2011

12. Analysis of Community Garden Soil and Leaves for Heavy Metals

Farwa Said
Technological University Dublin

Farwa Said

Compost Analysis of community garden soil and leaves for heavy metals.

List of Abbreviations

ICP-OES	Inductively Coupled Plasma Atomic Emission Spectroscopy
AAS	Atomic absorption spectroscopy
ATR	Infrared Spectroscopy
DSC	Differential Scanning Calorimetry
UV-Vis	Ultraviolet-visible spectroscopy

Abstract

Abstract

The purpose of this project is to determine the level of trace metals concentrations in soil samples and also in food. For this approach several soil samples and few leave samples were collected from an old community garden for this analysis. The samples were sieved in two fractions using sieve analysis and extracted using the nitric acid digestion. These samples were analysed by ICP-OES and AAS to determine the level of heavy metals present in soil. The results obtained indicated high level of Pb found in soil especially in patch A followed by B, C and D sample and very low level of copper. The plant sample was also found containing high level of Pb.

Furthermore tests were carried out on such as BRC Sequential extraction, Cation Exchange Capacity, Segregation and 1,2- phenylenediamine method in order to determine the type of Pb present in soil and the level of Pb found in the organic or inorganic matter. The results from the segregation and CEC method showed that most of Pb level is present in the inorganic of the soil and very little in organic matter.

The results of 1,2- phenylenediamine method showed the opposite results as the fluorescence intensity decreased with copper concentration instead of increasing. The technique proved to be not as simple as described in the paper and more information is required to make the method clear in term of degassing the solution.

The BCR results showed that the highest concentration of the lead level was found in residual fraction using nitric acid (~84%) and very little with other solution such as acetic acid extraction

The DSC gave the organic percentage for both the leave and the soil samples. Large amount of organic was found in leave samples (70%) and very little in the soil sample (~25%) as expected.

The level of Pb found in soil and plant sample are both way above the recommended literature values according to the health and food safety of Ireland and therefore serious action must be taken in order to minimise the risk on human and animals health.

Introduction

Introduction

Soil concept and Importance

Soils are a complex composite of loose mineral and organic material that constitutes the layer of the earth superimposed upon the earth's rocky crust. They provide nutrients for plants and also act as physical support and anchorage. Nutrients includes nitrogen (usually as nitrate and ammonia), phosphorous (as orthophosphate) and trace metals such as copper, iron, manganese and zinc.

The transport of materials in the soil is influenced by the acidity or alkalinity of the water in the soil structure. Soil pH is an important parameter which is frequently monitored. [1]

Through processes of physical and chemical deterioration of the firm, rocky layer, fragments of various sizes are created. The organic components derive from decaying plants parts, dead animals and microorganisms. Microbial decomposition affects all these organic materials, and animals that live on the ground break them down and digest them. Humus is composed of these decomposing organic materials. Both organic and inorganic materials form particles of various sizes, between which are hollows, the ''soil pores.'' Some of these pores are filled with air and some with water. This soil air and this soil water are the basis of life for plant roots and other organisms that live in the ground. In the course of time the humic layer of the soil mixes with the mineral layer that lies beneath it. Animals that burrow in the ground and plant roots that penetrate the soil are primarily responsible for the mixing process.

The soil particles form a fine mesh that filters solid materials out of seeping water, simultaneously the soil pores function as a storage site for materials. Lime and humus provide for a more firm fixation. Thus soil can hold harmful materials for years, without releasing them into the ground water. Soil have a high capacity for regeneration; the lager the number of life forms that live in the soil provide a wealth of different enzymes that metabolize more quickly than is possible in the air or water. [2]

Metals in Soil

In Soil the metals are present in a variety of forms. In some cases they are structural components of soil and minerals or minor constituents incorporated into soil organic matter. Environmental issues regarding soil trace metals often centre around their mobility and this is related to form in which it is present as well as the environmental situation. The most important environmental factors are the

amount, chemical nature and movement of water through the soil. Metals associated with the original inorganic material may not be readily available for uptake or leaching. [3]

Heavy Metal Contamination Sources

Heavy metal contamination *of* soil *is one of the most important environmental problems throughout the* world. The ability of heavy metals to accumulate and causes toxicity in biological systems- humans, animals, microorganisms and plants. As chemical hazards, heavy metals are non-biodegradable and can remain almost indefinitely in the soil environment. Therefore it is the most arduous challenge is contemplating a way to protect the planet from heavy metal contamination.

Soils contain a wide range of heavy metals with varying concentration ranges depending on the surrounding geological environment and anthropogenic and natural activities occurring or which have occurred. These metals can be Fe, Al, Cr, Mn, Ni, Zn, Cu, Pb, Cd, Hg. Metal transport is not only dependent on the physiochemical properties of the metals but mostly on the physical and chemical properties of the soil. [4]

Chemical and metallurgical industries are the most important sources of heavy metals in the environment. Heavy metals get accumulated in top layer of the soils and plants. This could have a negative influence on physiological activities of plants.

In small concentrations, the traces of the heavy metals found in soil such as iron, manganese and aluminium are not toxic in plants or animals. The most heavy metals commonly found at contaminated sites are metals such as lead, chromium, zinc, cadmium, copper, mercury and nickel. These metals found in contaminated soils are toxic even in very low concentrations. [5]

Metals Background

Accumulation of metals in the surface of soil at high concentration over a long period of time causes threat to the environmental quality and human health. Major pathways of exposure include plant uptake, inhalation of soil dust, or direct ingestion.

The major concern is to find ways in which enable to minimise or remove the level of contaminated metals that are toxic to humans and plants and protect the environment.

Table 1: Shows the recommended limits of metal concentration in Compost standard for Ireland. [6]

Heavy Metals (mg/kg dry matter)	
Mercury	**0.4**
Cadmium	**1.3**
Nickel	**56**
Chromium	**92**
Copper	**149**
Zinc	**397**
Lead	**149**
Pathogen	
Salmonella (in 25g)	**0**
Escherichia soil (cfu/g fresh mass)	**1,000**
Impurities	
Total glasses, metal and plastic >2 Mm diameter by weight	**0.5%**
Stability	
Oxygen uptake rate mmol O_2/kg organic solid/h)	**13***
Organic matter	
Organic matter (% dry weight)	**20% Minimum**

*By 2014 there is n objective of limit value of 10 mmol O_2/kg organic solid/h.

Environmental and Health risk of heavy metals – Sources

Lead

The most common source lead that comes from are solder, toys, dust, soils, Lead-based paint, combustion residue, sinkers, trinkets, car batteries, radiators and some inks etc. Lead salts are extremely toxic. The ingestion of a soluble lead salt can cause acute poisoning, and long term exposure to a source of the metal (e.g. old water pipes, lead based paints) may results in chronic poisoning. Organolead(IV) compounds such as Et_4Pb used as an anti-knocker additive to leaded motor fuels, attack the nervous system. [7]

The effect of lead even at relatively low levels can cause birth defects in unborn child and children under the age of seven years, partly because they absorb a greater percentage of dietary lead and partly because brains are growing rapidly. [8]

Lead exposure occurs when lead dusts are inhaled or a high level of lead is introduced into the body which can poison and kill humans and animals. The lead in the body can damage internal organs, damage the brain, nervous system and in a long term scenario it can cause reproductive disorders such as osteoporosis. [9]

Lead entering the respiratory and digestive systems is released to the blood and distributed throughout the body. More than 90% of the total body burden of lead is accumulated in the bones, where it is stored. Lead in bones may be released into the blood, re-exposing organ systems long after the original exposure. [10]

If swallowed, lead can be extremely toxic to aquatic organisms and may affect the life of living organisms by food poisoning. This can also lead to a reduction in the economy of the country as a reduction in the number of aquatic life is being observed.

Lead is present in the upper soils, there is also a small level of lead in the mineral soils. Plants and animals may be affected by lead if it reaches a level of 7.5 mg/kg for plants and 50mg/kg for a daily dosage on animals and humans. [11]

The presence of lead in the soil can lead to severe damage in the environment. Sources of lead in dust and soil include lead that falls to the ground from the air, and weathering and chipping of lead-based paint from buildings and other structures. Lead in dust may also come from windblown soil. Disposal of lead in municipal and hazardous waste dump sites may also add lead to soil. Deposits of lead in soil can harm both humans and animals by absorbing it into a body.

Mercury

Mercury is a naturally occurring element in the earth's crust. Mercury is the most volatile of metals, and its vapour is highly toxic. In nature, mercury is emitted into the atmosphere through soil erosion, volcanoes and forest fires. Volcanoes and oceans vents are the main source of naturally occurring mercury in our oceans.

Exposure to mercury is associated with serious health and developmental effects e.g. can damage to the nervous system and deformities in infants exposed to mercury in the womb. It affects unborn fetuses and their embryonic nervous systems, leading to learning difficulties and poor memory. Low level exposures also affect male fertility.

Industrial activity results in releases of mercury into the environment every year, in the form of air emissions from coal fired power plants. Mercury also is released into the environment by municipal and medical waste incineration, mining, and smelting. Once in the environment, elemental mercury can be transformed by microorganisms to organic forms compound called methylmercury. Methylmercury is of particular concern because it accumulates in plants, animals, fish, and the human body, and it is more toxic at low doses than other forms of mercury. [12]

Copper:

Copper is an important element that is found in only trace quantities (average of 63 μg g^{-1}) in the earth's crust. For both plants and animals it is required as a trace nutrient, but large amount are toxic at 20mg/kg dry measure. The mobility of copper is less in the upper humus of forest soils than in the mineral layers, therefore pollution of copper of soil is a serious matter.

Copper in high doses it can cause anaemia, cold sweat, weak pulse, liver and kidney damage, and stomach and intestinal irritation. Inhalation over long period or absorption can lead to death. [13]

Nitric Acid Digestion

Nitric acid disgestion method is commonly used to determine trace of metals in soils. The digestion procedure breaks down a organically bond substance and converts to substance to the analyzed form by using liquid oxidizing agent such as concentrated nitric acid. The mixture is heated under reflux for short period of time and extracted. The elements in nitric acid disgestion are measured with ICP. [14]

Soil Analysis Methods

There are several methods has been carried out for the soil analysis in order to obtain appropriate sets of results.

Inductively Coupled Plasma - Optical Emission Spectrometry (ICP OES)

Environmental analysis has become the number one priority throughout the world in many analytical laboratories. In order to monitor environment conditions and measure the impact up on it, an analytical technique called Inductively Coupled Plasma - Optical Emission Spectrometry has been developed which has a leading role in the analysis of environmental material.

ICP emission spectrometer is fast, multi element technique which permits the analysis of seventy different chemical elements at the trace, minor and major concentration levels can be determined quickly and accurately.

ICP-OES suffers from few chemical interferences and this which makes calibration an easy process and the superior calibration linearity of this technique means that extended concentration ranges may be covered by a single calibration graph.

The ICP technique is based on atomic spectrometry. The important fact is that atoms of the same element have similar energy levels whereas those of different elements each have their own unique set of energy levels. In ICP-OES the plasma is used to generate photons of light by the excitation of electron of a ground state atom to a higher energy level. The movement of electrons between these levels requires emission of energy. If the atoms in sample are excited using high energy source plasma, many of the atoms electrons will be excited to high energy levels. An atom in its excited state is unstable and remains there for an extremely short time. Almost immediately these excited state electrons will relax by returning to the ground state, wavelength specific photons are emitted, which are characteristic of the element of interest.

The plasma is very hot, partially ionized gas. It contains relatively high concentrations of ions and electrons. Argon ions, once formed in a plasma are capable of absorbing sufficient power from an external sources to maintain the temperature at a level at which further ionization sustains the plasma indefinitely. The plasma temperature is about 10,000 K.

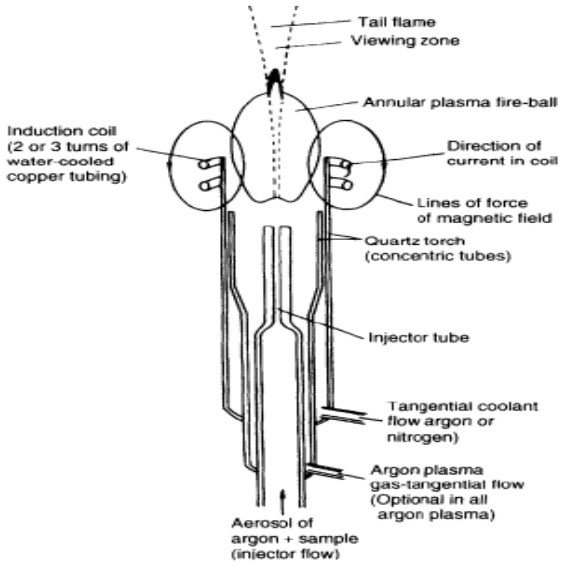

Figure 1: ICP Plasma Sources.

Instrumental Methods

- The spectrometer, which optically collects light from the plasma and separates the spectral lines produced by the different elements in the sample.
- The plasma source, which excites the atoms in a sample to produce an emission spectrum which is characteristic of the elements in that sample.
- The sample handling system, where a sample solution is converted into an aerosol capable of being excited by the source.
- The detector and signal processing where the light intensity is measured at each wavelength and ultimately converted to a digital results. [15]

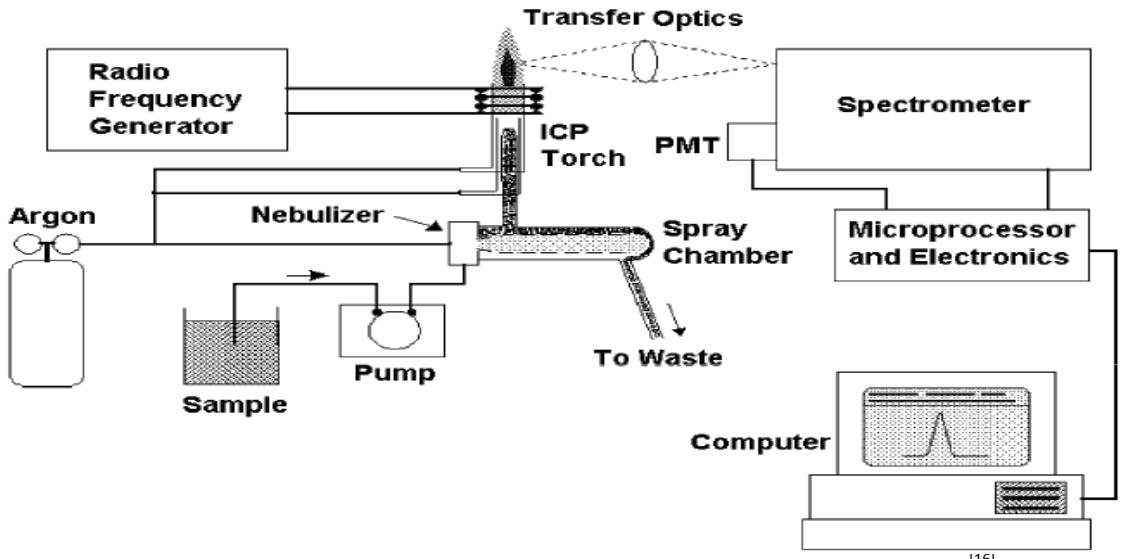

Figure 2: Schematic diagram of a typical IC-OES system, indicating the key components. [16]

Atomic Absorption Spectroscopy

Atomic absorption spectrometry (AAS) determines the presence of metals in liquid samples. It measures the concentrations of metals in the samples (e.g. concentrations in the mg/l range). In their elemental form, metals will absorb ultraviolet light when they are excited by heat. Each metal has a characteristic wavelength that will be absorbed. The AAS instrument looks for a particular metal by focusing a beam of uv light at a specific wavelength through a flame and into a detector. The sample of interest is aspirated into the flame. If that metal is present in the sample, it will absorb some of the light, thus reducing its intensity. The instrument measures the change in intensity and the computer data system converts the change in intensity into an absorbance.

