples, as showed in spectrum plot, as position two samples there is no significant peaks between 2000 and 2500 cm^{-1} which means the sample does not contain any C≡C, C≡N bonds, also the there is no O-H bond between 3600-3700. And that what we also have in previous position No1 and 2.

Table 4.13 showed these secondary beaks. For present study this position No.3 peaks position and intensities both were changed as other positions, which means that there was a difference between soil samples at different depths in peaks intensities and peak positions.

Peaks of samples with fertilizers of position No.3 showed a red shift for all peaks except peak (2) was a blue shift, peak(1) shifted by 2 wavenumber higher than control sample, peak(3) shifted by more than 10 wavenumber higher than control sample and peak (4) shifted by max. 7 wave number higher than control sample which indicate that there was a binding between fertilizers and soil at different depth which caused a strong effect of the bond that presented on the soil.

Most intense band in the spectrum was at depth 60 cm soil samples at all peaks positions and it is due to stretching of the C-H bond and the lower intense band was at depth 20 cm soil sample, the highest intense C=O stretching was at 80 cm sample with fertilizers while the lower intense was at control sample.

4.4 Position Four (P_4) Results and Discussion

4.4.1. Chemical analysis of P_4 samples:

According to the tentative values of the soil characterization and available nutrient concentration by (Hummel, Gaultney *et al.*,1996) ,(Kalra,1971) data presented in Table (4.14) indicate that the soil was loam in texture.

Table 4. 14: EC., pH and soil texture of Position four (P_4) soil samples.

Sample ID / Soil Tests	$B4D20P_4$	$B4D40P_4$	$N13D20P_4$	$N14D40P_4$	$N15D60P_4$	Soil type: **Loam** Of texture:
Depth (cm)	0-20	20-40	0-20	20-40	40-60	Sand % 46.60
EC. (1:5) (µS/cm)	20400	12770	9550	5020	4620	Silt % 31.81
Convert EC.(1:5) to ECSE by multiplied of factor then divided by 1000 for mmhos/cm						Clay % 21.60
$EC._{SE}$ (mmhos/cm)	181.15	113.6	84.9	44.7	41.1	
pH (1:5)	7.3	7.5	6.9	8.0	7.5	
Nitrogen (%)	0.245	0.231				
Phosphorus (ppm)	14.81	16.95				
Potassium (ppm)	579.91	523.66				

B: Blank sample, N: Number of treated sample, D: Depth of sample, P: Position of sample.
The Conversion Factor is derived from clay content, in this case for loam with around 20% clay content the factor = 8.9 ,

According to the values that showed in table 4.14, values of soil EC and pH indicated that soil of position No.4 is very strongly saline soils for all samples, with electrical conductivity EC of their saturated extract is extremely higher than 16 mmhos/cm at 25C° and pH less than 8.5 this may be because of the evaporation because this position is in the last part of the land, and also there is no irrigation system for the last part of the land.(Kalra,1971) Data also showed that control sample has medium range of phosphorus and high value of potassium and medium amount of nitrogen as also a notation that in this part of land was a new young Date palm tree were planted and may be the farmer don't care enough of this part as other parts. (Adjei-Nsiah, Kuyper *et al.*,2007).

4.4.2. ICPMS analysis of P_4 samples:

Macro elements of soil extracting 1:5 soil/water ratio for position three soil samples. Table 4.15 shows data soil analysis of the soil samples.

Table 4.15 presented data of macroelement for position four samples, table showed that all samples were contained a in range of high and medium amount of macro elements except Ca^{2+}. As previous positions calcium were in very low range at all depth and that indicate that soil suffers from the lack of calcium. The reason of these high content is maybe refer to the high electrical conductivity which effect negatively on plant absorption. (Figure 4.13)

Table 4. 15: Extractable macroelements soil data analysis of position four (P_4) samples.

Sample ID / Analysis	$B4D20P_4$	$B4D40P_4$	$N13D20P_4$	$N14D40P_4$	$N15D60P_4$
Depth(cm)	0-20	20-40	0-20	20-40	40-60
Extractable Macroelements (mg/100g)					
K^+	93.2 VH	66.5 VH	64.7 VH	35.4 H	28.7 M
Na^+	650 VH	622 VH	501.5 VH	310.4 VH	294.9 VH
Mg^{2+}	275.25 VH	153 M	96.9 M	33.5 M	27.9 L
Ca^{2+}	93.8 L	44.5 VL	32.1 VL	9.6 VL	7.97 VL

B: Blank sample, N: Number of treated sample, D: Depth of sample, P: Position of sample, VL= Very low, L=Low, M=Medium, H=High, VH= Very High (Ankerman and Large,1974)

Microelements for the same soil extracting 1:5 soil/water ratio for position four soil samples. Table 4.16 shows data soil analysis of the soil samples. Table 4.16 presented data of microelement for position four samples, tables showed that all samples depth contained a very low amount of microelements Data indicate that the soil of position four also was very nutrition poor

Table 4. 16: Extractable microelements soil data analysis of position four samples.

Sample ID / Analysis	$B4D20P_4$	$B4D40P_4$	$N13D20P_4$	$N14D40P_4$	$N15D60P_4$
Depth(cm)	0-20	20-40	0-20	20-40	40-60
Extractable Microelements (ppm)					
Fe^{3+}	7.4 L	3.6 VL	2.6 VL	1.01 VL	0.85 VL
Mn^{2+}	0.18 VL	0.009 VL	0.014 VL	0.02 VL	0.02 VL
Cu^{2+}	0.005 VL	0.008 VL	0.004 VL	0.01 VL	0.01 VL
Zn^{2+}	0.06 VL	0.05 VL	0.03 VL	0.04 VL	0.05 VL

VL= Very low, L=Low, M=Medium, H=High, VH= Very High

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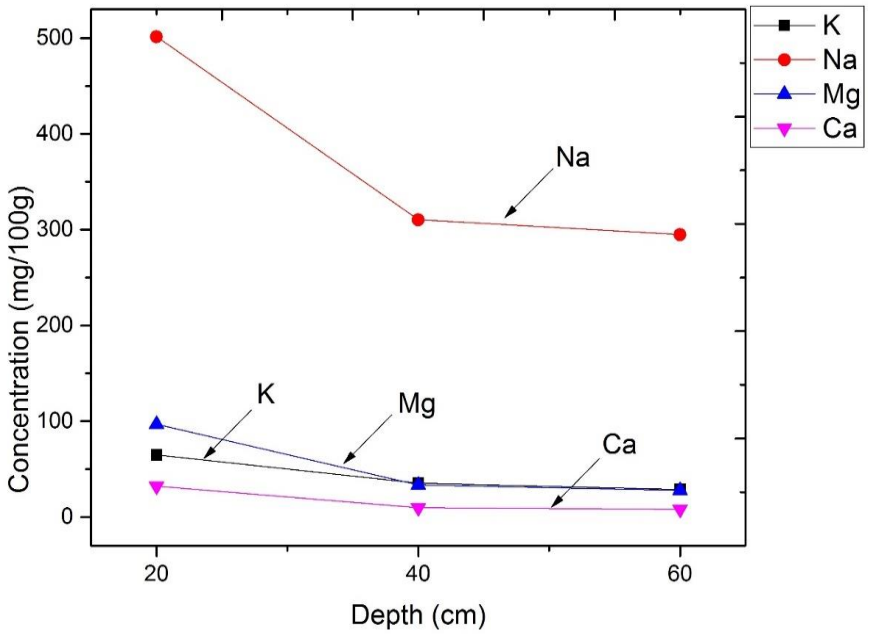

Figure 4.13: Extractable macroelements soil of position three samples with fertilizers.

4.4.3. Fluorescence analysis of P_4 samples:

Figure 4.14 showed fluorescence of soil samples of position four (P_4) were quenched in a depth dependent. The peak positions shows little or no change at all, fluorescence spectrum exhibiting the peak maximum at 450 and the intensity decreases as the depth increase. The intensity of soil at maximum started at depth 20 cm then it is begin to quenched until depth 80 cm as strong interaction.

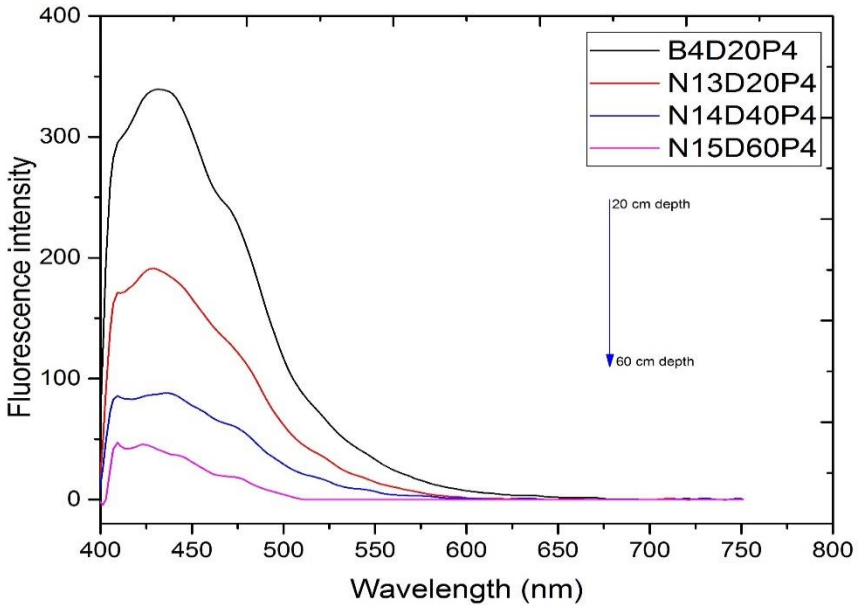

Figure 4.14: Fluorescence spectra of soil's samples at increasing depths.

4.4.4. FTIR analysis of P_4 samples:

Figure 4.15 show the FTIR spectra of position four soil samples in IR region 400-4000cm^{-1}

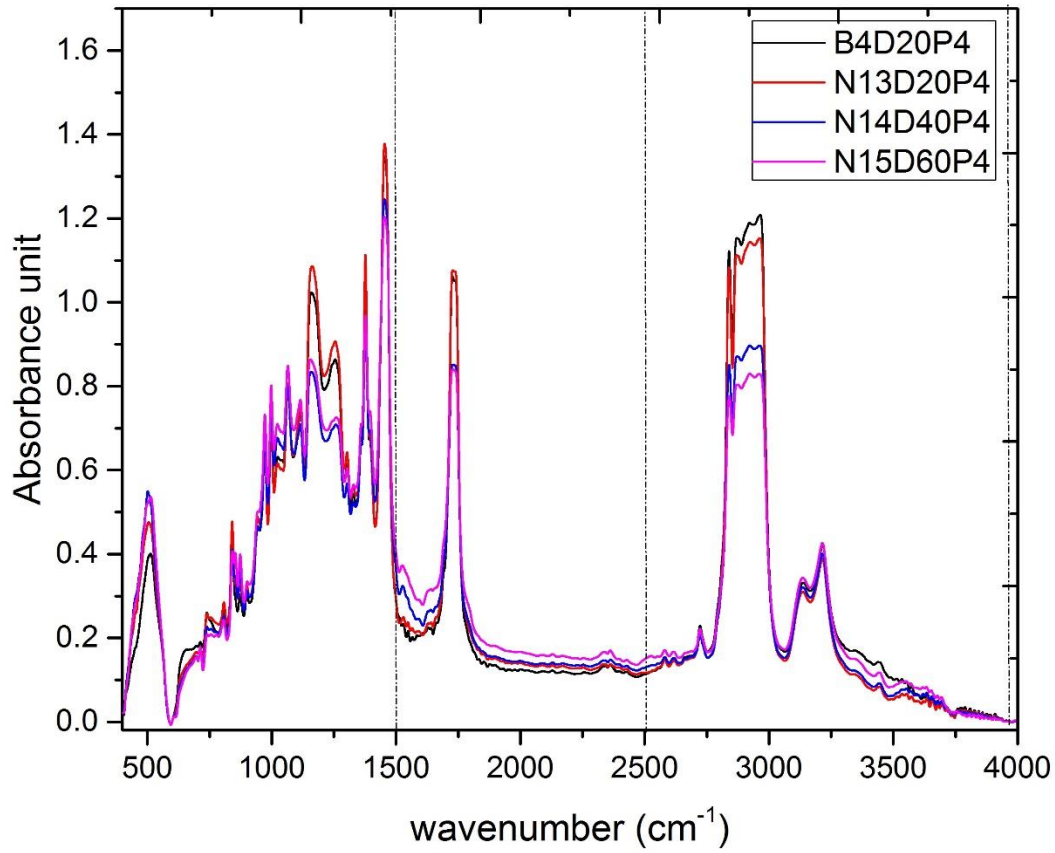

Figure 4.16: FTIR spectra of position four samples (400-4000 cm-1)

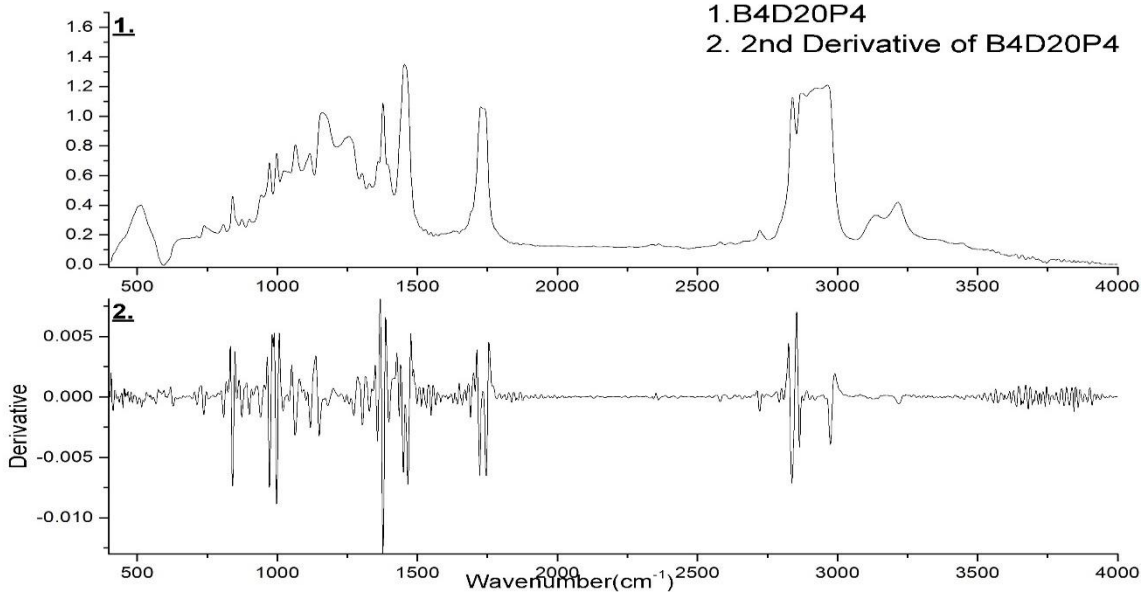

Figure 4.15: shows the 2nd derivative of position four control soil sample.

2^{nd} derivation beak analysis for position four soil samples, and 2^{nd} derivative assignments of the main bands observed in the FTIR spectra of all samples are shown in appendix E.

Table 4. 17: 2nd derivative assignments of the main bands observed in the FTIR spectra for organic compounds of soil samples

Max. peak observed (cm^{-1})	$B4D20P_4$ peak intensity	$N13D20P_4$ peak intensity	$N14D40P_4$ peak intensity	$N15D60P_4$ peak intensity	peak Mean value	Functional group
2836.77	1.10	1.06	0.84	0.74	2860	C-H stretching
2863.77	1.12	1.07	0.85	0.78		
2879.20	1.15	1.11	0.87	0.80		
1722.12	1.02	1.04	0.83	0.83	1738	C=O stretching
1745.26	0.99	1.01	0.82	0.81		

As assumed the change in the peak intensity usually means a change in the amount (per unit volume) of the functional group associated with the molecular bond. Table 4.17 showed that the most intense band in the spectrum was at depth 20 cm control soil sample at 2860 cm^{-1} and it is due to stretching of the C-H bond and the lower intense band of the same stretching bond was at depth 80 cm soil sample with fertilizers, while the most intense band at 1738 cm^{-1}due to stretching of the C=O bond in the spectrum was at depth 20 cm soil sample with fertilizers and the lower intense band of the same stretching bond was at depth 80 cm soil sample with fertilizers.

Table 4. 18: 2nd derivative assignments of the main bands observed in the FTIR spectra of soil samples

Sample ID	$B4D20P_4$	$N13D20P_4$	$N14D40P_4$	$N15D60P_4$	Functional group
peak (1) (cm-1)	2956.3	2960.2	2958.3	2958.3	C-H stretching
peak intensity	1.2	1.15	0.89	0.83	
peak (2) (cm-1)	2973.7	2975.6	2975.6	2977.5	
peak intensity	1.16	1.06	0.85	0.77	

Table 4. 17 and Table 18 showed the observable peaks in the all soil samples, as showed in spectrum plot, as position two samples there is no significant peaks between 2000 and 2500 cm^{-1} which means the sample does not contain any C≡C, C≡N bonds, also the there is no O-H bond between 3600-3700. And that what we also have in previous positions.

Table 4.18 showed these secondary beaks. For present study this position No.4 peaks position and intensities both were changed as other positions, which means that there was a difference between soil samples at different depths in peaks intensities and peak positions.

Peaks of samples with fertilizers of position No.4 showed a red shift for all peaks except peak (1) shifted by 2 wavenumber higher than control sample, peak (2) shifted by more than 4 wavenumber higher than control sample, which indicate that there was a binding between

fertilizers and soil at different depth which caused a strong effect of the bond that presented on the soil.

4.5 Major mineralogical composition of represent soil

It was performed to know the chemical compositions of the mineralogical soil. A set of soil samples are randomly chosen from position one (P_1) and position four (P_4) to be a representing samples for measuring the major mineral of the hole land and to study the sites characterization for the farm at different depths if there is any different composition in soil mineralogical, both X-ray fluorescence (XRF) and X-ray diffractometer (XRD) are used in order to measure the major soil mineral. Table 4.19 shows the chemical compositions in form of oxides for position one (P_1).

Table 4. 19: XRF chemical compositions for position one (P_1) soil samples at different depth.

Depth / Chemical Compositions	**B1D40P1**	**N2D40P1**	**N3D60P1**	**N4D80P1**
	0-40	20-40	40-60	60-80
	Weight (%)			
Silicon dioxide (SiO2)	39.1043	36.9157	36.4639	36.6923
Calcium oxide (CaO)	26.4093	26.8141	26.7872	27.0347
Aluminium oxide ($A_{l2}O_3$)	12.7707	13.1401	13.7823	12.3356
Iron(III) oxide (Fe_2O_3)	10.5869	11.9316	11.9885	12.2258
Magnesium oxide (MgO)	4.2717	4.0524	3.9152	4.6829
Potassium oxide (K_2O)	3.8123	3.6201	3.5954	3.6316
Titanium dioxide (TiO_2)	1.7664	2.0593	2.0566	1.8297
Phosphorus pentoxide (P_2O_5)	0.5063	0.4703	0.4115	0.388
sodium oxide (Na_2O)	0.2166	0.3111	0.2906	0.3441
manganese oxide (MnO)	0.1997	0.2551	0.2723	0.3039
Sulfur trioxide (SO_3)	0.1621	0.1553	0.1384	0.1491
Barium oxide (BaO)	0.081	-	-	-
Zinc oxide (ZnO)	0.0347	0.0885	0.098	0.0641
Chromium(III) oxide (Cr_2O_3)	0.0518	0.0641	0.0656	0.0592
Nickel(II) oxide (NiO)	0.0261	0.0354	0.038	0.0316
Chlorine (Cl)	-	0.0868	0.0963	0.1364
Erbium(III) oxide (Er2O3)	-	-	-	0.091
Total in each	99.9999			

B: Blank sample, N: Number of treated sample, D: Depth of sample, P: Position of sample

The data in table 4.19 showed that the silica and calcium oxides (SiO_2, CaO) are the dominant oxides followed by Al_2O_3, Fe_2O_3, and MgO, while other oxides are present in trace amounts. This confirms the chemical analysis of position No.1 soil and these oxides mimic with the soil type which is loamy soil.

The possible minerals present in the adsorbents are given in all plots of XRD figures which are founded in Appendix F for both P_1 and P_4. No quantitative estimation phases in these adsorbents have been made but their characterization of XRD patterns indicates the presence of quartz, calcite, Dolomite as the major phases for all samples. (Table 4.20)

As showed in table 4.20 wide mineralogical variability was founded, quartz is found as major mineral in all samples and as quartz chemical compositions consider as SiO_2 so from table 4.19 was appeared that silicon oxide was in maximum amount on the control sample, and as Calcite has a chemical composition which consist of lager than 50% of CaO and also this made the calcite as a major mineral for the position, Dolomite also has a chemical composition consist of 30% Calcium oxide and around 20% MgO and it was appear in larger amount on soil with fertilizers at depth 40 cm larger than control sample.

Table 4.20 showed that the Kaolinite was only appear in treated soil at depth 60 cm with it was not founded in control sample and Kaolinite has a chemicals composition consist of larger than 35% of AL_2O_3 and around 45% of SiO_2 and as SiO_2 appears in quartz also this made a mixture of two mineral peaks for quartz Kaolinite and finally sample of depth 60 cm appears as the most sample have a mixture of all mineral that presented on other samples.

Table 4. 20: XRD mineralogy for position one (P_1) soil samples at different depth.

Sample Name	Mineralogical Composition
B1D40P1	Quartz, Calcite, Dolomite
N2D40P1	Quartz, Calcite, Dolomite
N3D60P1	Quartz, Calcite, Dolomite, Kaolinite
N4D80P1	Quartz, Calcite, Dolomite

B: Blank sample, N: Number of treated sample, D: Depth of sample, P: Position of sample.

Position four soil samples (P_4) have a wide mineralogical variability, tables 4.21 and 4.22 shows the values of oxides and mineralogical soil for P_4.

Table 4.21 shows that Aragonite is found as major mineral in all samples and as Aragonite chemical compositions consist of more than 50% of CaO. The percentage of calcium oxide was larger than silicon oxide that because the appearance of Aragonite in larger amount than Quartz.

Table 4.21 appears that calcium oxide was in maximum amount on the treated soil sample at depth 60 cm which has larger amount than control, and Cristobalite is from the same group of quartz and its chemical form composition is SiO_2 and its also only appear on treated soil at depth 60 cm like position one other minerals were found in major amount such as Calcite, Kaolinite and Quartz, but Dolomite does not appear in the P_4.

Table 4. 21: XRF major oxide chemistry for position four (P_4) soil samples at different depth.

