## ABSTRACT

# Microwave Treatment of Hazardous Waste: Feasibility Studies - Mass Balance

**by**
**Liu Liu**

This laboratory has been developing processes for the remediation of soils contaminated with hazardous wastes using microwave treatment. The initial stage was to define situations in which microwave treatment could potentially have unique advantages, and to define the relevant physical chemical mechanisms. That having been accomplished, at the present stage, feasibility studies are being carried to determine whether or not on-site field testing is justified. To that end, mass balances on the processes are needed. In this study mass balance studies were carried out on the microwave assisted steam distillation of volatile organic chemicals (VOCs) and semi-volatile organics (SVOCs), respectively, from substrates.

The substrates studied were sand, clay, humus, clay containing-magnetite, and soil, respectively. These substrates were impregnated with naphthalene. The naphthalene concentration in the substrate was 2000 ppm:

taking into account the sample size, the total amount of naphthalene was 0.1 gram.

It was assumed that the naphthalene, after treatment, would be in three possible states: a. In the substrate, and recoverable by extraction; b. Volatilized. c. In the substrate, but not extractable. For the first state, the substrate was subjected to Soxhlet extraction; for the second, the gases were trapped in methanol-containing wash bottles situated outside the microwave cavity; and for the potential non-extractables, the substrates were investigated by DRIFT (Diffuse Reflectance Fourier Transform Spectroscopy).

It was found that approximately 85% of the naphthalene could be accounted for by extraction and trapping: no evidence for non-extractables in the substrates was found by DRIFT. Since the sample size was only 0.1 gram, the unaccounted material was approximately 0.015 grams. That amount could have easily been lost due to absorption on the tubes from the reaction vessel to the wash bottles or by diffusion through connections. It is concluded that mass balances can be carried out on this system in the manner developed in this study.

# MICROWAVE TREATMENT OF HAZARDOUS WASTES: FEASIBILITY STUDIES - MASS BALANCES

by
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A Thesis
Submitted to the Faculty of the Graduate Division of the
New Jersey Institute of Technology
in Partial Fulfillment of the Requirements for the Degree of
Master of Environmental Science
Department of Chemical Engineering, Chemistry,
and Environmental Science
April 1992

# APPROVAL PAGE

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# ACKNOWLEDGMENTS

I would like to thank Dr. Dauerman for his invaluable support and guidance to my thesis and research work. His encouragements and comments sharpened my mind and analysis. From him, I learned much, including what was important for research and what was not, and how to say it clearly.

I am obliged to Ms. Gabriele Windgasse who trained me to use GC/MS and helped me set up the experimental devices. Her important advice was always ready when I needed it.

Further thanks are due to Professor Trattner and Professor Schuring who read the thesis and gave helpful guidance.

I thank, too, my parents, whose moral support has sustained me during my entire education.

Above all, I am indebted to my husband, Yansan Xiong, who contributed to every stage of this thesis, from the encouragement to the useful discussions.

Special thanks to all who have helped in my thesis work.

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# CHAPTER 1. INTRODUCTION

There is a need for alternative treatments for the remediation of hazardous waste contaminated soil. The method that is generally recommended by the US EPA on Superfund sites is incineration, but that recommendation is usually resisted by the local community(1), therefore, resulting in the call for alternate technologies (2).

An alternate technology which has been under development in this laboratory is microwave treatment of soils contaminated with hazardous wastes. The wastes that have been studied are volatile organics, non-volatile organics, and heavy metals. The program is divided into three stages. In the first stage, approaches which optimize the advantages of microwave treatment have been sought, and the underlying mechanisms, chemical and physical, have been studied. The second stage involves determining the feasibility of the treatment processes: capital costs, operating costs, and operating conditions. The third stage entails going to a Superfund site and demonstrating how the system works under actual field conditions. The status of each of these stages will now be addressed.

The first stage involves the finding of appropriate strategems for the use of microwave treatment and defining the underlying chemical and physical mechanisms. For volatile organics and semivolatiles, the approach used is steam distillation. This is a non-destructive way of separating organics from a non-volatile substrate, utilized as a unit operation in the chemical industry for decades. It is based upon the principle that the vapor pressures of water and immiscible organics are additive, thus boiling will occur at a temperature below $100^0$ C, assuming that the ambient pressure is 1 atm., effecting mass transfer of the organic in proportion to its vapor pressure. Since water is a strong absorber of microwave energy, the formation of the steam is effected directly by the incident radiation. This is not the case with a rotary kiln incinerator. Heating of the soil is effected by hot gas. Thus there is a temperature gradient set up in the soil, that will cause the water to diffuse into the gas stream rather than to boil. This is a non-destructive process, and the volatiles, in principle at least, are recoverable. For the non-volatile organics, a different process is postulated. Soil consists of aggregates which contain humus, clay, etc. bound together by adhesion and cohesion water. The spilled hydrophobic organic forms multilayers, held together by weak Van der Waal's forces on the surfaces of the soil aggregates. Because the forces are relatively weak, the organics are mobile. Microwave radiation effects the removal of the water, thus unimolecular layer adsorption can take place. The humus is a microwave absorber and it will react with the organics to form new species which are not leachable: "chemical fixation" takes place. This model is based upon microwave treamtment studies and Fourier Transform Infra Red (FTIR) studies on surface interactions of the organic with clay and humus using DRIFT cells. For metal contaminated soil, the appropriate model is a soil which contains a strongly microwave absorbing mineral which can interact with the heavy metal to form a new mineral which is non-hazardous. Thus in studies on hematite-containing soils impregnated with chromates it was shown by a combination of X-ray spectroscopy, scanning electron spectroscopy, and x-ray image spectroscopy that microwave heating effects the formation of a new chromium containing mineral, namely, chromite, which is non-hazardous.

The presentations and publications from this laboratory on the above-described work is presented in Appendix II.

The second stage is the feasibilty investigations: operating costs, capital costs, and operating conditions. These studies are being carried out in our pilot plant. The pilot plant was fabricated by the Raytheon Corporation of Waltham, MA. It consists of 50 cubic foot cavity, powered by 8 magnetrons situated above a conveyor belt.

The total rated power is 6 kW, which can be doubled by adding a similar array of magnetrons below the conveyor belt. These studies are now in progress and it is too early to draw any conclusions. Initial investigations are being carried out on the process for the removal of volatile and semivolatile organics.

The third stage involves going to a Superfund site and determining under actual conditions the operations of the system. This stage will be carried out in cooperation the Raytheon Corporation. A 50 kW microwave generator operating at 915 MHz will be used. The depth of penetration increases as the wavelength of the incident radiation increases. In contrast to the 2450 MHz hitherto used, the depth of penetration should increase by approximately a factor of three. Such units are available only at high powers, therefore, it could not be used previously. This stage is basically now at the planning stage.

The purpose of the studies in this thesis is to carry out mass balance studies. Specifically, on the steam distillation process. Mass balances are necessary to characterize the process. Such studies carried out to-date have been of a tenuous nature. It is assumed that there are three routes for the organic: volatilization in the gas phase; in the soil, and extractable; in the soil, but not extractable. In a previous study(Gu's MS Thesis, Appendix II), the volatiles were adsorbed on granulated activated charcoal (GAC)

# CHAPTER 2. THE INTERACTION OF MATERIALS WITH MICROWAVES

Microwaves fall into the class of phemomena called electromagnetic radiation. Electromagnetic radiation can be defined as phenomena that obey Maxwell equations (3,4). The basic thrust of each of these equations will be discussed in non-mathematical terms. The first equation deals with a non-moving static charge. If a sphere is placed around the charge, the sum of the electric fields around the surface is equal to the magnitude of the enclosed charge. That is, the electric field associated with the electrical charge appears in its entirety on the surface of the sphere. The second equation deals with a magnetic dipole enclosed in a sphere. In contrast to the case with the electric charge, there is no magnetic field on the surface of the sphere. This is because the fields of the dipole are opposite to each other in magnitude and direction and thus will cancel each other on the surface. This equation is based upon the assumption that monopoles do not exist. The source of electric fields is electric charges; the source of magnetic fields is dipoles. The third and fourth equations deal with time-varying electric and magnetic fields. According to the third equation, a time-varying magnetic field produces an elcetrical field in an imaginary loop placed about the magnetic field. The fourth equation states that a time-varying electric field and current produce a magnetic field in an imaginary loop situated around the electric field and the electric current. It follows that since a time-varying electric field produces a time-varying magnetic field and vice versa, a wave is propagated that is self-sustaining. A wave that propagates in a sinusoidal form is referred to as electromagnetic radiation. That means that the time variable can be replaced by a phase variable, for situations in which wave propagation is not important.

The hardware to effect microwave treatment can be classified as follows: the microwave generator; the way the power is delivered to the applicator; the nature of the applicator; the load; the way in which microwave leakage is prevented. These will now be discussed sequentially.

The function of the microwave generator is to take 60 Hz line power, and increase it to 2450 MHz, with a minimal loss of power. The power source is a vacuum electric tube. For low power, the tube is a magnetron; for high power, a klystron. The principle of the magnetron is that electrons emitted from a filament are confined to a circular path by a perpendicular magnetic field. A surrounding circular anodic field contains vanes which are distributed radially. Fields set up in the vanes cause the electrons to bunch up in spokes, the number of spokes are 1/2 the number of vanes. The vane of the electron bunch approaches a spoke which is negatively charged; repulsion occurs and also, RF field energy is gained by the anode. In contrast, in the klystron the elecrons move linearly through the field of spokes. While the magnetron is more efficient, the klystron is needed when the power output is above 100 kW. Also, the klystron is longer lived because in the magnetron the elecron density is built up by the bombardment of emitted electrons on the filament: the resulting heating shortens the life of the filament and the tube.

Microwave power is transmitted in several ways: antennas; two-conductor transmission lines (coaxial line, twin-lead line, and microstrip line); waveguides (5). An antenna directs the radiant electromagnetic radiation from an oscillating LC resonating circuit into space by means of two relatively large conductors which tap into the circuit and are in the same axis (the dipolor antenna). For 60 cycle transmission a single wire conductor can be used, but not at 2450 MHz. The basic mode of operation (field configuration) in two conductor transmission lines is TEM transverse electromagnetic radiation): all electric and magnetic field configurations are transverse to the direction of propagation along the line. The electric fields radiate; the magnetic field are circular about the direction of propagation. The shortcoming of two-conductor transmission lines is that energy losses are high. A waveguide consists of a hollow metallic duct, the dimensions of which will insure that only one mode is transmitted. Power losses are relatively low if there is no discontinuity which the characteristic impedance of the mode. Such a change in the impedance causes reflections and standing waves. The reflections cause the fringing RF fields in the magnetron to change which can cause the electron cloud to radiate; the standing waves will stop the propagation of the microwaves. Unlike two-conductor transmission lines, one of the field must be axial direction.

The applicator is where the power is delivered to the load. The load is the material to be treated. There are three major types of applicators: travelling wave; resonant; multimode. In the travelling wave applicator the laod is treated in the waveguide. Given the mode, it is possible to cut slots in the waveguide which do not disturb the eddy currents on the surface of the waveguide, and through which a load can be continuously be passed.

After passing through the region in which the load is located, the radiation is "dumped" into a water load. The laod must be small both in dimensions and a low absorber. It has to be small because one of the slot dimensions can't be greater than a quarter of a wavelength, otherwise, leakage of radiation will occur. The power absorption must be low because if absorption is too great, the mode will change.

In a resonant applicator, one end of the waveguide is shorted by a metal plate causing the wave to be reflected. In turn, there is another reflecting plate whcih cut to allow the incoming wave to enter, which reflects the reflected wave. If the distance between the reflectors is an integral number of wavelengths, then a standing wave occurs. the amplitude of the standing wave increases with reflection, thus, relatively high power can be delivered to a properly situated from a relatively low power microwave generator. Again the shortcoming is that the load has to be small. In the multimode applicator, the load is in a cavity which is external to the waveguide. In that cavity the aim is to have a uniform distribution of energy. That means no distinct modes. Hence the need for as many modes as possible. This can be effected by stirring the incoming radiation (mode stirrer), roatating the load in the cavity, distributing the magnetrons with baffles to distribute the directions of the waves, and by using a large cavity.

Unlike thermal heating, the load has to be considered as an element in the system because of the fact that its nature affects the operation of the elements in the system. The impact of the load on traveling wave applicators and resonant applicators was pointed out above. In the multimode applicator, if the load does not absorb strongly, reflections can cause damage to the magnetron in the way discussed previously. Furthermore, the load is of the size of the incident wavelength. This leads to diffraction effects, bending of the wave around a load. The load affects the distribution of fields in the cavity. That distribution if established in the absence of a load can not be extrapolated to the situation when a load is present. An effect common to all applicators is when the load has sharp edges and electric charges so that the electrical fields are concentrated about that sharp edge. When this occurs, ions in the gas stream towards the field, causing ionization of air molecules by collision; the cascading effect results in an arc. Arcs are undesirable because waves are reflected back to the magnetron, combustion can be initiated if combustible gases are present within the flammability limits, and because they can cause holes in the applicator. On the other hand, continuous arcs, that is, plasmas, have been used to destroy volatile toxic gases (6).

Sources of possible leakage are: a door and the window which it contains to look into the cavity; the apertures through which the conveyor belt moves; ports for the thermocouples drilled into the cavity; the ducts for the entrance and exiting of forced convection air. The basic units used for preventing leakage are apertures which have a dimension less than a 1/4 of a wavelength; microwave absorbing materials; and shorting stubs. In the shorting stubs incoming radiation is reflected after travelling 1/4 of a wavelength. When it is reflected back to the entrance it has traveled a total of a half a wavelength. Thus it is $180^0$ out of phase with the incoming radiation. This causes annhilation of the wave by destructive interference. The aperture size can be greater than 1/4 of a wavelength if the other means of preventing leakage just described are combined with aperture. Thus if continuous operation were sought using a conveyor belt, if the only means for preventing leakage were the aperture, than the height of the material to be processed would be limited to 1/4 of a wavelength. But in practice, a tunnel is constructed both before and after the cavity through which the material passes on the conveyor belt. The size of the aperture depends to a large extent on the array of stubs and absorbing materials within the tunnel. In semicontinuous operation, the limits do not exist: the material is conveyed into a chamber; that chamber is sealed so that there can be no microwave leakage; then the material is conveyed into the cavity.

This thesis is limited to the applicability of microwave radiation to the effecting of the remediation of hazardous wastes. Other uses, some commercial and others potentially commercial, will now be discussed.

In the agri-food sector(7): sterilization, pasteurization, and cooking; also, the (tempering) thawing of frozen products.

In the rubber industry(7): vulcanization (cross-linking) of rubbers; addition polymerizations which involve the elimination of molecules which are strong microwave absorbers; regeneration of spent rubber to effect recycling.

In the chemical industry(7): drying of pharmaceuticals; polymerization of resins or glues; catalytic reactions; rearrangements on microwave absorbing clay substrates like Ca Montmorrillonite.

In the textile industry(7): drying; the setting of dyes.

In the wood industry(7): curing; drying-assist; laminating.

In the surface treatment industry(7): microwave plasmas for etching.

In the champagne industry(7): softening of corks.

In the ethanol industry(8): cooking of cassava roots as part of the production of ethanol.

In the ceramics industry(9): sintering to form ceramics; drying of ceramic products.

Also, as sensors and controllers(7): temperature, in contrast to infrared thermography, microwave provides a larger depth of penetration; dielectric constants; moisture; density.

To treat radioactive wastes: for calcination of the wastes (10); for reducing the volume of the waste (11).

To treat household wastes: a home incinerator(12).

To detoxify volatile hazardous wastes: fluidized bed reactor(13).

# CHAPTER 3. EXPERIMENTAL SECTION: OVERVIEW

## 3.1 INTRODUCTION

This Experimental Section covers the following aspects of carrying out the experiments: the setup; instruments; materials. Note that in each chapter there will be an additional experimental section, related to the specifics of the studies carried out.

## 3.2 EXPERIMENTAL SETUP

The experimental setup used in the whole experimental process is shown in the Figure 3.1.

## 3.3 EXPERIMENTAL INSTRUMENTS

**3.3.1** Microwave Oven: SHARP, Carousel # II

The microwave treatment was conducted in a modified domestic microwave oven: 2450 MHz, 700 W.

**3.3.2** GC/MS: Hewlett-Packard 5890/5970 GC/MS with 59970 ChemStation.

**3.3.3** FTIR: Digilab-40 Fourier Tansform Infrared Spectrometer was used with 3240 SPC data system. A model GRAPHTEC WX 4731 plotwriter and a model OKIDDATA, MICROLINE 182 TURBO printer were used in this study. The diffuse reflectance accessory designed exclusively for

Bio-Rad Spectrometers. The powder samples were held in stainless steel cups, 10 cm in diameter and 1 mm deep.

**3.3.4** Soxhlet Extractor: 34 - mm I.D., with 125 - ml round-bottom flask.

**3.3.5** Thermocouple: GLAS-col MODEL PR - 800

### 3.4 EXPERIMENTAL MATERIALS

**3.4.1** Naphthalene: $C_{10}H_8$; FW 128.17; Melting Point: 80.5 $^0C$; Boiling Point: 218.0 $^0C$: Vapor Pressure: 0.032 mmHg at 25 $^0C$; Recrystallized From Alcohol; CAS 91-20-3;

**3.4.2** Methanol: $CH_3OH$; FW 32.04; CAS 67-56-1; HR-GC; Product of EM Science.

**3.4.3** Sand: Play ground sand. Product of Quikrete & Quikwall.

**3.4.4** Sandy Soil: The sandy soil was taken from South Mountain Reservation in New Jersey. The properties of this kind of soil are as follows according to previous study:

* Moisture content: 8.5%;

* Clay Content: 9.9%;

* pH: 6.5 - 7.0;

* Metal elements content: Ti = 0.29% +/- 0.01 (wt/wt);
Mn = 147 +/- 8 (ug/g);
Fe = 2.10% +/- 0.01 (wt/wt);
Cu = 56 +/- 3 (ug/g);
Zn = 169 +/- 10 (ug/g).

**3.4.5** Clay Soil: The clay soil was taken from Aron Street, Middlessex County in New Jersey. The properties are listed as follows:

* Moisture content: 4.9%;

* pH: 6 - 6.5;

* Metal elements content: Ti = 0.79% +/- 0.01 (wt/wt);
Mn = 548 +/- 8 (ug/g);
Fe = 9.22% +/- 0.01 (wt/wt);
Cu = 69 +/- 3 (ug/g);
Zn = 191 +/- 10 (ug/g).