As concentration goes up, absorbance goes up. A calibration curve is constructed by running standards and observing the absorbance. [17]

BCR Sequential Extraction:

An important aim in inorganic environmental analysis is the determination of the potential for an element to be released from its matrix and migrate to a biological host where it may cause toxic effects.

The European Union's Community Bureau of Reference has proposed a harmonised sequential extraction procedure. The sequential extraction method can be used if there metals present in soil, in order to selectively leach metals held in different soil or sediment phases by the use of reagents with different leaching capabilities. The correspondence of the extractability of metals with potential for toxic effects is the eventual goal of these sequential extractions.

The sequential extraction procedure involves three steps. In the first step the soil sample is extracted with acetic acid where the water and acid soluble are extracted. The metals extracted at this stage are the ones with highest bioavailability and thus highest toxicity. In the second step the solid residue is extracted using a solution of hydrolyamine hydrochloride 0.1 M acidified with concentrated nitric acid to pH 2. In this step metal species bound to reducible matter in the soil are released where the species will be bound to iron and manganese oxyhydroixdes. In third step the solid residue is extracted with hydrogen peroxide in order to release metals bound to oxidisable matter, typically organic matter. Excess hydrogen peroxide is then removed and then extracted metals taken up in 1 M ammonium acetate acidified with concentrated nitric acid to pH 2.

The sequential extraction procedure is widely for the characterisation of the heavy metal pollution in soils, sediment and other environmental solid matrices. [18]

Cation Exchange Capacity of soil

Soils are a complex mixture of inorganic material, decaying organic matter water, air and living organisms. The composition of the soil is consistently changing due to biological and chemical processes taking place. One of the most important functions of soil is to deliver nutrients to the plant root. This is done through the exchange of cations from the soil to water in the soil. This is done through the exchange of cations from the soil to water in the soil. This is termed cation exchange capacity, the quantity of monovalent cation that can be exchanged by 100g of dry soil. The primary cations are calcium, potassium and magnesium along with some trace metals (Zn, Fe, Cu etc). When the metal is taken up by the plant hydrogen ions are released, making the soil more acidic.

The knowledge of soils cation exchange capacity is important as it indicates the degree of leaching of nutrients such as K. Typically values range between 10-30 meq/100g. This method involves measuring the amount of the sodium taken up and realised by the sample of soil. The sodium is later analysed by flame emission. [19]

A Nanoparticle Autocatalytic sensor for Ag^{+} and Cu^{2+} ions

A novel nanoparticle autocatalytic sensor is constructed for the detection of Ag^{+} and Cu^{2+} based on the oxidative ability of Ag^{+} and Cu^{2+} towards o- phenylenediamine (OPDA). The Ag^{+} and Cu^{2+} can be oxidised to zerovalent silver and copper, respectively and then zerovalent Ag and Cu species form silver and copper nanoparticles that can catalyse the reaction between OPDA and Ag^{+} and Cu^{2+}.

This method developed is described the literature as being simple, economical, sensitive and portable for the detection of two heavy metal ions selectively. This method is performed as it is simple for the analysis of Cu^{2+} determination.

The new method is developed for the analysis of Ag and Cu and it involves colour change of the test paper visible by the naked eye. The test paper is used just like the pH paper and is more economical.

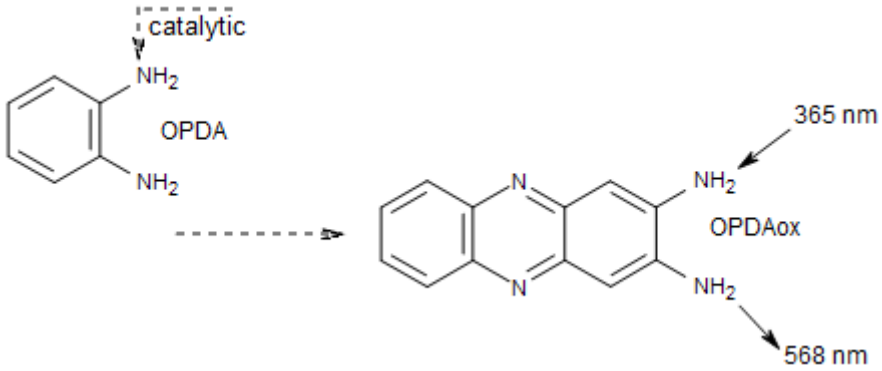

Figure 3: Shows the chemical reaction of OPDA oxidizing to Cu [20]

Fluorescence spectroscopy

Fluorescence is a spectrochemical method of analysis where the molecules of the analyte are excited by irradiation at a certain wavelength and emit radiation of a different wavelength. The emission spectrum provides information for both qualitative and quantitative analysis.

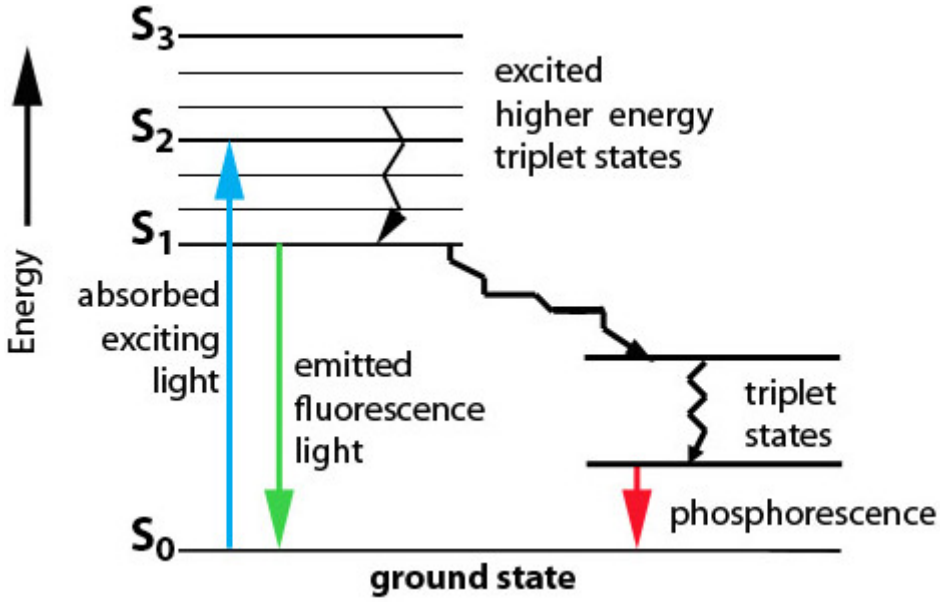

Figure 4: Shows Aleksander Jablonski diagram

If the photon emission occurs between states of the same spin state (e.g. S_1 ---> S_0) this is termed fluorescence. If the spin state of the initial and final energy levels are different (e.g. T_1 --> S_0), the emission is called phosphorescence.

The Jablonski diagram shows that the fluorescent state of a molecular entity is the lowest excited state from which the transition to the ground state is allowed, whereas the phosphorescent state is a metastable state below the fluorescent state, which is reached by radiationless transition.

In some cases the fluorescent state is the lowest singlet excited state and the phosphorescent state the lowest triplet state, the ground state being a singlet.

The Jablonski diagrams are frequently used and are actually state diagrams in which molecular electronic states, represented by horizontal lines displaced vertically to indicate relative energies, are grouped according to multiplicity into horizontally displaced columns. Excitation and relaxation processes that interconvert states are indicated in the diagram by arrows. The radiative transitions are generally indicated with straight arrows, while radiationless transitions are generally indicated with wavy arrows. [21]

Segregation method

Segregation simple method used for determining the level of organic and inorganic that is present in soil samples. The soil sample is placed into beaker containing water where the organic layer flows at top of the water and the inorganic layer remains at the bottom of the beaker. This determines whether the high level of lead is found in organic or inorganic layer of the soil.

Differential Scanning Calorimeters

Differential Scanning Calorimetry (DSC) measures the temperatures and heat flow flows associated with thermal transitions in a material as a function of time and temperature. In a DSC the difference in heat flow to the sample and a reference at the same temperature, is recorded as a function of temperature. The reference is an inert as just an empty aluminum pan. The temperature of both the sample and reference are increased at a constant rate.

DSC provides information about physical and chemical changes that involve a change in heat capacity. Depending on whether the heat absorbed or released during the process, they can be endothermic or exothermic. A chemical reaction is a process that one or more substances are converted to new chemical substances with different properties such as oxidation, decomposition and polymerization.

When the sample absorbs energy, the enthalpy change is said to be endothermic. Processes such as melting and vaporization are endothermic. When the sample releases energy, the process is said to be exothermic. Processes such as crystallization and oxidation are exothermic. [22]

Infrared Spectroscopy

Infrared Spectroscopy is the analysis of infrared light interacting with a molecule. This can be analyzed in three ways by measuring absorption and reflection. The main use of this technique for this project is to determine organic molecule which may be present in soil. Also it is used to determine functional groups region in an organic molecules. [23]

Project Objective

This project is to analysis soil samples obtained from community garden and ensuring that the soil is maintained safe in environment for the health safety of the humans and animals from hazardous caused by the heavy metal contamination in soil.

The aim is to map the garden, accurately and rigorously sample the garden and recorded at the known sites for compost. Sample to be taken in 15cm deep and control sample be taken at points remote from the area.

The soil sample must be sieved to two fractions and characterise these fraction by DSC and ATR spectrometry in order to identify the organic matter from the soil. The heavy metals can be determine by carrying out analysis of ICP-OES and AAS methods which determines the level of heavy metals present in these compost samples. Also attempt to speciate the type of metals found in the soil. The analysis for the plant samples would indicate if there is metal present in food.

The previous results obtained from the soil analysis on this community garden indicated high lead leave and this work is to confirm the presence of lead in these compost samples.

Experimental

Experimental Procedures

The available soil samples used for the purpose of the thesis were:

- Compost heap Community garden
- Herb Community garden
- Strawberry Community garden
- Ground soil Community garden

Nitric Acid Digestion

One gram of the soil sample was weighted out in weighting boat and the sample was transferred into a 100 cm^3 one neck round bottomed flask.

23 cm^3 of concentrated nitric acid was measured into a 50 cm^3 graduated cylinder; this was then added in drop wise while gently stirring the round bottomed flask containing the soil sample. Few anti bumping granules were added to the mixture solution. This mixture solution was heated for two hours using a heating source. Heat is supplied via a heating mantle. The reflux apparatus was set up in the fume hood. The condenser was connected with two condenser tubes together as shown below figure 5.

Figure 5: Reflux apparatus setup

After two hours of reflux the solution was allowed to cool at room temperature and the solution mixture was then filtered using a vaccum filtration technique, where the solids of the soil was separated from a liquid reaction mixture. The solution mixture was poured through a filter paper in a Buchner funnel.

The extracted liquid drawn through the funnel was transferred into a 100 cm^3 volumetric flask and filled up to mark with deionised water.

ICP Standard Solution Preparation

The 1000 µg/ml standard ICP solution containing As, Hg, Cd, Cu, Pb, Fe, Ni, Cr and Co was diluted to 100ppm.

Table2: Shows dilution prepared from 1000ppm standard ICP solution

Concentration (ml)	Volumetric flask (ml)	Concentration (ppm)
1	100	1
2	100	2
3	100	3
4	100	4
5	100	5

Table3: Second dilution prepared from 1000ppm standard ICP solution

Concentration (ml)	Volumetric flask (ml)	Concentration (ppm)
0.2	100	0.2
0.4	100	0.4
0.6	100	0.6
0.8	100	0.8
1.0	100	1.0

Series dilutions were prepared from the standard ICP solution as shown above table 1 and 2. For example 0.2ppm of the standard ICP solution was pipetted into a 100ml of volumetric flask and made up to the mark with deionised water.

Table 4: Instrument

Instrument	**Model**	**Made/Manufacture**
ICP-OES	Liberty 150	Varian
AAS	Spectra AA 110	Varian
Sieve	AS 200 – Control ''g''	Rhetsch analytical sieve shaker
ATR	Spectrum 100	Perkin Elmer – precisely
Fluorescence	Luminescence spectrometer LS 50 B	Perkin Elmer
DSC	DSC	Rheometric Scientific

The solutions were run on instrument listed in table 3. All other instrument used is also listed here.

AAS Pure lead Standard Solution Preparation

To make up 10ppm standard pure lead solution 1 cm^3 of the standard pure lead solution was taken and transferred into a 100 cm^3 of volumetric flask and made up to the mark with deionised water. From this a 100 cm^3 pure lead standard the following dilutions were prepared for the AAS analysis in 50 cm^3 of volumetric flask and made up to mark with deionised water.

Table5: Shows dilution prepared from 10ppm standard pure lead solution

Concentration (ml)	Volumetric flask (ml)	Concentration (ppm)
1	50	1
2	50	2
3	50	3
4	50	4
5	50	5

Cation Exchange Capacity

The following solutions were prepared in 250 cm^3 volumetric flask:

- Sodium acetate of 1.00 M (20.5075 grams) was weighted out into weighting boat and placed into the volumetric flask and made up to mark.

- Ammonium acetate of 1.00 M (19.27 grams) was weighted out into weighting boat and placed into the volumetric flask and made up to mark.