Depth / Major oxides	**B4D40P$_4$**	**N14D40P$_4$**	**N15D60P$_4$**
	0-40	20-40	40-60
	Weight (%)		
Calcium oxide (CaO)	31.2772	35.2579	39.4416
Silicon dioxide (SiO_2)	28.7146	33.1248	29.5543
Iron(III) oxide (Fe_2O_3)	14.4606	9.8587	9.1111
Aluminium oxide (Al_2O_3)	9.0964	7.8067	8.1253
Magnesium oxide (MgO)	5.7383	7.138	6.9575
Potassium oxide (K_2O)	3.9092	2.8305	2.5043
Chlorine (Cl)	2.9323	1.199	1.0762
Titanium dioxide (TiO_2)	1.8323	1.1715	1.2462
sodium oxide (Na_2O)	0.8716	0.8358	0.7371
Phosphorus pentoxide (P_2O_5)	0.3438	0.4764	0.393
manganese oxide (MnO)	0.3411	-	0.7371
Sulfur trioxide (SO_3)	0.31	0.2017	0.2057
Chromium(III) oxide (Cr_2O_3)	0.0743	0.0438	0.049
Zinc oxide (ZnO)	0.0535	0.0345	0.0436
Nickel(II) oxide (NiO)	0.0445	0.0206	0.0288
Cobalt(III) oxide (Co_2O_3)	-	-	0.0214
Total in each	99.9999		

B: Blank sample, N: Number of treated sample, D: Depth of sample, P: Position of sample.

Table 4. 22: XRD mineralogy for position No.4 soil samples at different depth

Sample Name	Mineralogical Composition
B4D40P$_4$	Aragonite, Calcite, Quartz
N14D40P$_4$	Aragonite, Calcite, Kaolinite, Quartz
N15D60P$_4$	Aragonite, Calcite, Kaolinite, Quartz, Cristobalite

B: Blank sample, N: Number of treated sample, D: Depth of sample, P: Position of sample, A: Aragonite, C: Calcite, Q: Quartz, K: Kaolinite, Cr: Cristobalite.

The second part of this study was conducted in the lab by using blank samples that were collected from filed and treats them by certain concentration of feed solutions that prepares in lab and then study the relation between these feed solutions and soil by using fluorescence spectroscopic technique

4.6 Control Experiment Fluorescence Analysis

Fluorescence spectra for control experiment shown in Fig.4.17 show the effect of fertilizers concentration that were added on the control soil samples of all positions. The fluorescence intensity of P_1 and P_2 (figures 4.17a, 4.17b) were increases as concentration of feed solutions increase and this indicate that there is an effect of samples concentrations on the fluorescence properties.

Figure 4.17 shows that the intensity remains almost unchanged at higher concentrations F1, F2 for both positions. While P3 and P_4 shows a different trend with maximum fluorescence intensity in the lowest concentration range (F5-F3) This behavior can may be attributed to a different fluorescence threshold for the various fluorophors in the positions soils. The spectra of all positions are dominated by a peak at around 450nm with shoulders of varying intensity on both sides.

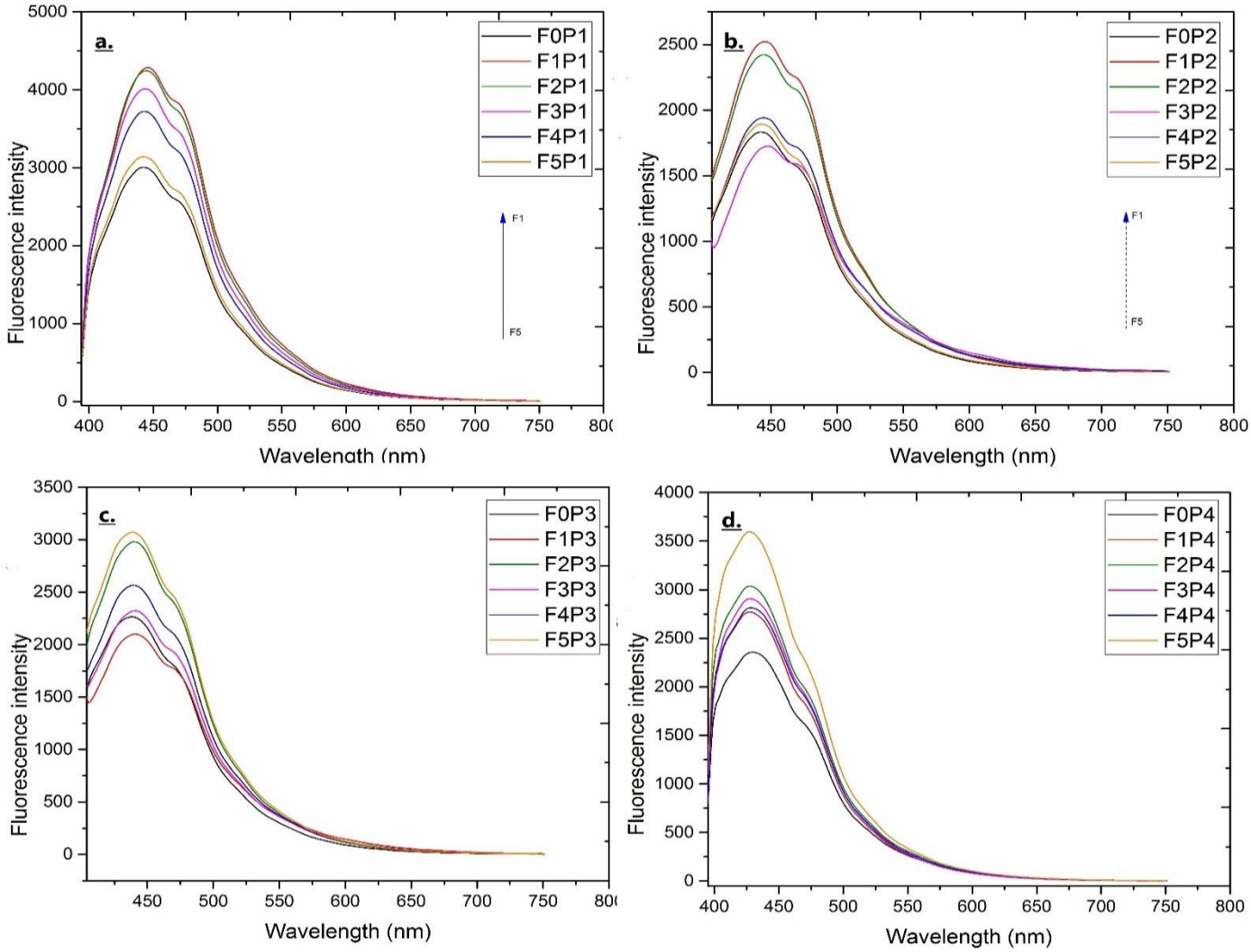

Figure 4.17: fluorescence spectra of control experiment samples for: (a): position one(P_1), (b) position two(P_2), (c): position Three(P_3), (d): position four(P_4). **(**F0: Blank, F1:280mg/L, F2:270mg/L, F3:160mg/L, F4:85mg/L, F5:32mg/L**)**.

4.7 Control Experiment ATR-FTIR Analysis

As mentioned before this part of study was aimed to study the relation between feed solutions that were prepared in lab and soil by using ATR-FTIR spectroscopic technique

4.7.1 Position one (P_1) ATR-FTIR Analysis:

ATR-FTIR spectra for control experiment shown in Fig.4.18 show the effect of fertilizers concentration that were added on the P_1 control soil sample, figure shows that there is three main band assignments for organic and in organic compounds of soil sample, table 4.23 show these main band and the beaks observed in the ATR spectra. Figure 4.18 showed the observable peaks in spectrum plot, no significant peaks between 2000 and 2500 cm^{-1} which means the sample does not contain any C≡C, C≡N bonds.

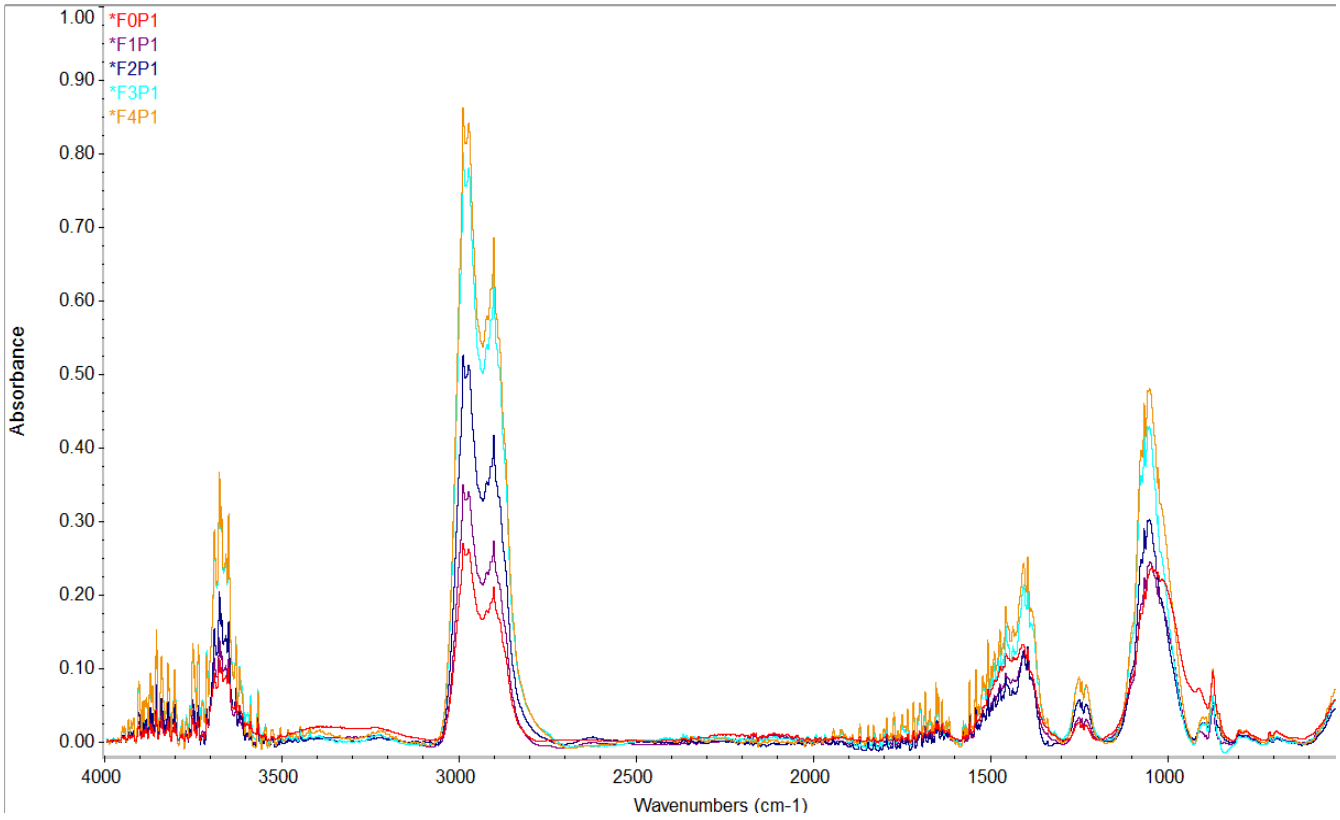

Figure 4.18: ATR spectra for position one (P_1) soil samples of control experiment.

Table 4.23 showed secondary beaks for position one (P_1) the intensities only was changed with fixed beaks position, most intense band in the spectrum was for adding F5 feed solution of concentration 32 mg/L, table also shows the oxides band that are appears around wavenumbers larger than 3300cm^{-1} and it was in the maximum intensities with adding F2 feed solution of concentration 270 mg/L and all oxides intensities was concentration dependent.

From table 4.23 we can say that when we added a low concentration of feed solutions we got a larger intense spectral beaks that due to organic C-H stretching this can be interpreted by with increasing the added fertilizers to the soil which is also has an amount of nutrients naturally the added fertilizers may covered the soil molecule and prevent it to absorb light so the lager concentration have small intensity in compered with lowest ones.

Table 4. 23: Assignment of the main bands observed in the ATR spectra of the organic and in organic compounds of position No.1 soil according to (Calderón et al.,2011b)

Max. peak observed (cm^{-1})	$F0P_1$ peak intensity	$F1P_1$ peak intensity	$F2P_1$ peak intensity	$F3P_1$ peak intensity	$F4P_1$ peak intensity	Functional group
2900	0201	0.266	0.409	0.625	0.683	organic C-H stretching
2971	0.252	0.336	0.509	0.528	0.838	
2987	0.260	0.346	0.523	0.771	0.859	
3649	0.062	0.086	0.147	0.792	0.210	In organic Oxides
3657	0.055	0.077	0.131	0.178	0.164	
3669	0.071	0.100	0.164	0.247	0.242	
3675	0.086	0.121	0.194	0.292	0.294	
3689	0.071	0.094	0.148	0.220	0.231	

(P: Position of samples, F0: Blank, F1:280mg/L, F2:270mg/L, F3:160mg/L, F4:85mg/L, F5:32mg/L).

4.7.2. Position Two (P_2) ATR-FTIR Analysis:

ATR-FTIR spectra for control experiment shown in Fig.4.19 show the effect of fertilizers concentration that were added on the P_2 control soil sample, figure shows that there is three main band assignments for organic and in organic compounds of soil sample, table 4.24 show these main band and the beaks observed in the ATR spectra.

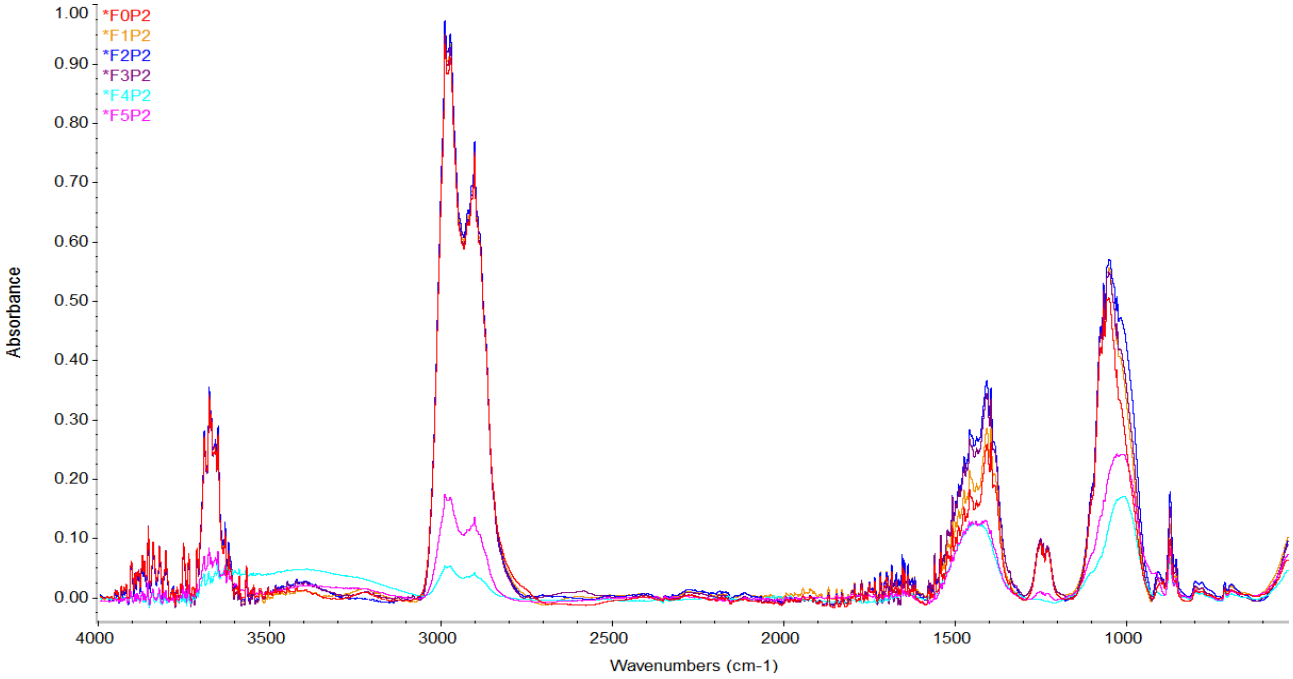

Figure 4.19: ATR spectra for position two (P_2) soil samples of control experiment.

From table 4.24 showed that the intensities that due to organic C-H stretching were concentration dependent except the feed solution of concentration 85mg/L. The most intense band was by adding the concentration 270 of feed solution.

Figure 4.20 also showed that no significant peaks between 2000 and 2500 cm^{-1} which means the sample does not contain any C≡C, C≡N bonds.

Table 4.24 showed secondary beaks for position No.2 the intensities only was changed with fixed beaks position, also shows the oxides band that are appears around wavenumbers larger than 3300cm^{-1} and it was in the maximum intensities with adding F2 feed solution of concentration 270 mg/L and all oxides intensities was concentration dependent.

Table 4. 24: Assignment of the main bands observed in the ATR spectra of the organic and in organic compounds of P_2 soil according to (Calderón et al.,2011b).

Max. peak observed (cm^{-1})	$F0P_2$ peak intensity	$F1P_2$ peak intensity	$F2P_2$ peak intensity	$F3P_2$ peak intensity	$F4P_2$ peak intensity	$F5P_2$ peak intensity	Functional group
2900	0.746	0.764	0.763	0.749	0.036	0.136	organic C-H stretching
2971	0.911	0.940	0.946	0.929	0.044	0.166	
2987	0.933	0.963	0.971	0.953	0.045	0.171	
3649	0.201	0.204	0.203	0.195	0.022	0.050	In organic Oxides
3657	0.189	0.188	0.190	0.179	ND	ND.	
3669	0.254	0.245	0.252	0.238	ND.	ND.	
3675	0.291	0.283	0.298	0.280	0.022	0.061	
3689	0.234	0.215	0.240	0.216	0.030	0.050	

(P: Position of sample, F0: Blank, F1:280mg/L, F2:270mg/L, F3:160mg/L, F4:85mg/L, F5:32mg/L).

4.7.3. Position Three (P_3) ATR-FTIR Analysis:

ATR-FTIR spectra for control experiment shown in Fig.4.20 show the effect of fertilizers concentration that were added on the P_3 control soil sample, figure shows that there is three main band assignments for organic and in organic compounds of soil sample, table 4.25 show these main band and the beaks observed in the ATR spectra.

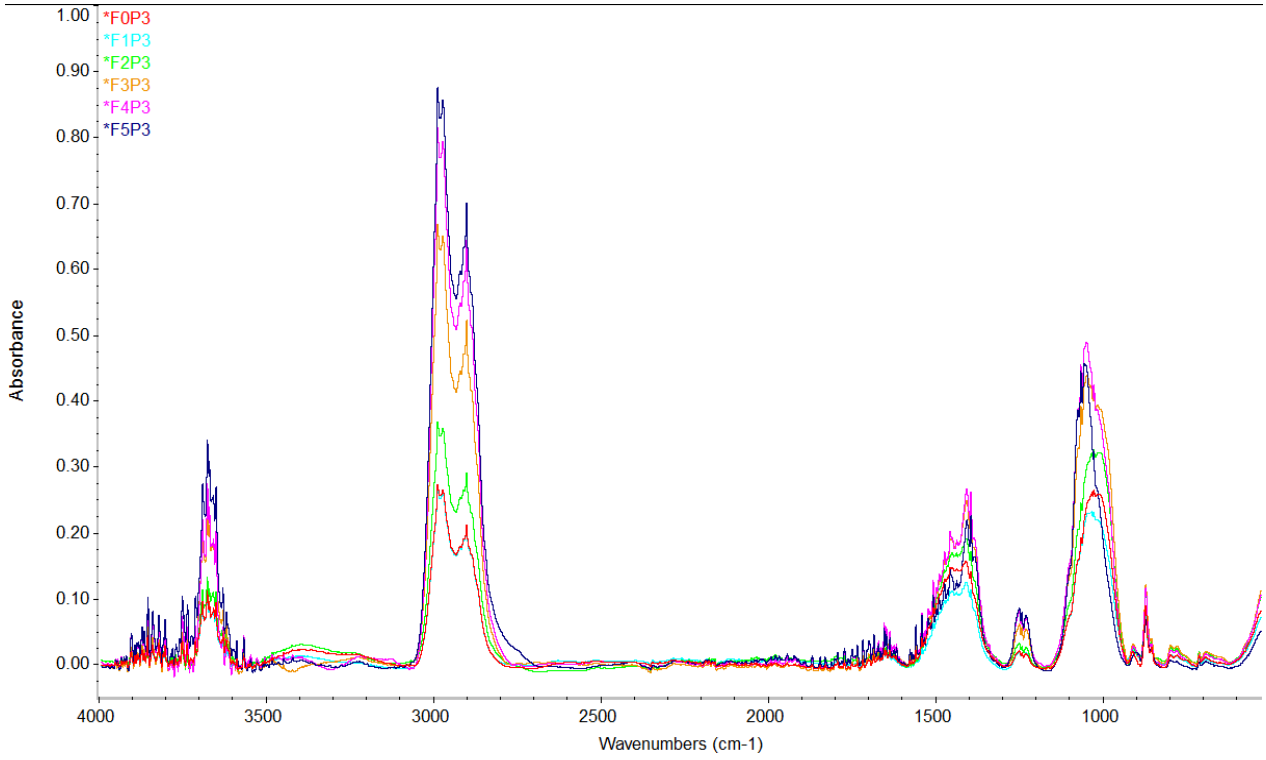

Figure 4.20: ATR spectra for position three (P_3) soil samples of control experiment.

From table 4.25 we have the same result like P_1 low concentration of feed solutions gots a larger intense spectral beaks that due to organic C-H stretching, intensities only was changed with fixed beaks position, most intense band in the spectrum was for adding F5 feed solution so intensity here also is concentration independent, table also shows the oxides band that are appears around wavenumbers larger than 3300cm^{-1} and it was in the maximum intensities with adding F5 feed solution of concentration 32 mg/L and all oxides intensities was concentration independent also.

Table 4. 25: Assignment of the main bands observed in the ATR spectra of the organic and in organic compounds of P_3 soil according to (Calderón et al.,2011b).

Max. peak observed (cm^{-1})	$F0P_3$ peak intensity	$F1P_3$ peak intensity	$F2P_3$ peak intensity	$F3P_3$ peak intensity	$F4P_3$ peak intensity	$F5P_3$ peak intensity	Functional group
2900	0.204	0.213	0.279	0.508	0.645	0.683	organic C-H stretching
2971	0.261	0.263	0.348	0.640	0.799	0.842	
2987	0.270	0.270	0.359	0.659	0.820	0.862	
3669	0.065	0.064	0.087	0.167	0.204	0.231	In organic Oxides
3675	0.085	0.081	0.108	0.196	0.241	0.268	
3689	0.076	0.068	0.097	0.164	0.190	0.210	

(P: Position of sample, F0: Blank, F1:280mg/L, F2:270mg/L, F3:160mg/L, F4:85mg/L, F5:32mg/L).