**3.4.6** Clay: The clay, namely, Kaolin (KGa-1) was obtained from the Clay Minerals Society Repository, Department of Geology, University of Missouri. The properties of Kaolin are as follows:

* Chemical Composition (%):

$SiO_2$: 44.2; $Al_2O_3$: 39.7; $TiO_2$: 1.39; FeO: 0.08; MnO: 0.002; MgO: 0.03; CaO: n.d.; $Na_2O$: 0.013; $K_2O$: 0.050; F: 0.013; $P_2O_5$: 0.034.

* Cation Exchange Capacity: 2.0 meg/100g.

* Surface Area $N_2$ area: 10.05 +/- 0.02m2/g.

* Thermal Analysis: DTA: endotherm at 630 $^0$C, exotherm at 1015 $^0$C; TG: dehydroxylation weigh loss 13.11% ( theory 14%) indicating less than 7% impurities.

* Infrared Spectroscopy: Typical spectrum for well crystallized Kaolonite, however not as well crystallized as a typical China Clay from Cornwall, as judged from the intensity of the 3669 $cm^{-1}$ band. Splitting of the 1100 $cm^{-1}$ band is due to the presence of coarse crystals.

**3.4.7** Humus: Product of Petruzzo Company.

**3.4.8** Magnetite: $Fe_3O_4$ (Spinel Group), obtained from Ward's natural science establishment, INC., has following properties:

* Crystallography: Isometric; 4/m32/m. Frequently in octahedral crystals; rarely dodecahedral. Commonly coarse- to fine-grained granular, massive.

* Physical Properties: Cleavage: None. Fracture subconchoidal to uneven; brittle. H.6.0. G. 5.18. Luster: Splendent to dull metallic. Color: Iron-black; opaque. Streak: Black.

* Composition/Features: A common iron oxide characterized by its strong magnetism, black color, and hardness. Slowly soluble in HCL. Infusible. Strongly magnetic varieties, which act as nature magnets, are known as lodestone.

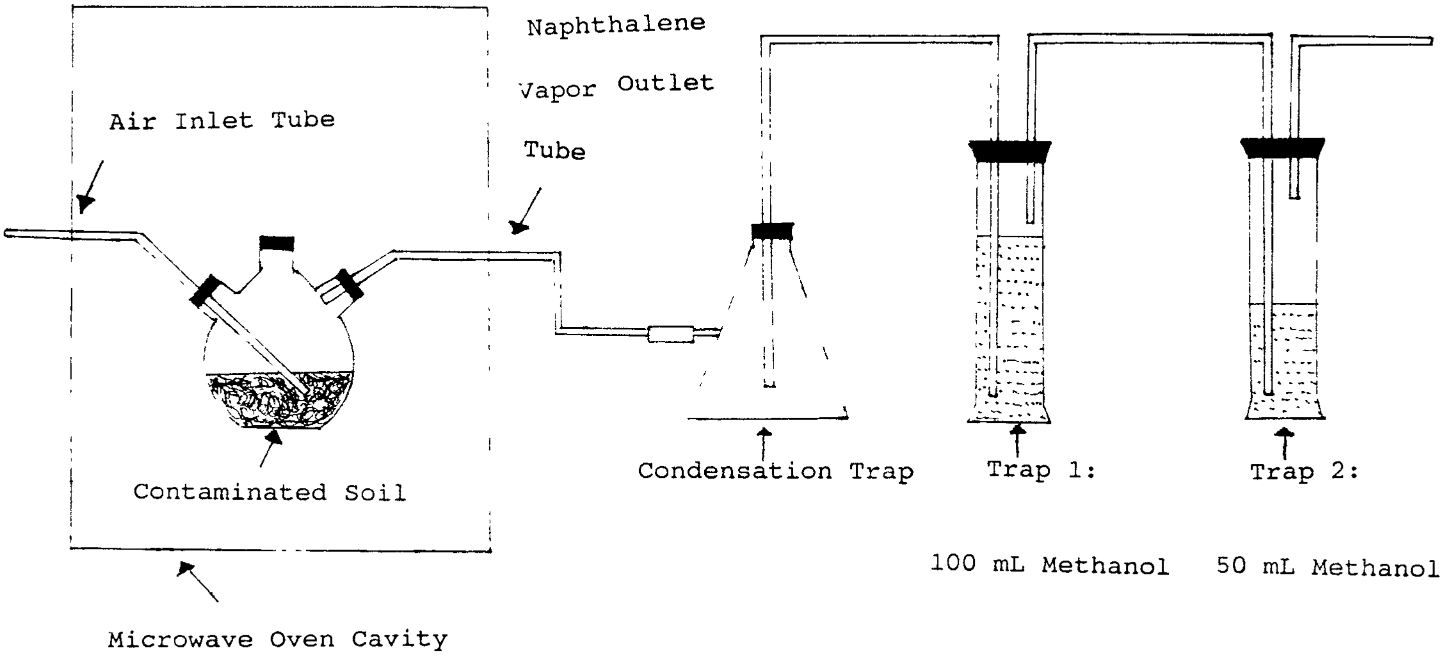

FIGURE 3.1 Off Gas Trapping System

# CHAPTER 4. EXPERIMENTAL SERIES I

# MASS BALANCE STUDIES: THERMALLY TREATED SAND IMPREGNATED WITH NAPHTHALENE

## 4.1 INTRODUCTION

The overall objective is to quantitatively measure the naphthalene vaporized during microwave treatment of contaminated soil under steam distillation conditions. Since such a measurement is more complicated than measuring the vapors resulting from thermal treatment, initially it will be determined if the experimental apparatus can trap thermally vaporized naphthalene under steam distillation conditions. To optimize the conditions for maximum vaporization, the substrate that will be used is sand because naphthalene should not be strongly sorbed on sand.

## 4.2 EXPERIMENTAL SECTION

**4.2.1** Two hundred (200 g) gram sand were impregnated with 20 ml naphthalene dissolved in methanol (20 mg/ml) in a round bottom flask. Methanol was not evaporated. Then 20 ml water was added. A thermometer was inserted into the sand and the vapors escaped through a glass tube: the vapors were trapped in two methanol spargers in series. Through another glass tube in the flask, air from a compressed air outlet was passed over the mixture.

**4.2.2** The mixture was heated with a heating mantle until the temperature reached 220 $^{0}$C; this temperature was maintained for 1.5 hr. The emerging vapors were passed through two wash bottles containing methanol; these traps will be referred to as "trap 1" and "trap 2," respectively.

**4.2.3** Ten (10) ml solution were pipetted from "trap 1" and diluted to 100 ml; 1 ul was injected into GC/MS, in triplicate: the results are listed in Table 4.1.

**4.2.4** Unlike the treatment of the solution in "trap 1," the "trap 2" solution was dilute, therefore, it wasn't necessary to dilute the sample before injection into the GC/MS: again, a 1 ul sample was injected into the GC/MS in triplicate: the results are listed in Table 4.1.

**4.2.5** A calibration curve of naphthalene solution was drawn in the range from 10 ng/ul to 1000 ng/ul.(See Figure 4.1).

## 4.3 RESULTS AND DISCUSSION

In Figure 4.1, the calibration curve of naphthalene is shown. The regression constant is 0.998, indicating that the curve is reliable.

In Table 4.1, trapping data after one and a half(1.5) hours thermal treatment are presented. For samples 1, 2, and 3, respectively, the total amounts of naphthalene found in trap 1 and trap 2 are 365 +/- 10, 362 +/- 9, and 367 +/- 12. The trapping percentages of the three samples are 91 +/- 2%, 90 +/- 2%, and 92 +/- 3%, respectively. Assuming that the sand does not retain the naphthalene, the total percentage of naphthalene recovery equals the percentage of naphthalene trapped. Hence, the total percentage of naphthalene recovery of the three samples are 91 +/- 2%, 90 +/- 2%, and 92 +/- 3%, respectively.

## 4.4 CONCLUSIONS

These experiments show that it is possible to account for up to 90% of the volatilized naphthalene quantitatively, and precisely. The 10% that is not accounted for may be due to trapping inefficiency, adsorption in the sand, or losses in the course of transportation from the sand to the trap.

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C A L I B R A T I O N   T A B L E   E D I T              Rev 3.1.1 31-Mar-86

        Calibration Table : DATA:LIU-LIU.Q

Ret Time Pk#    Signal Descr      Amt ng/ul  Lvl  RespFact  Pk-Type  Partial Name
[illegible]   1  127.00- 129.00 amu  10.00       1 16.45e-6        1
                                   15.00       2 14.06e-6
                                   40.00       3 23.59e-6
                                   50.00       3 24.58e-6
                                   200.0       4 24.26e-6
                                   400.0       5 19.55e-6
                                   800.0       6 21.88e-6
                                   1000        7 21.50e-6
                                   2000        8 24.57e-6
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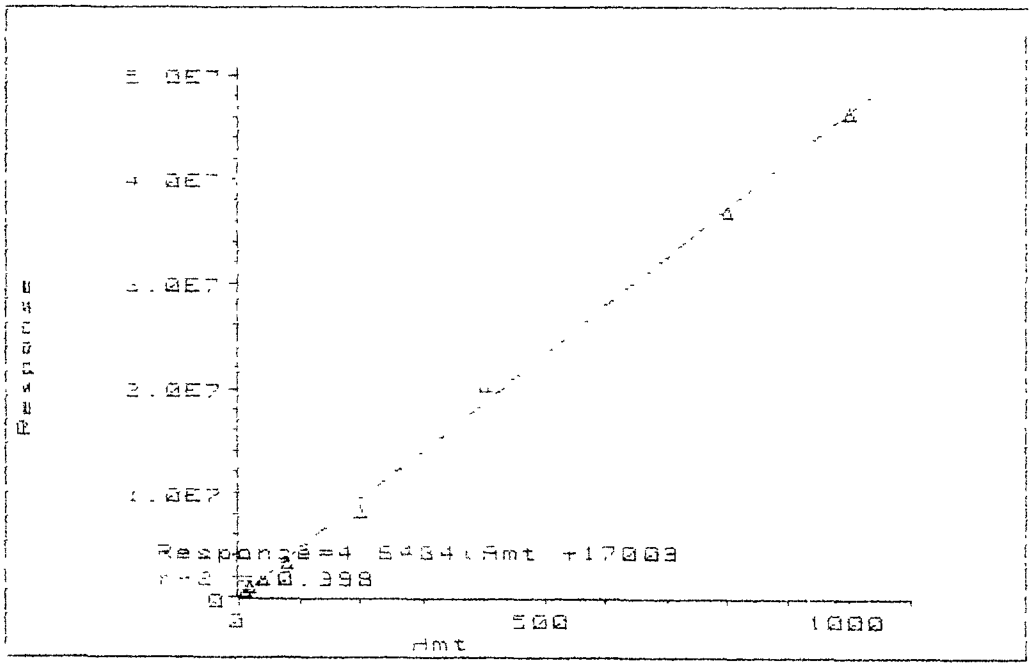


FIGURE 4.1 Calibration Curve

Table 4.1 Trapping Data: Thermal Treatment (1.5 hr.)

| | Sample 1 | | Sample 2 | | Sample 3 | |
|---|---|---|---|---|---|---|
| sample No. | trap1 | trap2 | trap1 | trap2 | trap1 | trap2 |
| No. of replication | 3 | 3 | 3 | 3 | 3 | 3 |
| naph amt. (ng/ul) | 270.4 | 2.215 | 277.6 | 1.854 | 284.0 | 2.012 |
| | 286.6 | 1.784 | 281.2 | 1.796 | 286.7 | 1.943 |
| | 275.3 | 1.873 | 262.3 | 1.796 | 270.2 | 1.866 |
| ave. | 277.4 | 1.957 | 274.0 | 1.855 | 280.3 | 1.947 |
| *s | 8 | 0.2 | 7 | 0.1 | 9 | 0.1 |
| *95% C.L. | 277+/- 8 | 2.0+/- 0.2 | 274+/- 7 | 1.8+/- 0.1 | 280+/- 9 | 1.9+/- 0.1 |
| vol. of solution (ml) | 131 | 52 | 132 | 50 | 131 | 50 |
| naph. amt in 100ml (mg) | 365 +/-10 | 0.10 +/-0.01 | 362 +/-9 | 0.090 +/-0.003 | 367 +/-12 | 0.097 +/-0.003 |
| sum of trap1, 2 | 365+/-10 | | 362+/-9 | | 367+/-12 | |
| orig. amt. (mg) | 400 | | 400 | | 400 | |
| Trapping % | 91+/-2 | | 90+/-2 | | 92+/-3 | |

*s: In this and subsequent studies, "s" represents the standard deviation based upon the results of the triplicate GC/MS analyses; the ranges reported for calculated parameters like "total recovery" are proportional to this standard deviation.

*95% C.L.: Here, 95% C.L. stands for confidence level, and it measures the posibility for the absolute deviation (x - $\overline{x}$) being equal to less than ts.

$$95\ \%\ \mathrm{C\ L.} = \overline{x} \pm \frac{ts}{\sqrt{n}}$$

# CHAPTER 5.EXPERIMENTAL SERIES II

# MICROWAVE ABSORPTION: DIFFERENT SUBSTRATES

## 5.1 INTRODUCTION

One factor that has to be considered in interpreting the microwave experiment data is the temperature that various substrates reach as a function of heating time. Obviously one could not expect significant removal of a volatile organic if the temperature of the substrate were lower than the steam distillation temperature.

## 5.2 EXPERIMENTAL SECTION

Fifty (50) grams of the following substrates were studied separately: sand; sandy soil; clay soil; clay; clay with magnetite and humus. Five (5) samples of each substrate were heated for 2, 4, 6, 8, and 10 minutes, respectively. Temperature measurements were made by thermocouples inserted into the substrates immediately after the radiation was turned off.

## 5.3 RESULTS AND DISCUSSION

In Figure 5.1, 5.2, 5.3, 5.4, 5.5, 5.6, the temperature of sand, sandy soil, clay soil, clay, clay and magnetite, humus as a function of heating time, respectively, are shown. Note that each point represents the result of a separate run. The maximum temperature reached after 10 minutes microwave treatment of sand, sandy soil, clay soil, clay, clay and magnetite, and humus are 77.7, 134.5, 107.5, 93.5, 195.2, and 86.3 $^0$C, respectively.

## 5.4 CONCLUSIONS

The highest temperature is that obtained for a mixture of clay and magnetite. Since clay alone reaches only a temperature of 93.5 $^0$C, the temperature reached of 195 $^0$C is due mainly to magnetite. Magnetite is a microwave absorber because it contains magnetic domains which can absorb energy from the magnetic fields associated with the electromagnetic energy. Sand reaches a significantly lower temperature than sandy soil, clay soil, clay, and humus, respectively. This difference in temperature may be due to the difference in the amounts of water: sand retains little, whereas in the others it may be considerable.