Standard Solution for Cation Exchanger Capcity

- 100 ppm of Na^+ was prepared by weighting out 0.025 grams of NaCl solids, which was transferred into 100 cm^3 volumetric flask and made up to mark with deionised water.
- From the stock solution 100 ppm NaCl solution 0.5, 1.0, 1.5, 2.0 and 2.5 ppm solutions were made up.

1. Soil sample of 5g was weighted out into a centrifuge tube. This step was carried out in duplicate for the two soil samples.
2. 30 cm^3 of 1 M sodium acetate was added into centrifuge tube and agitated with a stirring rod for 5 minutes.
3. The tubes were centrifuged for 3 minutes so that the supernatant liquid is clear. The sodium acetate was decanted off from the soil sample.
4. The step one to three was repeated once more with fresh sodium acetate. This ensured that all exchangeable cations are replaced by sodium.
5. 20 cm^3 of water added into the centrifuge tube and agitated with a stirring rod for 5 minutes.
6. The tubes were centrifuged for 3 minutes until the supernatant is clear. The supernatant was decanted off and was discarded.
7. The step five and six was repeated with fresh water. This removed any excess sodium acetate
8. 20 cm^3 of 1 M ammonium acetate was added to the soil sample and was agitated with a stirring rod for 5 minutes. The tubes were centrifuged for 3 minutes until the supernatant was clear. The liquid was decanted off and the supernatant was collected in a 100 cm^3 volumetric flask.
9. The step eight was repeated once more with fresh ammonium acetate and the extracts were collected in the same 100 cm^3 flask. The volumetric flask was made up to mark with deionised water.

BCR Sequential extraction method

- Step 1

  One gram of soil sample was weighted out onto weighting boat and transferred into a 100 ml one neck round bottom flask.

  80 cm^3 of acetic acid of 0.11 M was added to one gram of soil sample. This solution was refluxed for two hours.

  After two hours of heating, the extract was then separated from solid residue by filtration technique. The extracted liquid drawn through the funnel was transferred into a 100 cm^3 volumetric flask and filled up to mark with deionised water.

- Step 2

  8.68 gram of hydroxylammonium chloride (solution ll) of 0.5 M was weighted out and transferred onto 200 ml beaker. Nitric acid was slowly added in dropwise until the pH paper was 1.5. The solution was poured into 250 ml of volumetric flask and filled up to mark with deionised water.

  From step 1 the one gram of soil was transferred to centrifuge tube and 40 ml of the hydroxylammonium chloride was added to this tube. The tube was shaken and left at room temperature for 16 hours.

  The extract was separated from solid of soil by filtration and the supernatant was collected and placed onto a 100 cm^3 volumetric flask and filled up to mark with deionised water.

- Step 3

  10 ml of hydrogen peroxide of 8.8 M was added to residue from step 2 in a centrifuge tube.

  The digestion was allowed to proceed at room temperature for one hour, followed by digestion at 85 °C water bath for another one hour.

  NOTE: During the digestion the tube were not covered to prevent the substantial loss of hydrogen peroxide.

  The tubes were kept uncovered until the volume was reduced to 2-3 ml. When the volume was reduced, additional 10 ml hydrogen peroxide was added to tube and tube was digested at 85 °C water bath for another one hour until the volume reduced to 2-3 ml.

  50ml of ammonium acetate of 0.1 M was added to the mixture. The mixture stirred and left at the room temperature for 16 hours.

The extract was separated from solid of soil by filtration and the supernatant was collected and placed onto a 100 cm^3 volumetric flask and filled up to mark with deionised water.

- Step 4

  The step 4 which is treatment with concentrated nitric acid was not carried out on the residue from step 3 as it had been done with a fresh sample previously

Segregation method:

- 10g of soil sample was weighted out in a 300 cm^3pre weight beaker and 250 cm^3 of deionised water was added into the beaker.
- The soil sample was stirred with stirring rod for 10 minutes until all the organic layer flowed on top of the beaker and all the inorganic layer sank to the bottom of the beaker.
- The organic and inorganic layer were carefully poured off into separately beaker and filtered.
- The solids of the organic and inorganic were allowed to dry in oven temperature at 80 °C for 30 minutes. Once the solids were dried, 1g of organic and inorganic sample were weighted in a weighting boat.
- The 1g was placed into one neck round bottom flask and 22 cm^3 of concentrated nitric acid was added to flask with few anti bumping granules.
- This mixture was refluxed for 2 hrs. After the 2 hrs of refluxing the mixture was allowed to cool down at room temperature. The mixture was then filtered and supernatant liquid was collected and transferred into 100 cm^3 volumetric flask and made up to the mark with deionised water.
- The mixture of the organic layer was transferred into 50 cm^3 volumetric flask and made up to the mark with deionised water as very less of the organic layer was collected.

1,2- phenylenediamine method

Preparation of 1,2- phenylenediamine solution

0.0648g of 1,2 – phenylenediamine was weighted out in pre weighted beaker and 80 cm^3 of deionised water was added into the beaker and the solution mixture was stirred. About 0.1 cm^3 of 0.1 M HCl solution was added until the 1,2 – phenylenediamine was dissolved. The solution was then transferred into 100 cm^3 volumetric flask and made up to the mark with deionised water.

Preparation of Copper solution

The 10ppm of the copper solution was prepared by taking 1 cm^3 of the 100ppm stock copper solution placing into 100 cm^3 volumetric flask and made up to the mark with deionised water.

Preparation of the buffer solution:

6.0027g of sodium dihydrogen phosphate was weighted out in weighting boat and transferred to 50 cm^3 volumetric flask and made up to the mark with deionised water. From this solution (NaH_2PO_4), 10 cm^3 was taken and placed into a 100 cm^3 beaker. 80 cm^3 of deionised water was added to the beaker and 5 M of NaOH solution was added in dropwise until the pH was 7.4. The solution was then transferred into 100 cm^3 volumetric flask and made up to the mark with deionised water.

From the 10ppm of stock copper solution the following dilutions were made by taking 2 to 10ppm and transferring into 10 cm^3 volumetric flask and made up to the mark with deionised water. From these dilutions 0.1 cm^3 of the copper was taken and placed into test tubes. From the prepared 1,2 – phenylenediamine (OPDA) solution 0.3 cm^3 and 9.6 cm^3 of buffer solution was added to test tube. These test tubes were placed in a water bath at 50°C for 1 ½ hr and then were analysed by the fluorescence and Uv-vis.

Results & Discussion

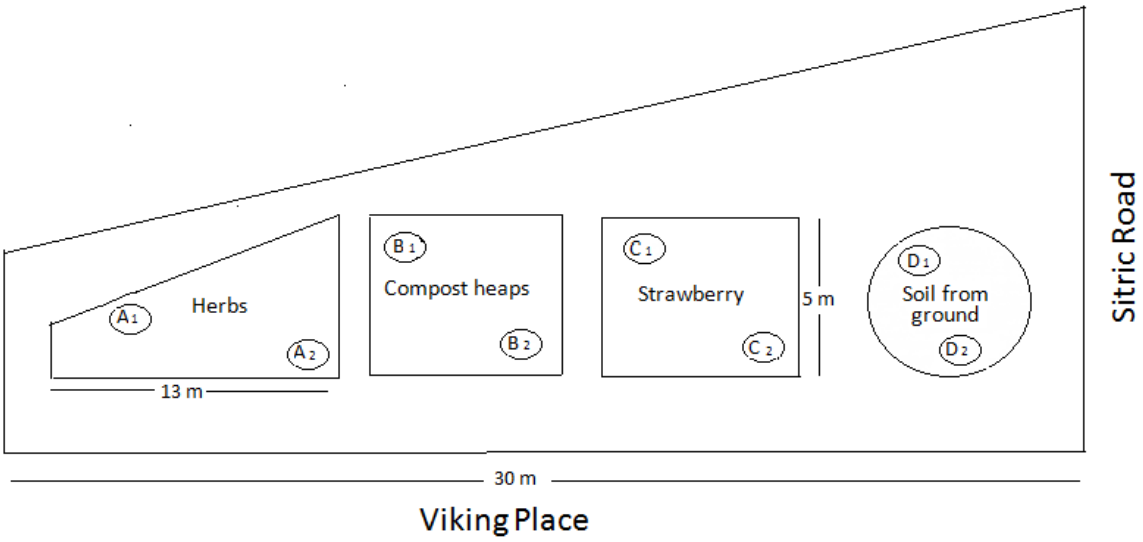

Figure 6: Map of Sampling Site – Stonybatter

The sampling position was carefully chosen with care where the area was subdivided into grids with sampling points at fixed locations within the grids. Control samples were taken at point remote from the area under investigation while ensuring that the control site is close to the sampling site. The control samples were taken to evaluate the area rather than relying on a single sample.

The analysis of AAS method shows a high level of consistency results between sample and control sample. This implies that the sampling method carried out is quite accurate and valid as it is relatively homogonous over the sampling area. The results obtained are significant because it indicates that the amount of lead obtained from the soil is distributed uniformly through the plot.

ICP-OES

An analytical instrument ICP-OES was used to determine concentration of trace elements in soil samples. The lead concentration in soil was determined by extracting lead from a sample, involving digesting a sample of soil with nitric acid to eliminate interference, filtering and analyzing with ICP-OES. When a sample was introduced to ICP-OES, the sample was nebulized and into an inductively coupled plasma torch where it is atomized and ionized. The excited atoms in the sample emitted photons, which were then analysed to determine the optical emission spectroscopy of the sample.

Multi element standard solutions, whose concentrations are traceable to primary reference standards was prepared for the ICP analysis by diluting the 1000 µg/ml ICP standard containing trace metals such as, Hg, Cd, Cu, Pb, Fe, Ni, Cr and Co with deionised water. The dilution factor that was used for standards were 1, 2, 3, 4 and 5 ppm. The results obtained are shown in table 1, and from figure 1 the calibration curve a linear straight line was obtained.

Table 6: Emission levels for metal standards in ICP

Standard Solution of ICP Reference				
Metals	Lead	Copper	Cadmium	Mercury
Wavelength nm	220.353	342.754	228.802	253.652
Concentration (mg/l)	Intensity	Intensity	Intensity	Intensity
5.00000	3790.66	5825.60	50007.6	1570.53
4.00000	2942.86	4528.49	37974.7	1174.20
3.00000	2245.90	3437.99	29148.8	939.774
2.00000	1567.31	2405.54	20440.9	708.968
1.00000	936.769	1462.50	11952.7	576.071
0.00000	83.2084	9.26638	203.124	265.235

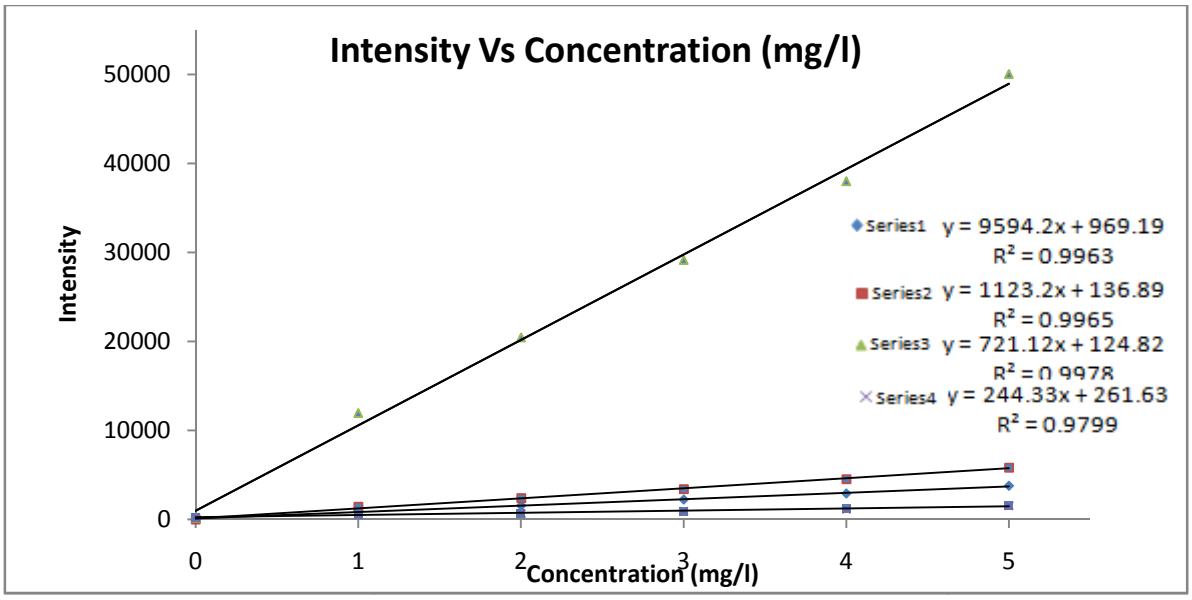

Figure 7: ICP Standard Solution

Due to large amount of metals present in soil, the optical emission spectrum of the soil were analysed at four different wavelengths that are specific wavelengths of emission for trace metals.

For lead metal the sample was analysed with ICP-OES at a wavelength 220.353 nm and 261.418 nm. These wavelengths were chosen because they were representative of emission wavelengths of lead. The sample were analysed for copper at wavelength 342.754 nm, for cadmium at wavelength 228.802 nm and mercury at wavelength 253.652 nm.

ICP-OES analysis was taken of the calibration solutions, and intensity of emission was found at each wavelength of lead emission.

Table 7: ICP intensity of each soil samples

Emission at Wavelength of Pb at 220.353	
Soil Samples	Intensity
A1 – Compost	13112.4
A2 – Compost	10401.4
B1 – Herbs	7049.29
B2 – Herbs	7024.89
C1 – Strawberry	4797.16
C2 – Strawberry	1845.13
D1 – Ground soil	8033.5
D2 – Ground soil	7985.36

When the concentrations were used to determine the amount of lead in the soil, the values for concentration obtain from lead analysis of the two wavelengths were then averaged, and used to estimate the overall concentration of lead in soil (table 7).

Table 8: Lead Concentration (ppm) in soil samples and corresponding dilution factors

Wavelength of Pb at 220.353		
Soil Samples	Concentration (mg/l)	Dilution Factor in Volume (cm^3)
A1 – Compost	~17.3	7.2
A2 – Compost	~13.7	9.1
B1 – Herb	~9.3	13.4
B2 – Herb	~9.2	13.5
C1 – Strawberry	~6.33	19.7
C2 – Strawberry	~2.23	25
D1 – Ground soil	~10.59	11.8
D2 – Ground soil	~10.53	11.8

The results from the ICP analysis indiacted that there is large amount of lead found in soil samples . The concentration of lead in soil samples were found extrmely high, therefore samples were diluted (as shown in table 8) to yield a concentration of about 2.5ppm and analysed by atomic absorption spectrometry.