4.7.4. Position four (P_4) ATR-FTIR Analysis:

ATR-FTIR spectra for control experiment shown in Fig.4.21 show the effect of fertilizers concentration that were added on the P_4 control soil sample, figure shows that there is three main band assignments for organic and in organic compounds of soil sample, table 4.26 show these main band and the beaks observed in the ATR spectra.

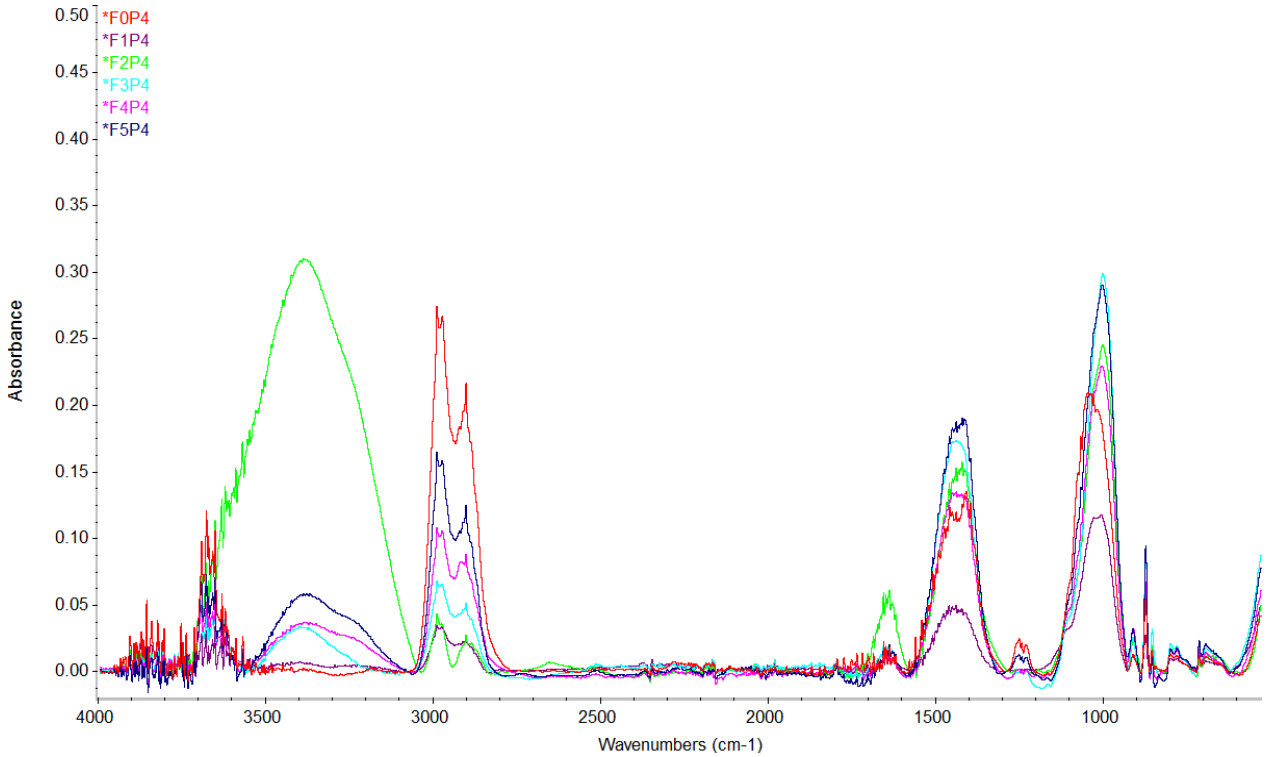

Figure 4.21: ATR spectra for position No.4 soil samples of control experiment.

From table 4.26 we have the same result like P_1 and P_3 low concentration of feed solutions gets a larger intense spectral beaks that due to organic C-H stretching, intensities only was changed with fixed beaks position, most intense band in the spectrum was for adding F5 feed solution so intensity here also is concentration independent, figure 4.21 showed the oxides band that are do not appears clearly.

Table 4. 26: Assignment of the main bands observed in the ATR spectra of the organic and in organic compounds of P_4 soil according to (Calderón et al.,2011b).

Max. peak observed (cm^{-1})	$F0P_4$ peak intensity	$F1P_4$ peak intensity	$F2P_4$ peak intensity	$F3P_4$ peak intensity	$F4P_4$ peak intensity	$F5P_4$ peak intensity	Functional group
2900	0.200	0.025	N.D	0.042	0.082	0.131	organic C-H stretching
2971	0.258	0.032	N.D	N.D	0.102	0.162	
2986	0.264	0.032	0.042	0.061	0.105	0.167	

(P: Position of sample, F0: Blank, F1:280mg/L, F2:270mg/L, F3:160mg/L, F4:85mg/L, F5:32mg/L).

Chapter Five:

Conclusion, Recommendations and Future Work

From the previous discussion, spectroscopic techniques appears as a useful tools for giving a better understanding of the relationship between soil and fertilizer based on vibrational mid-Infrared (IR) spectroscopy, fluorescence spectroscopy, X ray spectroscopy, mass spectrometer (ICPMS) . It was clear that the soils dose not receive a great attention as far as macro and micro nutrients resulted in low concentrations rates so this indicted that Date Palm tree grown under farm conditions suffer from nutrients deficiency.

So we recommended to give a higher attention for macro and micro nutrients addition. A deficiency in these essentials can be corrected by the addition of commercial or organic fertilizers. Most commercial fertilizers indicate the quantity of N: P: K in ratio form. These essentials are in a less concentrated form in organic additives such as compost.

The most common method of correcting micronutrient deficiencies is by adding chemical nutrients. Crop rotation is another method used to correct an imbalance.

The soil analysis indicates the over salinity of soil farm and this may refer to an increase of the underground level caused by excessive drought situations (high evaporation); and also refer for the using of high salts content water. This high values of salinity make a negative impact on soil such as high concentrations of soluble salts, and high soil pH, and a negative effect of sodium on the plant metabolism.

From results of the four positions on the study area it was clear that the applied fertilizers are not site- specific and not finely tuned to local soil chemical conditions. So it need a specific information on soil nutrients and improving soil fertility using agroforestry techniques.

We recommended also to make a up scaling study for all Date Palm trees areas in order to be soured if this deficiency presents in all sites or not.

For future work it’s useful if study the relation between fertilizers and soil through a simulation study based on leaf/soil analysis and date palm requirements using these same spectroscopic techniques.

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Appendices

Appendix A:

Standard rating values

Table A. 1(a): Concentrations of elements in soil associated with deficiency, optimum and excess in soil, Table A.1 (b): Tentative rating values of soil fertility status

Table A.1(a): Concentrations of elements in soil associated with deficiency, optimum and excess in soil					
Nutrition	Units	Low	Medium	High	Excessive
Nitrogen	(%)	0.2 >	0.2-0.3	0.3-0.5	0.5<
Phosphorus	ppm	10 >	10 – 20	20 – 40	40<
Potassium	ppm	150>	250– 150	250 – 800	800<

Table A.1 (b): Tentative rating values of soil fertility status					
Element	Rating				
	Very low	Low	Medium	High	Very high
Electric conductivity (E.C.) dS/m	<0.1	0.1-0.2	0.3-0.4	0.5-0.7	>0.7
pH	<5.8	5.9-6.6	6.7-7.2	7.3-8.5	>8.5
Macronutrients (mg/100g)					
Potassium (K)	<11.7	11.8-20	21-30	31-47	>47
Calcium (Ca)	-	<100	100-200	>200	-
Magnesium (Mg)	<11	11- 29	30-180	>180	-
Sodium (Na)	<20	20-25	26-30	>30	-
Micronutrients (ppm)					
Iron (Fe)	<5	5- 10	11- 16	17-25	>25
Manganese (Mn)	<5	5- 8	9- 12	13-30	>30
Zinc (Zn)	<0.5	0.5-1.5	1.6-3	3.1-6	> 6
Copper (Cu)	<0.3	0.3-0.8	0.9-1.2	1.3-2.5	>2.5

Sources: (Ankerman and Large,1974), (Adjei-Nsiah, Kuyper et al.,2007)

Appendix B:

The 2nd derivation beak analysis for position one soil samples are shown, and 2nd derivative assignments of the main bands observed in the FTIR spectra of all samples:

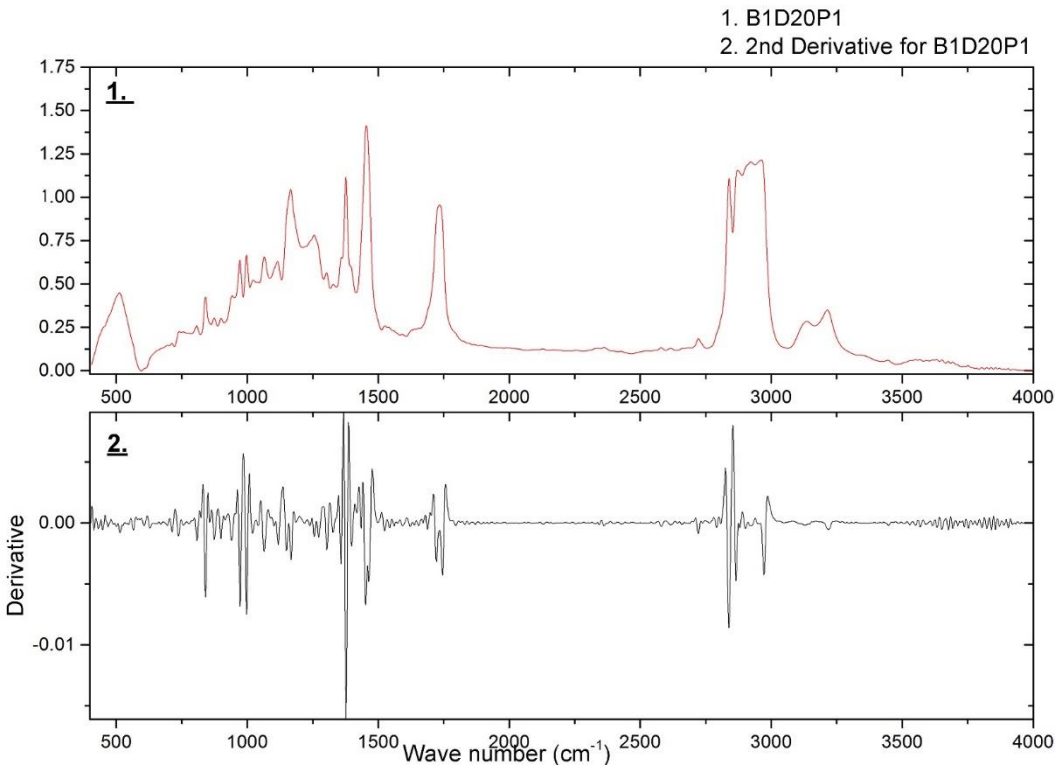

Figure B.2: FTIR spectra for 2nd derivative of B1D20P1

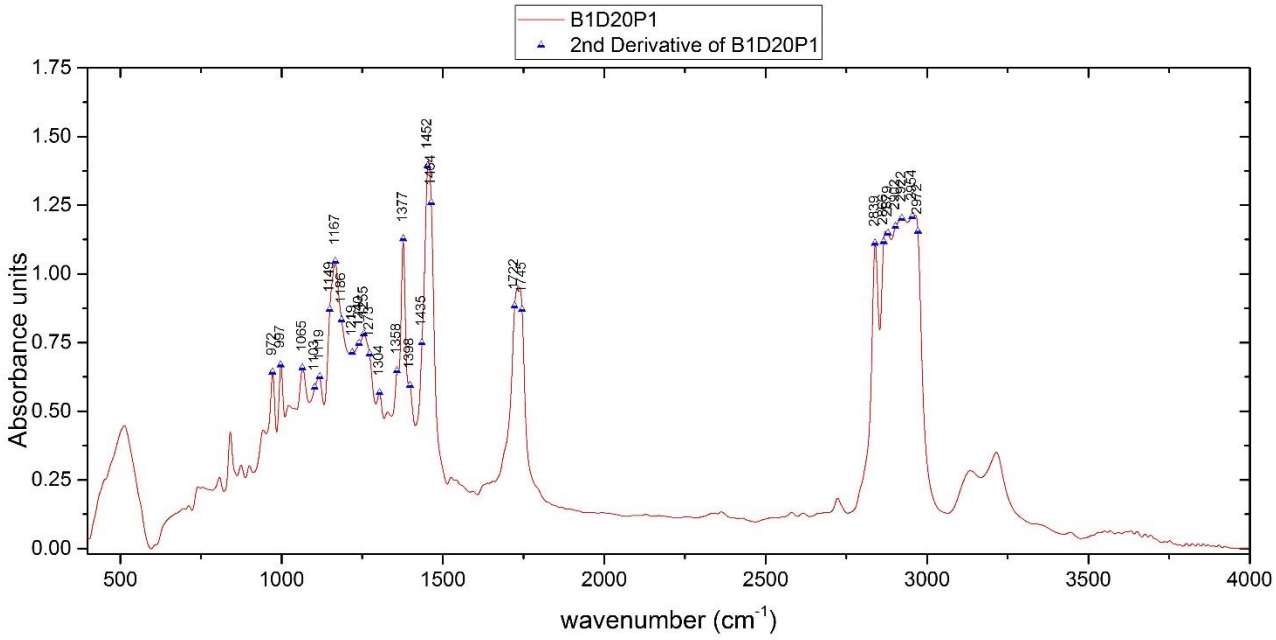

Figure B.1: FTIR spectra for 2nd derivative peaks of B1D20P1

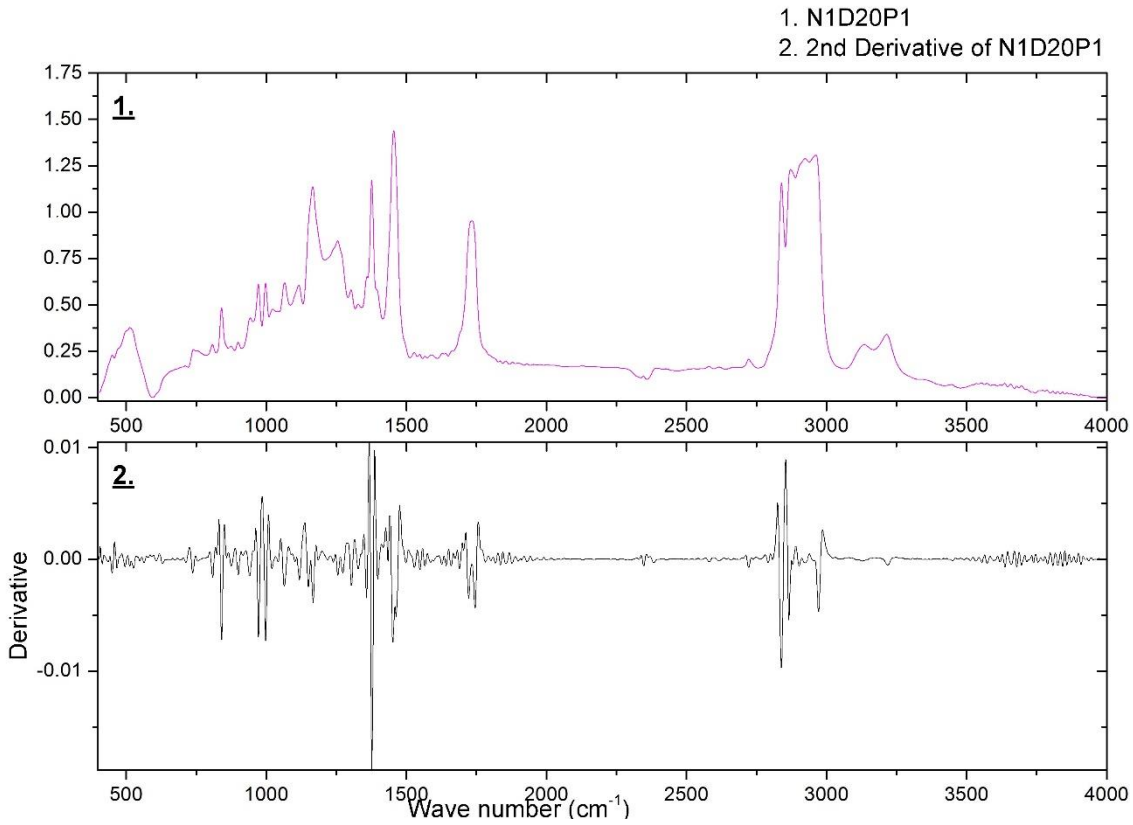

Figure B.4: FTIR spectra for 2nd derivative of N1D20P1

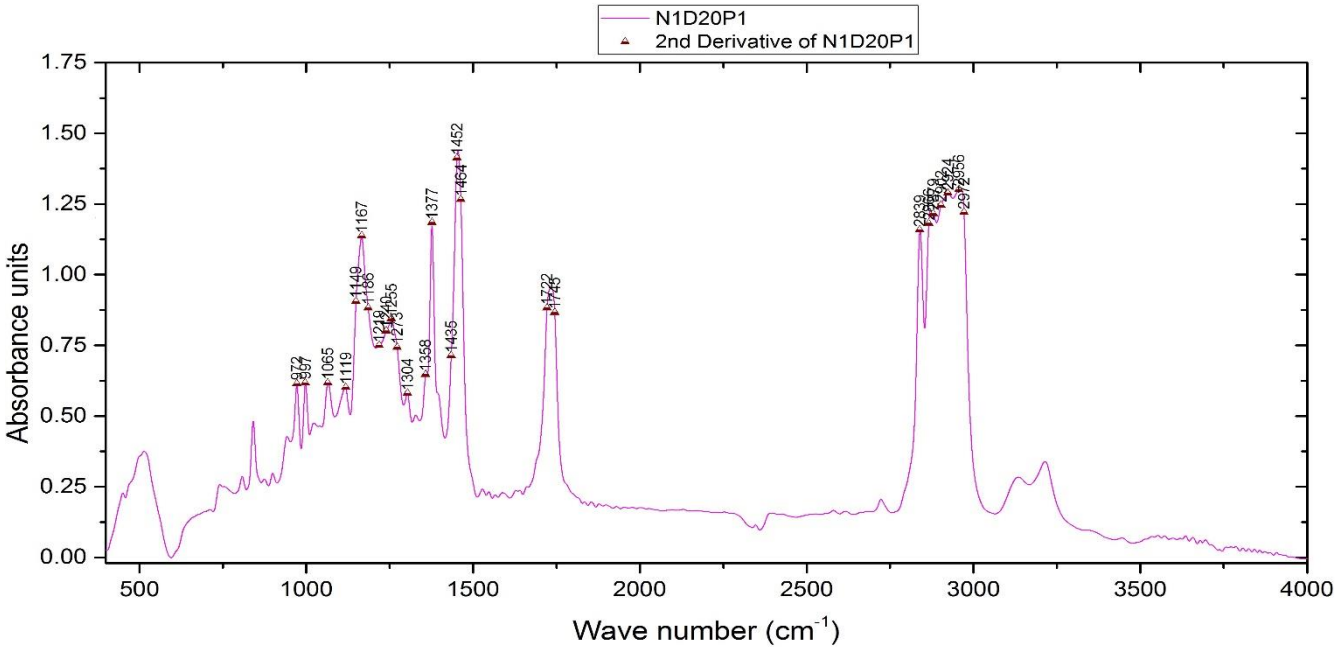

Figure B.3: FTIR spectra for 2nd derivative beaks of N1D20P1

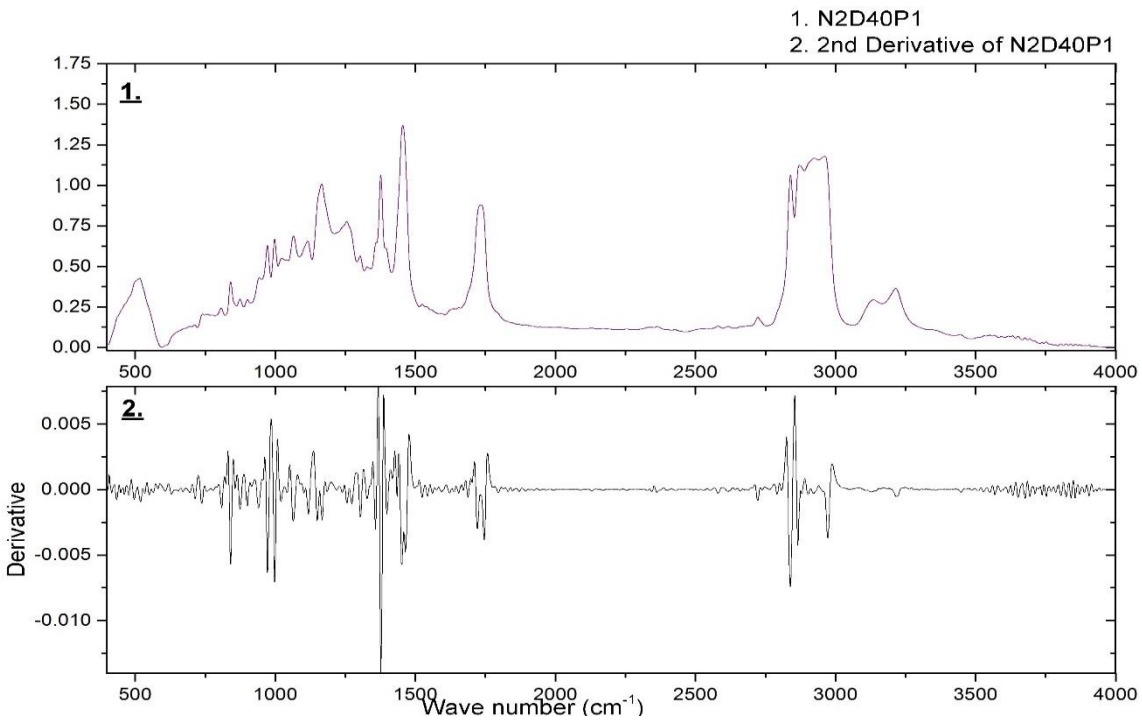

Figure B.6: FTIR spectra for 2nd derivative of N2D40P1

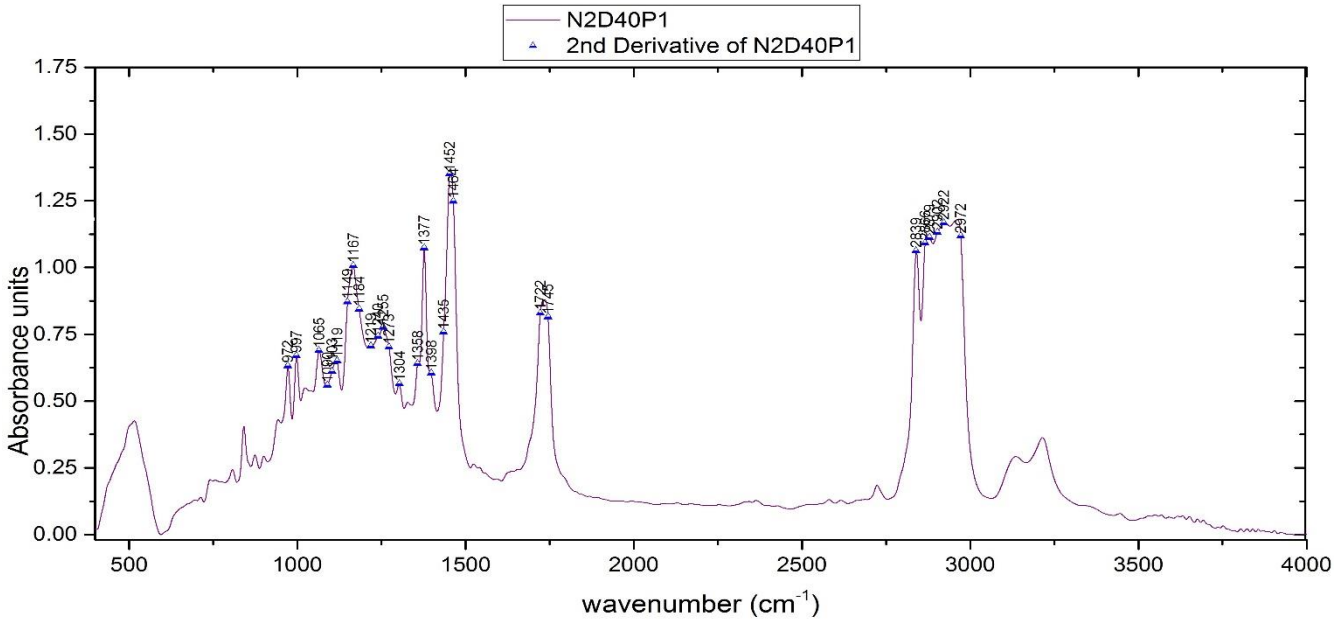

Figure B.5: FTIR spectra for 2nd derivative peaks of N2D40P1

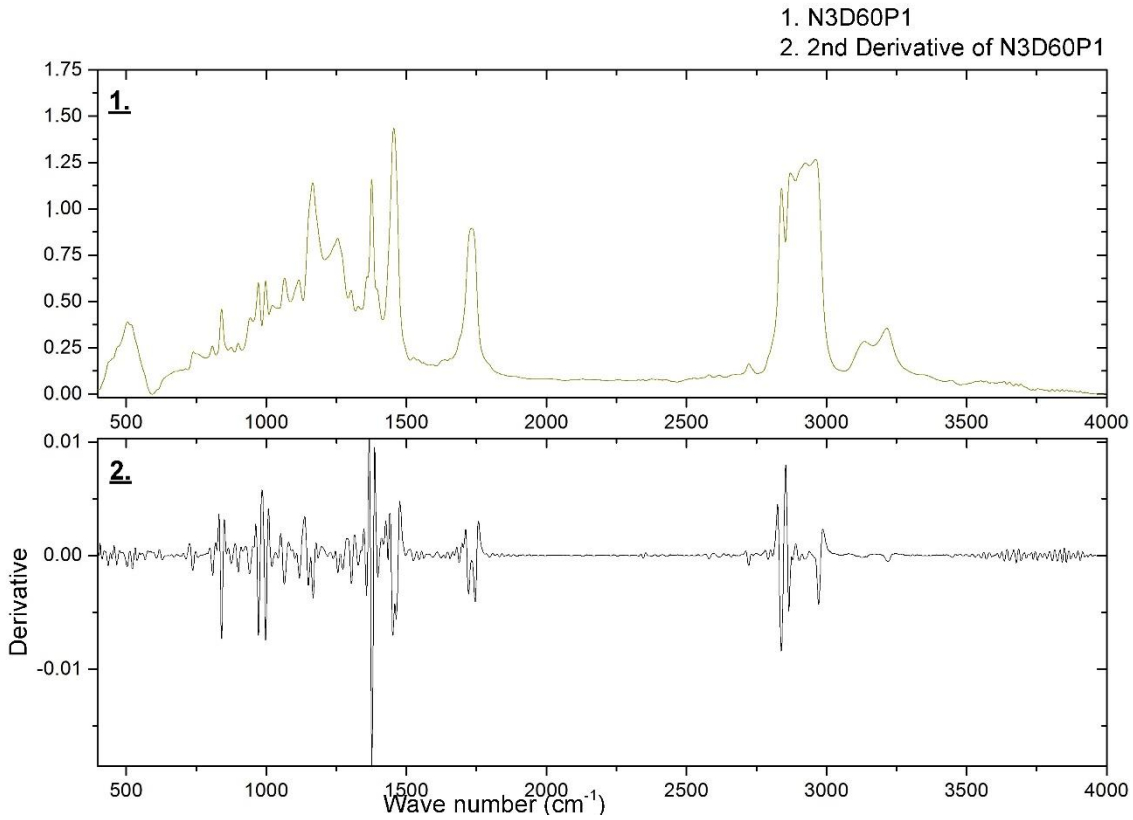

Figure B.8: FTIR spectra for 2nd derivative of N3D60P1

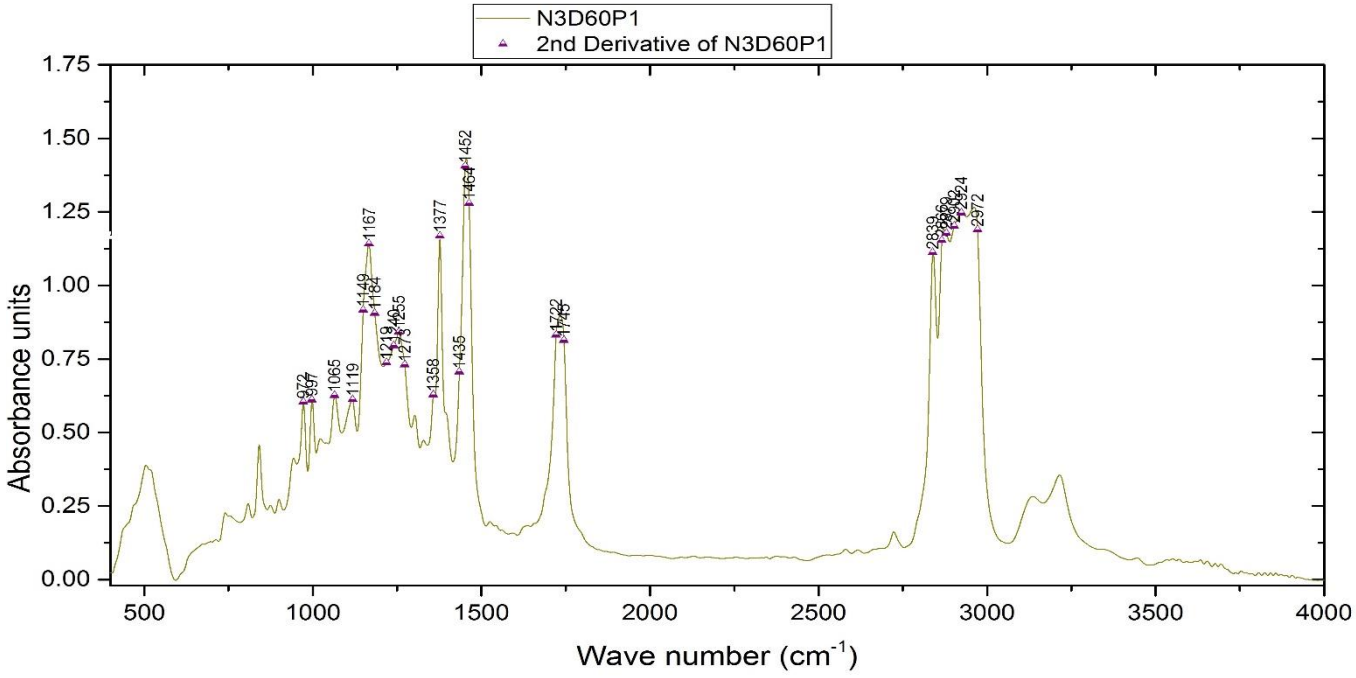

Figure B.7: FTIR spectra for 2nd derivative peaks of N3D60P1

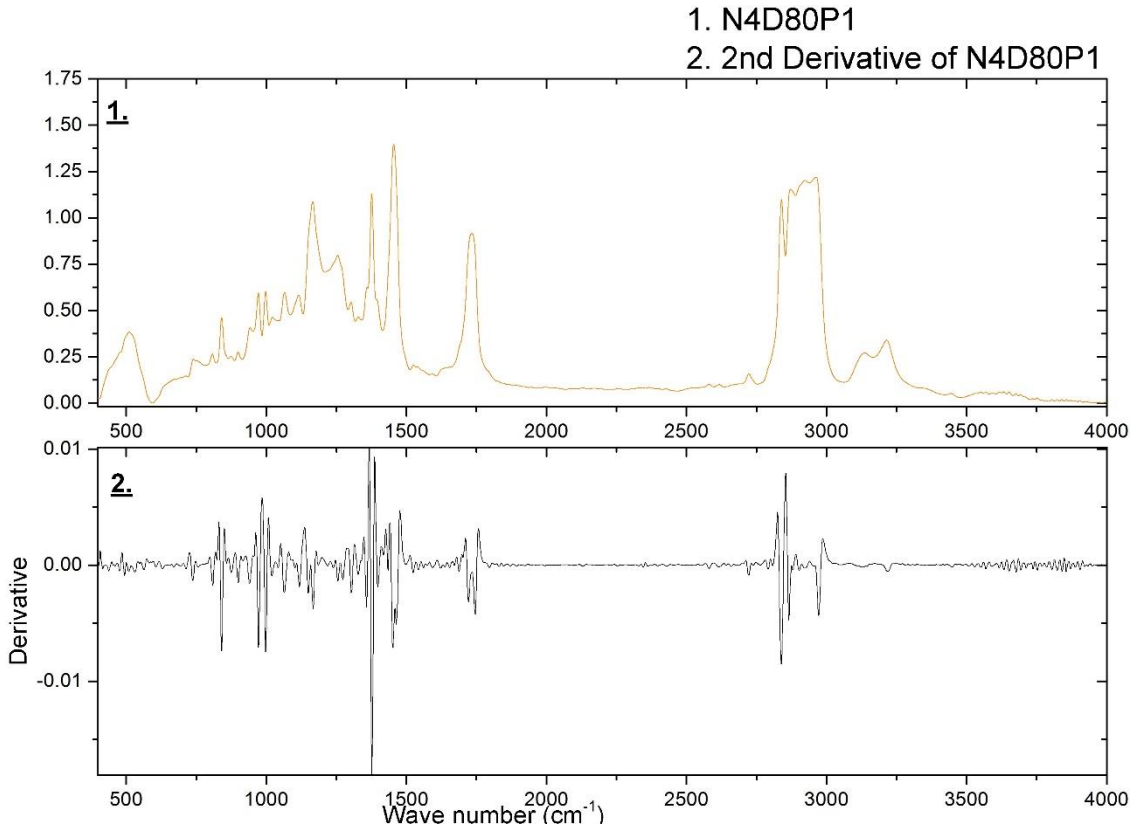

Figure B.9: FTIR spectra for 2nd derivative of N4D80P1

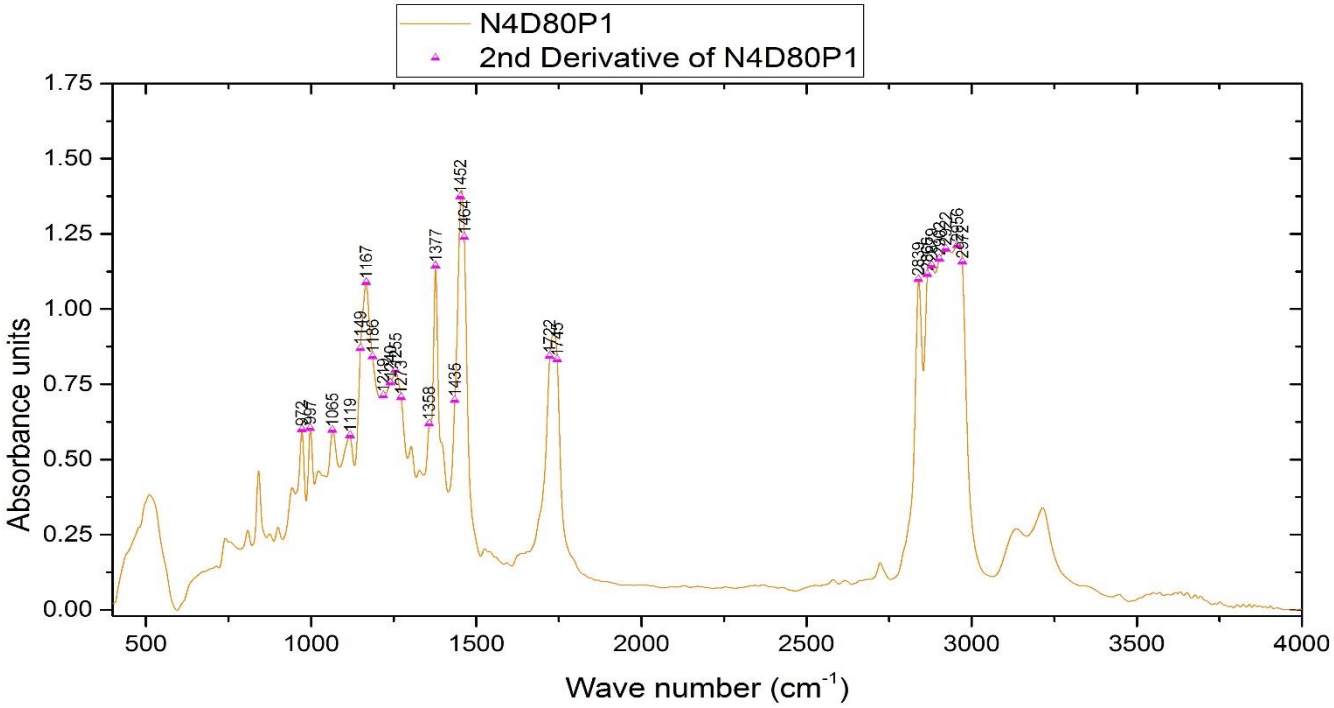

Figure B.10: FTIR spectra for 2nd derivative peaks of N4D80P1

Appendix C:

2nd derivation beak analysis for position two soil samples, and 2nd derivative assignments of the main bands observed in the FTIR spectra of all samples:

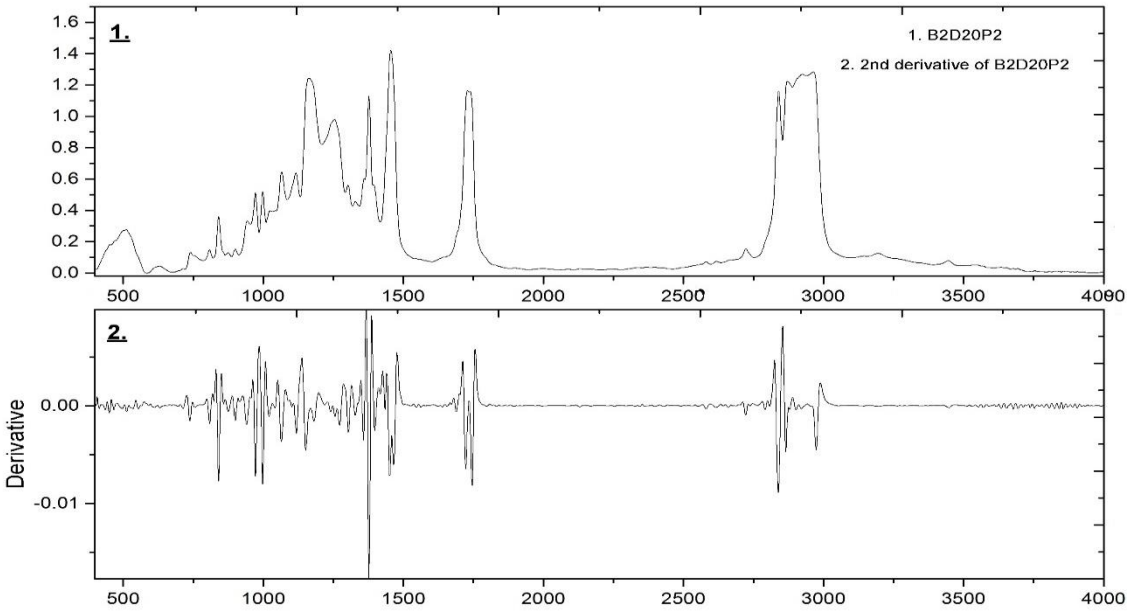

Figure C.1: FTIR spectra for 2nd derivative of B2D20P2

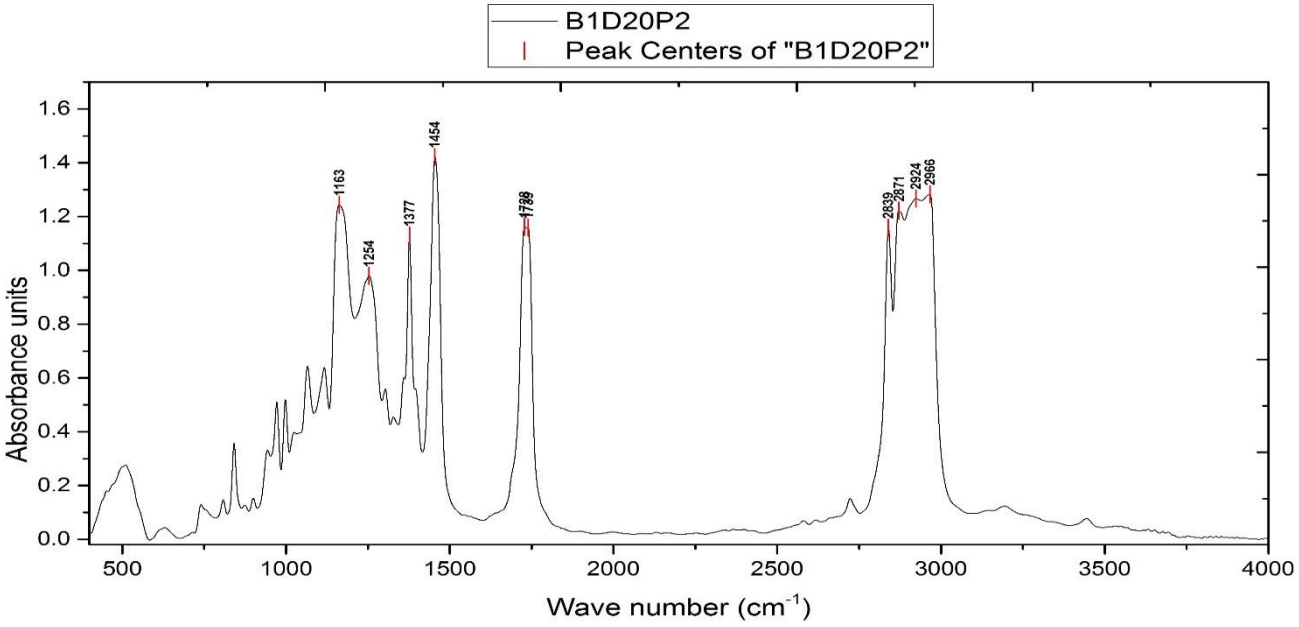

Figure C.2: FTIR spectra for 2nd derivative peaks of B2D20P2

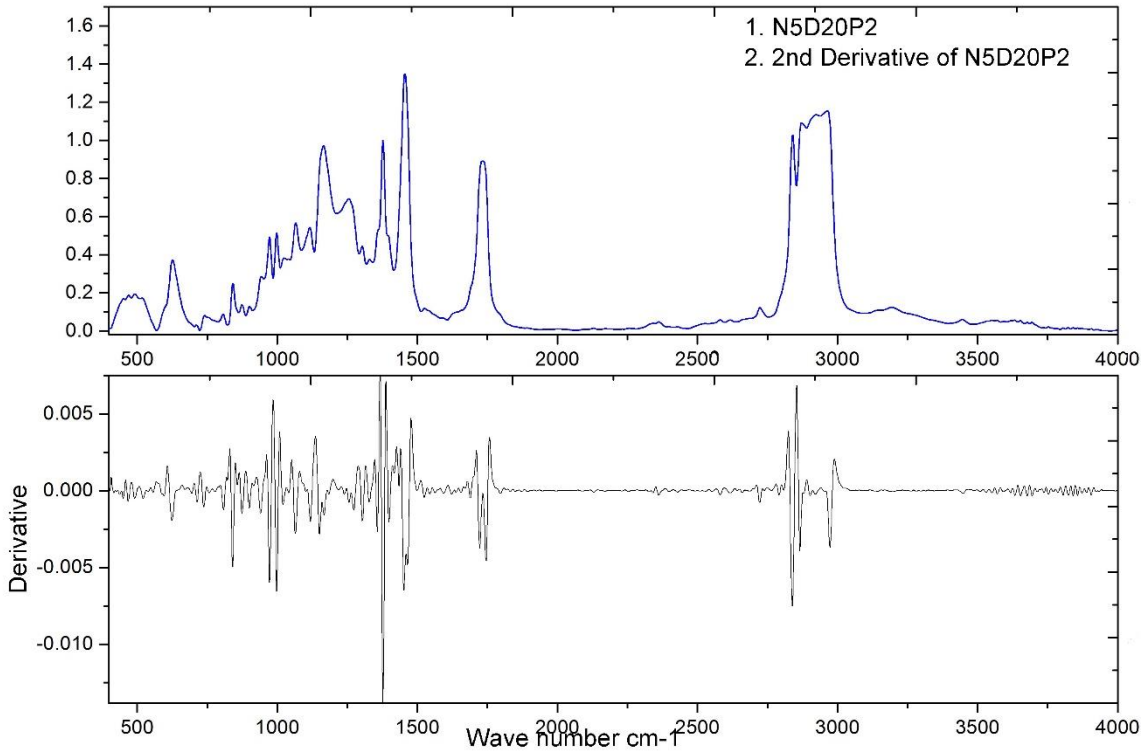

Figure C.4: FTIR spectra for 2nd derivative of N5D20P2

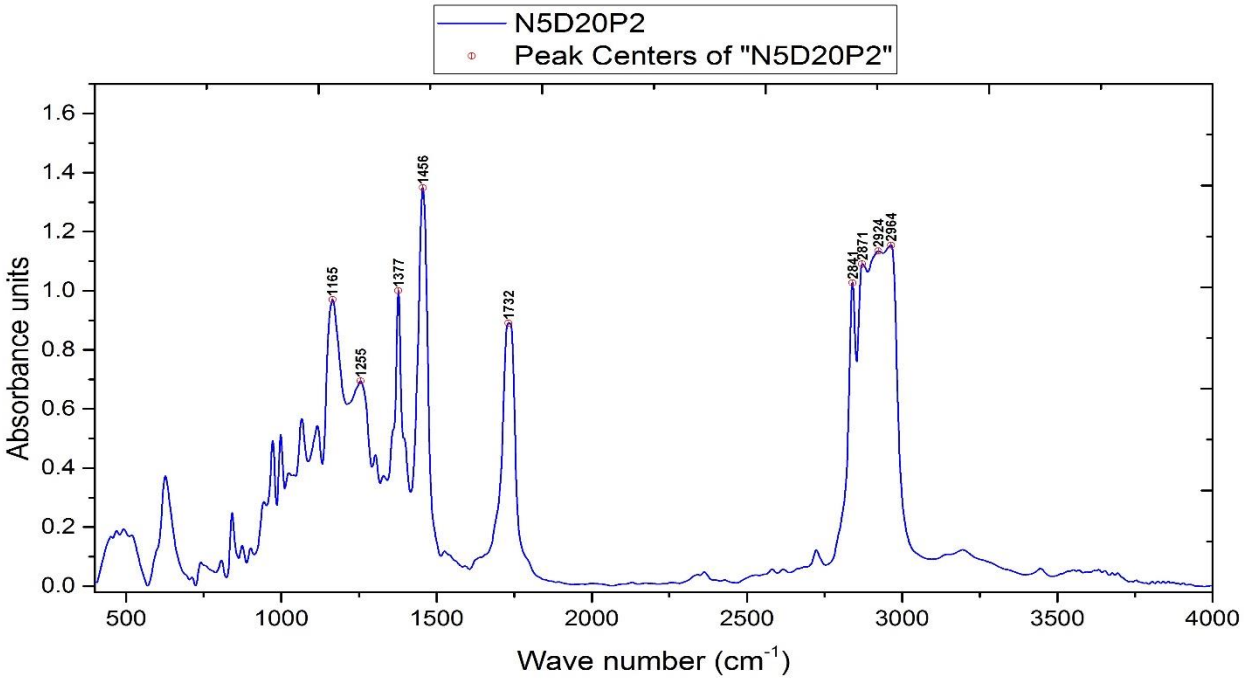

Figure C.3: FTIR spectra for 2nd derivative peaks of N5D20P2

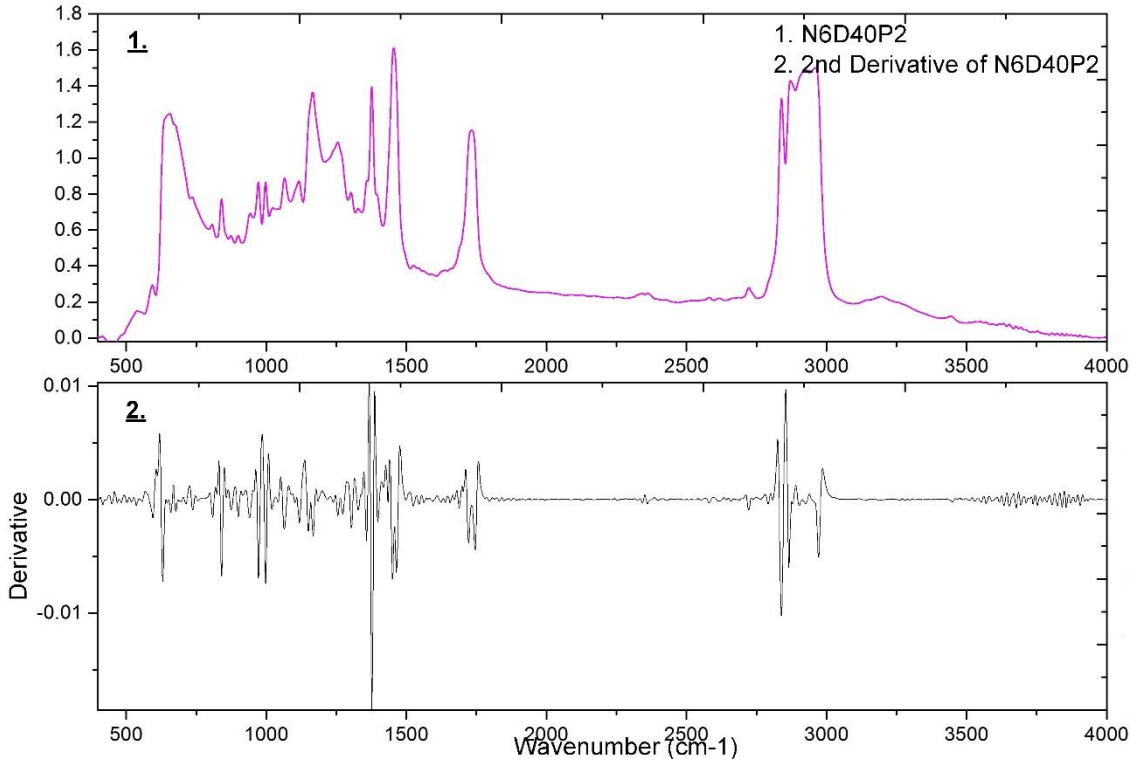

Figure C.5: : FTIR spectra for 2nd derivative of N6D40P2

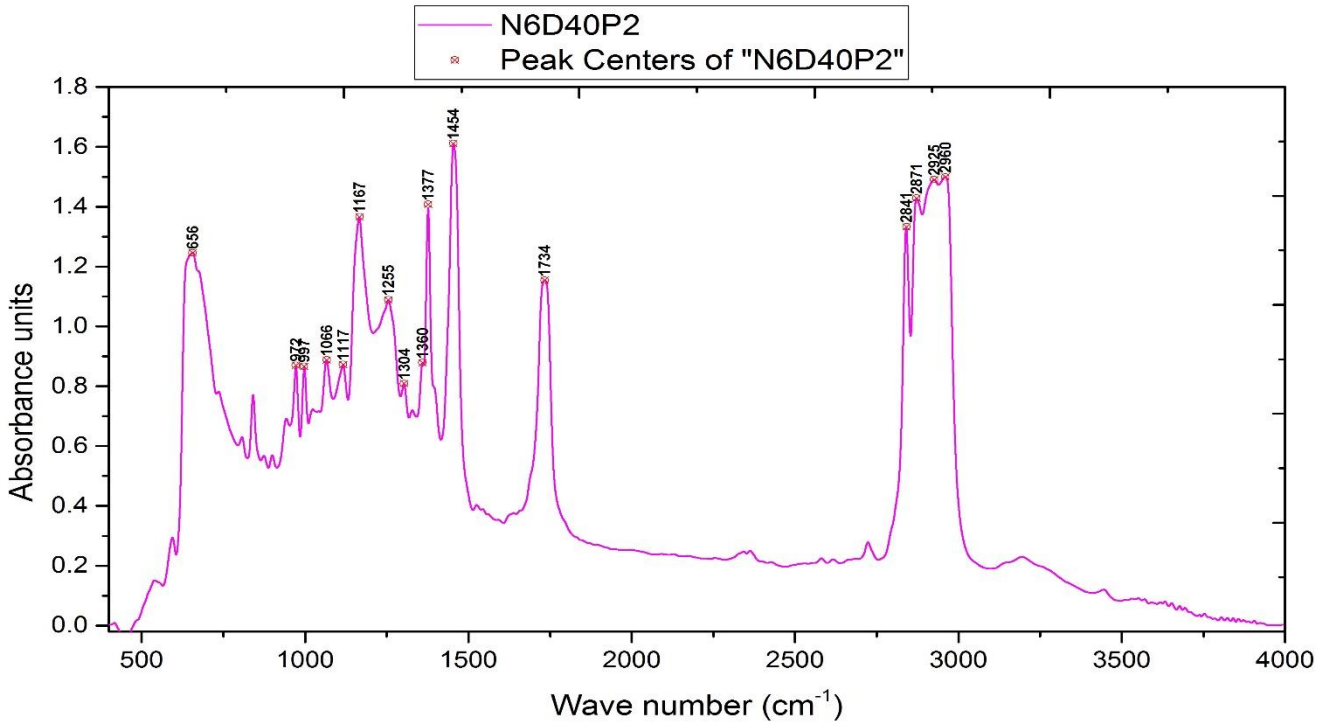

Figure C.6: FTIR spectra for 2nd derivative peaks of N6D40P2

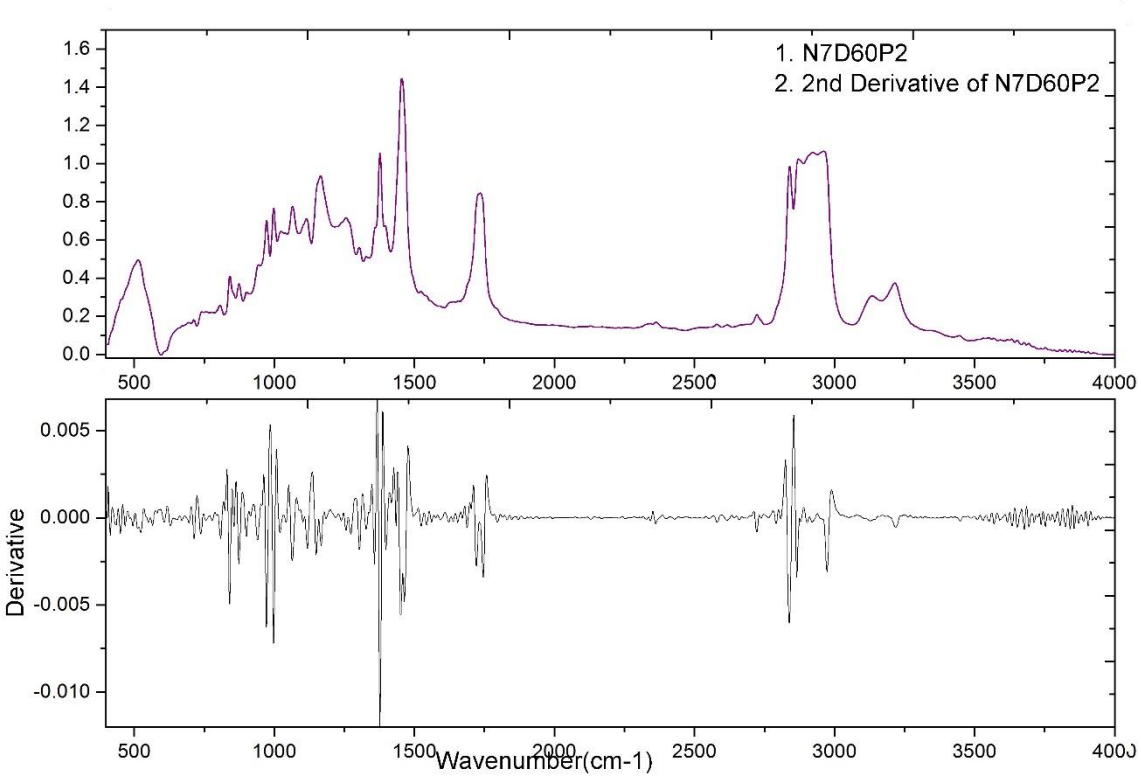

Figure C.7: FTIR spectra for 2nd derivative of N7D60P2

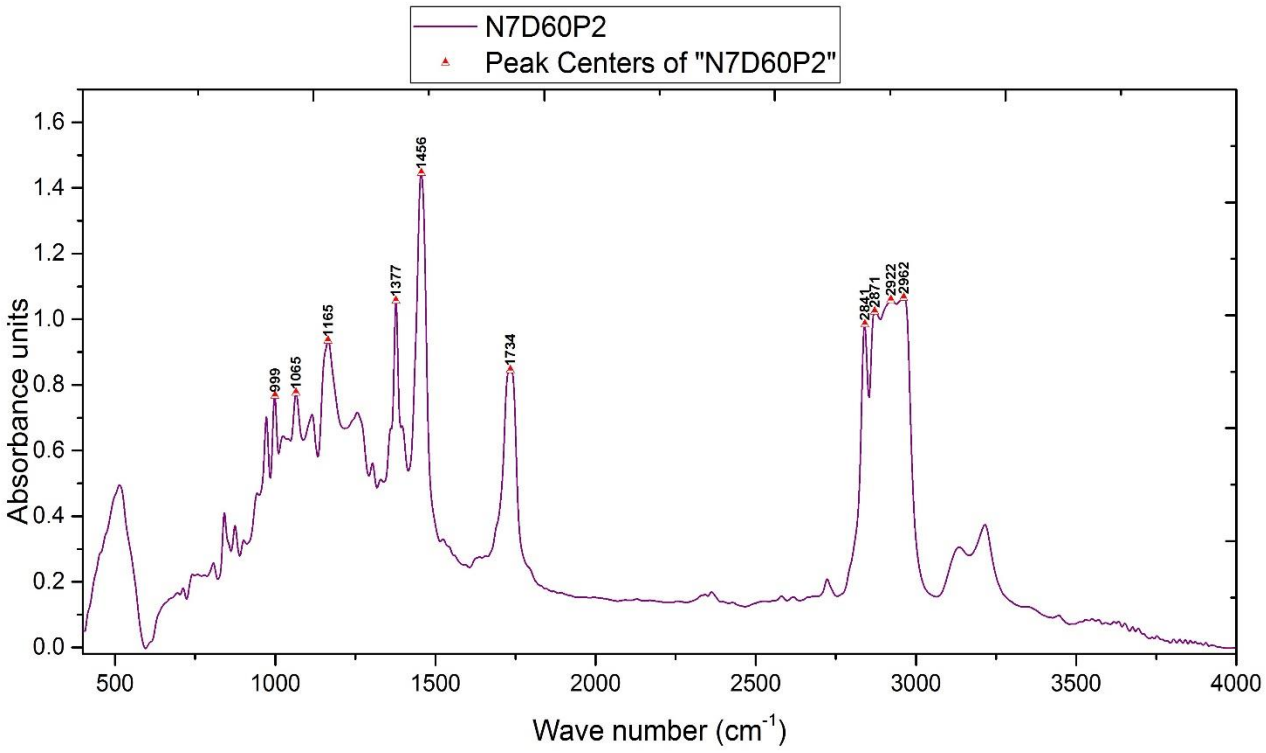

Figure C.8: FTIR spectra for 2nd derivative peaks of N7D60P2

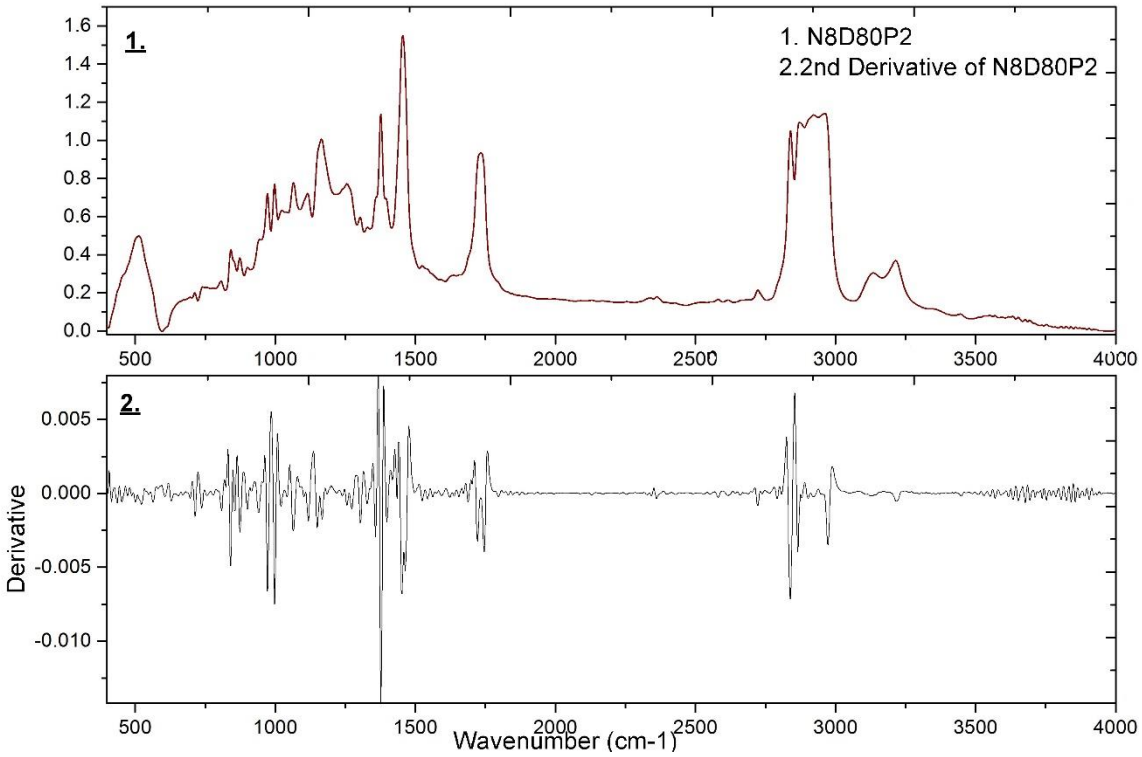

Figure C.10: FTIR spectra for 2nd derivative of N8D80P2

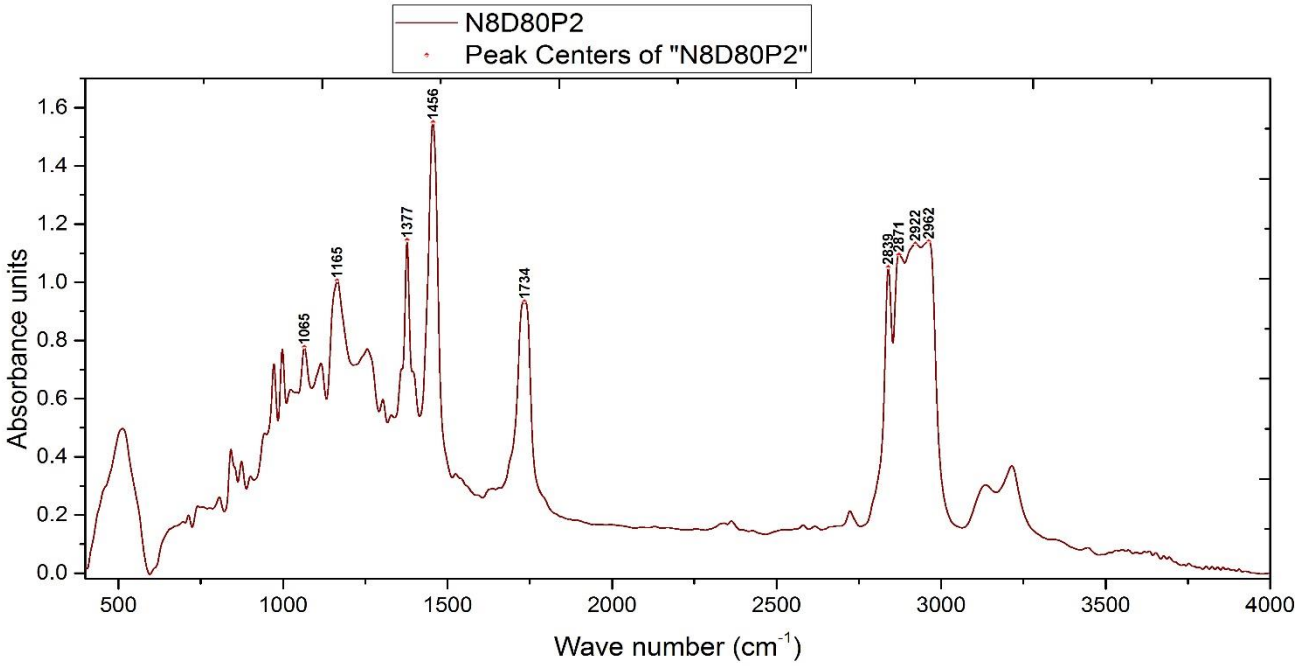

Figure C.9: FTIR spectra for 2nd derivative peaks of N8D80P2

Appendix D:

2nd derivation beak analysis for position three soil samples are shown, and 2nd derivative assignments of the main bands observed in the FTIR spectra of all samples:

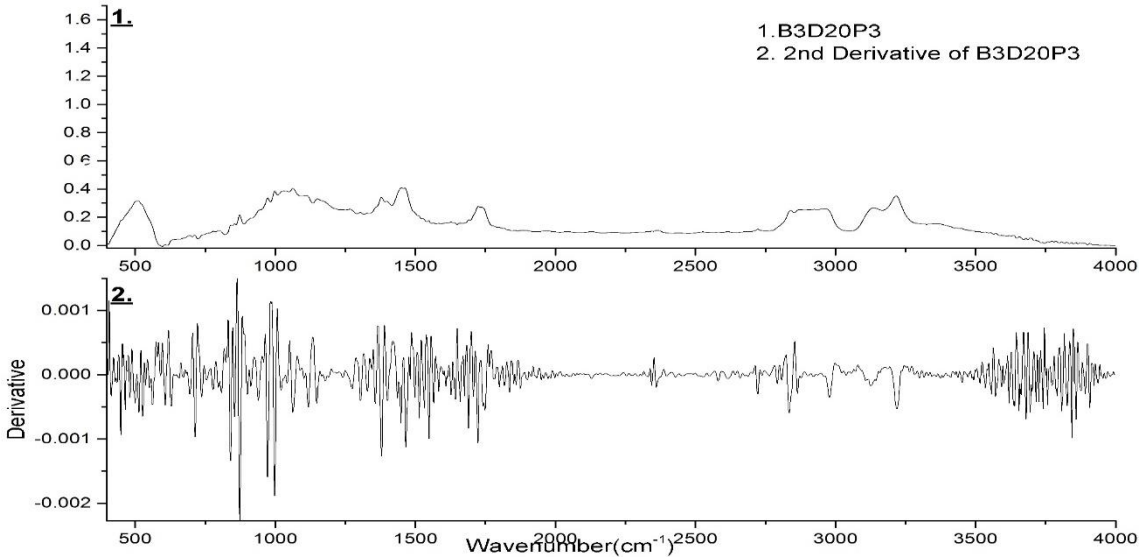

Figure D.2: FTIR spectra for 2nd derivative of B3D20P3

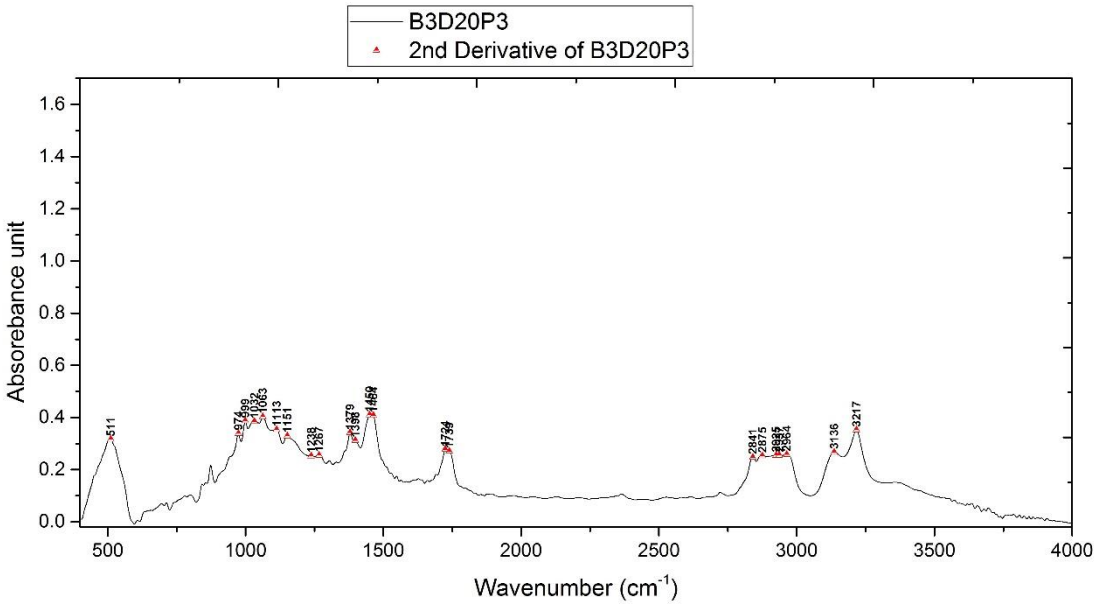

Figure D.1: FTIR spectra for 2nd derivative peaks of B3D20P3

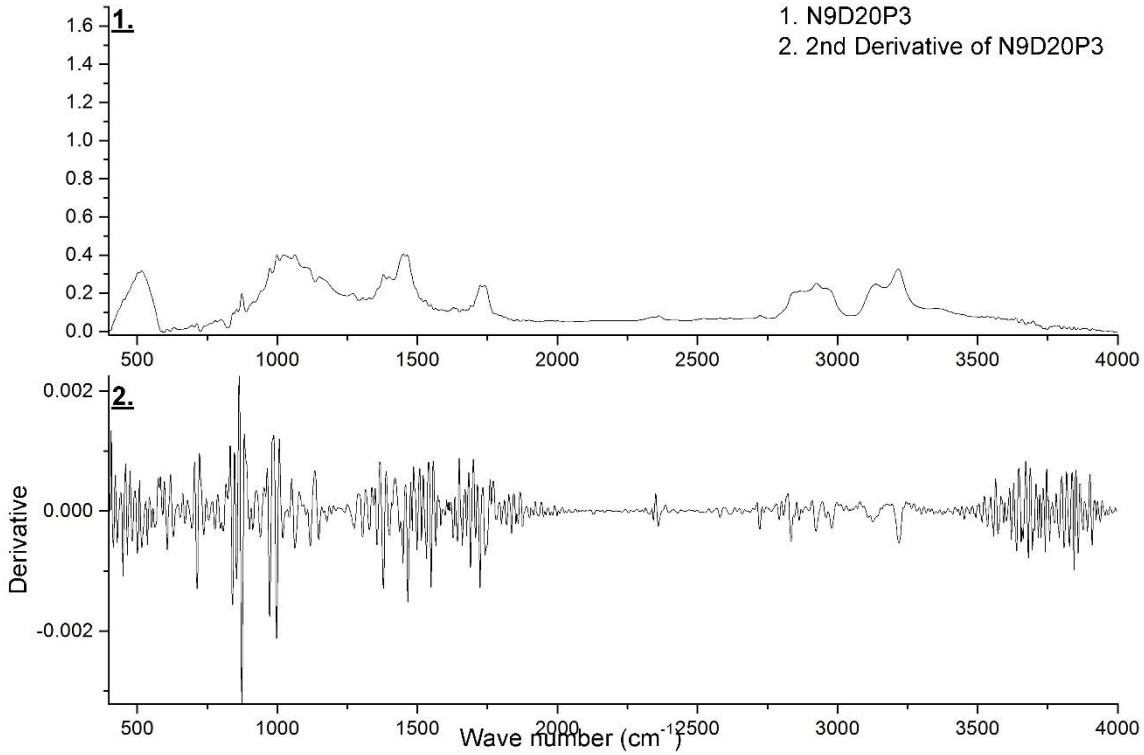

Figure D.3: FTIR spectra for 2nd derivative of N9D20P3

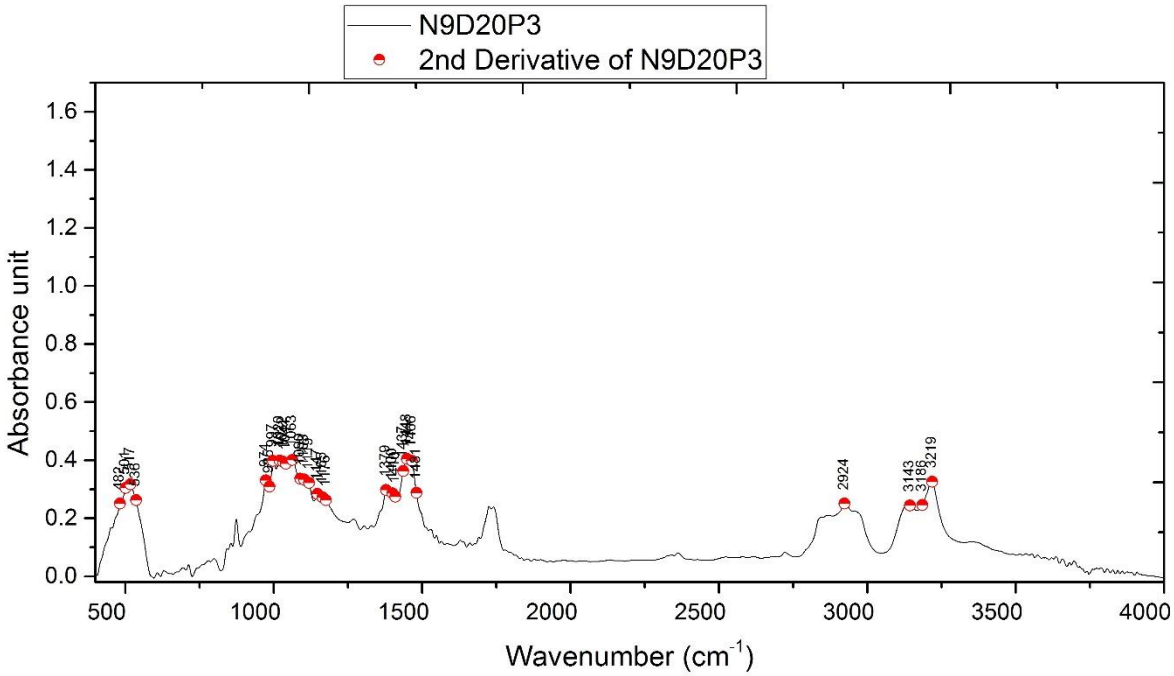

Figure D.4: FTIR spectra for 2nd derivative peaks of N9D20P3

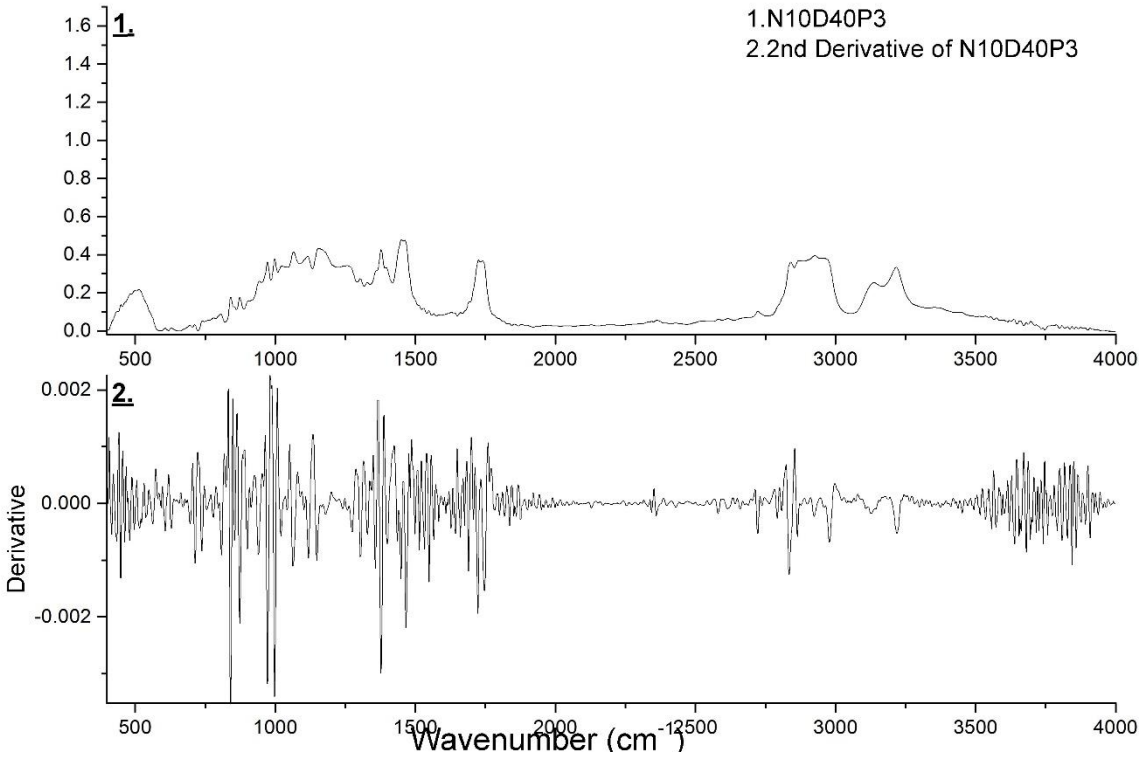

Figure D.5: FTIR spectra for 2nd derivative of N10D40P3

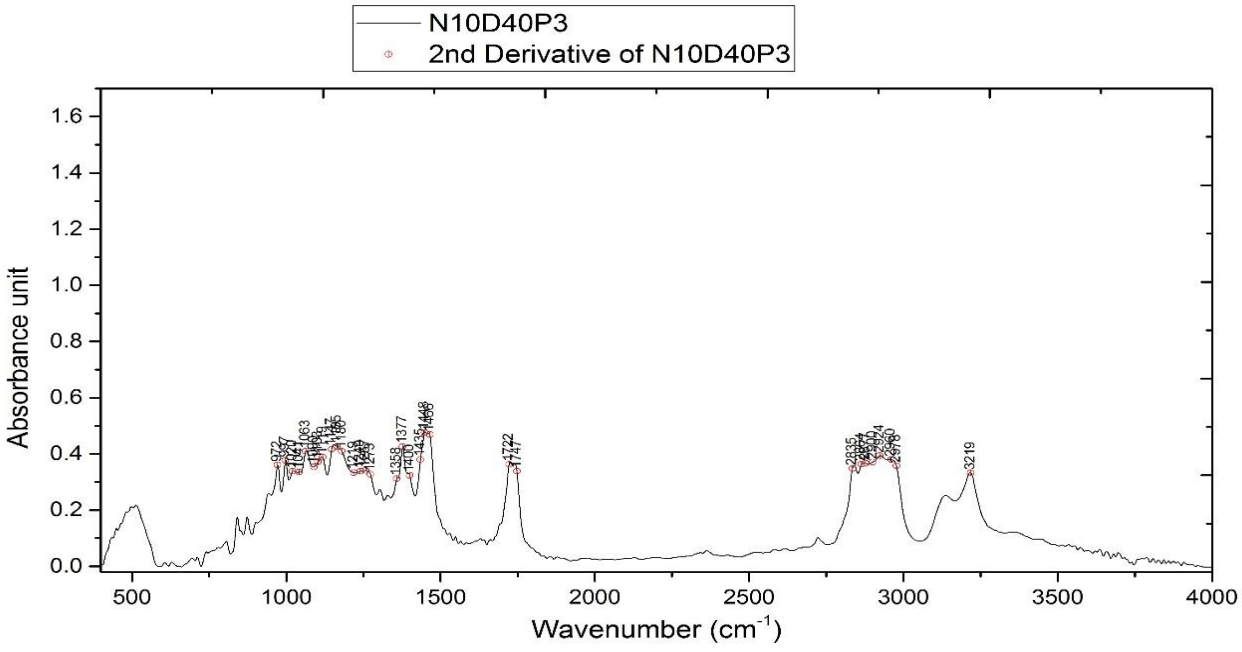

Figure D.6: : FTIR spectra for 2nd derivative peaks of N10D40P3

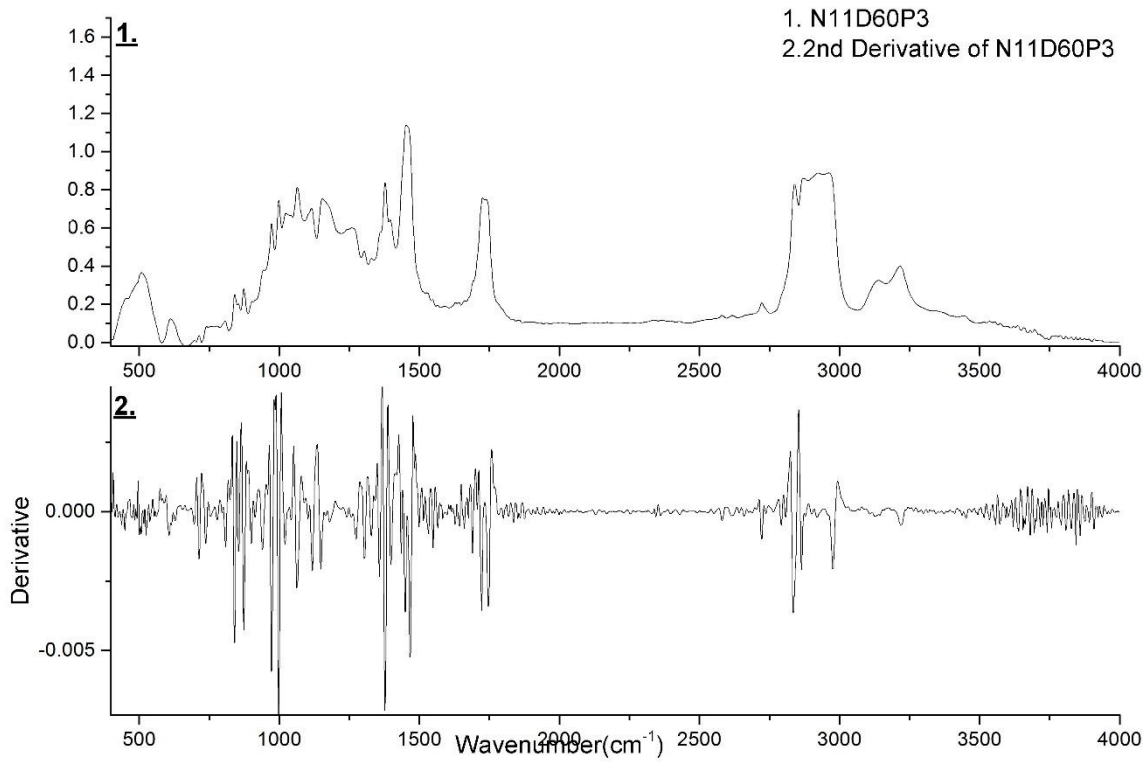

Figure D.8: FTIR spectra for 2nd derivative of N11D60P3

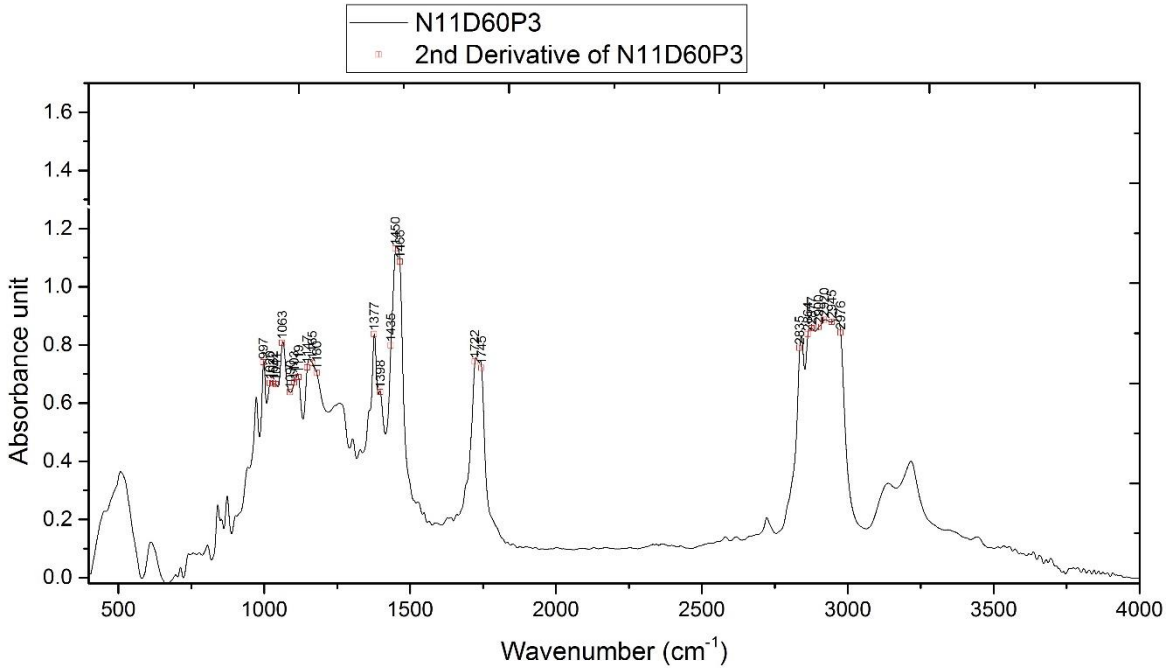

Figure D.7: FTIR spectra for 2nd derivative peaks of N11D60P3

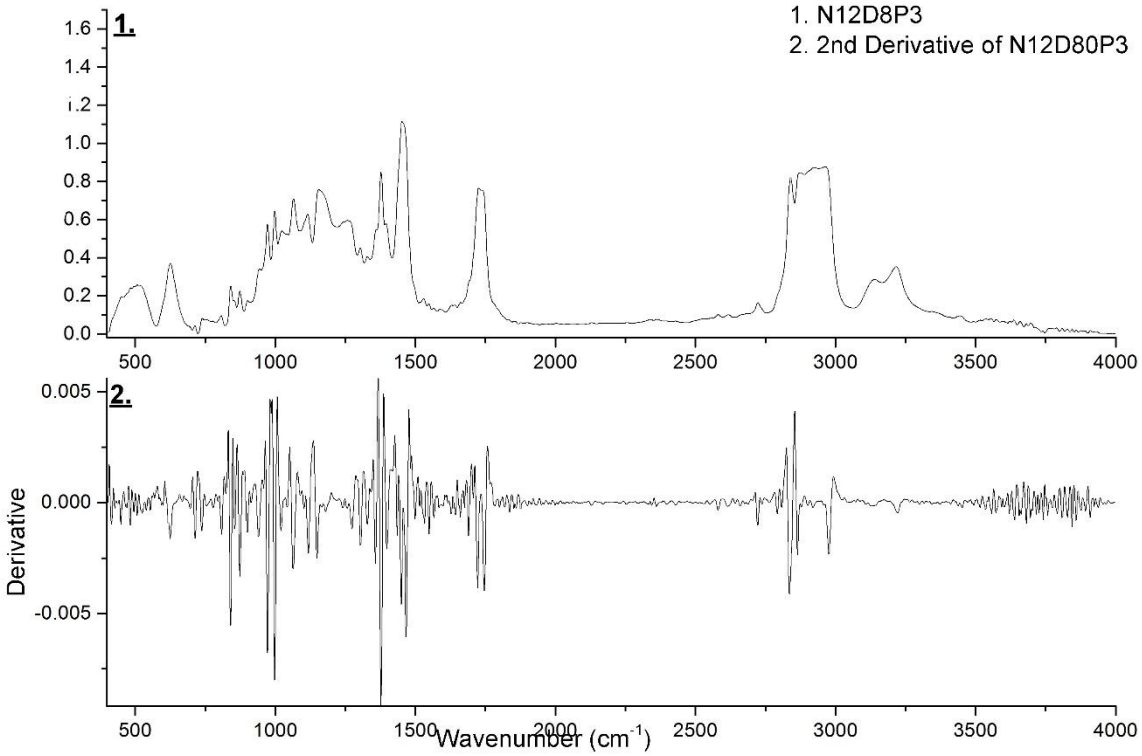

Figure D.10: FTIR spectra for 2nd derivative of N12D80P3

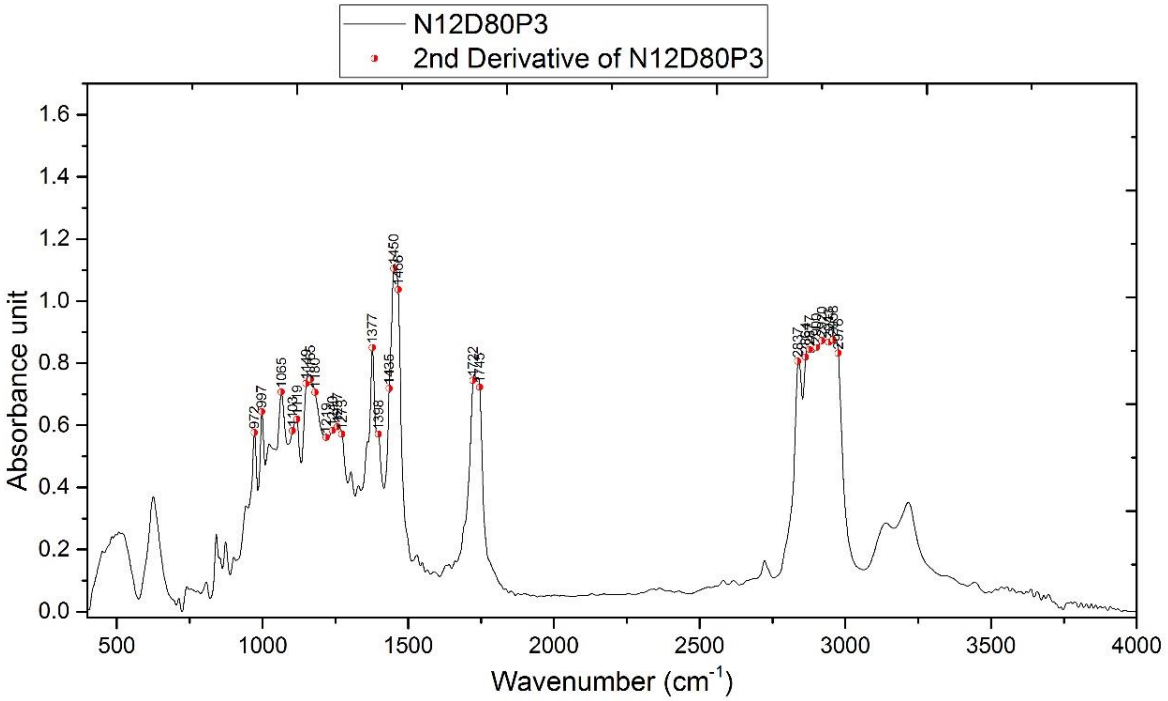

Figure D.9: FTIR spectra for 2nd derivative peaks of N12D80P3

Appendix E:

2nd derivation beak analysis for position four soil samples, and 2nd derivative assignments of the main bands observed in the FTIR spectra of all samples:

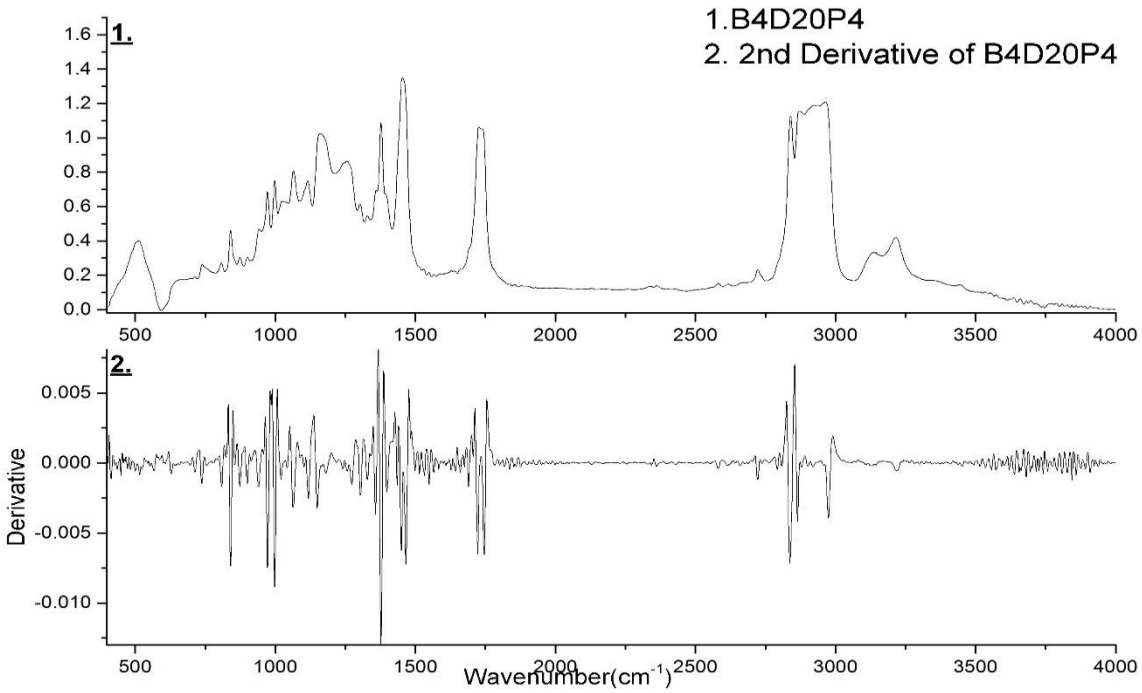

Figure E.2: FTIR spectra for 2nd derivative of B4D20P4

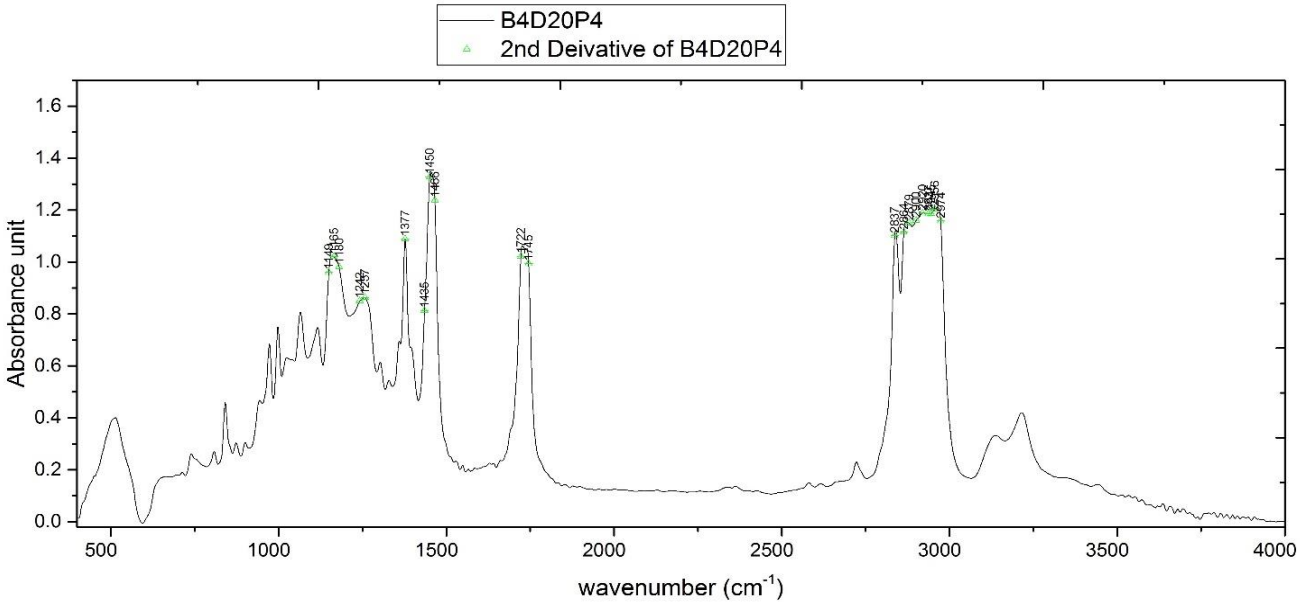

Figure E.1: FTIR spectra for 2nd derivative peaks of B4D20P4

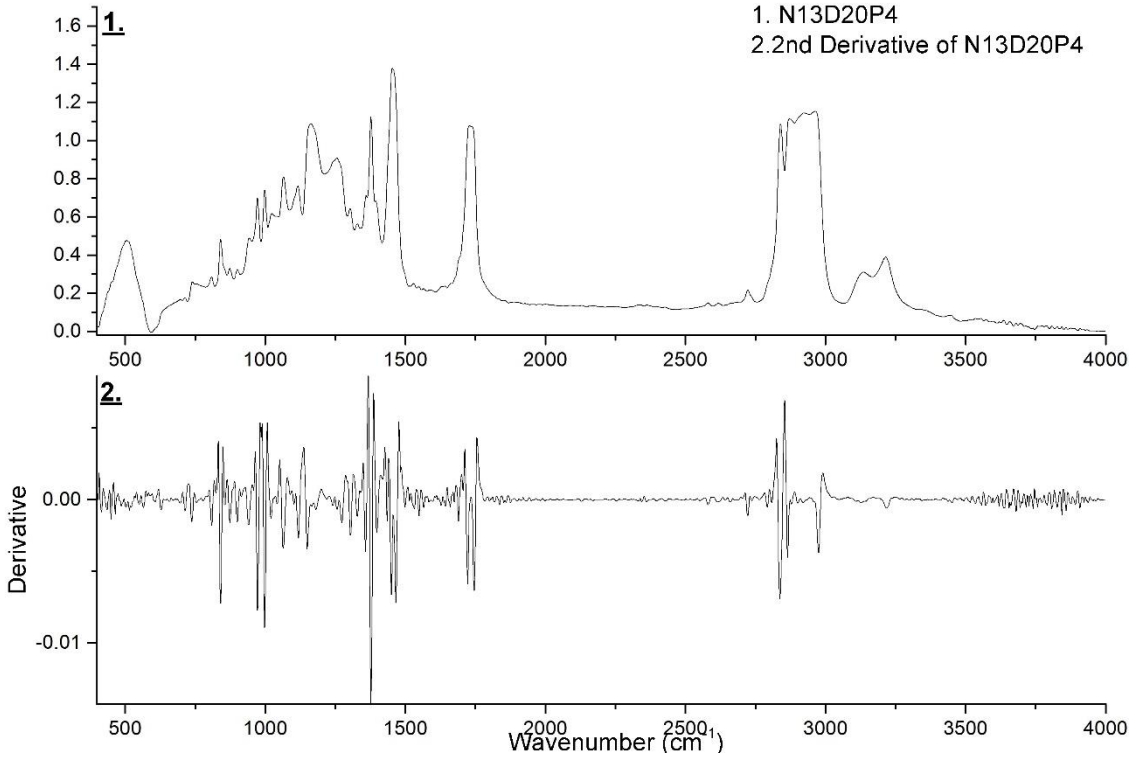

Figure E.4: FTIR spectra for 2nd derivative of N13D20P4

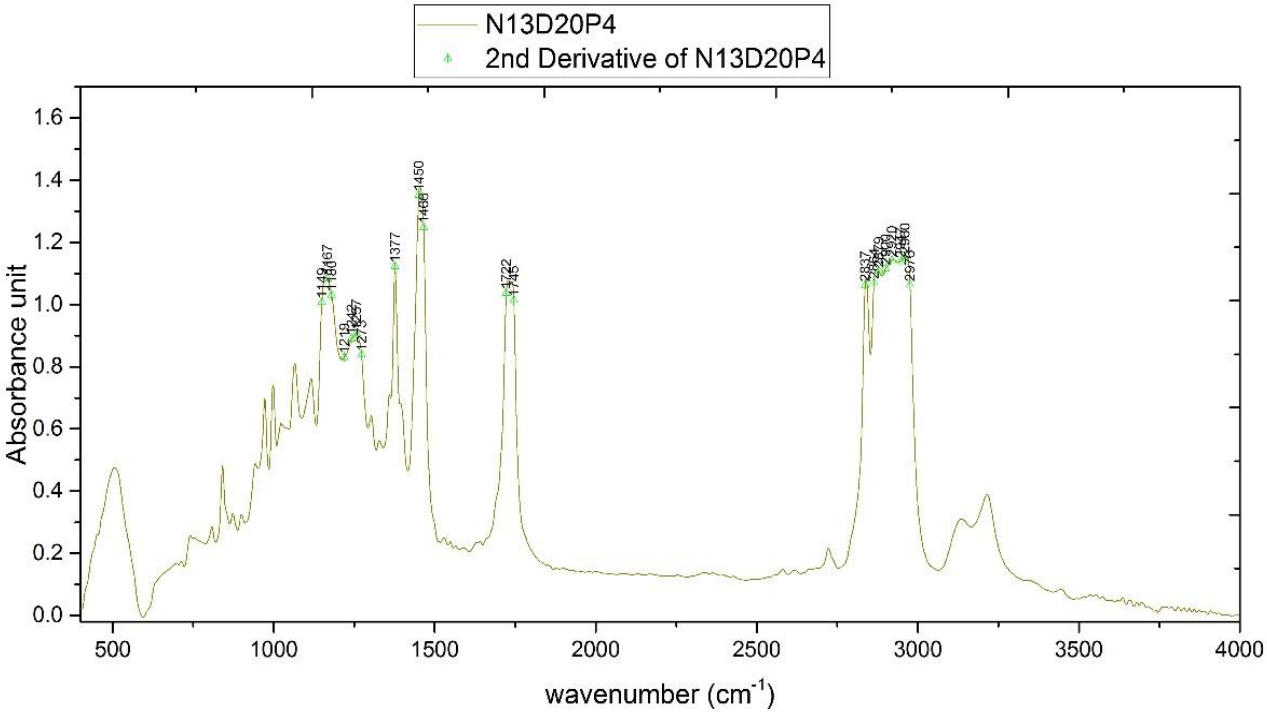

Figure E.3: FTIR spectra for 2nd derivative peaks of N13D20P4

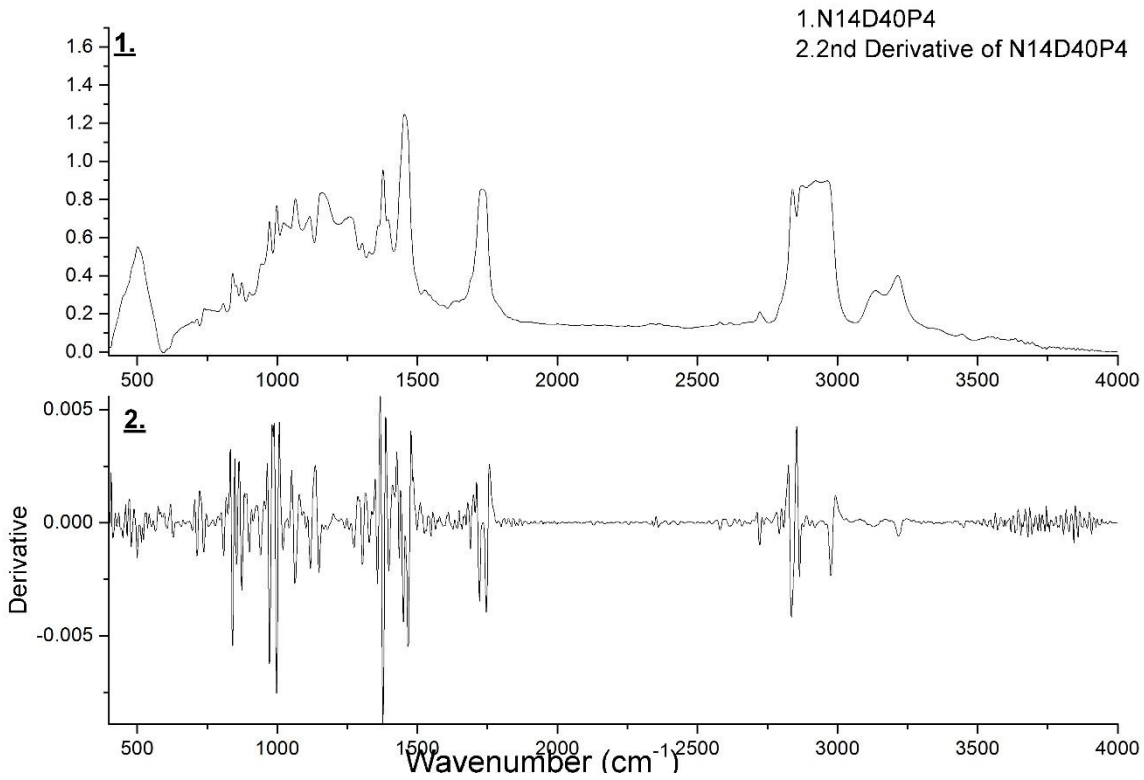

Figure E.6: FTIR spectra for 2nd derivative of N14D40P4

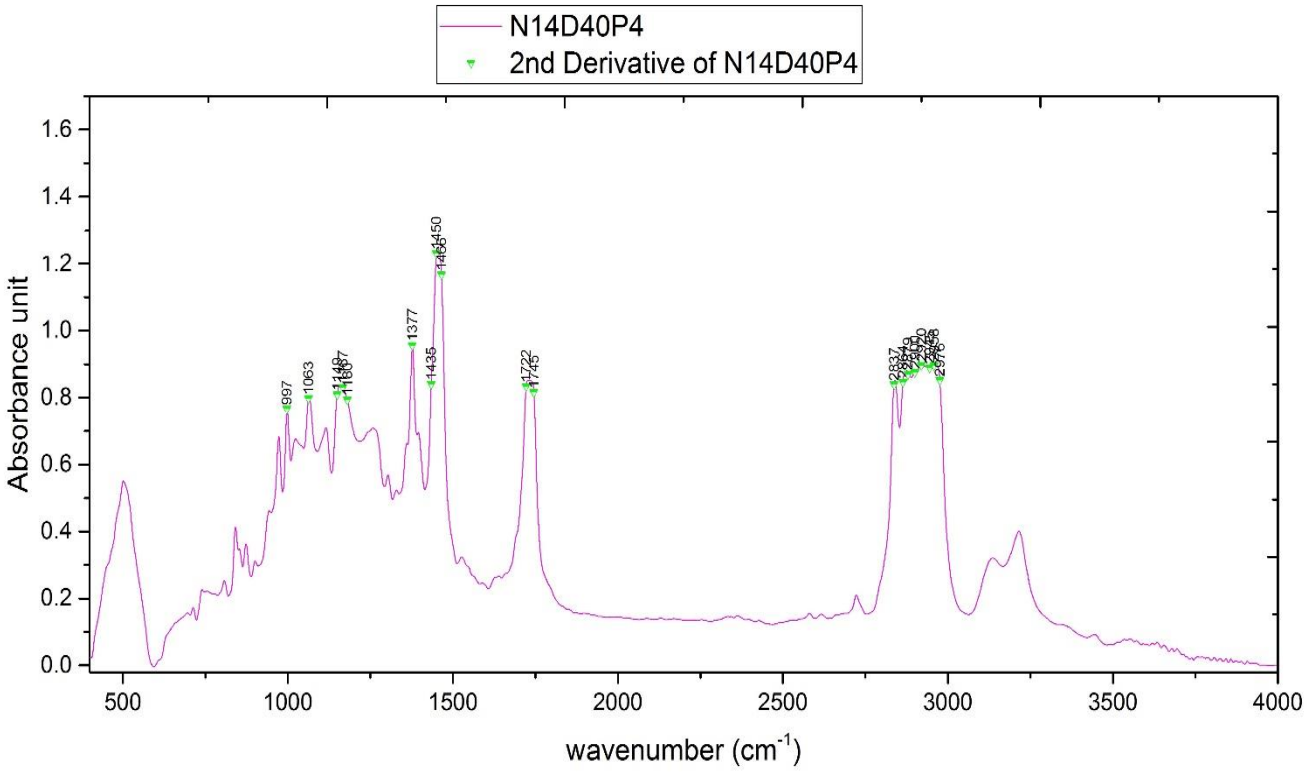

Figure E.5: FTIR spectra for 2nd derivative peaks of N14D40P4

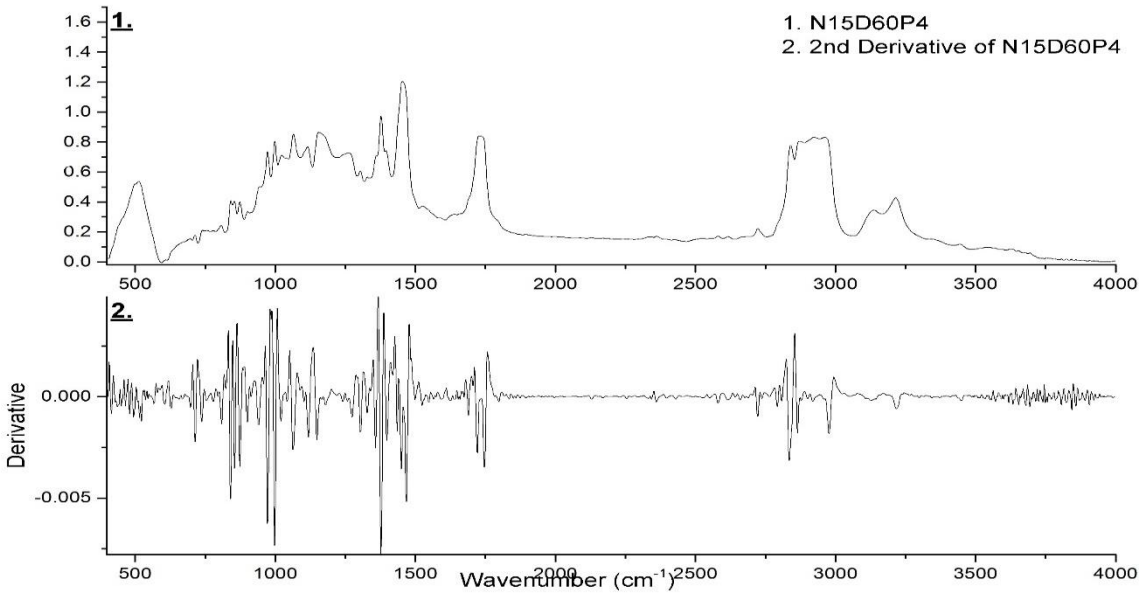

Figure E.8: FTIR spectra for 2nd derivative of N15D60P4

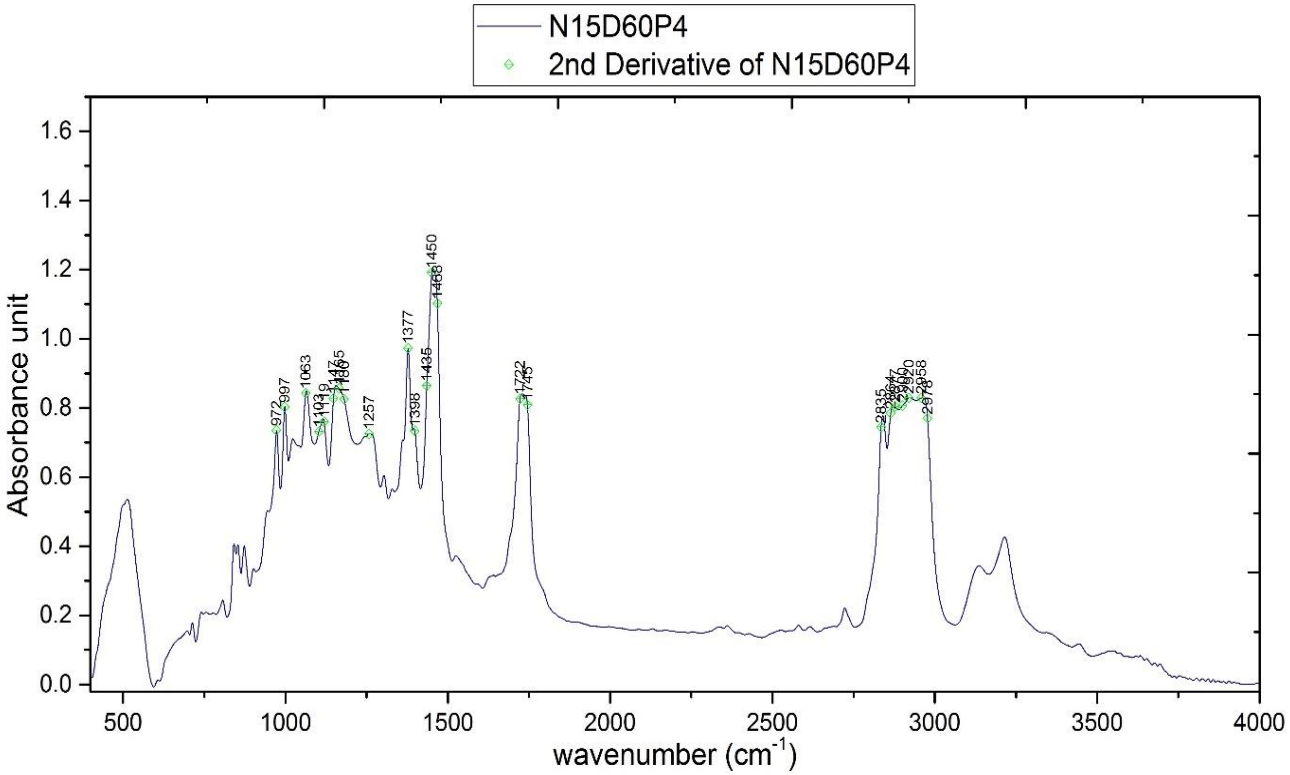

Figure E.7: FTIR spectra for 2nd derivative peaks of N15D60P4

Appendix F:

XRD mineral for positions No.1 and No.4

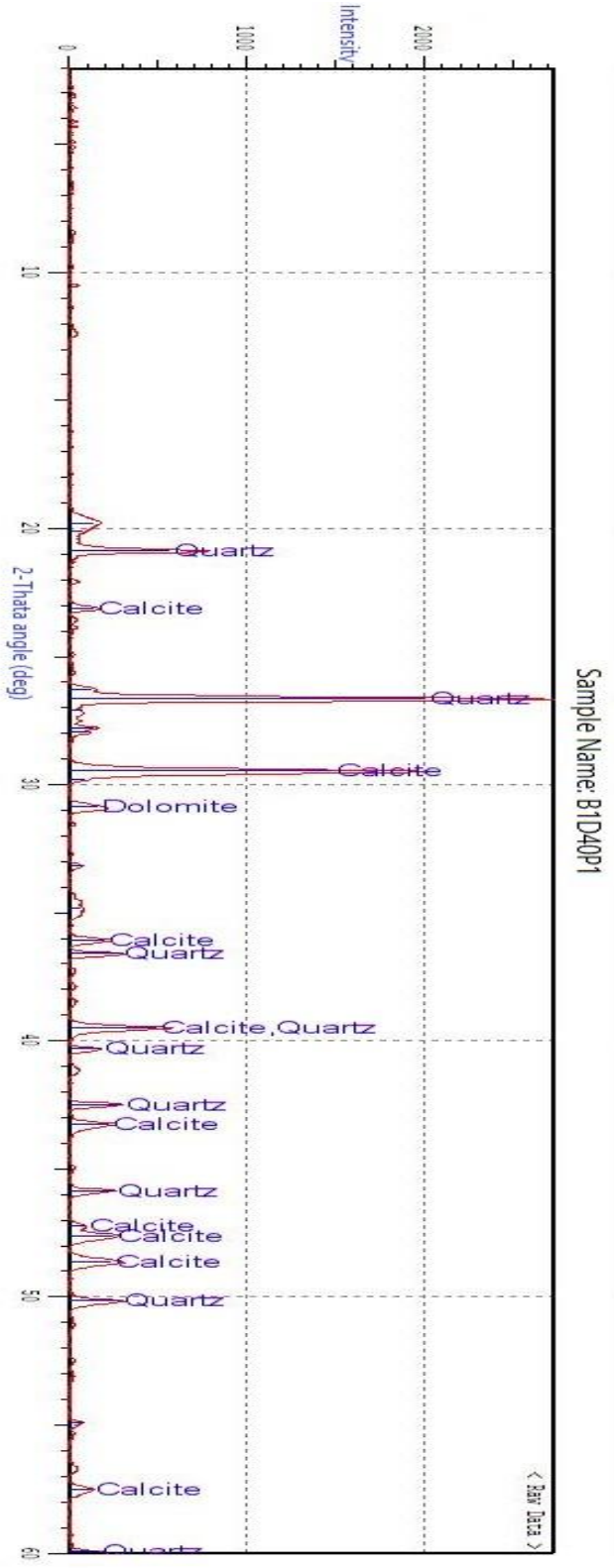

Figure F.1: : XRD mineral of B1D40P1 soil sample

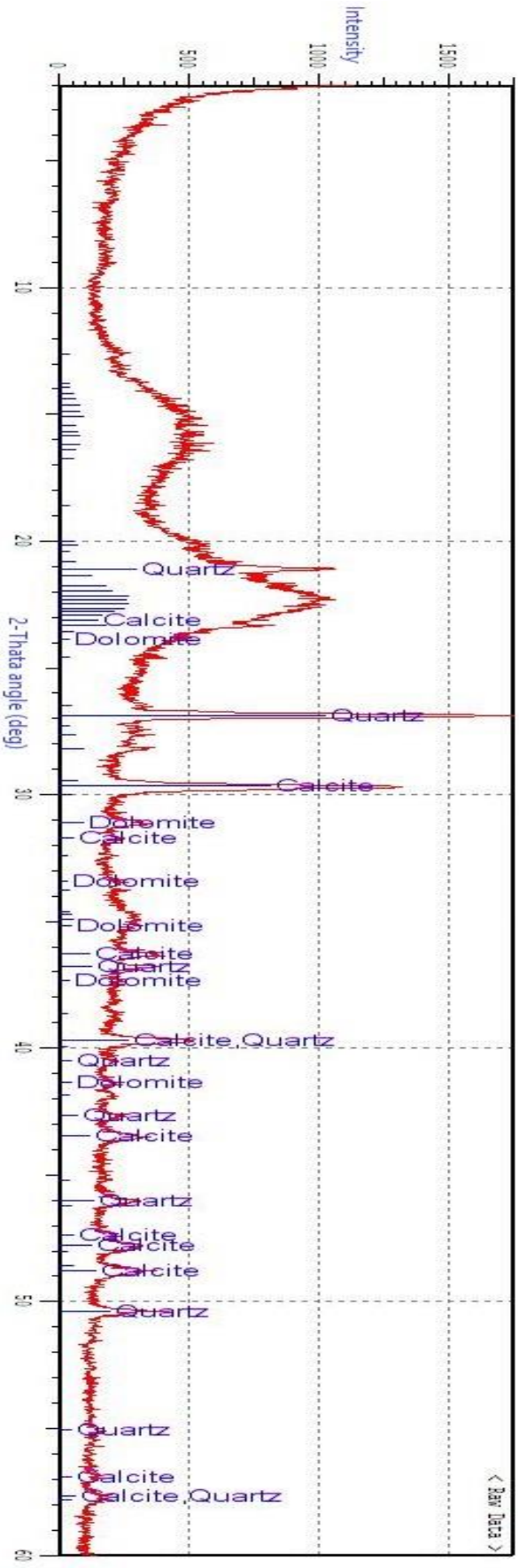

Figure F.2: XRD mineral of N2D40P1 soil sample

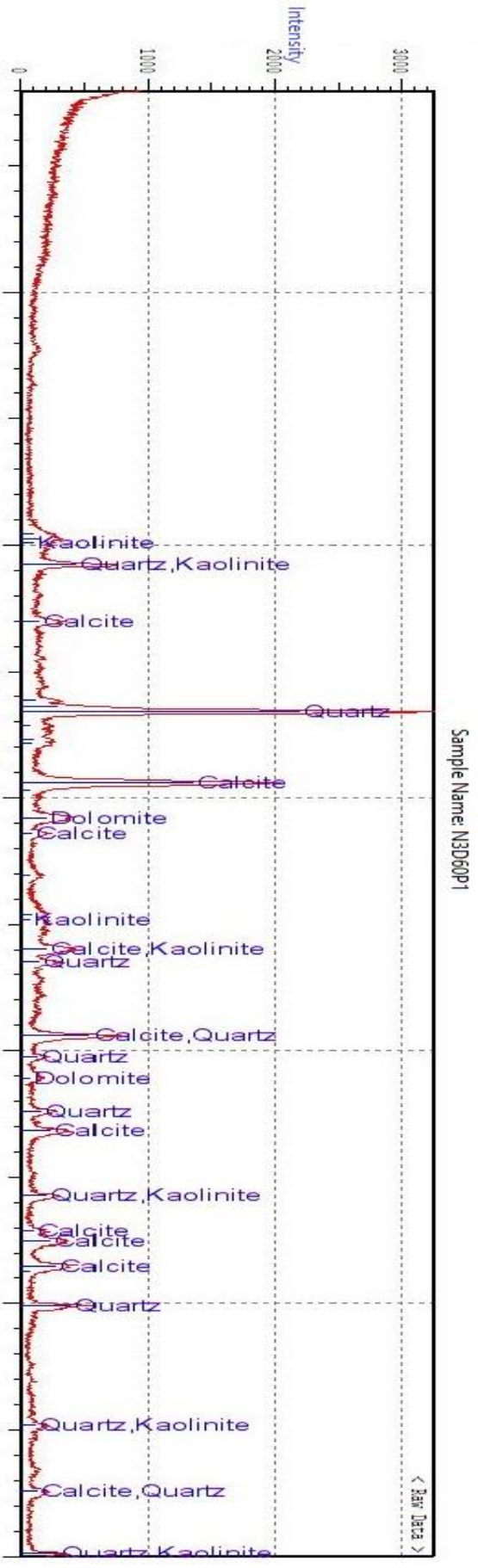

Figure F.3: XRD mineral of N3D60P1 soil sample

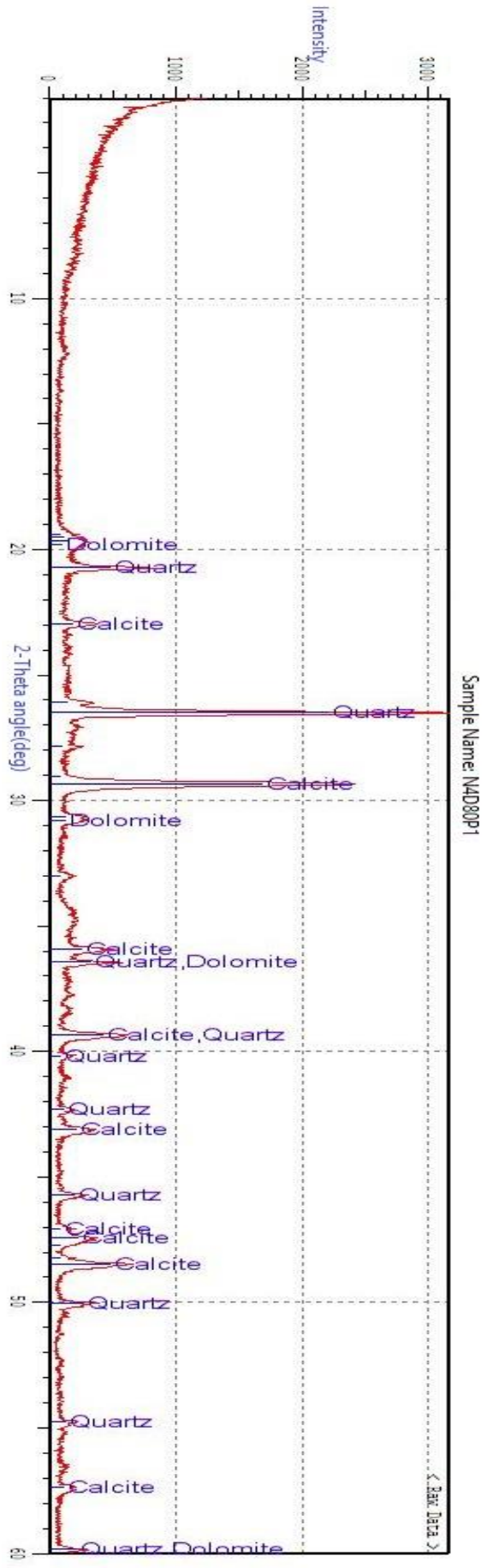

Figure F.4: XRD mineral of N4D80P1soil sample

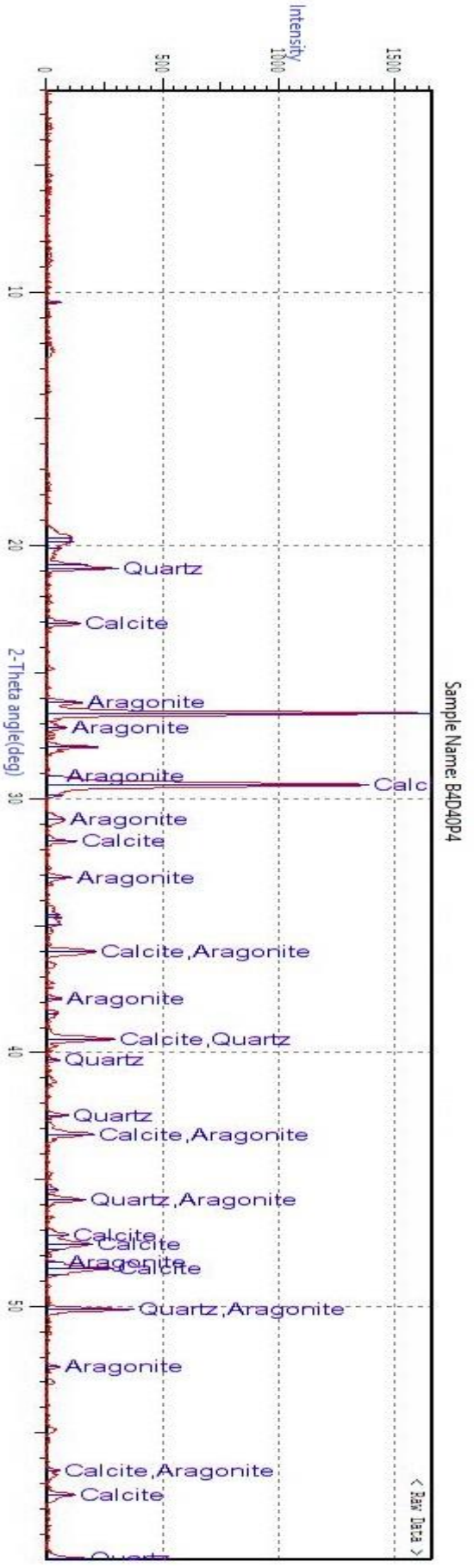

Figure F.5: XRD mineral of B4D40P4 soil sample

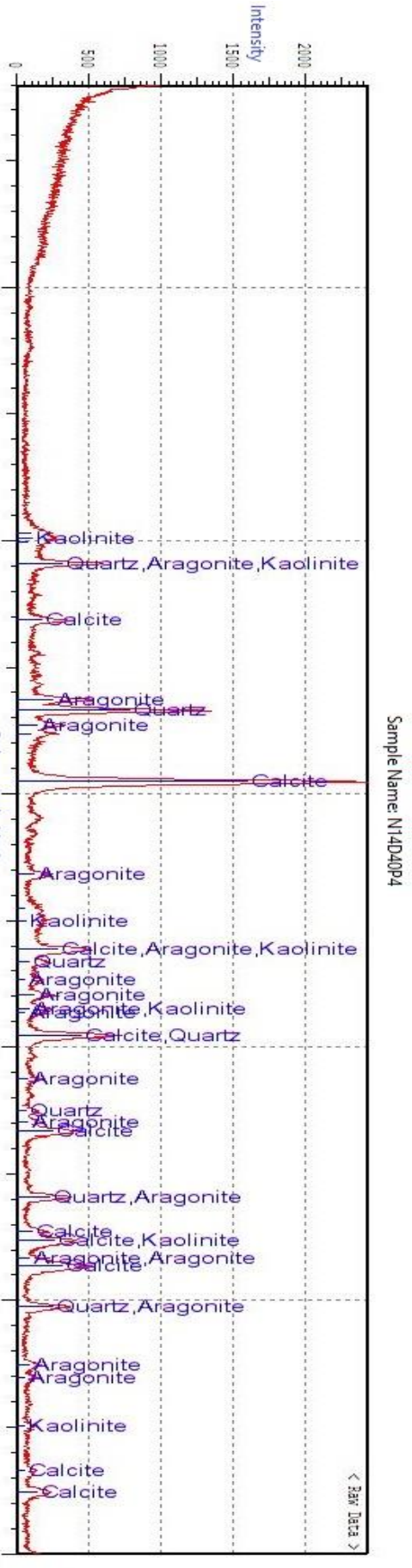

Figure F.6: XRD mineral of N14D40P4 soil sample

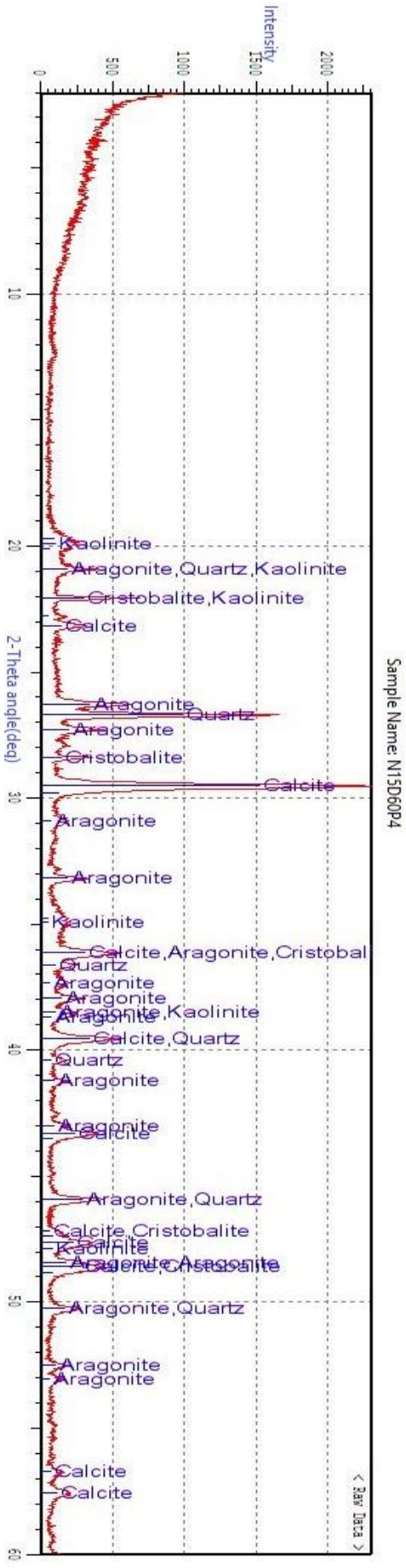

Figure F.7: XRD mineral of N15D60P4 soil sample

دراسة طيفية للمغذيات الكبيرة والمغذيات الدقيقة في تربة منطقة العوجا لإشجار النخيل

إعداد: أسماء محمود ابوحماد

إشراف: أ.د.عامر مرعي

ملخص:

في هذه الدراسة، تم جمع عينات تربة من مزرعة نخيل التمر في منظقة العوجا من مواقع مختلفة من المزرعة مقسمة الى اربع مواقع، عينات التربة التي تم جمعها من اعماق مختلفة تتراوح ما بين 0-20 سم، 20-40 سم، 40-60 سم، 60-80 سم من مسافات متساوية قريبة من جذع الشجرة.

كان الهدف الرئيسي لهذه الدراسة هو تطوير منهجية جديدة تستخدم لاول مرة في فلسطين تحدد اهم المغذيات النباتية الاساسية للنبات وزيادة فهم العلاقة بين عمق التربة والتفاعل ما بين التربة والاسمدة المغدية بالإضافة الى فهم العلاقة بين اضافة تراكيز مختلفة من الاسمدة للتربة باستخدام تقنيات التحليل الطيفي القائمة على التحليل الطيفي للاشعة تحت الحمراء(IR) الاهتزازية، مطافية الفلورة(FS)، مطيافية الاشعة السنينة بالإضافة الى مطياف الكتلة(ICPMS) المستخدم في قياس العناصر المغذيات الكبيرة والدقيقة ايضاً. حيث اظهرت هذه الدراسة ان التقنيات الطيفية شكلت ادوات بحث مفيدة لإعطاء فهم أفضل للعلاقة بين الاسمدة والتربة.

اشتملت الدراسة على قسمين لكل قسم هدف يرمو اليه، القسم الاول هدف الى دراسة العلاقة ما بين عمق التربة والاسمدة المغدية والقسم الثاني كان الهدف منه هو دراسة العلاقة ما بين تركيز الاسمدة المغذية والتربة.

بالنسبة للقسم الاول من الدراسة، أظهر التحليل المخبري لعينات التربة ان التربة كانت طميية رملية وطميية في القوام، وأن رواسب الملوحة كانت تتراوح ما بين التربة المالحة والمالحة جدا مع درجة حموضة ما بين 7-8.5 وكانت خصائص التربة الكيميائية هذه جيدة نوعا ما لإنبات محصول النخيل. ومن تحليل ICPMS أضهرت النتائج ان كل المواقع في منطقة الدراسة تعاني من نقص نسبة المغذيات الدقيقة وايضا مستويات المغذيات الكبيرة كانت حول المدى المنخفض والمنخفض جدا بإستثناء مستويات الصوديوم التي كانت عالية جداً من جميع المواقع.

كما وأظهرت نتائج تحاليل الفلوريسنت ان كثافة الفلورة تتناقص مع زيادة العمق وهذا ما يشير الى وجود ارتباط قوي بين الاسمدة والتربة مع زيادة العمق وخاصة في العمق 80 سم. وأظهرت تحاليل FTIR ثلاثة مناطق لذروة الاطياف في جميع المواقع وتم دراسة التاثيرات الناجمة عن زيادة العمق على القمم المختلفة الموجودة في مناطق الذروة. حيث أظهرت النتائج الارتباط القوي الواضح الناجم عن الاعماق المختلفة للتربة مع الاسمدة.

وأظهر تحليل الاشعة السينية، بيانات قوية ومفيدة جداً أظهرت معادن التربة في مواضع بداية ونهاية منطقة الدراسة المتمثلة في الموقع الاول والموقع الرابع، حيث عثر على معظم المعادن متمركزة في العمق 60 سم لكلا الموقعين، كما وأظهرت انواع مختلفة من المعادة ظهرت في الموقع الرابع ولم تثبت ظهورها في الموقع الاول وهذا ما يدعي الى الاهتمام بالاختلاف بنسبة التسميد ما بين بداية ونهاية موقع الدراسة.

أما بالنسبة للقسم الثاني من الدراسة، كان من الصعب دراسة العلاقة بين تراكيز الاسمدة المختلفة والتربة بسبب وجود عدد من العوامل الاخرى المؤثرة على هذه العلاقة مثل درجة الحموضة او البيئة المحيطة للتجربة، جيث أظهر تحليل

الفلورة اعتماد كثافة الفلورة على التركيز حيث زادت نسبة الكثافة مع زيادة التركيز للمواقع الاولية من منطقة الدراسة، بينما اظهرت علاقة مختلفة تماما في المواقع الاخرى.

كما وظهر تحليل ATR-FTIR كأداة قوية واكثر افادة من FTIR لتزويده بمعلومات عن المواضع التي تظهر بها ذروة الاكاسيد على مدى رقم موجي اكبر من 3300سم$^{-1}$ كما وكانت النتائج تعطي ان الكثافة لا تعتمد على زيادة التراكيز.

اما بالنسبة للتوصيات الناتجة عن هذه الدراسة، فإننا نوصي بزيادة الاهتمام بإضافة المعذيات الكبيرة واعطاء المزيد من الاهتمام لإضافة المغذيات الدقيقة ايضاً .

نقترح في دراسة مستقبلية دراسة العلاقة ما بين إضافة الاسمدة وتأثيرها على نبتة تمر النخيل كنبات وكثمرة وذلك باستخدام ذات الاساليب الطيفية من اجل الحصول على صورة واضحة لتأثير إضافة الاسمدة على التربة والنبات على حدٍ سواء.