FIGURE 5.1 MICROWAVE HEATING TIME VS TEMPERATURE OF SAND

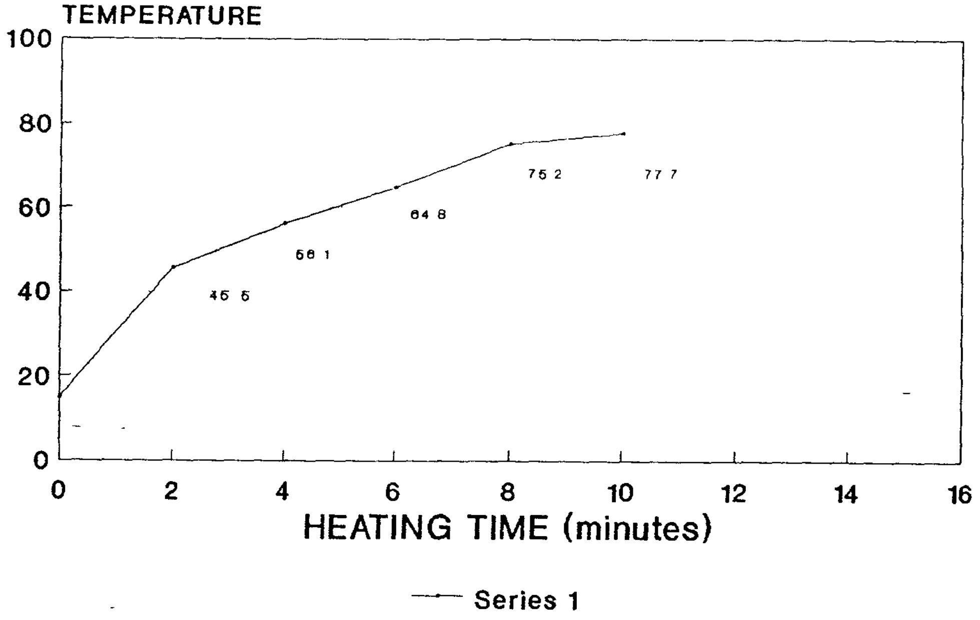


FIGURE 5.2 MICROWAVE HEATING TIME vs TEMPERATURE OF SANDY SOIL

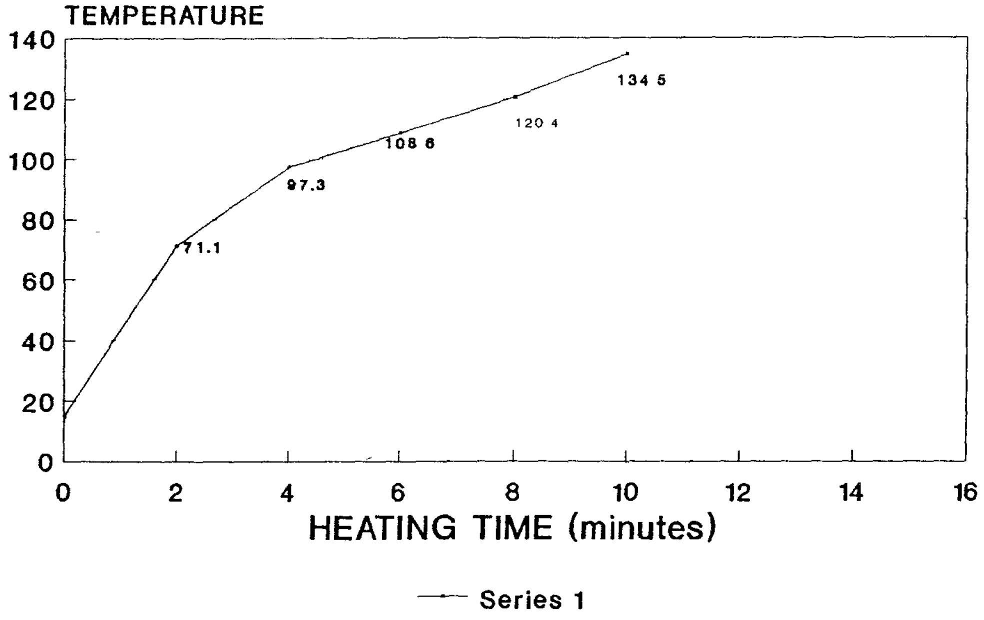


FIGURE 5.3 MICROWAVE HEATING TIME vs TEMPERATURE OF CLAY SOIL

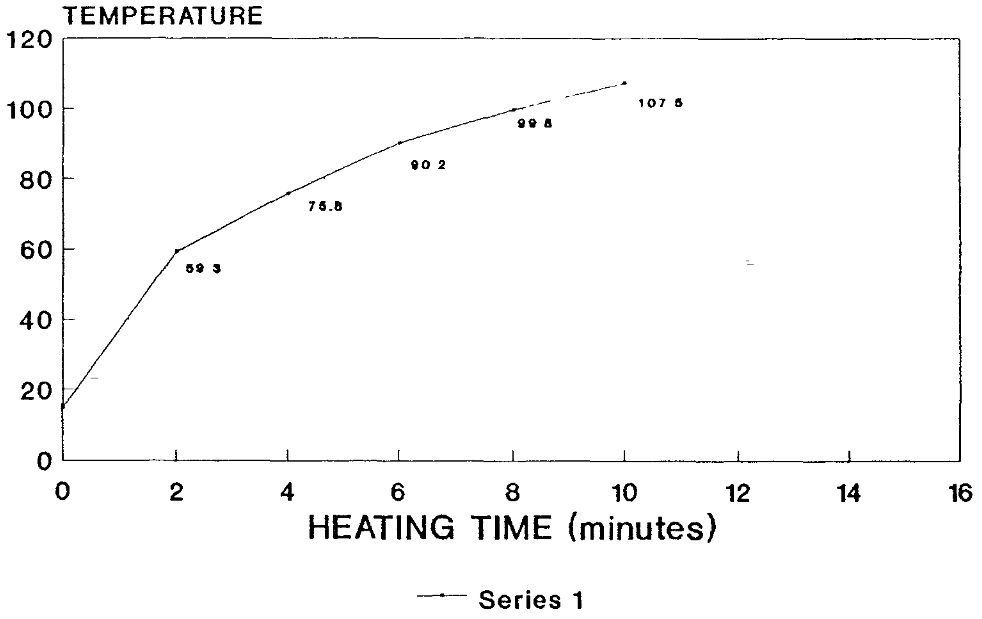


FIGURE 5.4 MICROWAVE HEATING TIME vs TEMPERATURE OF HUMUS

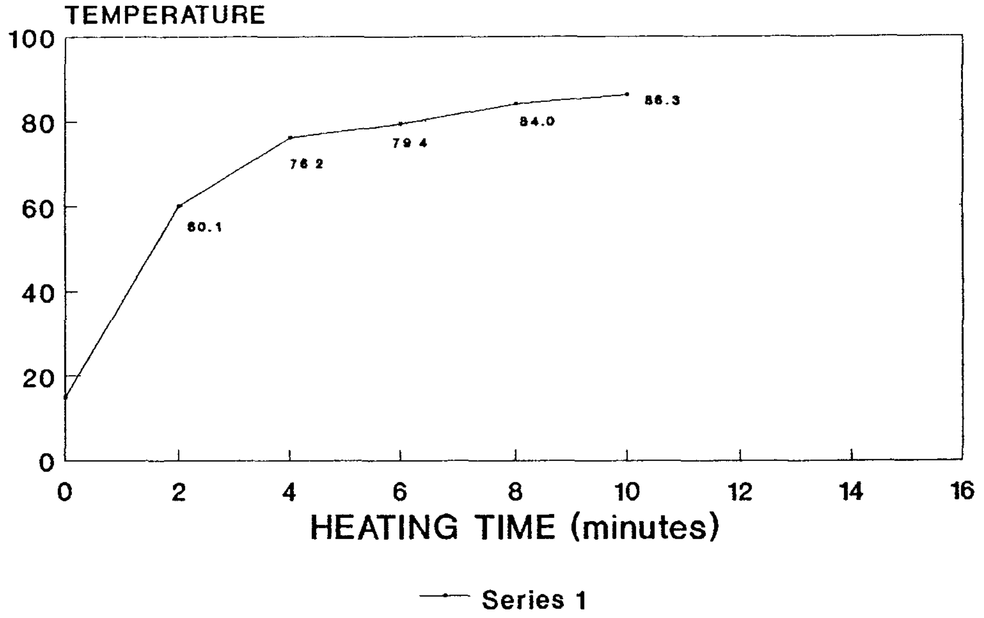


FIGURE 5.5 MICROWAVE HEATING TIME vs TEMPERATURE OF CLAY

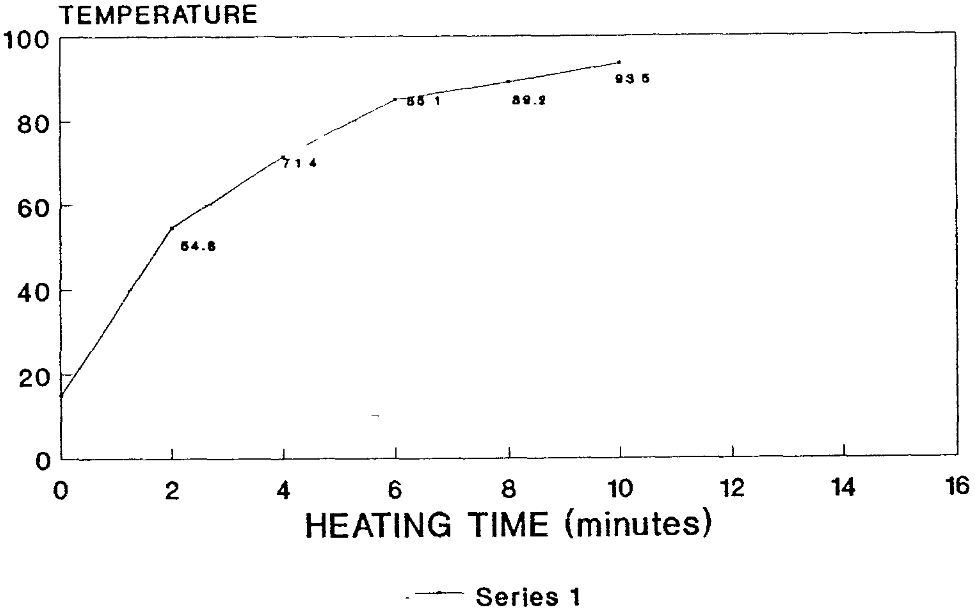
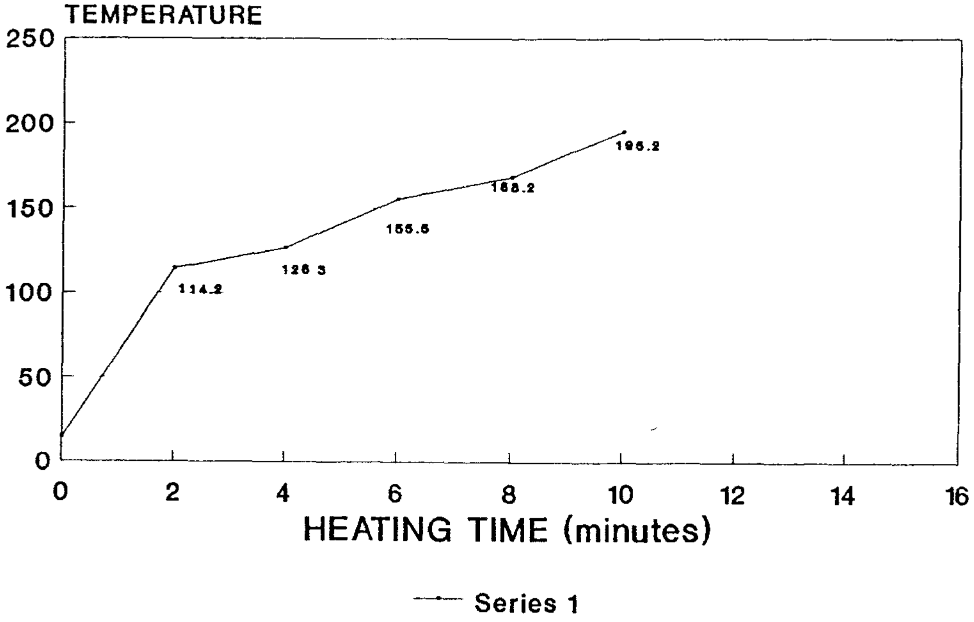


FIGURE 5.6 MICROWAVE HEATING TIME vs. TEMPERATURE OF CLAY & MAGNETITE



# CHAPTER 6. EXPERIMENTAL SERIES III

## MASS BALANCE STUDIES: MICROWAVE TREATMENT OF SAND IMPREGNATED WITH NAPHTHALENE

### 6.1 INTRODUCTION

Two different substrates are considered in this thesis, namely, sand and soil. It was assumed that there might be a problem in obtaining a mass balance with soil because soil sorbs organics strongly therefore the organics would not be accounted for in the volatiles or the soil extract. It was thought that the problem of strong sorption would not occur with sand because sand is mainly inorganic crystalline silica, to which organic bonding forces were expected to be weak.

### 6.2 EXPERIMENTAL SECTION

**6.2.1** Each sand sample was prepared by adding 5 ml of a solution of 20 mg naphthalene/ml methanol to 100 grams of sand; each sample was then put into a fume hood at room temperature for 24 hours to allow the solvent to evaporate.

**6.2.2** This experiment was run in duplicate. In each run a sand sample after solvent evaporation was put into a three neck round-bottom flask which was then placed into a microwave oven. In that flask, one neck served as the inlet for the compressed air, another, as the outlet for the naphthalene vapor. The third one was not used. It was sealed by a stopper. 5 ml water was added to each sample before microwave treatment.

**6.2.3** Refer to Figure 3.1. The external filter flask acted as a safety trap in the event that solutions flowed back from the traps as a result of a pressure drop in the apparatus in the microwave oven. Two washing bottles were connected with the filter flask. One bottle contained 100ml methanol, the other one contained 50 ml methanol.

**6.2.4** After 5 minutes microwave treatment, the round-bottom flask was taken out of the oven and the temperature of the sand was determined by a thermocouple immediately. Half of the sand sample was extracted by Soxhlet extractor for 48 hrs. using 80 ml methanol. In the meantime, a blank extraction was prepared by using half of the untreated sample. The amount of naphthalene recovered from the blank was taken as the 100% reference point.

**6.2.5** The extracted solutions were diluted to 100 ml volumetric flasks and 1ul was injected into GC/MS. The results are listed in Table 6.1.

**6.2.6** The residues after the extraction were put in the hood to let dry for 24 hrs. The dry sample was sifted by a 38 um sieve, and then studied by DRIFT.

**6.2.7** The diffuse reflectance data were collected at 16.0 $cm^{-1}$ resolution for 64 scans, using potassium bromide powder as the background and diluent (The samples were diluted to approximately 5 - 10% by weight in KBr).

**6.2.7.1** The spectrum of sand was collected by DRIFT (see Figure 12.1).

**6.2.7.2** The spectrum of neat naphthalene spectrum was collected by DRIFT (see Figure 12.2).

**6.2.7.3** The spectra of blank extraction residue and sample extraction residue were collected by DRIFT (see Figure 12.3 and Figure 12.4).

**6.2.7.4** The spectrum of the mixture of pure sand and the pure solid naphthalene were collected by DRIFT (see Figure 12.5).

**6.2.7.5** The spectra of Figure 12.6 to Figure 12.9 were obtained by gradually diluting (by the addition of sand) the pure solid naphthalene concentration in the afforested mixture (6.2.7.4).

**6.2.8** One (1) ul samples of the solutions in the two traps, respectively, were injected in triplicate into the GC/MS. The results are listed in Table 6.2.

## 6.3 RESULTS AND DISCUSSION

In Table 6.1 data for the extraction after 5 minutes microwave treatment is presented. Runs on the blanks and two samples were run in duplicate. The temperature was measured.

It is seen that for the blank at the 95% C. L., 395+/-2 is found. For the two samples, 388 +/- 2 and 364 +/- 1, respectively. Both samples are lower than the blank but the range of difference between the two samples is 24 based upon the means. The difference between the means of the upper sample value and the blank is 7. It appears that based upon this data, the sample was not affected by microwave treatment.

In Table 6.2 data for the trapping after five(5) minutes microwave treatment is presented. For each sample two duplicate injections were made. For sample one, no detectable naphthalene was found. For sample two, the 95% C.L. for "trap 1" is 2.3 +/- 0.1, which is negligible compared with the naphthalene amount in the extraction. No detectable naphthalene was found in "trap 2."

Table 6.1 Sand Studies: Naphthalene Recovery at Position 1 (5 minutes microwave treatment time)

| Sample No. | Blank | Sample 1 | Sample 2 |
|---|---|---|---|
| Temp. of sand ( $^0$C ) | | 51 | 53 |
| No. of replication | 2 | 2 | 2 |
| amt. of naph. (ng/ul) | 394.6<br>395.7 | 386.7<br>388.6 | 364.9<br>363.9 |
| ave. | 395.2 | 387.6 | 364.4 |
| s | 0.8 | 1 | 0.7 |
| 95% C.L. | 395+/-2 | 388+/-2 | 364+/-1 |
| naph amt. in 100ml(mg) | 39.5+/-0.2 | 38.8+/-0.2 | 36.4+/-0.1 |
| orig. amt of naph.(mg) | 50 | 50 | 50 |
| ext. percent (% ) | 79+/-1 | | |
| rec. percent ( % ) | | 98+/-1 | 92+/-1 |

Table 6.2 Data of trapping after 5 min microwave treatment

| | Sample 1 | | Sample 2 | |
|---|---|---|---|---|
| sample No. | trap1 | trap2 | trap1 | trap2 |
| No. of replication | 2 | 2 | 2 | 2 |
| naph amt. (ng/ul) | N.D.<br>N.D. | N.D.<br>N.D. | 2.310<br>2.215 | N.D.<br>N.D. |
| ave. | N.D. | N.D. | 2.262 | N.D. |
| s | N.D. | N.D. | 0.06 | N.D. |
| 95% C.L. | | | 2.3+/-0.1 | |
| vol. of solution(ml) | 100 | 50 | 100 | 50 |
| amt. of naph (mg) | N.D. | N.D. | 0.23+/-0.01 | N.D. |

## 6.4 CONCLUSIONS

From the results, we can see that most of the naphthalene is still in the sand after 5 minutes microwave treatment. The reason is that the temperature is too low to evaporate naphthalene: It is assumed that there exists an energy distribution in the microwave oven, and that it is possible that the samples were placed in a area in which the incident energy was low. This effect was studied in the following experiment.

# CHAPTER 7. EXPERIMENTAL SERIES IV

# ENERGY DISTRIBUTION IN THE MICROWAVE OVEN

## 7.1 INTRODUCTION

As stated in the conclusion of the previous section, the effect of the energy distribution within the microwave oven was of concern in interpreting data. The nonhomogeneous distribution of energy in a microwave oven is a problem as a result of "moding," a problem unique to heating by relatively long wavelength electromagnetic energy. "Moding" occurs when the reflected waves forms standing waves, resulting in an uneven distribution of energy.

## 7.2 EXPERIMENTAL SECTION

The principle of the method used to study the distribution of the energy within the microwave oven is the fact that a chemical, cobaltous chloride, changes from pink to blue as a result of dehydration. By placing that chemical in solution state on paper distributed throughout the oven, the pattern of energy distribution is evidenced by color patterns on the paper.

## 7.3 RESULTS AND DISCUSSION

After 1 minute treatment, the paper changed in color from pink to blue, but the degree of blueness varied from dark to light. The area used in the previously reported experiments on naphthalene-impregnated sand was on the lighter side.

## 7.4 CONCLUSIONS

It would appear that in the previously reported experiments on sand that the temperature reached was relatively low because the sample was placed in a region where the incident energy was relatively low. However, such a conclusion is at best tenuous because the distribution of the energy in a microwave field is dependent on the load, thus patterns obtained in the absence of a load have doubtful significance. But if a load is present these pattern experiments can't be carried out at all. Thus, at best, the results are suggestive.

# CHAPTER 8. EXPERIMENTAL SERIES V

# ENERGY DISTRIBUTION EFFECT: MASS BALANCE, MICROWAVE TREATMENT OF NAPHTHALENE-IMPREGNATED SAND

## 8.1 INTRODUCTION

One of the problems associated with carrying out studies in a microwave energy environment is that the electromagnetic waves are long, and are susceptible to forming interference patterns as a result of being reflected from surfaces. This results is an inhomogeneous distribution of energy. In the following study, mass balances were carried out on the sand substrate in different positions in the cavity to determine whether or not interferences were significant. Additionally, studies were carried out for longer times than the ones reported above.

## 8.2 EXPERIMENTAL SECTION

**8.2.1** Each sand sample was prepared by adding 5 ml of a solution of 20 mg naphthalene/ml methanol to 50 grams of sand, and then was put into hood at room temperature to allow the solvent to evaporate for ca. 24 hr.

**8.2.2** Four series of experiments were carried out: 7 min and 9 min microwave treatment at position 1 in the microwave oven; 5 min microwave treatment at position 2 and position 3, respectively, in the same microwave oven.

**8.2.3** This experiment was run in triplicate. In each run a sand sample after solvent evaporation was put into a three neck round-bottom flask which was then placed into a microwave oven. In that flask, one neck served as the inlet for the compressed air, another, as the outlet for the naphthalene vapor. The third one was not used. It was sealed by a stopper. 5 ml water was added to each sample before microwave treatment.