The results obtained for the strawberry patch sample (C2) was found to be highly inaccurate value. This may have been due to some technical problem with ICP-OES machine and bubbles in ICP-OES. Therefore 5ppm value was used instead of 2.43ppm value in order to obtain dilution factor.

Atomic Absorption Analysis

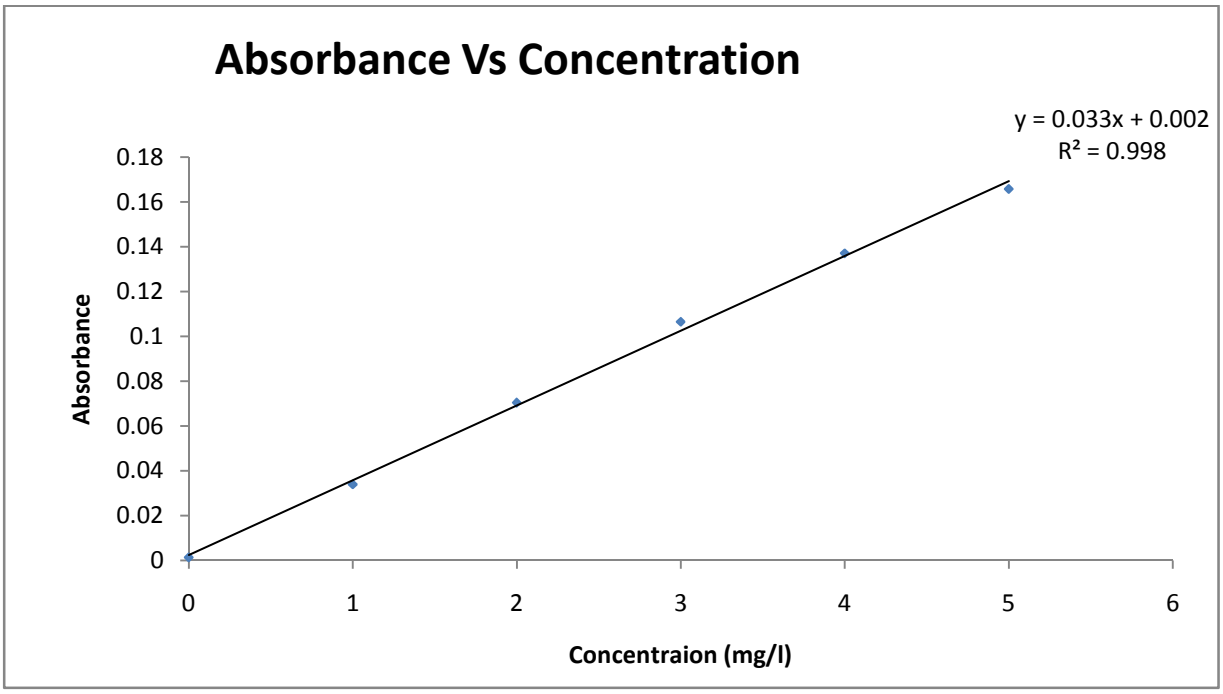

Figure 8: Pure Pb standard for atomic absorption spectroscopy

The calibration cruve of the pure lead standrad (shown in figure 3) gave good straight line as the R^2 is almost 1 and the intercept is zero, therefore the correlction is well behaved.

Table 9: Soil samples by Atomic absportion spectromtry

Soil Samples	Concentration (mg/l)	Original Cocentration (mg Pb/kg) compost
A1 – Compost	3.38	2347
A2 – Compost	3.35	1840
B1 – Herbs	3.21	1190
B2 – Herbs	3.34	1237
C1 – Strawberrys	3.02	766
C2 – Strawberrys	3.21	642
D1 – Ground soil	3.55	1504
D2 – Ground soil	3.36	1423.72
1 PPM ICP standrad	1.46	1.46

When the ICP standard of 1ppm was analysed in AAS it gave higher value than 1ppm. This could have been due to some interference of other metals which could be present in the sample.

In the table 9 it can be seen that the greastest lead levels are found in patch A followed by D, B and then C. Also sampling is very important as consistant results are found for the duplicate samples. The results shows that these levels of lead found soil are way above the Ireland's recommendated level for compost 149 mg/kg.[7] Thus the level of lead is sufficiently high which can be harmful to the people who plants food in the garden.

Analysis of leave samples by Atomic Absorption spectroscopy

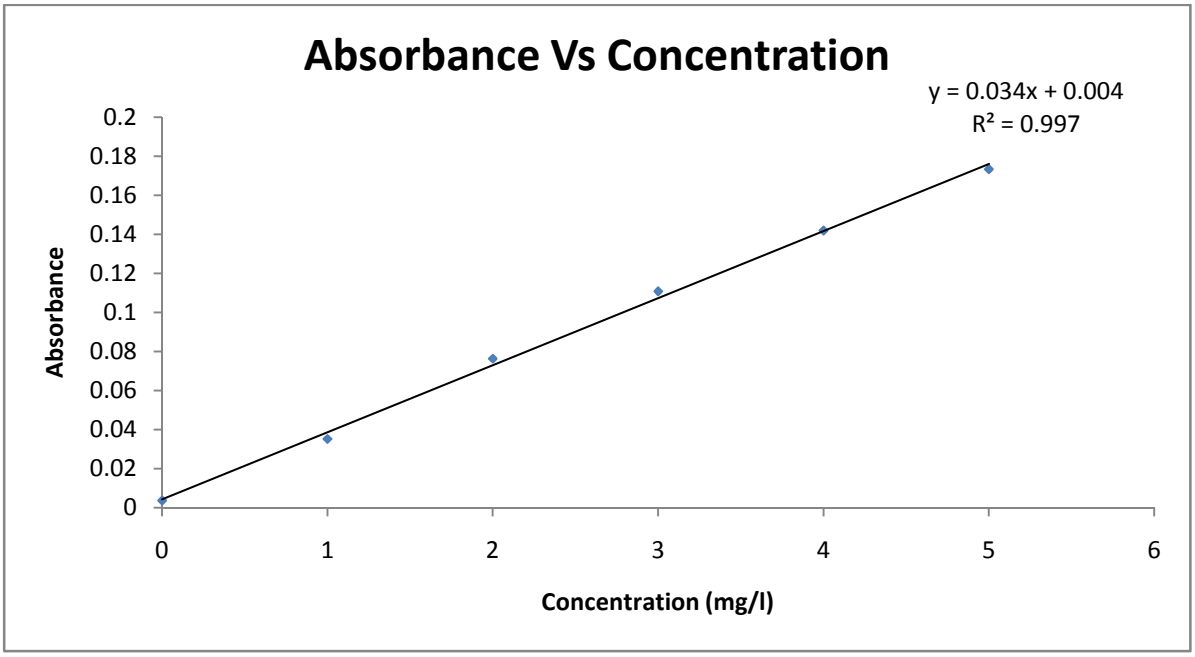

Figure 9: Standards of Pure Lead for leave analysis

The calibration for the pure lead sandards as shown in figure 9 gave nice straight line with R^2 is ~1 and inectercept almost zero.

Table 10: Analysis of leave for sample A3 and B3

Leave Samples	Concentration (mg/l)	Level of Pb in Leaves (mg/kg)	
A3 – Compost	0.58	Sample A3	Sample B3
A3 – Compost	0.56	58.3	64.6
A3 – Compost	0.61		
B3 – Herbs	0.64		
B3 – Herbs	0.64		
B3 – Herbs	0.66		

The leave samples were made up to 100 ml in vloumetric flask with deionised water. The analysis for leave samples showed extremely high level of lead in leaves which are above the ireland's recommendated level for food safety 3mg/kg.[24] This result indicates that leaves are not eatable as food as it is hazardous to the health of humans and animals, therefore serious action must be taken.

BCR method

Table 11 : **Sequential extraction**

Soil Sample	Concentration (mg/l)	Original Cocentration (mg Pb/kg) compost
Sample A_1 – Acetic Acid	3.63	363
Sample A_2 – Acetic Acid	2.83	283
Sample A_1 – Hydroxylammonium Chloride	0.35	35
Sample A_2 – Hydroxylammonium Chloride	0.41	41
Sample A_1 – Hydrogen peroxide	0.17	17
Sample A_2 – Hydrogen peroxide	0.18	18
Sample A_1 – Nitric acid	3.38	2347
Sample A_2 – Nitric acid	3.35	1840

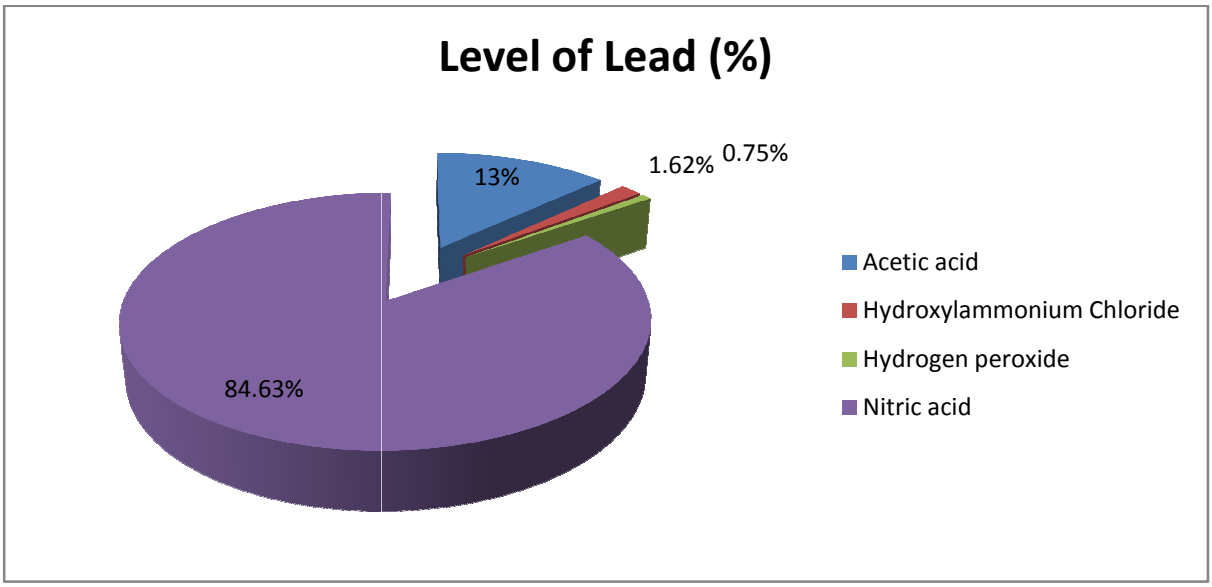

Figure 10: The percentage level of lead extracted in BCR steps

The pie chart (figure 10) represent the percentage level of lead obtained from using the three stage modified BCR sequential extraction method at different sediment. The Lead in the extract was measured by atomic absorption spectrometry (AAS). The result shows that the highest concentration of the lead level was found in residual fraction using nitric acid. The fact that high levels of lead extracted only with nitric acid indicates that the soil samples are highly contaminated, therefore it requires strong reagent to remove lead from the soil.

The extraction for the lead with acetic acid shows about 13% is the most toxic in which is easily bioavailable.

In the step two, the metals bound to amorphous Fe and Mn oxides and hydroxides were leached. The higher metal concentration may have sobbed by more Fe-Mn oxides in the top sediments than at the deeper depths. This could mean that the reductive dissolution of Fe-Mn oxides will occur at deeper positions in the absence of significant sulphide which could fix the Fe and Mn as sulphide phase followed by precipitation upon crossing the oxic/anoxic boundary.

The lead obtained in oxidisable fraction is bound to organic matter by bioaccumulation in certain living organisms through different ways. Therefore the variation of lead in this fraction became more complex and irregular.

In fourth step, the lead which is difficult to dissolve and not very bioavailable is extracted using concentrated nitric acid to determine the lead is present as Pb or Pb^0 and/ or Pb^2.

Segregation method:

The segregation analysis was only carried out for sample A1 and A2 as the results obtained from the ICP-EOS and AAS showed that these two samples contained high level of lead than other samples. From the Segregation analysis very little of organic matter layer flow on top of water whereas large amount of inorganic matter layer flow at the bottom. The results obtained from the AAS showed that the level of lead is found in the inorganic layer 24436.4 mg/kg are much higher than organic layer 767.7 mg/kg. This indicates that high level of lead is mainly found in inorganic layer and very little in organic layer.

Cation Exchange capacity

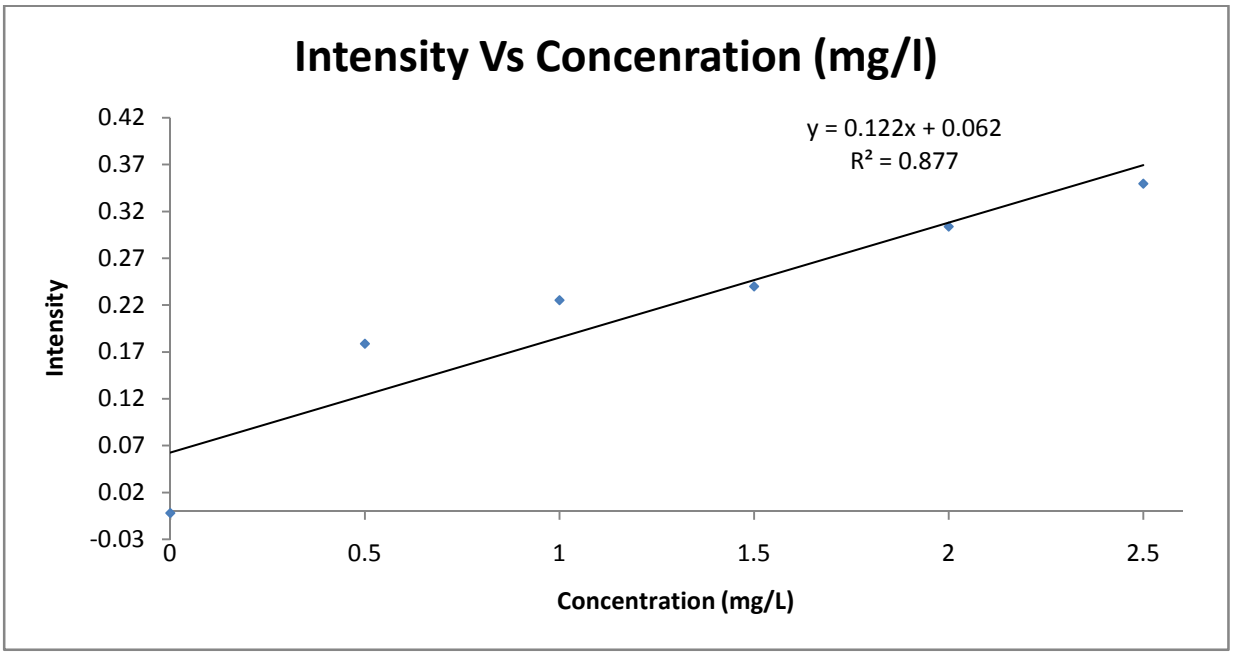

Figure 11: Standards for Cation Exchange Capacity

The standard for the cation exchange capacity were carried out from dilution 0.5 to 2.5 ppm for sodium emission. These dilutions for the calibration curve did not give linear plot as shown above figure 11 as the range concentration is limited. The slope is very sensitive from the 0 to 1ppm where as above the 1ppm the slope is not so very sensitive, this could be due to some sodium interference with the sodium in the flame resulting in self absorption. Self absorption is where at high concentration small amount of the sodium ion (Na^+) is being excited by the flame in which it causes the energy being transferred to the next sodium.

The sensitivity for the analyte in the soil sample is not equal to the sensitivity of the analyte in a standard solution. The matrix effect caused improper calibration curve, therefore the soil sample solution were diluted further more in order to improve the calibration curve.

The dilution factors for the standards were repeated from 0.2 to 1ppm and the soil sample solution was diluted by ¼.

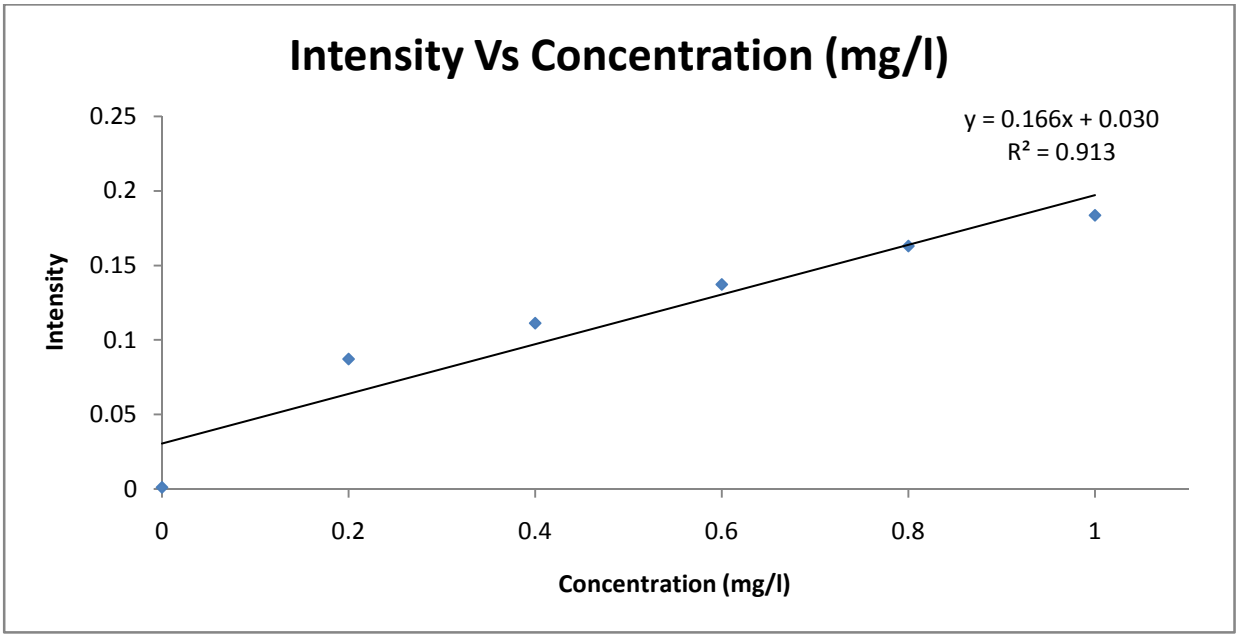

Figure 12: CEC standard with dilution factor

The calibration cruve did not give a straight line as the data points are scattered and do not lie perfectly on a straight line. This could be due to the method carried out which caused some error during dilution. The R^2 value represnt the best fit of a straight line in the calibration cruve.

Table12: Results from AA for CEC concentration of samples

Samples	Concentration (mg/l)	Cation Exchange Capcity concentration (millimoles of Na^+/100g soil)
A1 – Compost	0.21725	37.7
A2 – Compost	0.30675	53.3
B1 – Herbs	0.6208	107.9
C1 – Strawberrys	0.3002	52.2
C2 – Strawberrys	0.53065	92.2
D1 – Ground soil	0.0665	11.5
D2 – Ground soil	0.15135	26.3

The Cations used by plants in the largest amounts and are positively charged ions such as calcium (Ca2+), magnesium (Mg2+), and potassium (K+). The cation exchange capacity is the ability of soil colloids to attract and hold positively charged ions. These cations are held by the negatively charged clay and organic matter particles in the soil through electrostatic forces. The cations on the CEC of the soil particles are easily exchangeable with other cations. Thus, the CEC of a soil represents the total amount of exchangeable cations that the soil can adsorb.

The Sodium cations may replace adsorbed magnesium (Mg^{2+}) cations. The replaced magnesium ions can then combine with Cl^- ions to form magnesium chloride. This compound is soluble and can be leached from the soil when rain occurs.

Soils containing a high percentage of organic matter have high cation exchange capacity. The collected soil samples contains a low of clay and organic matter, indicating low CEC of sandy textured soil that requires more organic matter to improve water holding capacity.

The values obtain for the CEC are variable from one another soil sample from different position as the samples are homogeneous due to large particle sizes. However the value of the CEC for the sample D is found to be much lower than the rest of the samples as shown in table 12. This could have been due to sampling position as sample D was collected from the ground soil from almost same position.

The percentage of organic matter content in soil for both sample compost (A) and ground soil (D) is similar to percentage obtained from the DSC ~ 25% of organic matter.

Table 13: Differential scanning calorimetry (DSC)

Samples	Sample weight (mg)	Sample ash weight (mg)	Organic Percentage (%)
A1 – Compost	8.82	6.8	35
A2 – Compost	8.8	5.72	22
A3 – Herb leaves	8.4	2.2	73
B1 – Herbs	8.19	4.59	43
B2 – Herbs	8.8	5.21	40
B3 – Herb leaves	8.14	1.7	79
C1 – Strawberry	8.4	4.7	44
C2 – Strawberry	9.1	5.9	35
D1 – Ground soil	8.3	7.5	9.6
D2 – Ground soil	9.5	6.9	27

The DSC curves obtained by heating the soil sample where the thermic decomposition of organic matter in soil occurred between 150 to 500 °C and the Isotherm observed up to 1500 °C. The soil sample curves did not vary much from each other for all the samples as there was very little of organic matter was present in soil samples. The results of the analyses indicate that these soil samples contain a very low percentage of organic matter.

Further analysis was carried out in DSC for the herb leaves of the sample A and B to determine the percentage for the comparison to the soil sample. The result showed that leave samples did not contain 100% of organic matter as was expected, this could have been due to temperature not being high enough to burn all of the organic matter and some of the organic are stable which does not get lost at 500 °C.

1,2- phenylenediamine

In the reaction the OPDA is oxidised to 2,3-diaminophenazine (OPDAox) by the copper (Cu^{2+}) selectively. As the reaction continued Cu^{2+} is reduced to zerovalent copper and forms copper nanoparticles. Thus the formed copper nanoparticles catalyse the reaction between the OPDA and $Cu^{2+}$and shows good selectively towards Cu^{2+}.

To determine the level of Cu^{2+} the excitation wavelength was set at 365 nm and fluorescence emission was measured at 568 nm to monitor the fluorescence intensities. The figure 13, 14 and 15 shows that the fluorescence intensity at 568nm decreased instead of increasing as the Cu^{2+} concentration was increased. However the results obtained from the UV-visible gave good linearity.

The results from the fluorescence proved that this method is not suitable method for analysis of copper as not enough detail is provided in the paper related to degassing the nitrogen. This method was repeated several times with and without the buffer solution, in order to obtain better results but the results showed no difference and were same as the previous results.

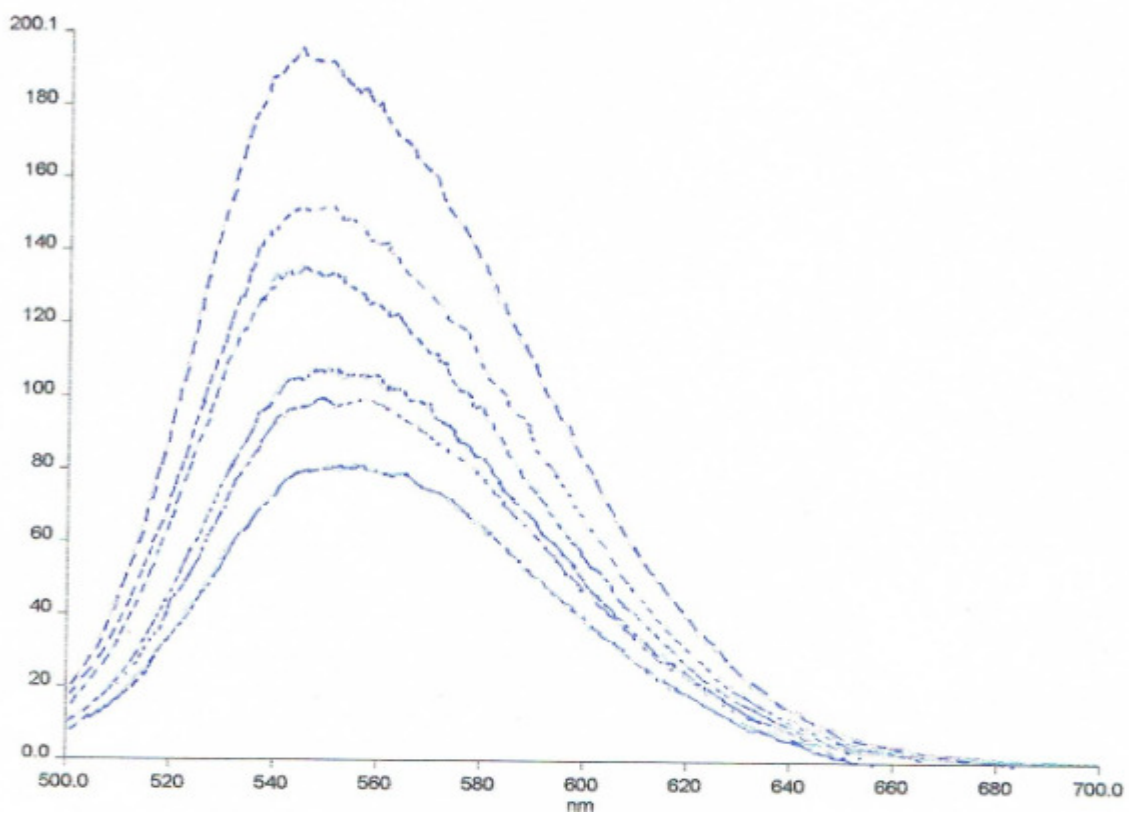

Figure 13 fluorescence of OPDA without Buffer (0.5 - 2.5ppm)

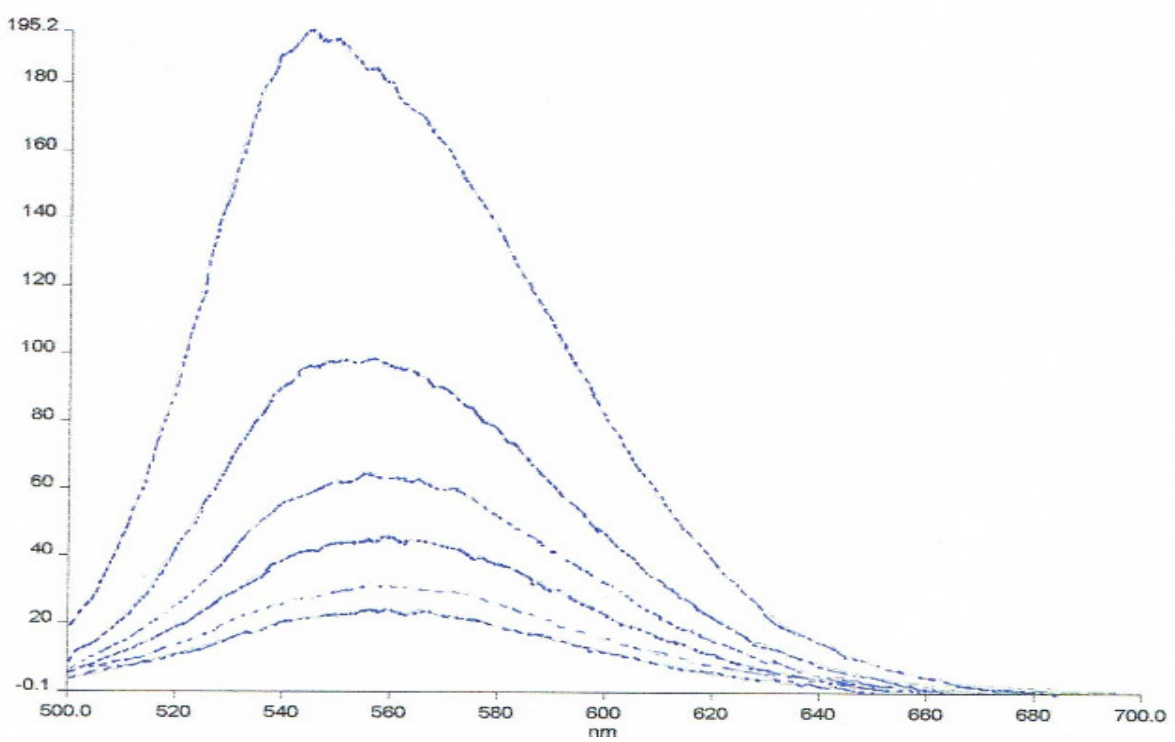

Figure 14 fluorescence of OPDA without Buffer (2 - 10ppm)