**8.2.4** Refer to Figure 3.1. The external filter flask acted as a safety trap in the event that solutions flowed back from the traps as a result of a pressure drop in the apparatus in the microwave oven. Two washing bottles were connected with the filter flask. One bottle contained 100 ml methanol, the other one contained 50 ml methanol.

**8.2.5** After 5 min microwave treatment, the round-bottom flask was taken out of the oven and the temperature of the sand was detected by a thermocouple immediately. The sand sample was extracted by Soxhlet extractor for 48 hrs. using 80ml methanol. In the meantime, a blank extraction was prepared by using untreated sample. The amount of naphthalene recovered from the blank was taken as the 100% reference point.

**8.2.6** The extracted solutions were diluted to 100 ml volumetric flasks and 1 ul was injected into GC/MS. The results were listed in Table 8.1a - 8.4a

**8.2.7** The residues after the extraction were put in the hood to let it dry for 24 hrs. The dry sample was sifted by a 38 um sieve and then studied by DRIFT.

**8.2.8** The diffuse reflectance data were collected at 16.0 $cm^{-1}$ resolution for 64 scans, using potassium bromide powder as the background and diluent (The samples were diluted to approximately 5 - 10% by weight in KBr).

**8.2.8.1** The spectrum of sand was collected by DRIFT (see Figure 12.1).

**8.2.8.2** The spectrum of neat naphthalene spectrum was collected by DRIFT (see Figure 12.2).

**8.2.8.3** The spectra of the blank extraction residue and the sample extraction residue, respectively, were collected by DRIFT (see Figure 12.3 and Figure 12.4).

**8.2.8.4** The spectrum of the mixture of pure sand and the pure solid naphthalene was collected by DRIFT (see Figure 12.5).

**8.2.9** One (1) ul solution in the two traps, respectively, were injected in triplicate into the GC/MS. The results are listed in Table 7.2b - 7.4b

### 8.3 RESULTS and DISCUSSION

In Table 8.1a extraction data after seven (7) minutes microwave treatment are presented. One blank and three sample extractions were made. The temperature of each sample were 68, 68, and 64 $^{0}$C, respectively. For each sample and blank, two duplicate injections were made. For blank extraction, the 95% C.L. is 890 +/- 1; the efficiency of the extraction is 89 +/-1 % which is taken as the 100% reference point. The 95% C.L. of the three samples were 783 +/- 32, 748 +/- 18, and 723 +/- 15, respectively. Hence, the percentage of the extraction from the three samples are 87 +/- 3%, 84 +/- 2%, and 81 +/- 2%, respectively.

No detectable naphthalene could be found in the two traps after seven minutes (7) microwave treatment at position 1.

In table 8.2a extraction data after nine (9) minutes microwave treatment at position 1 is present. The efficiency of extraction is 89 +/- 1% which is taken as the 100% reference point. Thus the percentage of the extraction of the three samples are 72 +/- 1%, 68 +/- 1%, and 70 +/- 1%, respectively.

In Table 8.2b trapping data after nine(9) minutes microwave treatment at position 1 is presented. For samples 1, 2 and 3, the total amount of naphthalene found in "trap 1" and "trap 2" are 11 +/- 1, 11 +/- 1, and 10 +/- 1, respectively. The percentage of trapping of the three samples are 11 +/-1%, 11 +/- 1% and 10 +/- 1%, respectively. The total percentage of naphthalene recovery should be the sum of the percentage of extraction and trapping. Hence, the total percentage of naphthalene recovery of the three samples are 83 +/1 %, 79 +/- 1% and 78 +/- 1%, respectively.

In table 8.3a extraction data after five(5) minutes microwave treatment at position 2 is presented. The efficiency of extraction is 86 +/- 2, which is taken as the 100% point. The percentage of the extraction of the three samples are 67 +/- 2%, 76 +/- 4% and 63 +/- 3%, respectively.

In Table 8.3b trapping data after five(5) minutes microwave treatment at position 2 is presented. For samples 1, 2 and 3, the total amount of naphthalene found in "trap 1" and "trap 2" are 18 +/- 1, 15 +/- 1 and 20 +/-

3, respectively. The percentage of trapping of the three samples are 18 +/- 1%, 15 +/- 1% and 15 +/- 3%, respectively. The total percentage of naphthalene recovery should be the sum of the percentage of extraction and trapping. Hence, the total percentage of naphthalene recovery of the three samples are 85 +/- 2%, 91 +/- 4% and 93 +/- 3%, respectively.

In table 8.4a extraction data after five(5) minutes microwave treatment at position 3 is presented. The efficiency of extraction is 86 +/- 2% which is taken as the 100% reference point. So, the percentage of the extraction of the three samples are 46 +/- 2%, 43 +/- 2% and 48 +/- 2%, respectively.

In Table 8.4b trapping data after five(5) minutes microwave treatment at position 3 is presented. For sample 1, 2 and 3, the total amount of naphthalene found in " trap 1" and "trap 2" are 44 +/- 1, 53 +/- 1 and 43 +/- 4, respectively. The percentage of trapping of the three samples are 44 +/- 1%, 53 +/- 1% and 43 +/- 4%, respectively. The total percentage of naphthalene recovery should be the sum of the percentage of extraction and trapping. Hence, the total percentage of naphthalene recovery of the three samples are 90 +/- 2%, 96 +/- 3% and 91 +/- 4%, respectively.

Table 8.1a Sand Studies: Naphthalene Recovery at Position 1 (7 minutes microwave treatment)

| Sample No. | Blank | Sample 1 | Sample 2 | Sample 3 |
|---|---|---|---|---|
| Temp. of sand ( $^{0}$C ) | | 68 | 68 | 64 |
| No. of replication | 2 | 2 | 2 | 2 |
| amt. of naph. (ng/ul) | 890.8 | 766.9 | 738.5 | 715.1 |
| | 888.9 | 799.0 | 756.8 | 731.3 |
| ave. | 889.8 | 783.0 | 7476 | 723.2 |
| s | 1 | 23 | 13 | 11 |
| 95% C.L. | 890+/-1 | 783+/-32 | 748+/-18 | 723+/-15 |
| naph amt. in 100ml(mg) | 89.0+/-0.1 | 78+/-3 | 75+/-2 | 72+/-2 |
| orig. amt of naph.(mg) | 100 | 100 | 100 | 100 |
| ext. eff. (% ) | 89+/-1 | | | |
| ext. percent | | 87+/-3 | 84+/-2 | 81+/-2 |

Table 8.2a Sand Studies: Naphthalene Recovery at Position 1 (9 minutes microwave treatment)

| sample No. | Blank | Sample 1 | Sample 2 | Sample 3 |
|---|---|---|---|---|
| Temp. of sand ( $^{0}$C ) | / | 78 | 74 | 75 |
| No. of Inj. | 2 | 2 | 2 | 2 |
| amt. of naph. (ng/ul) | 890.8<br>889.9 | 636.6<br>643.2 | 600.1<br>603.2 | 601.9<br>605.8 |
| ave. | 889.8 | 639.1 | 601.6 | 603.8 |
| s | 1 | 5 | 2 | 3 |
| 95% C.L. | 890+/-1 | 639+/-7 | 602+/-3 | 604+/-4 |
| naph. amt. in 100ml (mg) | 89+/-1 | 64+/-1 | 60+/-1 | 60+/-1 |
| orig. amt. (mg) | 100 | 100 | 100 | 100 |
| ext. eff. (%) | 89+/-1 | | | |
| ext. percent | | 72+/-1 | 68+/-1 | 68+/-1 |

Table 8.2b Sand Studies: Naphthalene Recovery at Position 1 (9 minutes microwave treatment)

| | Sample 1 | | Sample 2 | | Sample 3 | |
|---|---|---|---|---|---|---|
| sample No. | trap1 | trap2 | trap1 | trap2 | trap1 | trap2 |
| No. of replication | 2 | 2 | 2 | 2 | 2 | 2 |
| naph amt. (ng/ul) | 77.43 | 5.677 | 97.16 | 2.528 | 98.77 | 1.655 |
| | 86.31 | 3.856 | 96.31 | 1.368 | 109.2 | 1.917 |
| ave. | 81.87 | 4.766 | 96.74 | 1.948 | 104.0 | 1.719 |
| s | 6 | 1 | 0.6 | 0.8 | 7 | 0.2 |
| 95% C.L. | 82+/-8 | 5+/-1 | 96.7+/-0.8 | 2+/-1 | 104+/-10 | 1.8+/-0.3 |
| vol. of solution (ml) | 100 | 52 | 102 | 54 | 100 | 50 |
| naph. amt in 100ml (mg) | 8.2 +/-0.8 | 2.6 +/-0.5 | 9.86 +/-0.08 | 1.08 +/-0.05 | 10.4 +/-0.1 | 0.09 +/-0.02 |
| sum of trap1,2 | 11+/-1 | | 11+/-1 | | 10+/-1 | |
| orig. amt. (mg) | 100 | | 100 | | 100 | |
| Trapping % | 11+/-1 | | 11+/-1 | | 10+/-1 | |
| Total rec. % | 83+/-1 | | 79+/-1 | | 78+/-1 | |

Table 8.3a Data of extraction after 5 min microwave treatment at position 2

| Sample No. | Blank | Sample 1 | Sample 2 | Sample 3 |
|---|---|---|---|---|
| Sand temp. ( $^0$C ) | / | 85 | 83 | 88 |
| No. of Injection | 2 | 2 | 2 | 2 |
| amt. of naph (ng/ul) | 869.0<br>848.8 | 576.9<br>575.2 | 590.9<br>561.1 | 547.8<br>530.0 |
| ave. | 858.9 | 576.1 | 576.0 | 538.9 |
| s | 14 | 1 | 21 | 12 |
| 95% C.L. | 859+/-19 | 576+/-1 | 576+/-29 | 539+/-1 |
| naph amt. 100ml(mg) | 86+/-2 | 57.6+/-0.1 | 58+/-3 | 54+/-2 |
| orig.amt. (mg) | 100 | 100 | 100 | 100 |
| ext. eff.% | 86+/-2 | | | |
| ext. percent | | 67+/-2 | 76+/-4 | 63+/-3 |

Table 8.3b Sand Studies: Naphthalene Recovery at Position 2 (5 minutes microwave treatment)

| Sample No. | Sample 1 | | Sample 2 | | Sample 3 | |
|---|---|---|---|---|---|---|
| | trap1 | trap2 | trap1 | trap2 | trap1 | trap2 |
| No. of Inj. | 2 | 2 | 2 | 2 | 2 | 2 |
| naph. amt (ng/ul) | 167.1<br>173.4 | 10.07<br>11.48 | 144.4<br>150.8 | 7.028<br>9.272 | 177.9<br>207.6 | 16.58<br>14.30 |
| ave. | 170.2 | 10.78 | 147.6 | 8.150 | 192.8 | 15.44 |
| s | 4 | 1 | 4 | 1 | 21 | 2 |
| 95% C.L. | 170+/-6 | 11+/-1 | 148+/-4 | 8+/-1 | 193+/-29 | 15+/-3 |
| Solution V(ml) | 103 | 51 | 100 | 50 | 100 | 50 |
| naph amt. (mg) | 17.5 +/-0.6 | 0.55 +/-0.05 | 14.8 +/-0.4 | 0.40 +/-0.05 | 19 +/-3 | 0.8 +/-0.2 |
| sum of trap1,2 | 18+/-1 | | 15+/-1 | | 20+/-3 | |
| orig. amt. (mg) | 100 | | 100 | | 100 | |
| trapping % | 18+/-1 | | 15+/-1 | | 20+/-3 | |
| Total recovery% | 85+/-2 | | 91+/-4 | | 93+/-3 | |

Table 8.4a Sand Studies: Naphthalene Recovery at Position 3 (5 minutes microwave treatment)

| Sample No. | Blank | Sample 1 | Sample 2 | Sample 3 |
|---|---|---|---|---|
| sand temp. ( $^0$C ) | / | 96 | 97 | 93 |
| No. of Injection | 2 | 2 | 2 | 2 |
| amt. of naph (ng/ul) | 869.9<br>848.4 | 402.9<br>403.4 | 360.0<br>375.0 | 415.0<br>417.1 |
| ave. | 858.9 | 403.2 | 367.5 | 416.0 |
| s | 14 | 0.4 | 11 | 1 |
| 95% C.L. | 859+/-19 | 403.2+/-0.6 | 368+/-15 | 416+/-1 |
| naph in 100ml(mg) | 86+/-2 | 40.32+/-0.06 | 37+/-2 | 41.6+/-0.1 |
| orig. amt. (mg) | 100 | 100 | 100 | 100 |
| ext. eff.% | 86+/-2 | | | |
| ext. percent | | 46+/-2 | 43+/-2 | 48+/-2 |

Table 8.4b Sand Studies: Naphthalene Recovery at Position 3 (5 minutes microwave treatment)

| Sample No. | Sample 1 | | Sample 2 | | Sample 3 | |
|---|---|---|---|---|---|---|
| | trap1 | trap2 | trap1 | trap2 | trap1 | trap2 |
| No. of Inj. | 2 | 2 | 2 | 2 | 2 | 2 |
| naph amt. (ng/ul) | 430.1<br>427.1 | 27.92<br>34.51 | 493.3<br>507.1 | 17.46<br>25.67 | 384.7<br>420.0 | 13.74<br>15.58 |
| ave. | 428.6 | 31.21 | 500.2 | 21.56 | 402.4 | 14.64 |
| s | 2 | 5 | 8 | 6 | 25 | 1 |
| 95% C.L. | 429+/-3 | 31+/-7 | 500+/-11 | 22+/-8 | 402+/-35 | 15+/-1 |
| Solution V(ml) | 103 | 52 | 104 | 53 | 104 | 52 |
| naph. amt. (mg) | 44.2 +/-0.3 | 1.6 +/-0.3 | 52 +/-1 | 1.2 +/-0.4 | 42 +/-4 | 0.78 +/-0.05 |
| sum of trap1,2 | 44+/-1 | | 53+/-1 | | 43+/-4 | |
| orig. amt. (mg) | 100 | | 100 | | 100 | |
| trapping% | 44+/-1 | | 53+/-1 | | 43+/-4 | |
| Total rec.% | 90+/-2 | | 96+/-3 | | 91+/-4 | |

## 8.4 CONCLUSIONS

The effect of the energy distribution is inferred from the data obtained by placing the sample in three different positions in the oven, run in triplicate at each position. Table 6.1 refers to position 1; Table 8.3a, b, to position 2; Table 8.4 a, b, to position 3. There appears to be a slight variation in the total amount of naphthalene accounted for based upon the position of the sample in the microwave oven. On the one hand, the differences in the averages of the triplicate samples for positions 2 and 3 are 90 and 92%, respectively: but the precision is of the order of 2 - 4%. On the other hand, the total recovery average at position 3 is 95%, and the precision is of the order of 3%, suggesting that there might be a significant difference.

The temperature at position 1 is significantly lower than those observed at positions 2 and 3, respectively. The average temperature at position 1 was 52 $^0$C; at position 2, 85 $^0$C; at position 3, 95 $^0$C. This is indicative of a non-homogeneous distribution of energy. This effects the distribution of the naphthalene recovered. A greater amount is volatilized and thus found in the traps at the higher temperatures: at position 1, a negligible amount is found in the traps; at position 2, 18%; position 3, 47%.

Also, as expected, increasing the time at a given position, leads to an increase in temperature and, also, an increase in the proportion of naphthalene volatilized which is evidenced by the increase in the amount of naphthalene found in the traps. Refer to Table 6.1, five minutes; Table 8.1a, seven minutes; Table 8.2a, nine minutes. The total recoveries are 95.2%, 84%, and 80%, respectively. The corresponding temperatures and percents found in the traps are as follows: after 5 minutes, 52 $^{0}$C and non-detectable; 7 minutes and 67 $^{0}$C, non-detectable; 9 minutes, 76 $^{0}$C and 11%.

# CHAPTER 9 EXPERIMENTAL SERIES VI

## MASS BALANCE STUDIES: MICROWAVE TREATMENT OF SANDY AND CLAY SOIL IMPREGNATED WITH NAPHTHALENE

### 9.1 INTRODUCTION

The substrates used in this study were sandy soil and clay soil, respectively. These are the types of substrates which have the actual hazardous waste remediation problems. These substrates should have stronger absorption forces, especially, clay soil, so that by comparison with the results obtained with the sand substrate the effect of absorption which resists extraction can potentially be estimated.

### 9.2 EXPERIMENTAL SECTION

**9.2.1** Moisture Measurement: Three samples of each soil were put in the thermal oven for 48 hours at 110 $^0$C. Results are listed in Table 9.1 and 9.2.

**9.2.2** Sample Preparation: Sandy soil and clay soil were crushed by a electrical grinder and sifted by a electrical shaker. The aperture of the sieve is 125 um.

**9.2.3** To each 35 g soil sample, 5 ml of a solution of 20 mg naphthalene/ml methanol was added, and then was put into hood at room temperature to allow the solvent to evaporate for ca. 24 hr.

**9.2.4** This experiment was run in triplicate. In each run a soil sample after solvent evaporation was put into a three neck round-bottom flask which was then placed into a microwave oven. In that flask, one neck served as the inlet for the compressed air, another, as the outlet for the naphthalene vapor. The third one was not used. It was sealed by a stopper. 5 ml water was added to each sample before microwave treatment.

**9.2.5** Refer to Figure 3.1. The external filter flask acted as a safety trap in the event that solutions flowed back from the traps as a result of a pressure drop in the apparatus in the microwave oven. Two washing bottles were connected with the filter flask. One bottle contained 100 ml methanol, the other one contained 50 ml methanol.

**9.2.6** After 5 min microwave treatment, the round-bottom flask was taken out of the oven and the temperature of the sand was detected by a thermocouple immediately. The soil sample was extracted by Soxhlet extractor for 48 hrs. using 80 ml methanol. In the meantime, a blank extraction was prepared by using untreated sample. The amount of naphthalene recovered from the blank was taken as the 100% reference point.

**9.2.7** The extracted solutions were diluted to 100 ml volumetric flasks and 1 ul was injected into GC/MS. The results were listed in Table 9.3a and Table 9.4a.

**9.2.8** The residues after the extraction were put in the hood to let it dry for 24 hrs and were studied by DRIFT.

**9.2.9** The diffuse reflectance data were collected at 16.0 $cm^{-1}$ resolution for 64 scans, using potassium bromide powder as the background and diluent (The samples were diluted to approximately 5 - 10% by weight in KBr).