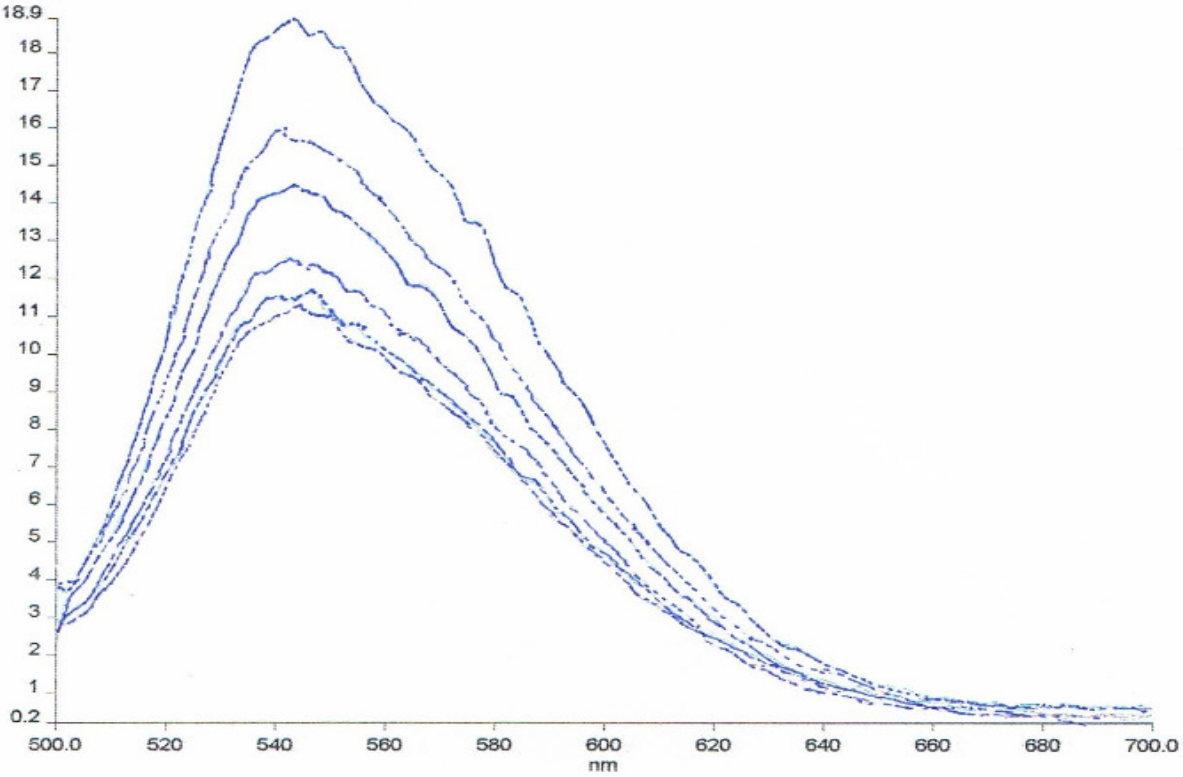

Figure 15 fluorescence of OPDA with Buffer (2 - 10ppm)

Anlaysis of 1,2- phenylenediamine by uv-vis

The analysis of OPDA without buffer was carried out first by Uv-vis in order to compare absorption with the observed intensity results by the fluorescence. The results obtained from uv-vis (in figure 16) showed the opposite results from the fluorescence as the absorption increased with copper concentration whereas in fluorescence the intensity decreased with the copper concentration.

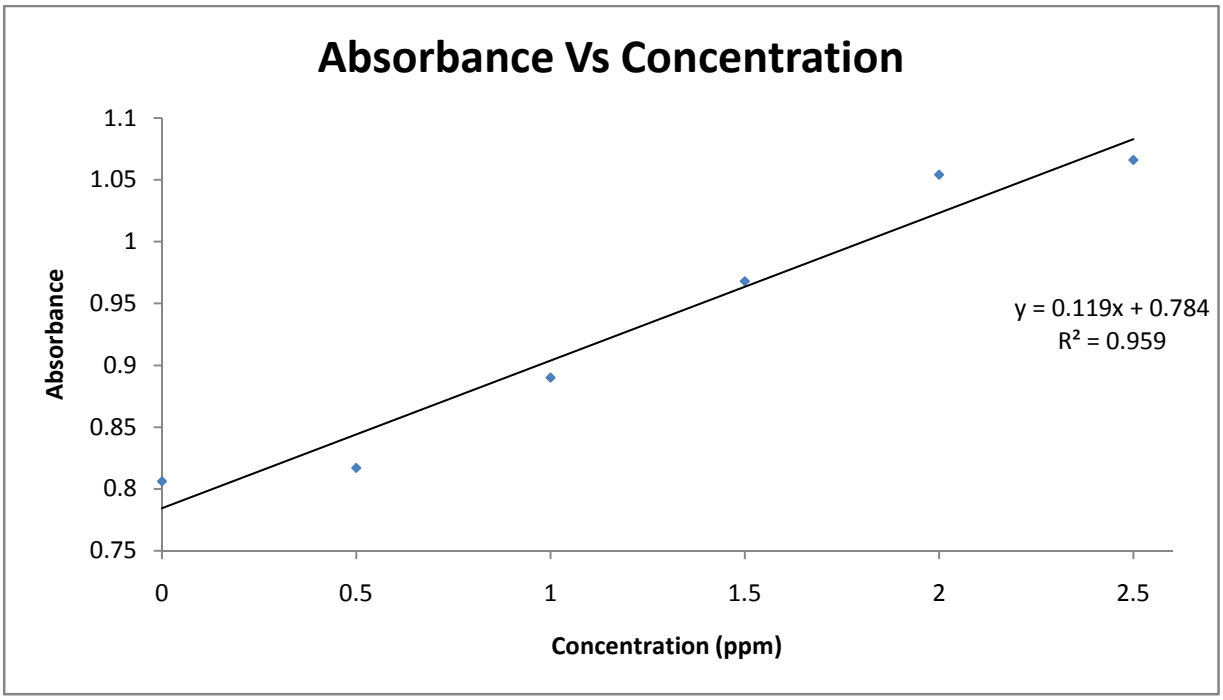

Figure 26 OPDA without Buffer (0.5 - 2.5ppm)

The calibration curve for the analysis of OPDA with buffer showed that the absorption increased with an increase of copper concentration (as shown in figure 17 and 18) and obeys Beer Lambert law as absorbance is directly proportional to the concentration of the absorbing species in the solution and the path length. The calibration plot of absorbance against concentration gave a straight line and intercept which is not zero. The line should have had passed through origin as the concentration of the copper at the start was zero. Also the slope's varies from each other when comparing the calibration plots of the OPDA with buffer in figure 17 and 18.

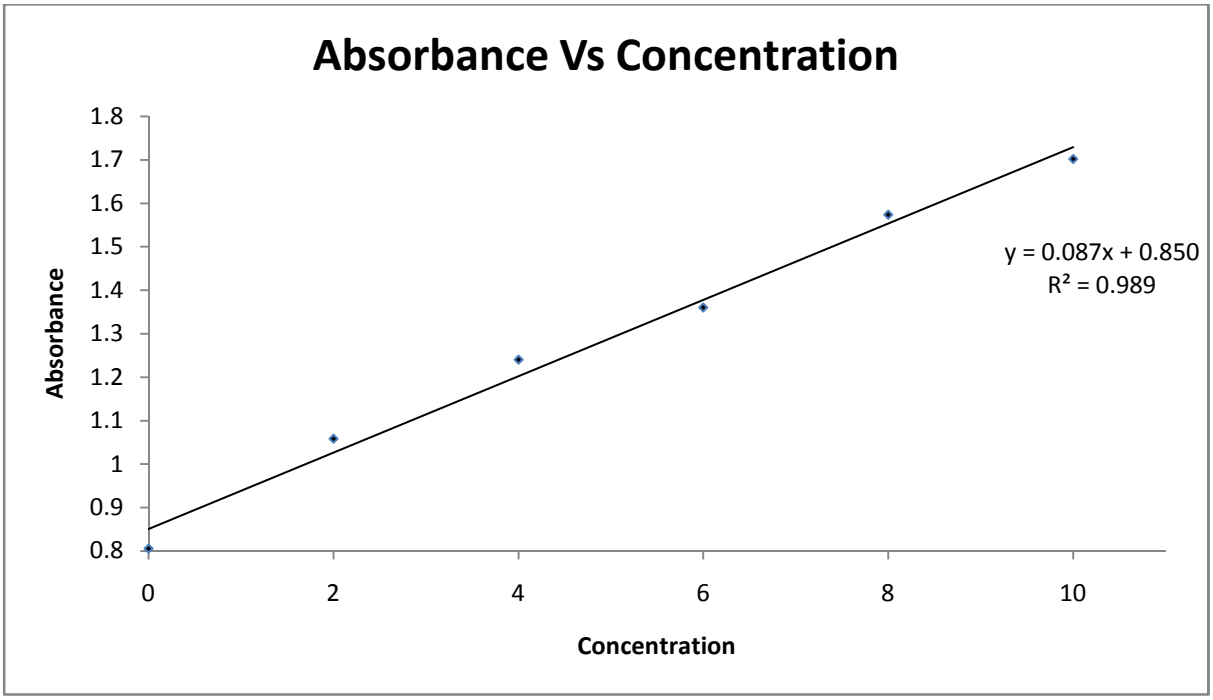

Figure 17: OPDA without buffer (2 - 10ppm)

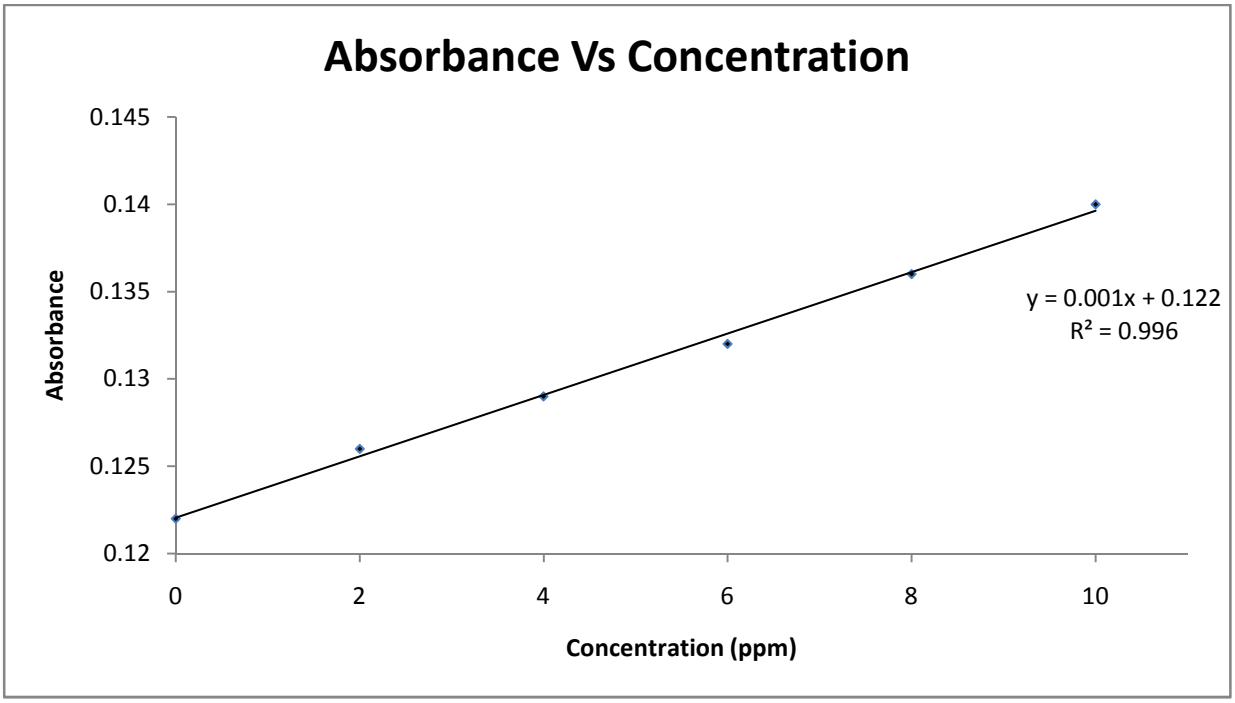

Figure 18: OPDA with Buffer (2 - 10ppm)

Infrared spectra

The ATR was run for the each soil samples and the peaks were assigned. The absorption peaks of the soil for sample A and B showed no difference between the peaks in spectrum (as shown in figure 21 and 22). Whereas the peaks for the soil sample C and D varied a little from A and B. However all the soil samples A, B, C and D had one peak in common at 100 cm^3, this could maybe due to Si-O stretch found in the soil.

The ATR was run for the leave samples of A and B (in figure 19 and 20) which showed very different peaks bands compared to the soil samples due to the level organic matter present in the leaves. The peak which are found in soil and not in leaves samples it could be due to level of inorganic in the soil.

Table 14 Shows the Assigned peaks for leave sample A3

Compost - Leave Sample A3	
Bonding	Frequency (cm^{-1})
C = O Ester	1735.28
C = C Aromatic	1587.45
C – H Alkane	1396.64
C – O Carboxylic acid	1233.34
C – O Ether	1094.11

Table 25 Shows the Assigned peaks for leave sample B3

Compost - Leave Sample B3	
Bonding	Frequency (cm^{-1})
C – H Alkane	2917.24
C = C Aromatic	1587.85
C – H $-CH_3$	1394.74

Table 36 Shows the Assigned peaks for Soil sample A1

Compost - Soil Sample A1	
Bonding	Frequency (cm^{-1})
Carbonate	1416.64
Inorganic Clay	1007.32
Carbonate	778.60

Table 47 Shows the Assigned peaks for Soil sample B1

Herbs - Soil Sample B1	
Bonding	Frequency (cm^{-1})
Carbonate	1420.21
Inorganic Clay	1025.69
Carbonate	776.36

Table 58 Shows the Assigned peaks for Soil sample C2

Strawberry - Soil Sample C2	
Bonding	Frequency (cm^{-1})
C = C Benzene	1634.22
Carbonate	1408.59
Inorganic Clay	1013.23
Carbonate	873.23

Table 69 Shows the Assigned peaks for Soil sample D1

Ground soil - Soil Sample D1	
Bonding	Frequency (cm^{-1})
Aldehyde	1740
Carbonate	1407.22
Carbonate	873.12

Conclusion

Conclusion

The nitric acid digestion method was proved successful for the determining level of heavy metals present in soil and plant samples.

The results obtained from the ICP-OES and AAS confirmed that there is large amount of the Pb level present in soil aswell as in plant samples. In compost (A) sample was found to contain highest level of Pb followed by ground soil (D), herbs (B) and strawberry (C) samples. These obtained results are beyond the recommended literature value for soil 149 mg/kg and for plant 2mg/kg. The results indicated that these samples are highly contaminated with lead and action must be taken to minimise serious damages to the humans and animals.

The BCR sequential extraction method was applied to the analysis of metal in order to obtain a distribution pattern in non residual fraction. The results showed that the most of the lead was extracted in residual fraction by using nitric acid and small level of lead by exchangeable, reducible and oxidizable fraction.

The 1,2- phenylenediamine method was not successful in giving accurate results as the intensity of the fluorescence decreased with copper concentration instead of increasing. However the uv-vis worked giving a straight line as absorption increased with the copper concentration.

The results from the segregation and CEC method showed that large amount of Pb concentration is present in the inorganic of the soil and very little in organic matter.

The DSC method was carried out to determine the percentage of organic presented in soil and plant samples. The results showed that plant samples contained high level of organic and the soil samples only small amount of organic matter.

The soil and plant samples were both run in infrared spectrometry and the peaks were assigned.

Bibliography and References:

[1] Environmental Chemistry by Dr Barry Foley, Lecture Notes; year 2012

[2] The chemistry of pollution, by Gunter Fellenberg: Page 101-102

[3] Gary W. VanLoon and Stephen J.Duffy. Environmental Chemistry; a global perspective

[4] Gary W. VanLoon and Stephen J.Duffy. Environmental Chemistry; a global perspective

[5] ISRN Ecology article journal, Heavy Metals in Contaminated Soils: A Review of Sources, Chemistry and Risks- 19 pages, 2011; http://www.isrn.com/journals/ecology/2011/402647/ (10^{th} April 2012)

[6] Development of an Industry Led Quality Standard for Source- Separated Biodegradable Material Derived Compost. Author – Munoo Prasad and Percy Foster
Journal - Environmental Protection Agency STRIVE programme 2007 – 2013

[7] Catherne E.Housecroft and Alan G.Sharpet, Inogrnic Chemistry, 3^{rd} Edition. 2008

[8] Colin Baird and Michael Cann, Environmental Chemistry, 4^{th} Edition. Page 689

[9] http://www.belleville.k12.wi.us/bhs/health/environment/leadpollution.htm (11th April 2012)

[10] http://www.health.ny.gov/publications/2584/ (11th April 2012)

[11] http://www.sigmaaldrich.com/catalog/DisplayMSDSContent.do (11th April 2012)

[12] Colin Baird and Michael Cann, Environmental Chemistry, 4^{th} Edition. Page 664-674

[13] The chemistry of pollution, by Gunter Fellenberg: Page 106-107.

[14] Fundamentals of Environmental Sampling and Analysis by CHUNLONG ZHANG

[15] Quality Assurance in Environmental Monitoring, Instrumental Methods. Edited by G. Subramanian Page 95-100

[16] Concepts, Instrumentation, and Techniques in Inductivity Coupled Plasma Pptical Emission Spectrometry by Charles B. Boss and Kenneth J. Fredeen page 3.

[17] http://www.gmu.edu/depts/SRIF/tutorial/aas/aas.htm (24^{th} April 2012)

[18] Title - Speciation of heavy metals by modified BCR sequential extraction procedure in different depths of sediments from Sungia Buloh, Selangor, Malaysia.
Authors - Keivan Nemdati, Nor Kartini Abu Bakar, Mhd. Radzi Abas, Elham Sobhanzadeh
Journal of Harzardous Materials 192(2011) 402 – 410

[19] http://www.ctahr.hawaii.edu/mauisoil/a_factor_mineralogy.aspx (12^{th} April 2012)

[20] Article - A Nanoparticle Autocatalytic Sensor for Ag^{+} and Cu^{2+} Ions in Aqueous Solution with High Sensitivity and Its Application in Test Paper
Authors – Xuan Yang and Erbang Wang

[21] http://www.shsu.edu/~chm_tgc/chemilumdir/JABLONSKI.html by Dr. Thomas G. Chasteen at Sam Houston State University, Huntsville, Texas (10^{th} May 2012)

[22] http://publicpartner.mt.com/content/mailings/UK/Lab/Introduction%20to%20DSC.pdf (12^{th} April 2012)

[23] Organic Chemistry by Dr Claire McDonnell, Lecture Notes 2010

[24] European Food Safety, http://www.efsa.europa.eu/fr/scdocs/doc/1570.pdf (24th April 2012)

Appendix

Calculation example for the ICP standard solution (ppm) in table 3

$M_1V_1 = M_2V_2$

$(100)*(0.2) = M_2*(100)$

$M_2 = \frac{(100)(0.2)}{100}$

$M_2 = 0.2$ppm

Calculation example of pb concentration (ppm) for intensity of compost sample A1 obtained in table 7.

$\left(\frac{5}{3790.66}\right) * (13112.45)$

Compost sample A1 = 17.3 ppm

Calculation of the original concentration in soil samples; dilute sample to yield 50 cm^3

$M_1V_1 = M_2V_2$

$(17.7) *(V_1) = (2.5)*(50)$

$V_1 = \left(\frac{(2.5)*(50)}{(17.3)}\right)$

$V_1 = 7.2\ cm^3$

Cacluation example of sample A1 from the table 9.

From the analysis of AA, the concentration for A1 was obtain to be 3.38 ppm. However the original concentration is:

$\frac{(50)(3.38)}{7.2} = 23.47$ ppm

Original concentration = 23.47 mg/dm of Pb

100 ml was prepared from the soil sample of the one gram

23.47 mg/100 cm^3

23.47 mg/g of compost

23.47 * 1000 = 2347 mg Pb/Kg

Calculation example in table 12: An estimate of the cation exchange capacity of a soil can be made from soil test results.

Sample A1 - The concentration obtain for sample A1 from atomic absorption was 0.21725 mg/l