**9.2.9.1** The absorbance, transmittance and Kubelka-Munk spectra of sandy and clay soils, respectively, were collected by DRIFT (see Figure 12.10 to Figure 12.15).

**9.2.9.2** The spectrum of neat naphthalene spectrum was collected by DRIFT (see Figure 12.2).

**9.2.9.3** The absorbance, transmittance and Kubelka-Munk spectra of blank extraction residue and sample extraction residue were collected by DRIFT (see Figure 12.16 to Figure 12.27).

**9.2.9.4** The absorbance and Kubelka-Munk spectrums of the mixture of pure sandy soil and the pure solid naphthalene were collected by DRIFT (see Figure 12.28 and Figure 29).

**9.2.9.5** The absorbance and Kubelka-Munk spectrums of the mixture of pure clay soil and the pure solid naphthalene were collected by DRIFT (see Figure 12.30 and Figure 12.31).

**9.2.10** One (1) ul samples from the solutions in the two traps, respectively, were injected in triplicate into the GC/MS. The results are listed in Table 9.3b and Table 9.4b.

## 9.3 RESULTS AND DISCUSSION

In Table 9.1 and Table 9.2 the moisture levels of sandy soil and clay soil are shown. The average moisture level of
sandy soil is 0.7%. The average moisture level of clay soil is 2.3%.

In Table 9.3a data of extraction after five(5) minutes microwave treatment of sandy soil at position 3 is presented. The efficiency of extraction is 90 +/- 1% which is taken as the 100% point. So, the extraction percentage of the three samples are 55 +/- 1%, 55 +/- 1% and 60 +/- 1%, respectively.

In Table 9.3b trapping data after five(5) minutes microwave treatment of sandy soil at position 3 is presented. For samples 1, 2, and 3, the total amount of naphthalene in "trap 1" and "trap 2" are 28 +/- 2, 27 +/- 1, and 28 +/- 2, respectively. The percentage of trapping of the three samples are 28 +/- 2%, 27 +/- 1%, and 28 +/- 2%, respectively. The total percentage of naphthalene recovery should be the sum of the percentage of extraction and trapping. Hence, the total percentage of naphthalene recovery of the three samples are 85 +/- 2%, 82 +/- 1% and 88 +/- 2%, respectively.

In table 9.4a data of extraction after five(5) minutes microwave treatment of clay soil at position 3 is presented. The efficiency of extraction is 87 +/- 1% which is taken as the 100% point. So, the percentage of the extraction of the three samples are 49 +/- 2%, 54 +/- 2% and 56 +/- 2%, respectively.

In Table 9.4b data of trapping after five(5) minutes microwave treatment of clay soil at position 3 is present. For sample 1, 2 and 3, the total amount of naphthalene of trap 1 and trap 2 are 32 +/- 1, 31 +/- 2 and 29 +/- 1, respectively. The percentage of trapping of the three samples are 32 +/- 1%, 31 +/-2 % and 29 +/- 1% respectively. The total percentage of naphthalene recovery should be the sum of the percentage of extraction and trapping. Hence, the total percentage of naphthalene recovery of the three samples are 81 +/- 2%, 85 +/- 2% and 85 +/- 2%, respectively.

## 9.4 CONCLUSIONS

The total recoveries for both the sandy soil and the clay soil is similar: the average values are 85 and 83%, respectively. Since the standard deviations are of the order of 2%, the difference in the means cannot be considered significant. Compared to the sand (Table 8.4b), these recoveries are lower: for sand, 92%, maximum standard deviation of an individual result is 4%. Thus there appears to be a significant difference. That difference can be ascribed to the "fixation" of the naphthalene in the soils. "Fixation" is not possible in the sand because silica can not interact with naphthalene in any way other than forming weak Van der Waal's bonds. However, in soils there are humus and clay fractions, both which are known to be capable of "fixing" organics.

Table 9.1 Sandy Soil: Moisture Content

| No. | weight before heating g | weight after heating g | moisture % |
|---|---|---|---|
| 1 | 50.2 | 49.9 | 0.6 |
| 2 | 50.4 | 49.9 | 1 |
| 3 | 50.1 | 49.8 | 0.6 |
| ave. | | | 0.7 |

Table 9.2 Clay Soil: Moisture Content

| No. | weight before heating g | weight after heating g | moisture % |
|---|---|---|---|
| 1 | 50.1 | 49.0 | 2.2 |
| 2 | 50.8 | 49.7 | 2.2 |
| 3 | 50.2 | 49.0 | 2.4 |
| ave. | | | 2.3 |

Table 9.3a Sandy Soil: Naphthalene Recovery at Position 3 (5 minutes microwave treatment)

| Sample No. | Blank | Sample 1 | Sample 2 | Sample 3 |
|---|---|---|---|---|
| Sand Temp. ( $^{0}$C ) | / | 130 | 128 | 119 |
| No. of Injection | 2 | 2 | 2 | 2 |
| amt. of naph (ng/ul) | 650.8<br>642.9 | 513.1<br>505.0 | 493.4<br>492.6 | 534.0<br>543.1 |
| ave. | 646.9 | 509.1 | 493.0 | 538.6 |
| s | 6 | 6 | 1 | 6 |
| 95% C.L. | 647+/-8 | 509+/-8 | 493+/-2 | 539+/-8 |
| naph amt. 100ml(mg) | 65+/-1 | 51+/-1 | 49+/-1 | 54+/-1 |
| orig.amt. (mg) | 72 | 100 | 100 | 100 |
| ext. eff.% | 90+/-1 | | | |
| ext. percent | | 55+/-1 | 55+/-1 | 60+/-1 |

Table 9.3b Sandy Soil: Naphthalene Recovery at Position 3
(5 minutes microwave treatment)

| Sample No. | Sample 1 | | Sample 2 | | Sample 3 | |
|---|---|---|---|---|---|---|
| | trap1 | trap2 | trap1 | trap2 | trap1 | trap2 |
| No. of Inj. | 2 | 2 | 2 | 2 | 2 | 2 |
| naph. amt (ng/ul) | 272.3 | 9.342 | 260.4 | 20.15 | 276.5 | 41.42 |
| | 287.8 | 8.568 | 267.7 | 27.76 | 252.6 | 37.42 |
| ave. | 280.1 | 8.955 | 264.1 | 23.96 | 264.6 | 39.42 |
| s | 11 | 1 | 5 | 5 | 17 | 3 |
| 95% C.L. | 280+/-15 | 9+/-2 | 264+/-7 | 24+/-7 | 265+/-23 | 39+/-4 |
| Solution V(ml) | 100 | 50 | 100 | 50 | 100 | 50 |
| naph amt. (mg) | 28+/-2 | 0.4+/-0.1 | 26+/-1 | 1.2+/-0.3 | 26+/-2 | 2.0+/-0.2 |
| sum of trap1,2 | 28+/-2 | | 27+/-1 | | 28+/-2 | |
| orig. amt. (mg) | 100 | | 100 | | 100 | |
| trapping % | 28+/-2 | | 27+/-1 | | 28+/-2 | |
| Total rec.% | 85+/-2 | | 82+/-1 | | 88+/-2 | |

Table 9.4a Clay Soil: Naphthalene Recovery at Position 3
(5 minutes microwave treatment)

| Sample No. | Blank | Sample 1 | Sample 2 | Sample 3 |
|---|---|---|---|---|
| Temp. of sand ( $^0$C ) | | 153 | 142 | 137 |
| No. of replication | 2 | 2 | 2 | 2 |
| amt. of naph. (ng/ul) | 783.4<br>736.6 | 423.3<br>437.3 | 461.4<br>475.9 | 495.2<br>485.9 |
| ave. | 760.0 | 430.3 | 469.6 | 492.1 |
| s | 33 | 10 | 10 | 6 |
| 95% C.L. | 760+/-45 | 430+/-14 | 469+/-14 | 492+/-8 |
| naph amt. in 100ml(mg) | 76+/-4 | 43+/-1 | 47+/-1 | 49+/-1 |
| orig. amt of naph.(mg) | 87 | 100 | 100 | 100 |
| ext. eff. (% ) | 87+/-4 | | | |
| ext. percent ( % ) | | 49+/-2 | 54+/-2 | 56+/-2 |

Table 9.4b Clay Soil: Naphthalene Recovery at Position 3 (5 minutes microwave treatment)

| Sample No. | Sample 1 | | Sample 2 | | Sample 3 | |
|---|---|---|---|---|---|---|
| | trap1 | trap2 | trap1 | trap2 | trap1 | trap2 |
| No. of Inj. | 2 | 2 | 2 | 2 | 2 | 2 |
| naph. amt (ng/ul) | 308.6<br>327.1 | 12.34<br>10.86 | 318.5<br>202.5 | 10.29<br>12.49 | 282.8<br>292.9 | 13.24<br>13.60 |
| ave. | 317.8 | 11.60 | 305.5 | 11.39 | 287.8 | 13.42 |
| s | 13 | 1 | 18 | 1 | 7 | 0.2 |
| 95% C.L. | 317+/-18 | 12+/-2 | 306+/-25 | 11+/-2 | 288+/-9 | 13+/-1 |
| Solution V(ml) | 100 | 50 | 100 | 50 | 100 | 50 |
| naph amt. (mg) | 32+/- 2 | 0.6+/- 0.2 | 31+/- 3 | 0.10+/- 0.05 | 29+/- 1 | 0.70+/- 0.01 |
| sum of trap1,2 | 32+/-1 | | 31+/-2 | | 29+/-1 | |
| orig. amt. (mg) | 100 | | 100 | | 100 | |
| trapping % | 32+/-1 | | 31+/-2 | | 29+/-1 | |
| Total rec.% | 81+/-2 | | 85+/-2 | | 85+/-2 | |

# CHAPTER 10 EXPERIMENTAL SERIES VII
# MASS BALANCE STUDIES: MICROWAVE TREATMENT OF HUMUS IMPREGNATED WITH NAPHTHALENE

## 10.1 INTRODUCTION

That part of the soil which can be expected to "trap" organics to the greatest extent is humus. Humus represents a complex mixture of thousands of chemicals held within a complex polymeric framework derived mainly from lignin, the decay product of wood. Thus studies on the mass balance were expected to shed light on the capability of humus to "fix" organics as a result of microwave treatment.

## 10.2 EXPERIMENTAL SECTION

**10.2.1** Sample Preparation: The humus was crushed by a electrical grinder and sifted by a electrical shaker, The aperture of the sieve is 38 um.

**10.2.2** To each 35 g humus sample, 5 ml of a solution of 33 mg naphthalene/ml methanol was added, and then was put into hood at room temperature to allow the solvent to evaporate for ca. 24 hr.

**10.2.3** This experiment was run in triplicate. In each run a sand sample after solvent evaporation was put into a three neck round-bottom flask which was then placed into a microwave oven. In that flask, one neck served as the inlet for the compressed air, another, as the outlet for the naphthalene vapor. The third one was not used. It was sealed by a stopper. 5 ml water was added to each sample before microwave treatment.

**10.2.4** Refer to Figure 3.1. The external filter flask acted as a safety trap in the event that solutions flowed back from the traps as a result of a pressure drop in the apparatus in the microwave oven. Two washing bottles were connected with the filter flask. One bottle contained 100 ml methanol, the other one contained 50 ml methanol.

**10.2.5** After 5 min microwave treatment, the round-bottom flask was taken out of the oven and the temperature of the sand was detected by a thermocouple immediately. The humus sample was extracted by Soxhlet extractor for 48 hrs using 80 ml methanol. In the meantime, a blank extraction was prepared by using untreated sample. The amount of naphthalene recovered from the blank was taken as the 100% reference point.

**10.2.6** The extracted solutions were diluted to 100 ml volumetric flasks and 1 ul was injected into GC/MS. The results were listed in Table 10.1.

**10.2.7** The residues after the extraction were put in the hood to let it dry for 24 hrs and then studied by DRIFT.

**10.2.8** The diffuse reflectance data were collected at 16.0 $cm^{-1}$ resolution for 64 scans, using potassium bromide powder as the background and diluent ( The samples were diluted to approximately 5 - 10% by weight in KBr).

**10.2.8.1** The absorbance and Kubelka-Munk spectrums of pure humus were collected by DRIFT (see Figure 12.32 and Figure 12.33).

**10.2.8.2** The spectrum of neat naphthalene spectrum was collected by DRIFT (see Figure 12.2).

**10.2.8.3** The absorbance and Kubelka-Munk spectrums of blank extraction residue and sample extraction residue were collected by DRIFT (see Figure 12.34 to Figure 12.37).

**10.2.8.4** The absorbance and Kubelka-Munk spectra of the mixture of pure humus and the pure solid naphthalene were collected by DRIFT (see Figure 12.38 and Figure 12.39).

**10.2.9** One microliter samples from the two traps were injected in triplicate into the GC/MS.

Table 10.1 Humus Studies: Naphthalene Recovery at Position 3 (5 minutes microwave treatment)

| Sample No. | Blank | Sample 1 | Sample 2 | Sample 3 |
|---|---|---|---|---|
| Temp. of sand ( $^0$C ) | | 132 | 129 | 117 |
| No. of replication | 2 | 2 | 2 | 2 |
| amt. of naph. (ng/ul) | 1388<br>1266 | 1097<br>1025 | 949.2<br>1123 | 1026<br>1144 |
| ave. | 1327 | 1061 | 1036 | 1085 |
| s | 86 | 51 | 88 | 60 |
| 95% C.L. | 1327+/-119 | 1061+/-71 | 1036+/-123 | 1085+/-83 |
| naph amt. in 100ml(mg) | 133+/-12 | 106+/-7 | 104+/-12 | 108+/-8 |
| orig. amt of naph.(mg) | 165 | 165 | 165 | 165 |
| ext. eff. (% ) | 80+/-7 | | | |
| ext. percent | | 80+/-8 | 79+/-7 | 82+/-4 |

## 10.3 RESULTS and DISCUSSION

In Table 10.1 data of extraction after five (5) minutes microwave treatment is present. One blank and three sample extractions were made. The temperature of each sample were 132, 129 and 117 $^0$C, respectively. For each sample and blank, two duplicate injections were made. For blank extraction, the 95% C.L. is 1327 +/- 119, the efficiency of the extraction is 80 +/- 7% which is taken as 100% point. The 95% C.L. of the three samples were 1061 +/- 71, 1036 +/-123 and 1085 +/- 83 respectively. Hence, the percentage of the extraction from the three samples are 80 +/- 8%, 79 +/- 7% and 82 +/- 4% respectively.

No detectable naphthalene could be found in the two traps after five minutes (5) microwave treatment at position 3.

The total percentage of naphthalene recovery of three samples are 80 +/- 8%, 79 +/- 7% and 82 +/- 4%, respectively.

## 10.4 CONCLUSIONS

The average of total recovery from humus, namely, 80%, is lower than for the sandy soil and clay soil, 83 and 85%, respectively. But the standard deviations for the humus are large so that it is hard to conclude that there is a significant difference. There is a significant difference in the trapping: for humus, non-detectable; for sandy soil, 28%; for clay soil, 31%. The respective temperatures are 126 °C; 126 °C; 144 °C. Thus it does not appear that the failure to find naphthalene in the traps from the humus experiment is due to temperature in the light of the observation that for sandy soil the trapped amount is 28% when the temperature is the same as the humus. It would appear that the vapor pressure of naphthalene is lowered in the humus due to the formation of relatively strong sorption forces. Thus although the substrate temperatures are the same, the naphthalene in the humus is less volatile.

# CHAPTER 11 EXPERIMENTAL SERIES VIII

# MASS BALANCE STUDIES: MICROWAVE TREATMENT OF CLAY AND MAGNETITE IMPREGGNATED WITH NAPHTHALENE

## 11.1 INTRODUCTION

Many studies on clay have shown that clay can "fix" organics. However, that effect is reversible. Furthermore it is confined to a single type of clay the montmorillonites. This clay has a layer of aluminum oxide separated from a layer of silica by a layer of hydrated alkali metal ions. Reversible absorption occurs when an organic replaces water in the hydration shell. In this study, the clay kaolinite was chosen because the middle layer of hydrated alkali metal ions is not present. The object was to determine if irreversible absorption occurred, not reversible absorption. Kaolinite will not absorb microwave energy. To effect the heating of the kaolinite, magnetite (iron oxide) was added. It was assumed that if the organics were to undergo irreversible absorption it would be with clay and not a basic metallic oxide.

## 11.2 EXPERIMENTAL SECTION

**11.2.1** Sample Preparation: The Kaolin clay was sifted by a electrical shaker, the aperture of the sieve is 125 um. The magnetite was sifted by 250 um sieve.

**11.2.2** To each 50 g sample, 5 ml of a solution of 20 mg naphthalene/ml methanol was added, and then was put into a fume hood at room temperature to allow the solvent to evaporate for ca. 24 hr.

**11.2.3** This experiment was run in triplicate. In each run a sand sample after solvent evaporation was put into a three neck round-bottom flask which was then placed into a microwave oven. In that flask, one neck served as the inlet for the compressed air, another, as the outlet for the naphthalene vapor. The third one was not used. It was sealed by a stopper. 5 ml water was added to each sample before microwave treatment.

**11.2.4** Refer to Figure 3.1. The external filter flask acted as a safety trap in the event that solutions flowed back from the traps as a result of a pressure drop in the apparatus in the microwave oven. Two washing bottles were connected with the filter flask. One bottle contained 100ml methanol, the other one contained 50 ml methanol.

**11.2.5** After 5 min microwave treatment, the round-bottom flask was taken out of the oven and the temperature of the sand was detected by a thermocouple immediately. 20.7 grams of the mixture sample was extracted by Soxhlet extractor for 48 hrs. using 80 ml methanol. In the meantime, a blank extraction was prepared by using untreated sample. The amount of naphthalene recovered from the blank was taken as the 100% reference point.

**11.2.6** The extracted solutions were diluted to 100 ml volumetric flasks and 1 ul was injected into GC/MS. The results were listed in Table 11.1.

**11.2.7** The residues after the extraction were put in the hood to let it dry for 24 hrs. The dry sample was then studied by DRIFT.

**11.2.8** The diffuse reflectance data were collected at 16.0 $cm^{-1}$ resolution for 64 scans, using potassium bromide powder as the background and diluent ( The samples were diluted to approximately 5 -10 % by weight in KBr).

**11.2.8.1** The absorbance and Kubelka-Munk spectra of the mixture of Kaolin and magnetite(ratio by weight: 25:1) were collected by DRIFT (see Figure 12.40 and Figure 12.41).

**11.2.8.2** The spectrum of neat naphthalene spectrum was collected by DRIFT (see Figure 12.2).

**11.2.8.3** The absorbance and Kubelka-Munk spectra of blank extraction residue and sample extraction residue were collected by DRIFT (see Figure 12.42 to Figure 12.45).

**11.2.8.4** The absorbance and Kubelka-Munk spectra of the mixture of pure Kaolin, magnetite and the pure solid naphthalene were collected by DRIFT (see Figure 12.46 and Figure 12.47).

**11.2.9** One microliter samples of the solutions in the two traps, respectively, were injected, in triplicate, into the GC/MS.

## 11.3 RESULTS AND DISCUSSION

In Table 11.1 data of extraction after five (5) minutes microwave treatment is presented. One blank and three sample extractions were made. The temperature of each sample were 174, 170 and 182 $^0$C, respectively. For each sample and blank, two duplicate injections were made. For blank extraction, the 95% C.L. is 272 +/- 16, the efficiency of the extraction is 89 +/-1 % which is taken as 100% point. The 95% C.L. of the three samples were 249 +/- 4, 193 +/- 22 and 168 +/- 22 respectively. Hence, the percentage of the extraction from the three samples are 93 +/- 3, 70 +/- 2 and 63 +/- 2 respectively.

No detectable naphthalene could be found in the two traps after five minutes(5) microwave treatment at position 3.

The total percentage of naphthalene recovery of three samples are 93 +/- 3%, 70+/-2% and 63+/-2% respectively.

## 11.4 CONCLUSIONS

The total recoveries for two of the samples are on the low side, average 67%; one on the high side, 93%. The temperatures were relatively high, averaging 176 $^0$C. Volatilization apparently did not occur because naphthalene was not detected in the traps. Clays can catalyze organic reactions. The effect of the addition of magnetite is unknown in the literature. A possible explanation is that the substrate acted as a catalyst in two of the experiments for the partial decomposition of naphthalene, but not for the third.

Table 11.1 Clay and Magnetite Substrate: Naphthalene Recovery at Position 3 (5 minutes microwave treatment)

| Sample No. | Blank | Sample 1 | Sample 2 | Sample 3 |
|---|---|---|---|---|
| Temp. of sand ( $^0$C ) | | 174 | 170 | 182 |
| No. of replication | 2 | 2 | 2 | 2 |
| amt. of naph. (ng/ul) | 263.4<br>280.7 | 251.4<br>247.0 | 204.5<br>181.6 | 157.2<br>179.7 |
| ave. | 272.1 | 249.2 | 193.1 | 168.4 |
| s | 12 | 3 | 16 | 16 |
| 95% C.L. | 272+/-16 | 249+/-4 | 193+/-22 | 168+/-22 |
| naph amt. in 100ml(mg) | 27+/-2 | 25+/-1 | 19+/-2 | 17+/-2 |
| orig. amt of naph.(mg) | 41.5 | 41.5 | 41.5 | 41.5 |
| ext. eff. (% ) | 65+/-4 | | | |
| ext. percent | | 93+/-3 | 70+/-2 | 63+/-2 |

## CHAPTER 12 EXPERIMENT SERIES VIIII

## SURFACE SPECTRA STUDIES: DIFFUSE REFLECTANCE INFRARED FOURIER TRANSFORM SPECTROSCOPY ( DRIFT )

### 12.1 INTRODUCTION

Assuming that there are no losses in the transport of the vapors to the traps, then, the organic compound should be found in the traps, in the extract from the soil, and "fixed" in the soil, respectively. It is difficult to study organics in the soil qualitatively, impossible now to carry out quantitative studies. The purpose of this series of experiments was to follow up previous studies conducted in this laboratory on microwave treatment of non-volatile, insoluble organics in soil, specifically, 9,10-anthraquinone. In those studies it was possible to obtain DRIFT spectra of that organic on clay and on humus. Also, to observe spectral changes as a result of microwave treatment. In the case of the clay, to facilitate the heating of the clay a strong microwave absorber, namely, magnetite was added. Here the organic is volatile. Approximately 90% can be accounted for in the traps and by extraction. In addition, the organic, naphthalene, unlike 9, 10-anthraquinone does not contain distinct functional groups like the carbonyls, which are distinct markers in an infrared spectra. Nevertheless, these studies were carried out in the slight hope that changes in the spectra might be observed, and, also, to point out that this is an important aspect of mass balancing which has to be tackled in the future with diligence and effort.

## 12.2 DRIFT PRINCIPLES

The problem is to obtain the infrared spectrum of materials sorbed on substrates such as soil and sand. To that end, sample preparation which will change the nature of the sorption must be minimized. Additionally, the method must be capable of obtaining surface spectra with relatively high sensitivity. With a minimum of sample preparation, powders and rough surface solids exhibit diffuse reflection, i.e. incident light is scattered in all directions as opposed to specular (mirror-like) reflection where the angle of the incidence equals the angle of the reflection. With the advent of Fourier Transform Spectroscopy, the sensitivity of infrared, a major shortcoming until now, is increased so that it has been reported that materials in the ppm range can be detected. The mating of diffuse reflectance and Fourier Transform Infrared Spectroscopy is called Diffuse Reflectance Infrared Fourier Transform Spectroscopy (DRIFT).

Diffuse reflectance spectra are more complicated than infrared transmission spectra. DRIFT spectra are affected by sample preparation, particle size, sample concentration and optical geometry effects. Another complication is the occurrence of specular reflection. Reflections from mirror-like surfaces produces inverted bands("reststrahlen band") in diffuse reflectance spectrum which reduce the usefulness of traditional transmission reference spectra. For highly absorbing samples these reststrahlen bands are strong. Grinding and diluting the sample with non-absorbing powder such as KBr, KCL, Ge or Si can minimize or eliminate these effects. Grinding reduces the contribution of reflection from large particle faces. Diluting ensures the deeper penetration of incident beam, thus increasing the contribution to the spectrum of the transmission and internal reflection components. The resulting spectra have an appearance more similar to that of the transmittance spectra than bulk reflectance spectra.

The Kubelka-Monk (K-M) function can be used for accurate quantitative analysis. However, the particle size and packing method must be strictly controlled.

## 12.3 EXPERIMENTAL SECTION

The instrument used is discussed in the Chapter 3, Experimental Section. The powder samples were held in stainless steel cups, 10 mm in diameter and 1 mm deep.

Experimental procedures were elaborated in each chapter's EXPERIMENTAL SECTION.

## 12.4 RESULTS AND DISCUSSION

**12.4.1 Sand:** The purpose of this study was to see whether or not after microwave treatment and extraction, naphthalene was still adsorbed on the substrate following up the earlier discussed series of experiments. To that end, the first task is to show that it can be observed in prepared samples. The spectra of sand is shown in Figure 12.1. The spectra of pure naphthalene in Figure 12.2. A mixture of the sand and solid naphthalene is shown in Figure 12.5. The spectrum of naphthalene is observed. To the latter mixture, methanol was added to dissolve the naphthalene: the solvent was evaporated for 24 hours in a fume hood. The resulting spectrum is shown in Figure 12.48 . Naphthalene is no longer observed. Furthermore, when solutions of naphthalene in methanol were added to sand, and evaporated, again, the spectrum of naphthalene was not observed (See Figure 12.3 and Figure 12.4). It is concluded that in the adsorbed state on the sand, naphthalene becomes too weak an infrared absorber to be observed.

**12.4.2 Sandy Soil:** Comparing Figure 10, pure sandy soil, and Figure 28 , representing the sandy soil to which pure solid naphthalene was added, it is seen that the sharpest spectral difference occurs in the 3000 $cm^{-1}$ region, the aromatic carbon - hydrogen stretch region. In the spectra of the sandy soil residue after microwave treatment (from the studies discussed in section 9.2.8 of this thesis), this absorption band cannot be observed (see Figure 18). Either there is no naphthalene residue or it is too low in concentration to be detected or it is in a physical or chemical state which cannot be detected.

**12.4.3 Clay Soil:** It is seen that the sharpest spectral difference between clay soil and clay soil to which naphthalene has been added is the aromatic C-H stretching band in the 3000 $cm^{-1}$ region. That band is not observed in the residue from the microwave treatment (Figure 20), from the study discussed in detail in section 9.2.9. Again, the explanation is similar to the previous one: too low a concentration, or there is no residue to detect, or in a physical or chemical state which cannot be detected.

**12.4.4 Humus:** Here the humus has strong absorption bands in the 3000 $cm^{-1}$ region and throughout the spectrum (Figure 32). Thus when pure solid naphthalene is added

(Figure 38), no distinct bands can be ascribed to naphthalene. Therefore, no inferences can be drawn from the spectrum (Figure 36) of the residue after microwave treatment (see section 10.2.8 for details of this series of experiments).

**12.4.5 Clay and Magnetite:** There are sharp differences between the absorption spectra of the clay/magnetite mixture (Figure 40), and that when pure solid naphthalene is added (Figure 47) : for example, the 3000 $cm^{-1}$ region. However, in the residue after microwave treatment (see section 11.2.8 for details of this study), there is no evidence for naphthalene (Figure 44). It is possible that the concentration is too low, or there is no naphthalene left, or it is in a physical or chemical state in which it is non-detectable.

## 12.5 CONCLUSIONS

The spectra of naphthalene cannot be observed in the substrates studied and reported upon previously. Those substrates being sand, sandy soil, and clay soil, respectively. Therefore, it is not possible to determine whether or not, in addition, to naphthalene extracted, and naphthalene volatilized and trapped, naphthalene was "fixed" in those substrates. There are two problems: a) the spectrum of naphthalene is too similar to the spectra of the soil substrates, presumably, because of the presence of organic matter absorbing in the carbon-hydrogen stretch and bending regions; b) naphthalene adsorbed from solution on a substrate like sand is not a strong enough infrared absorber to be detected.

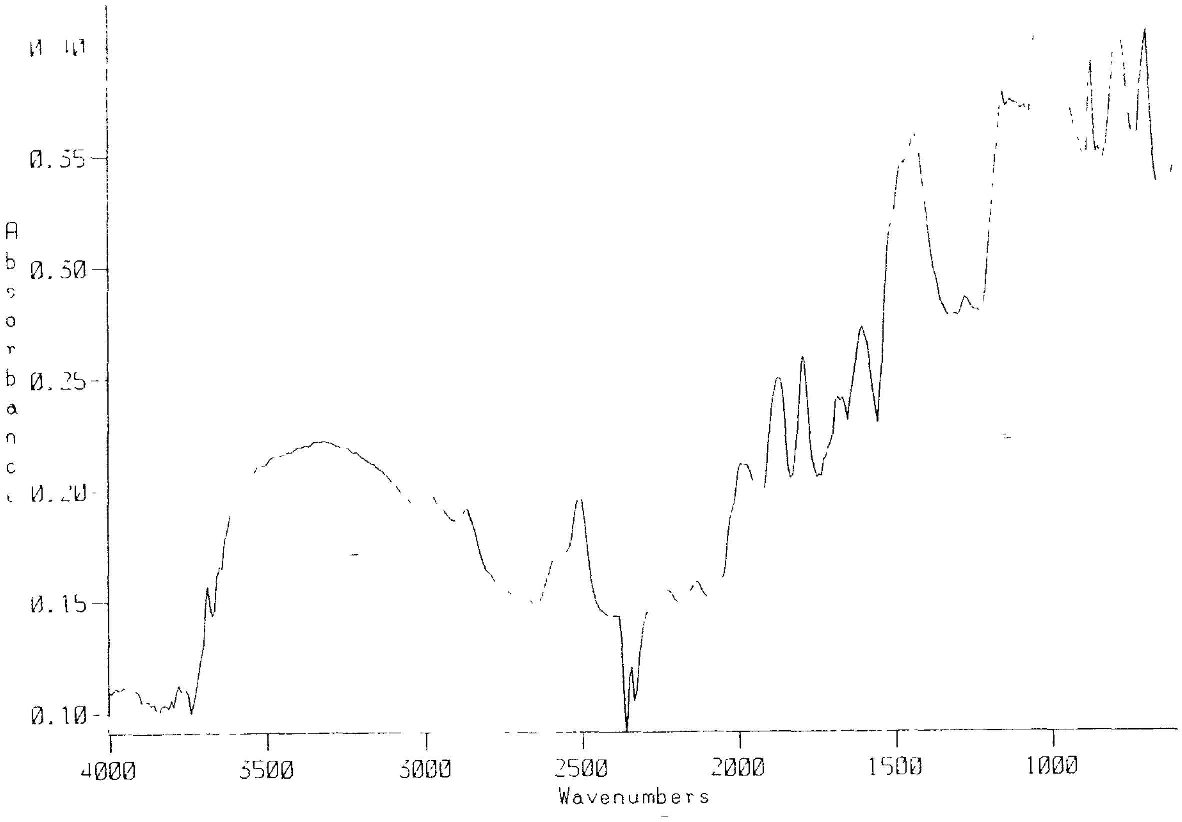


**Figure 12.1 The Diffuse Reflectance Spectrum of the Pure Sand in Absorbance Format**

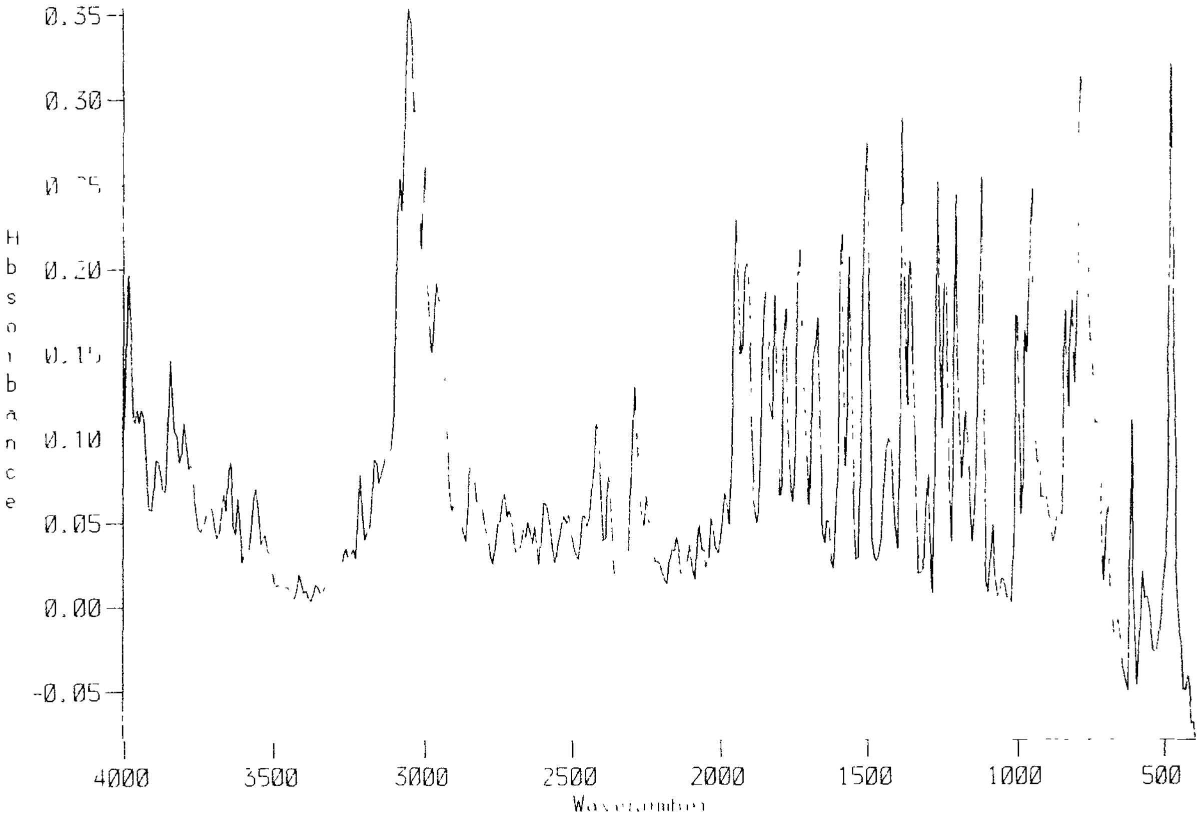


**Figure 12.2 The Diffuse Reflectance Spectrum of the Pure Naphthalene in Absorbance Format**

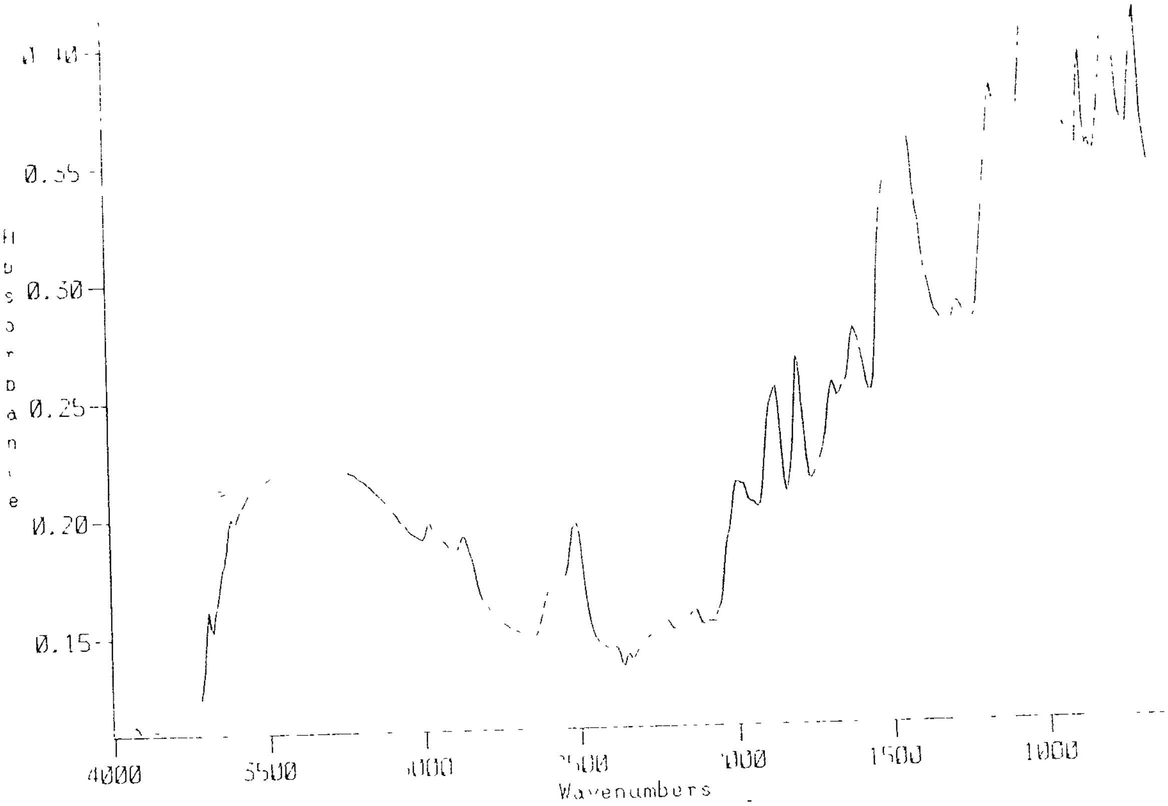


**Figure 12.3** The Diffuse Reflectance Spectrum of the Sand Blank Extraction Residue in Absorbance Format without Microwave Treatment