0.21725 mg/Na^+/dm^3 * 4

0.869 mg Na^+/dm^3 * 100

0.869 mg $Na^+/100cm^3$

86.9 mg Na^+/grams

869 mg Na^+/100 g

The molcular weight for Na^+ = 23 mole/g

Cation Exchange Cacpity: $\frac{869}{23}$ = 37.7 millimoles of Na^+/100g

Infrared spectra

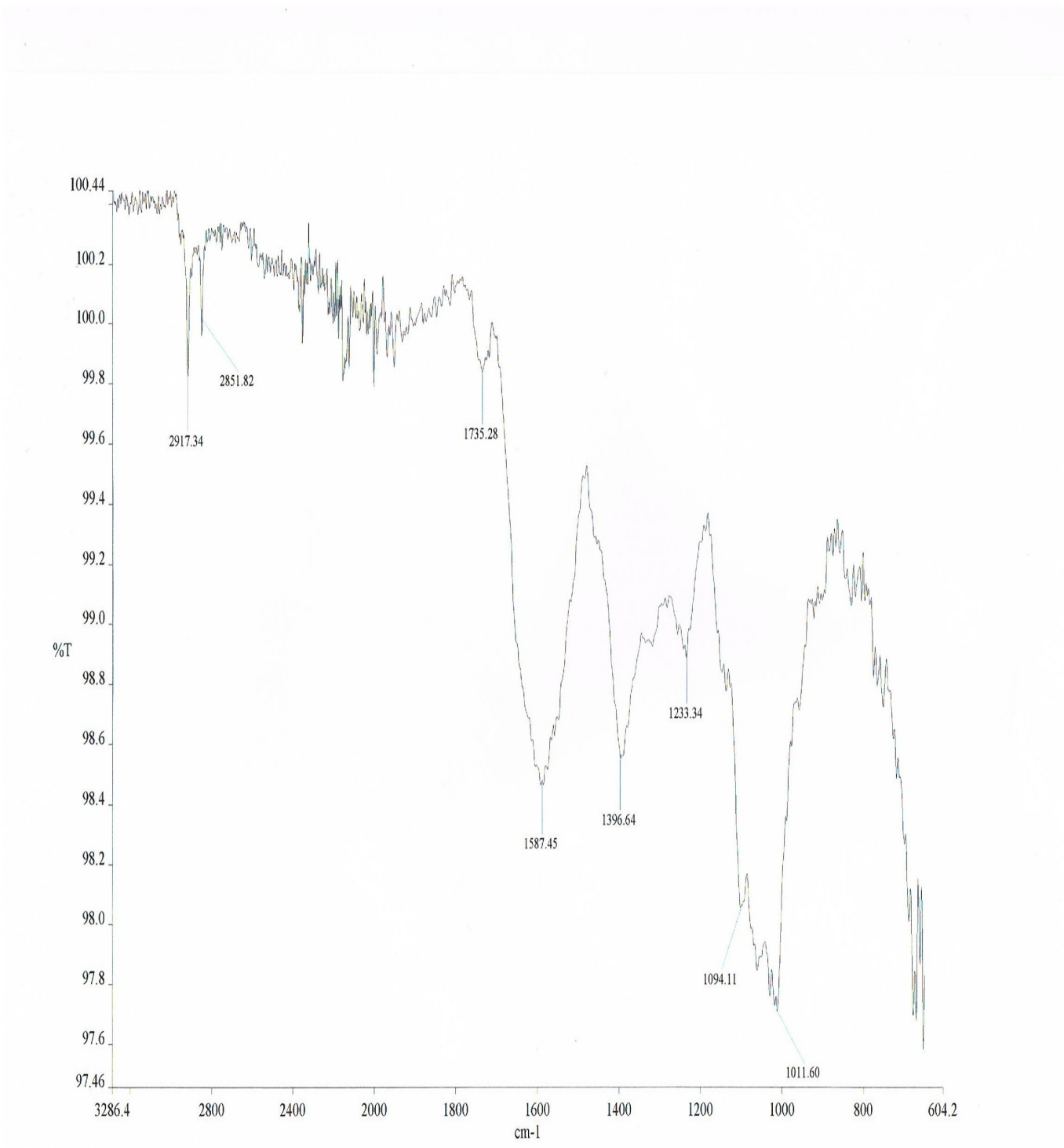

Figure 19 Leave Sample A3 spectrum

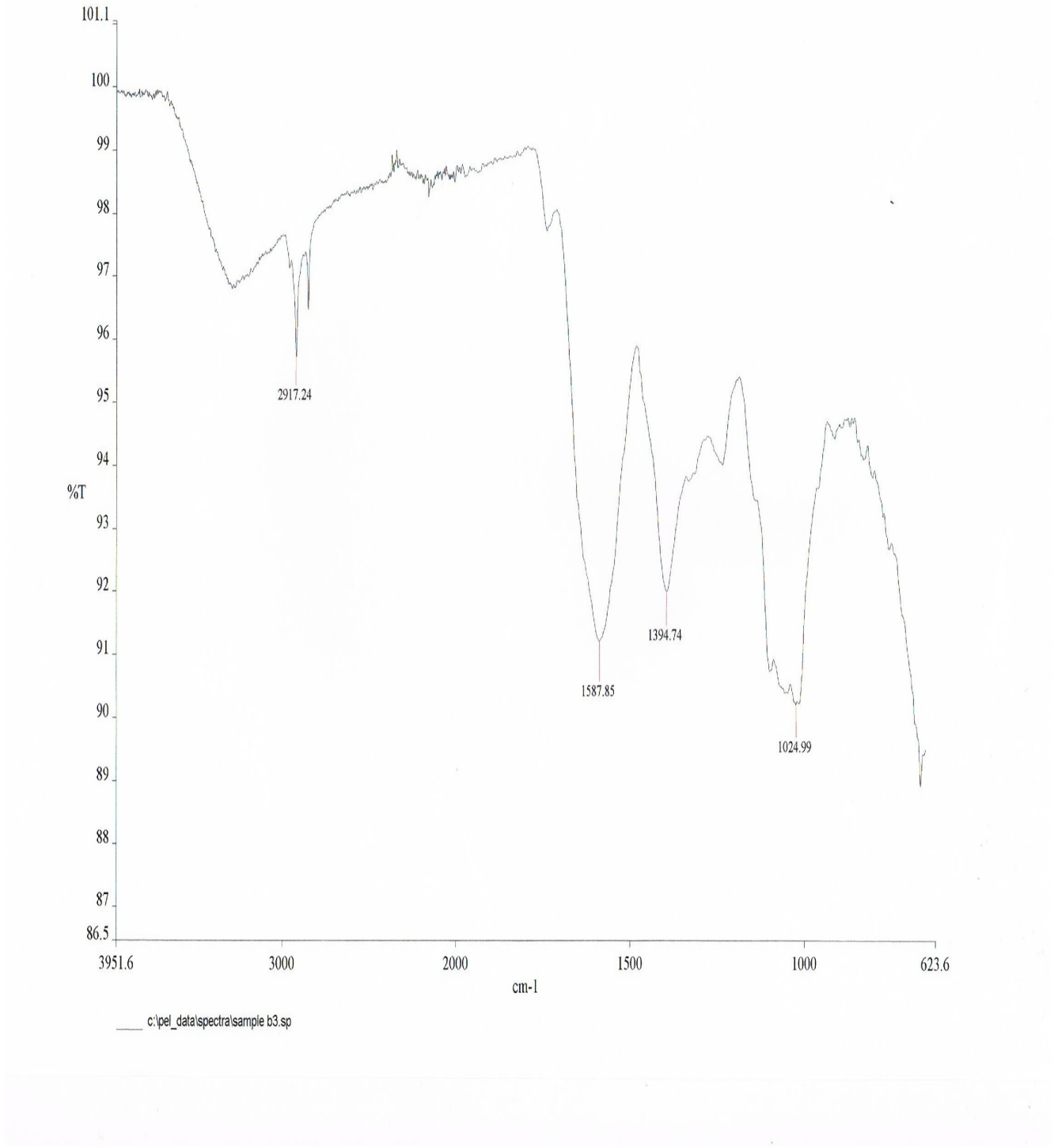

Figure 20 Leave Sample B3 spectrum

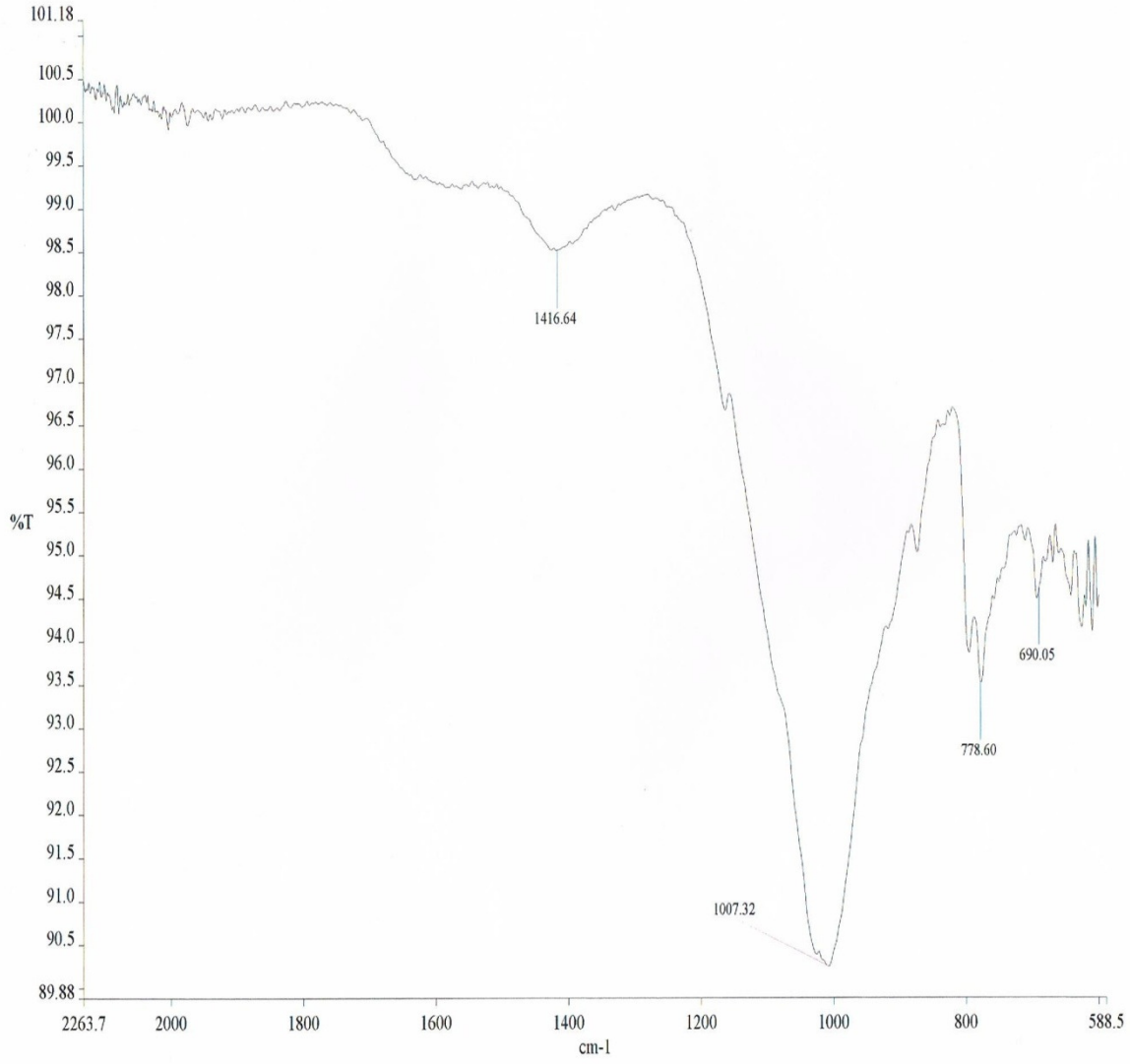

Figure 21 Soil Sample A1 spectrum

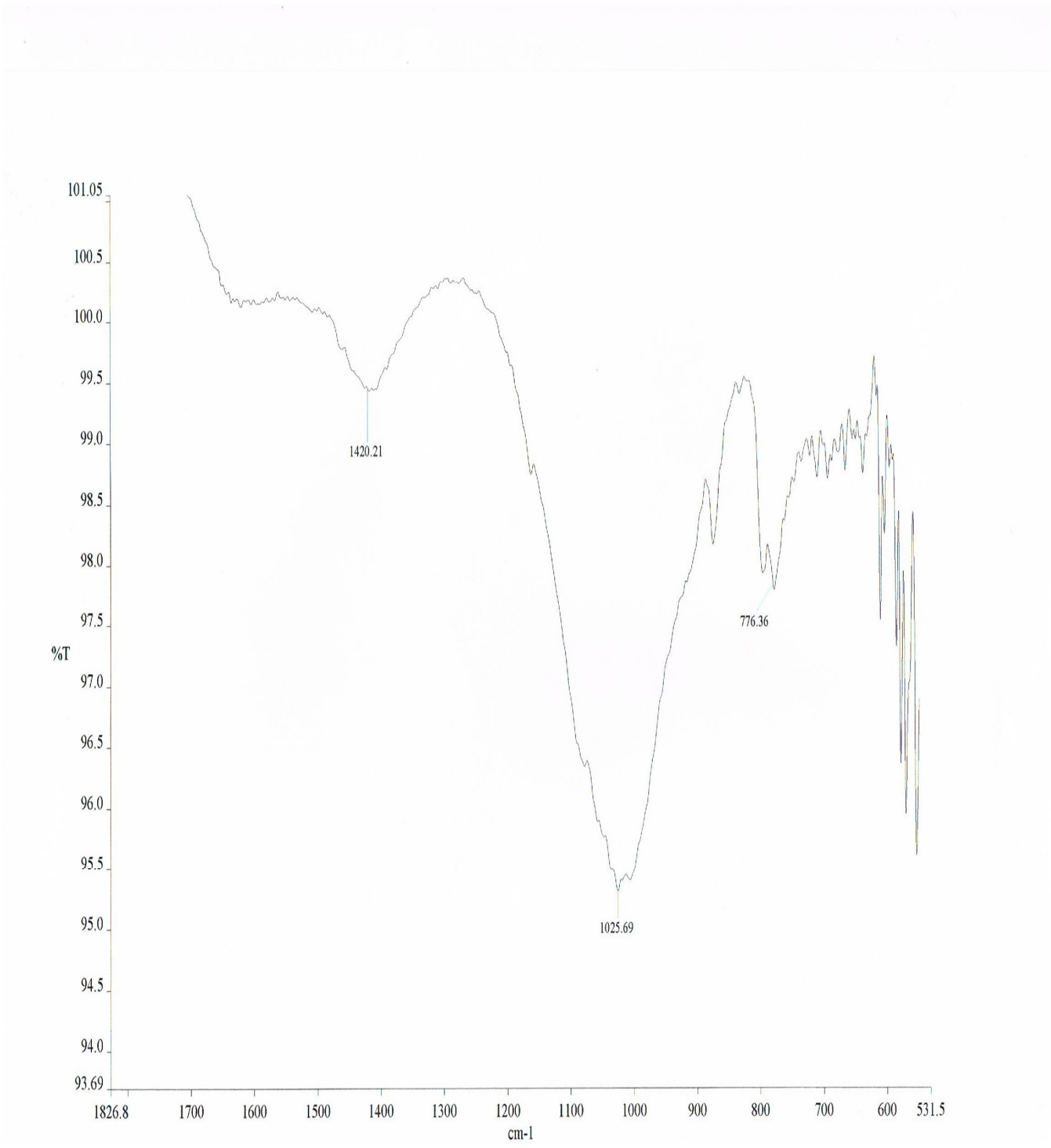

Figure 22 Soil Sample B1 spectrum

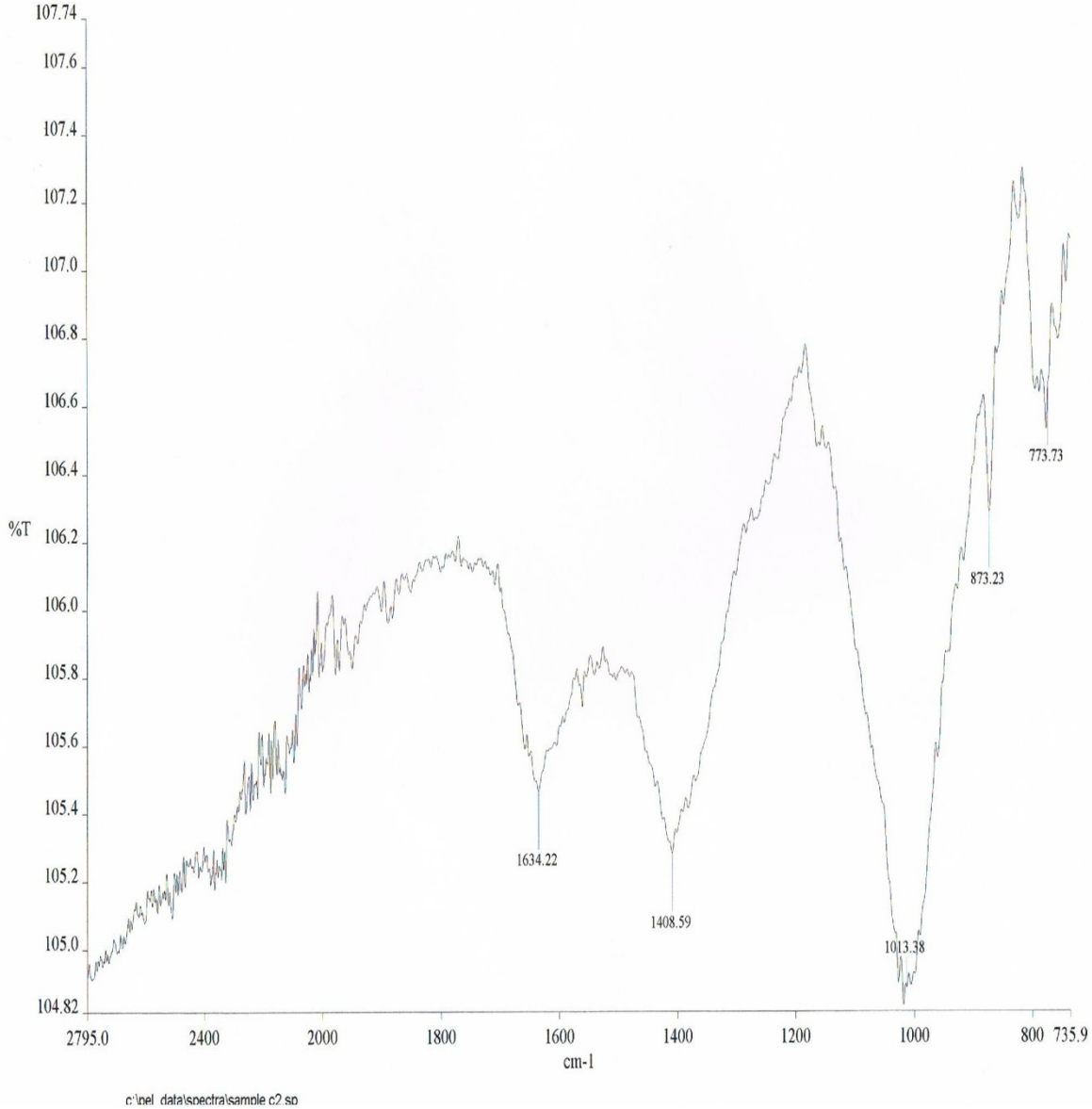

Figure 23 Soil Sample C2 spectrum

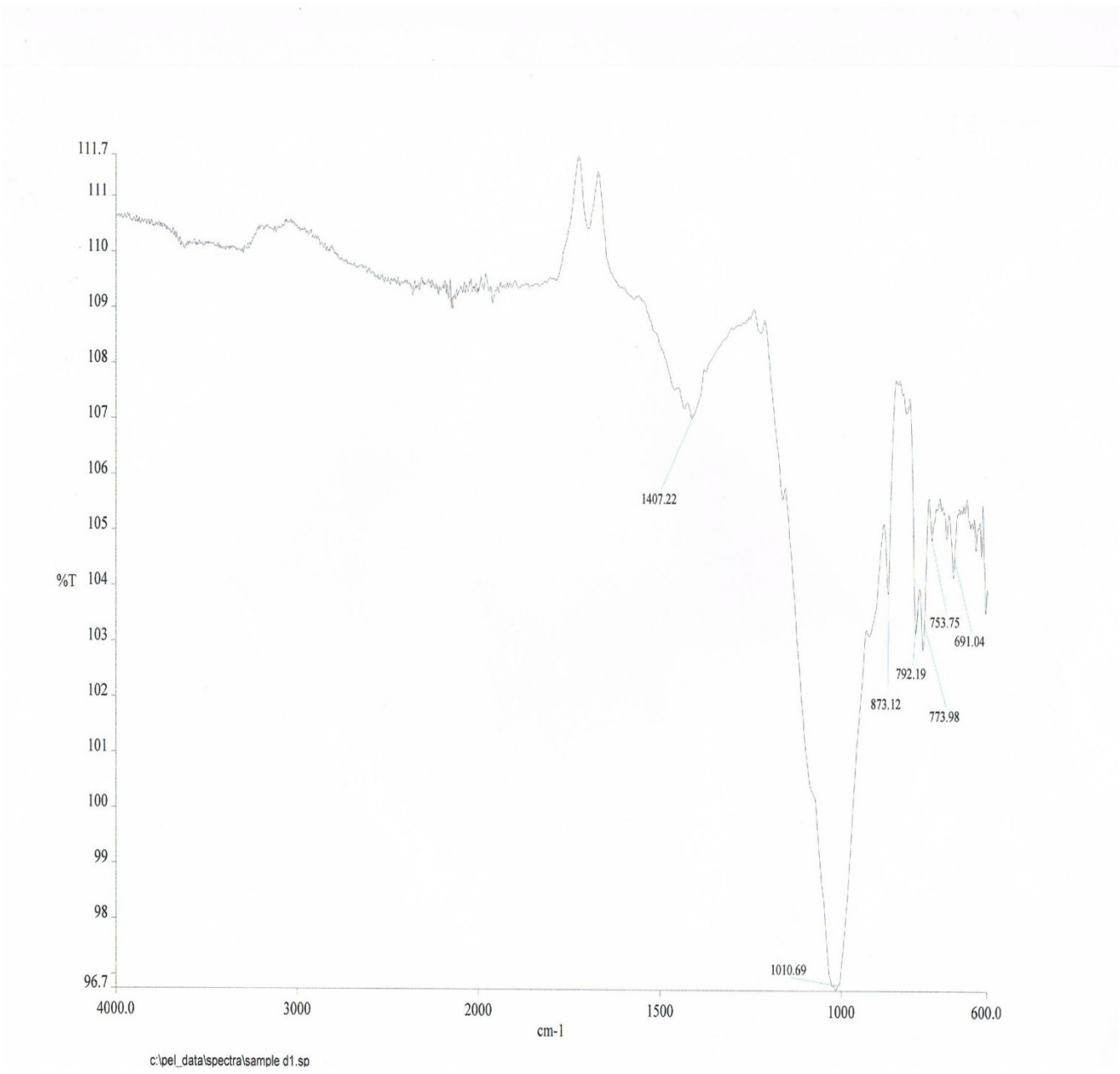

Figure 24 Soil Sample D1 spectrum

Soil Collection Area

Figure 25 Compost Sample A

Figure 26 Herb Patch Sample B

Figure 27 Strawberry Patch Sample C

Figure 28 Ground Soil Sample D