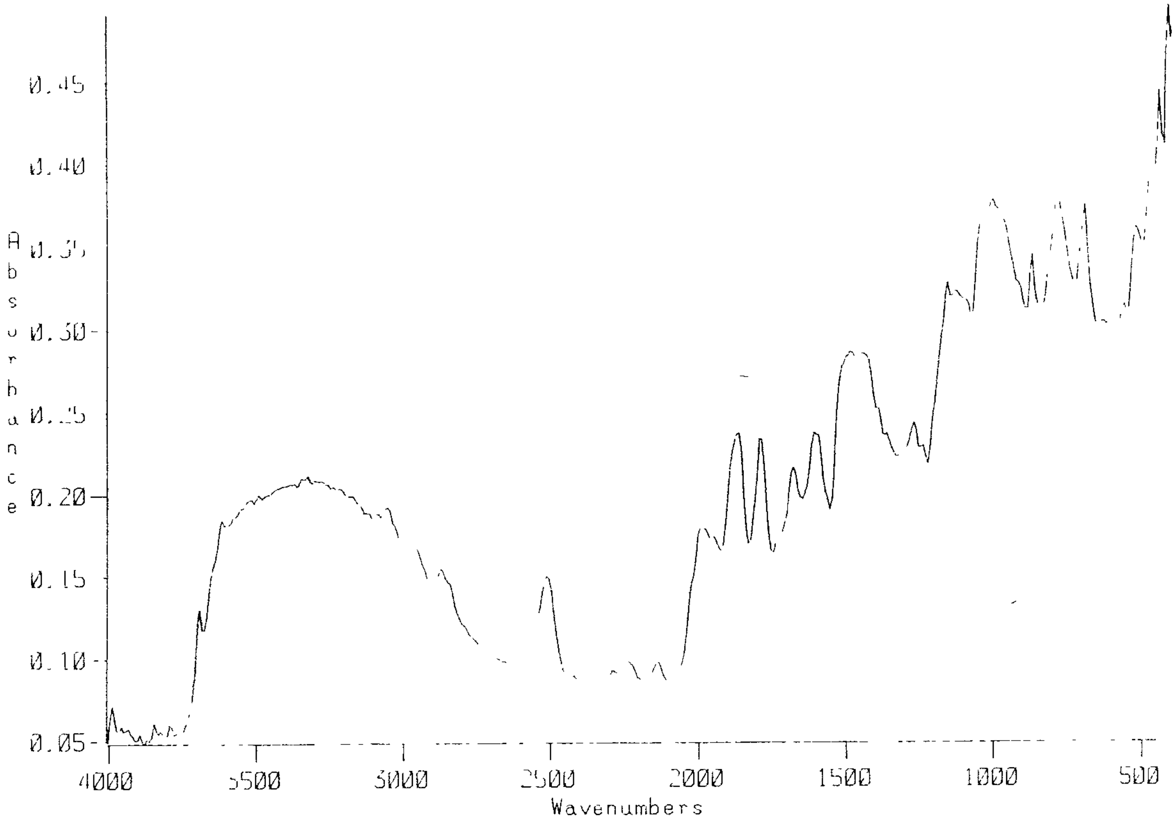


**Figure 12.4** The Diffuse Reflectance Spectrum of the Sand Extraction Residue in Absorbance Format after Microwave Treatment

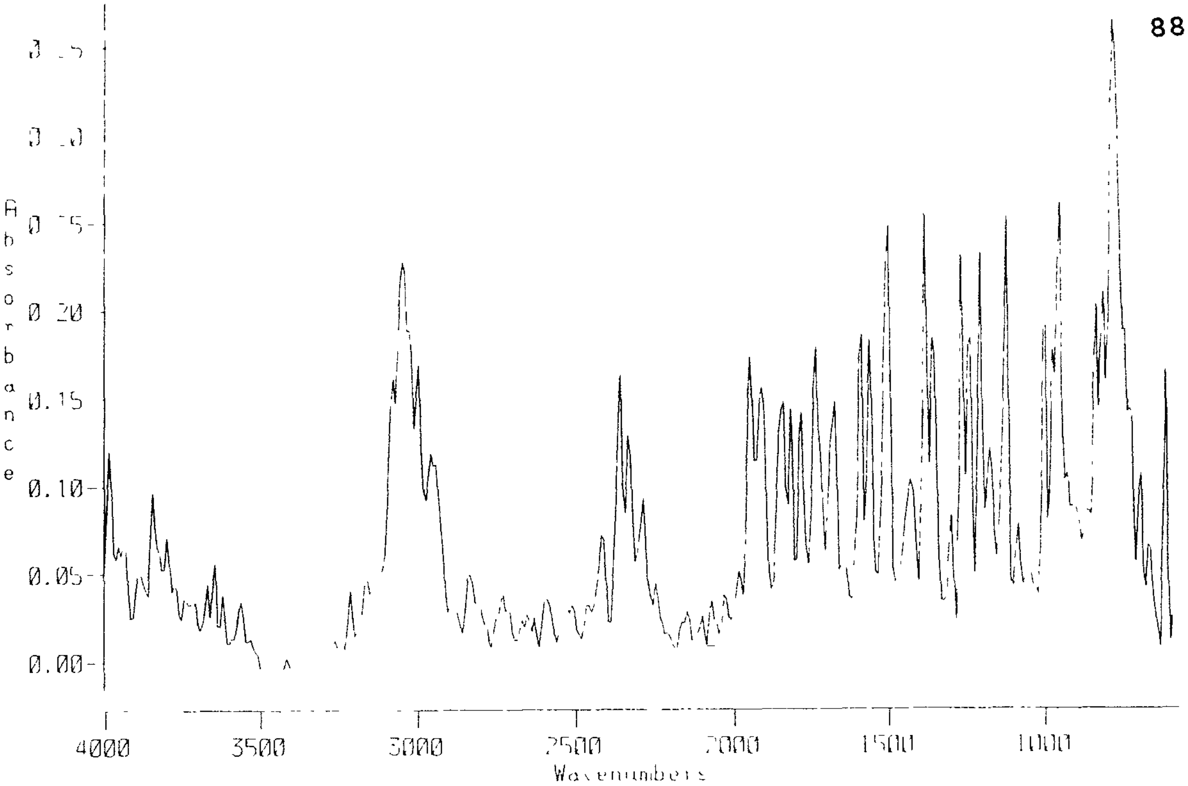


Figure 12.5 The Diffuse Reflectance Spectrum of the Mixture of the Pure Sand and Pure Naphthalene in Absorbance Format without Microwave Treatment

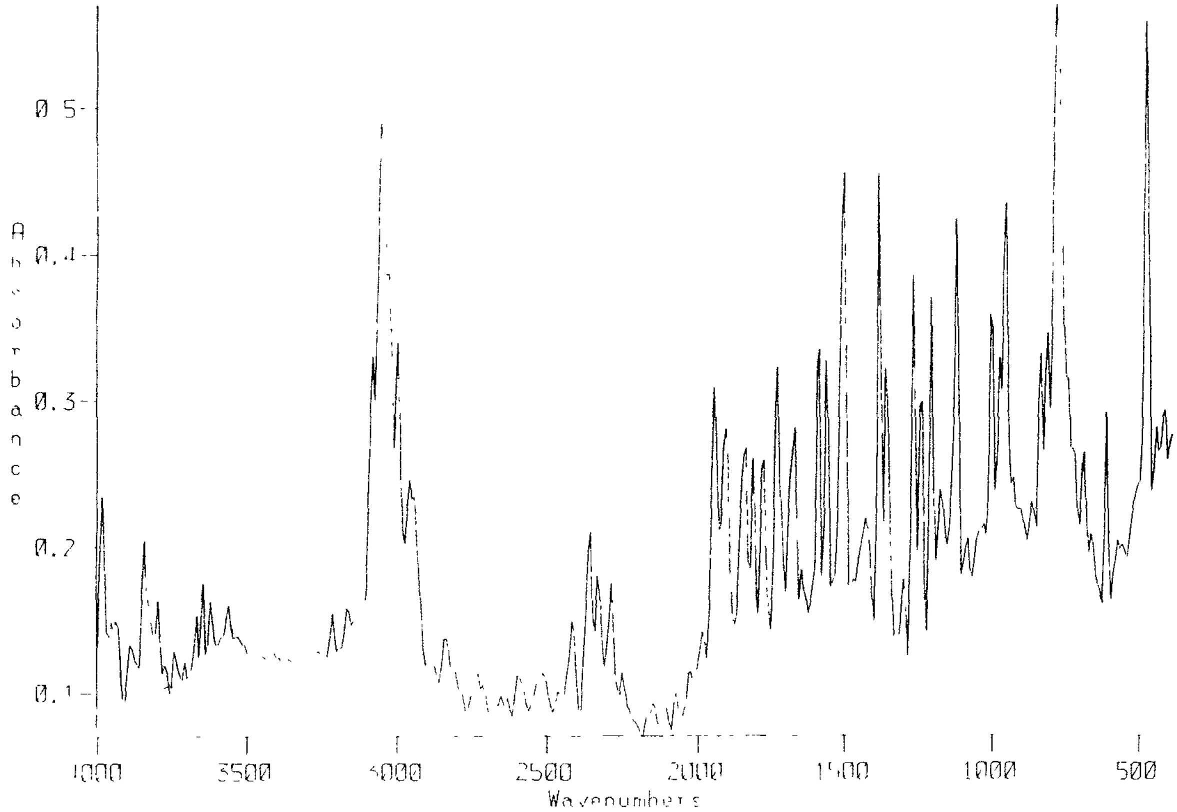


Figure 12.6 The Diffuse Reflectance Spectrum of the Mixture of the Pure Sand and Pure Naphthalene in Absorbance Format without Microwave Treatment

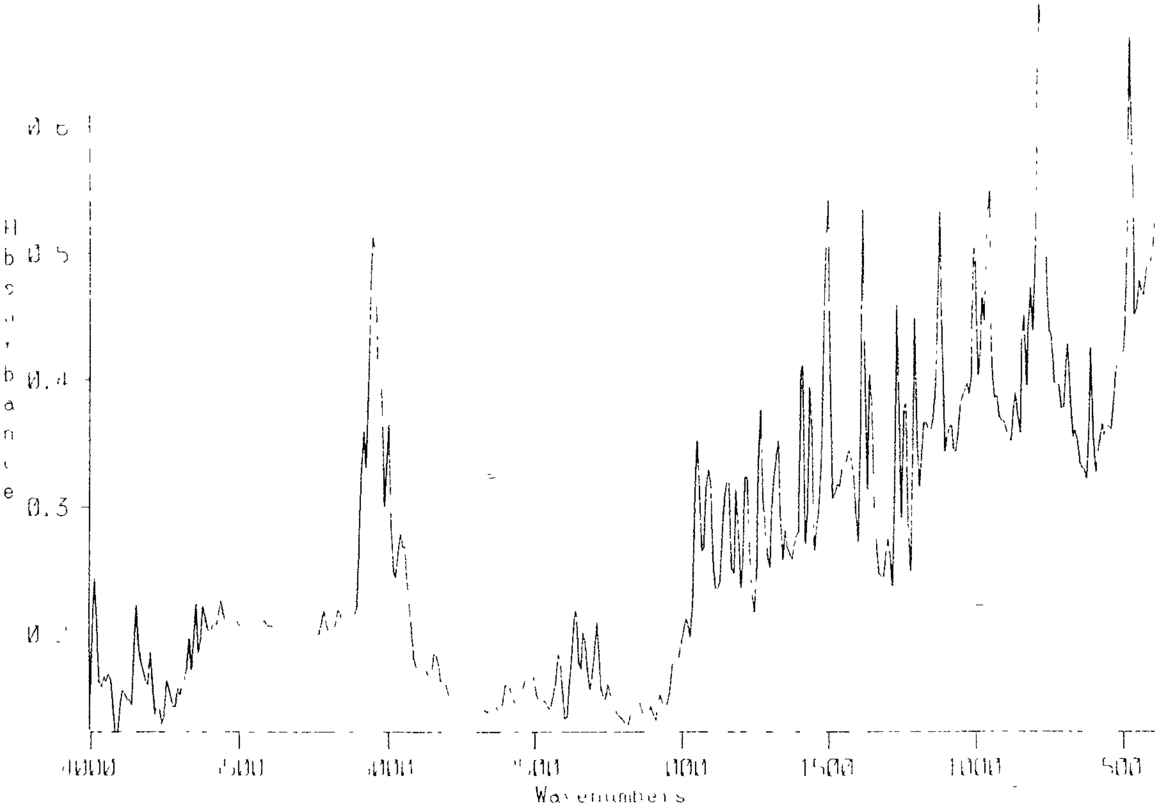


Figure 12.7 The Diffuse Reflectance Spectrum of the Mixture of the Pure Sand and Pure Naphthalene in Absorbance Format without Microwave Treatment

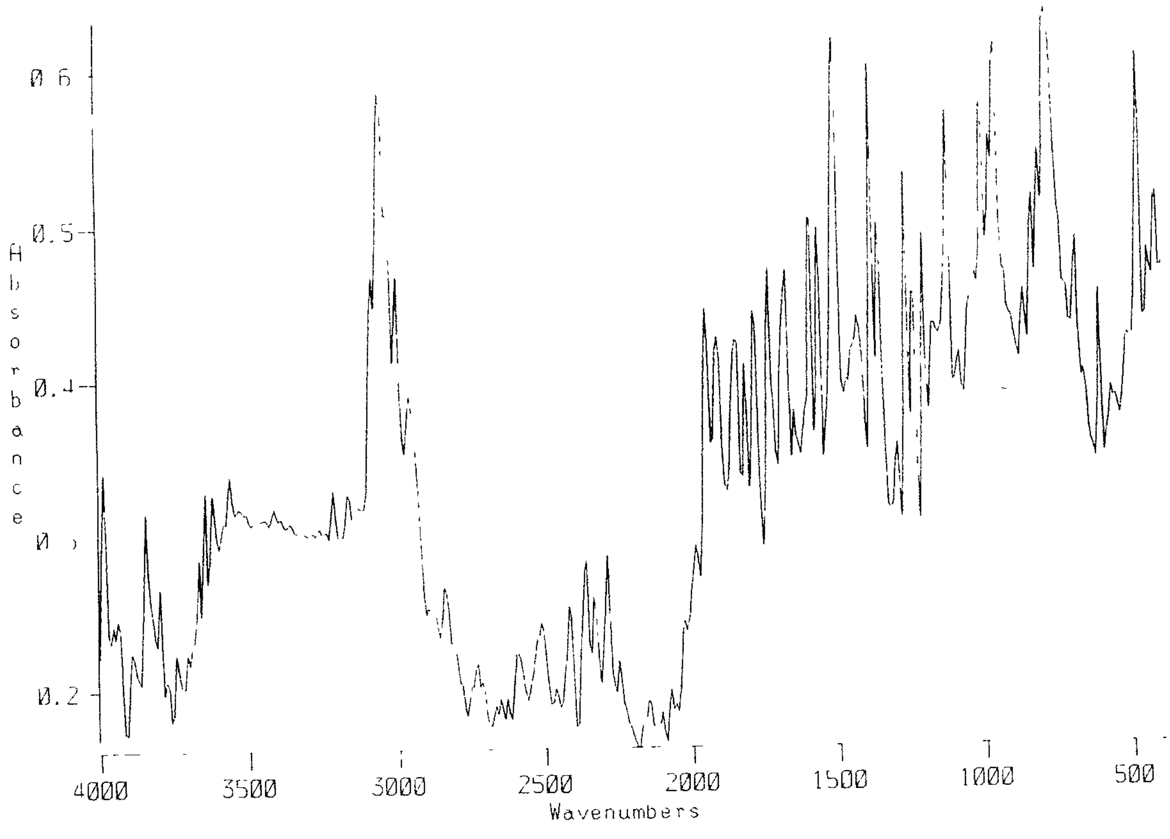


Figure 12.8 The Diffuse Reflectance Spectrum of the Mixture of the Pure Sand and Pure Naphthalene in Absorbance Format without Microwave Treatment

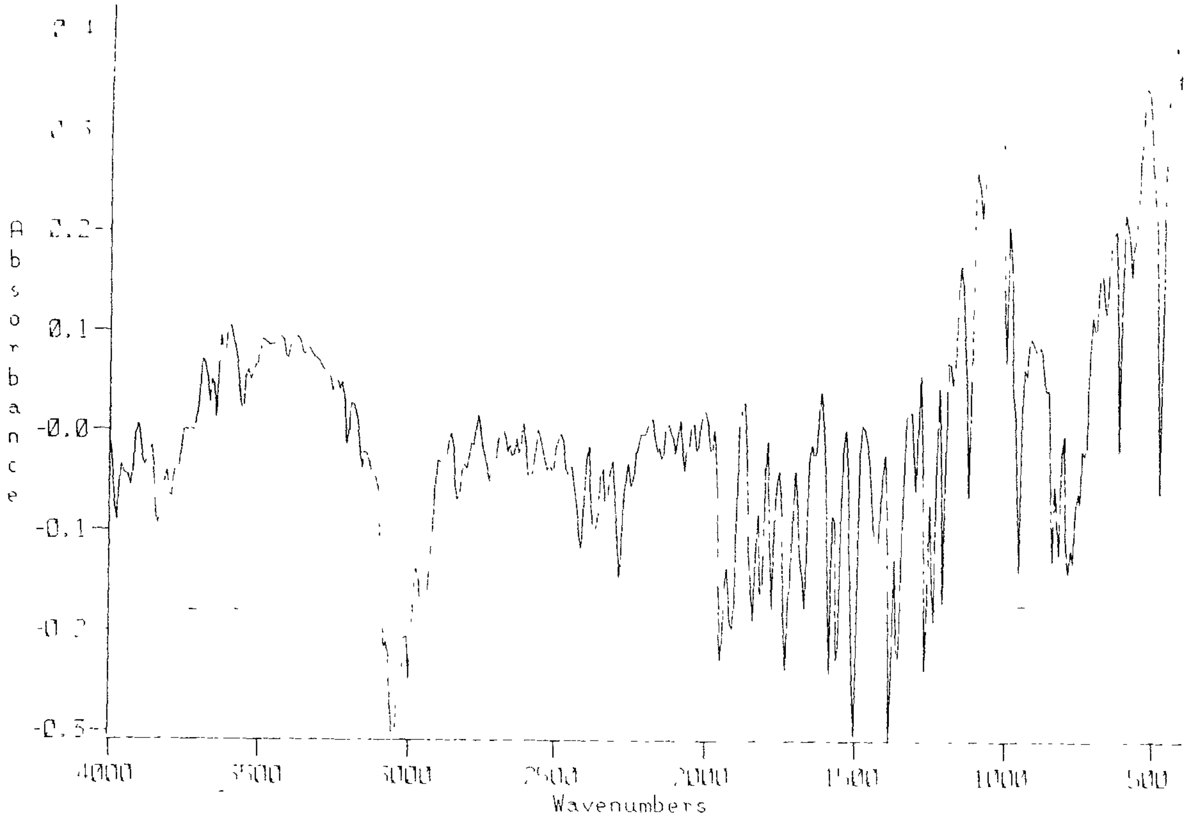


Figure 12.10 The Diffuse Reflectance Spectrum of the Pure Sandy Soil in Absorbance Format without Microwave Treatment

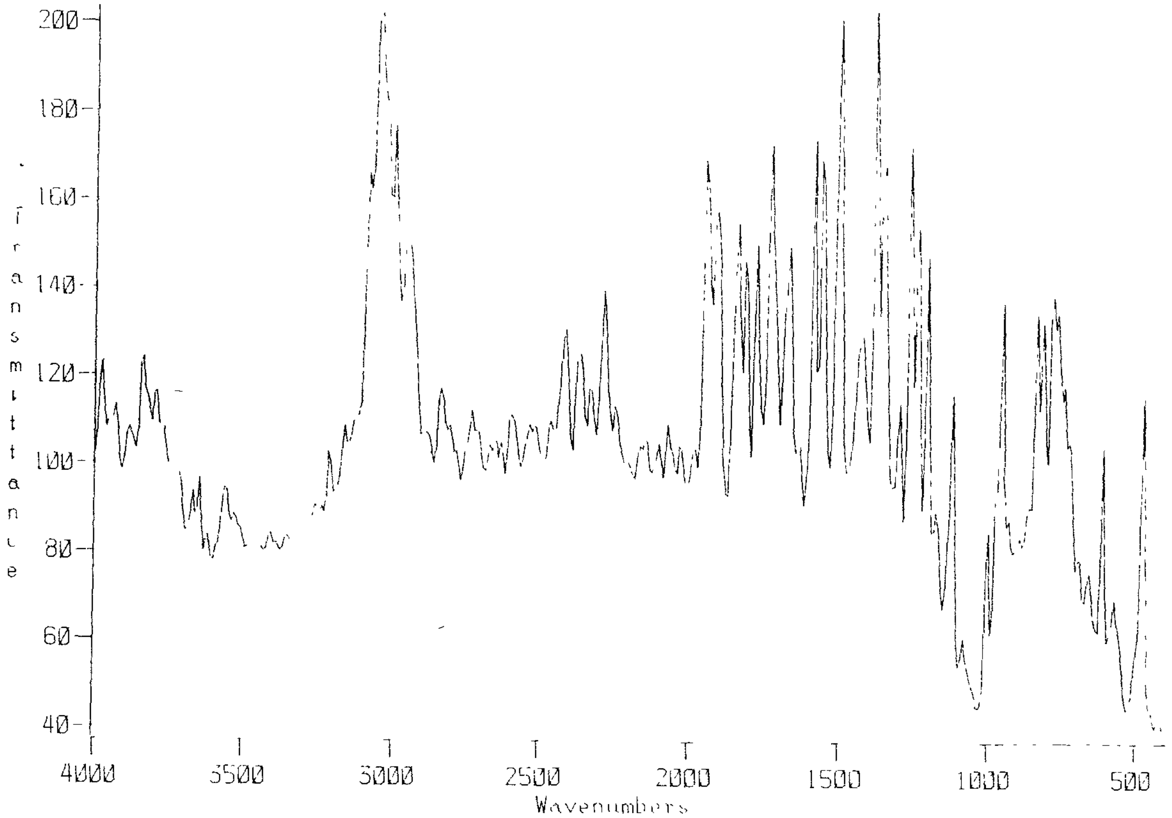


Figure 12.11 The Diffuse Reflectance Spectrum of the Pure Sandy Soil in Transmittance Format without Microwave Treatment

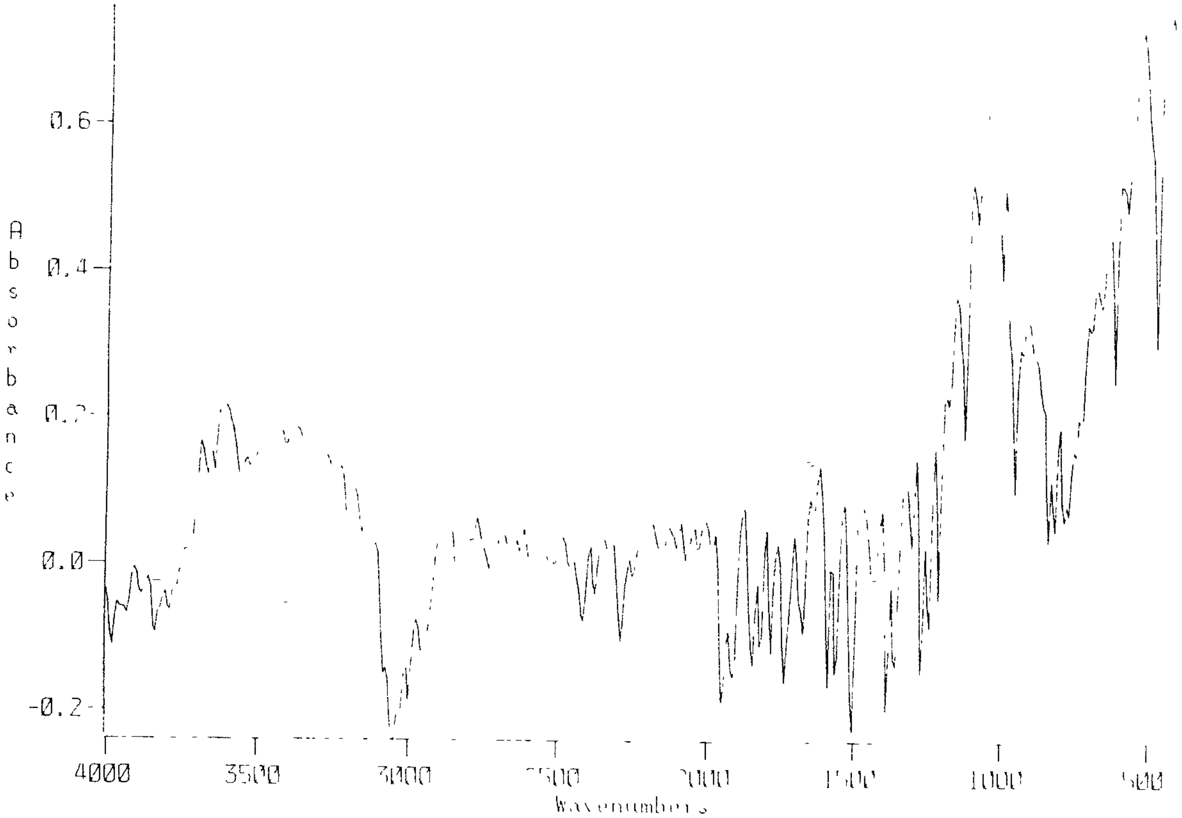


Figure 12.12 The Diffuse Reflectance Spectrum of the Pure Clay Soil in Absorbance Format without Microwave Treatment

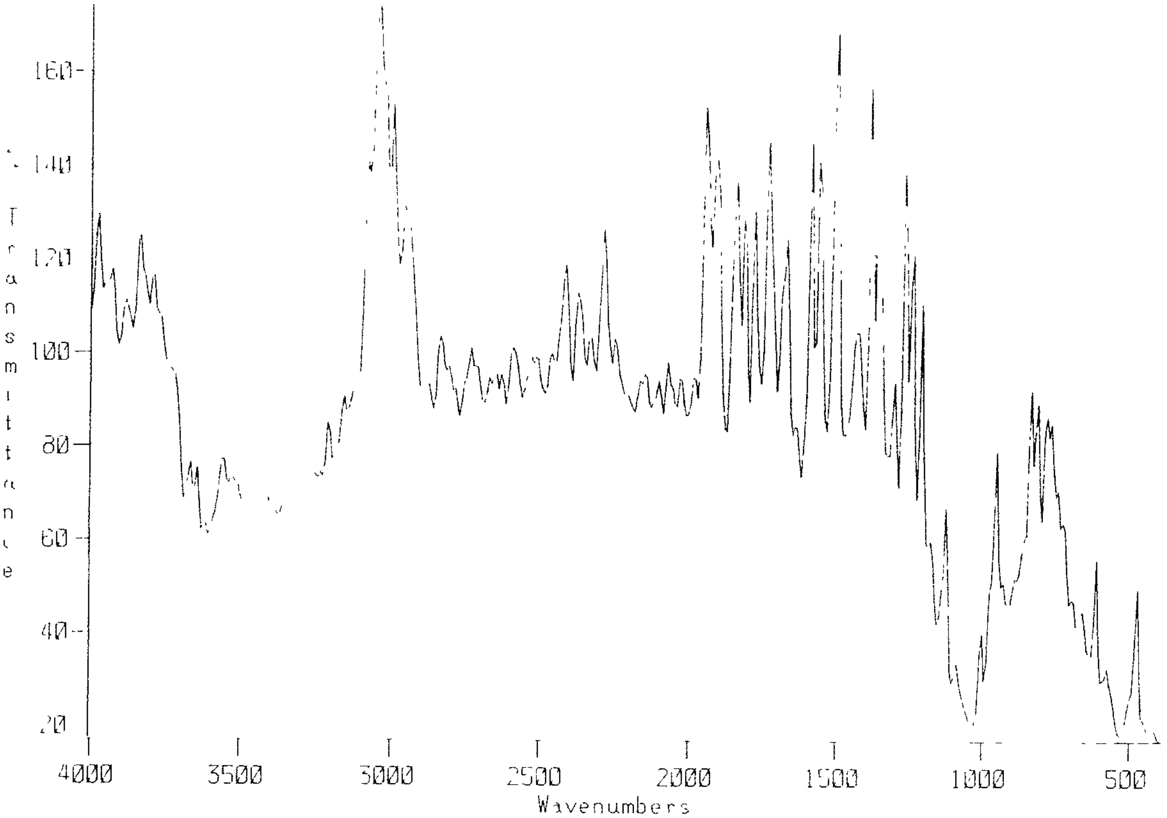


Figure 12.13 The Diffuse Reflectance Spectrum of the Pure Clay Soil in Transmittance Format without Microwave Treatment

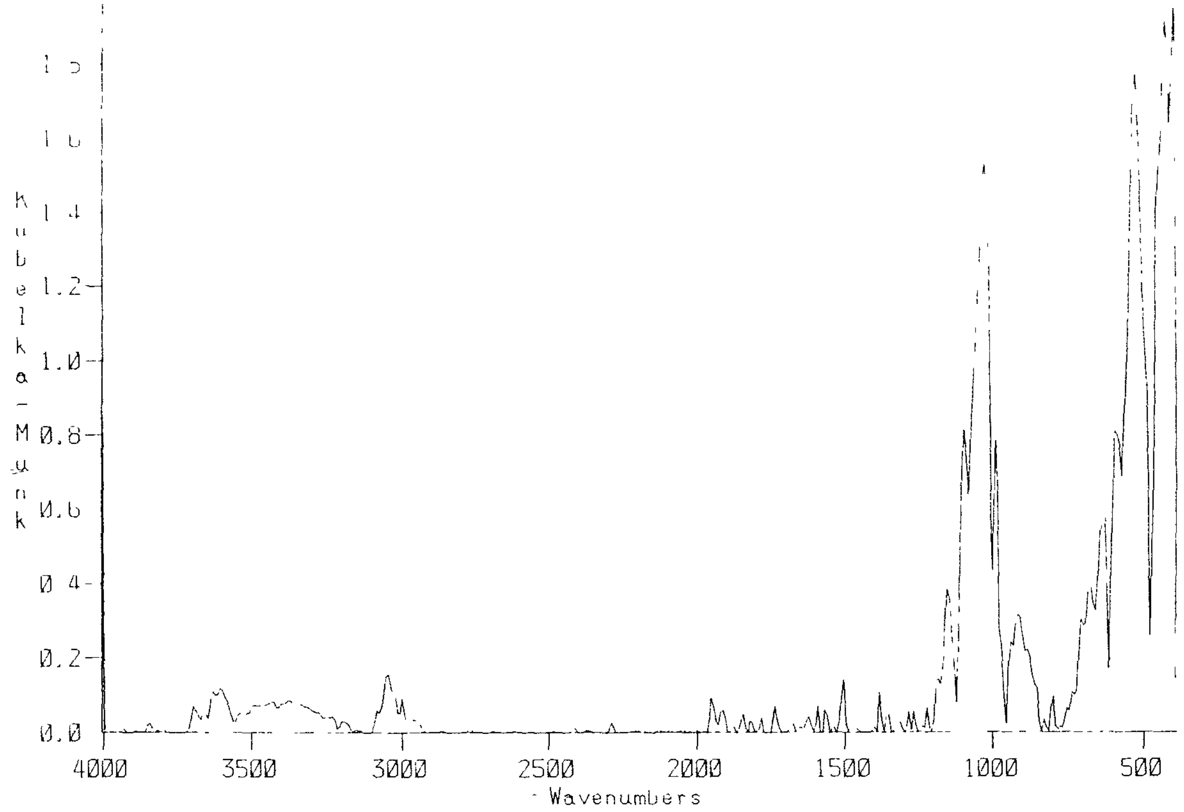


Figure 12.14 The Diffuse Reflectance Spectrum of the Pure Clay Soil in Kubelka-Munk Format without Microwave Treatment

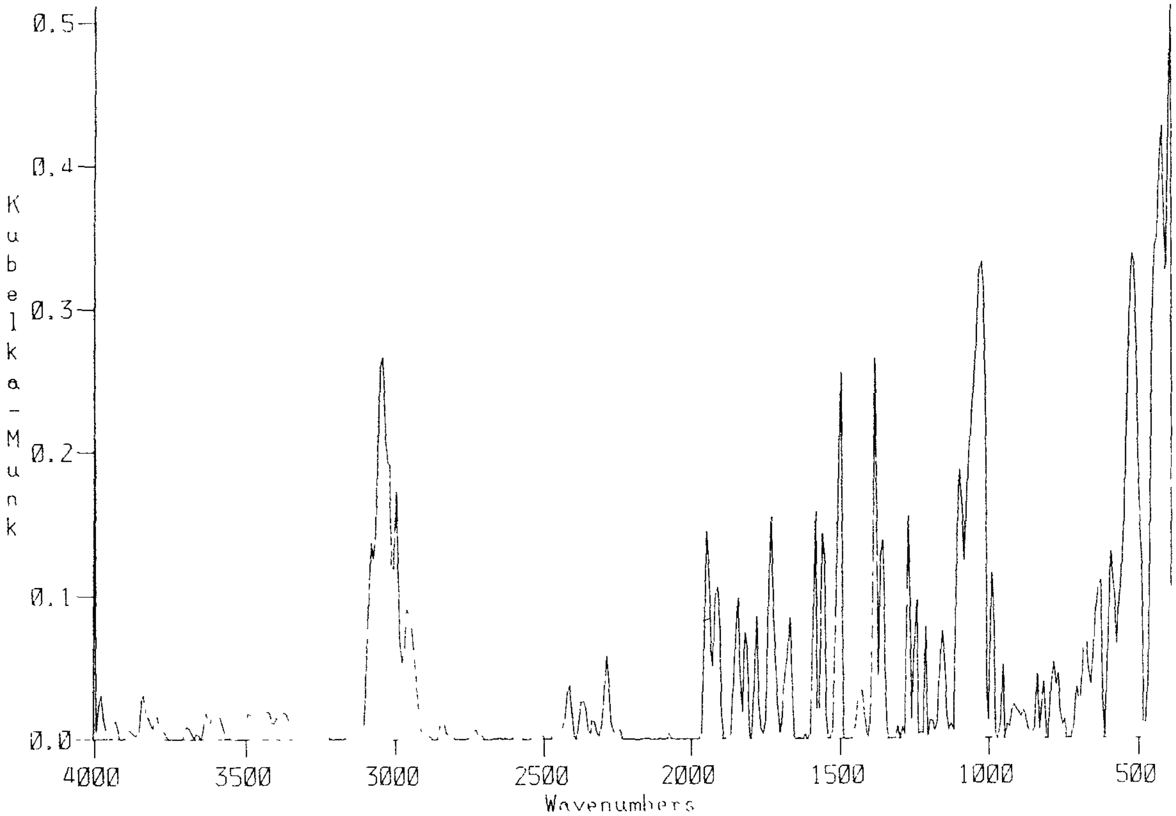


Figure 12.15 The Diffuse Reflectance Spectrum of the Pure Sandy Soil in Kubelka-Munk Format without Microwave Treatment

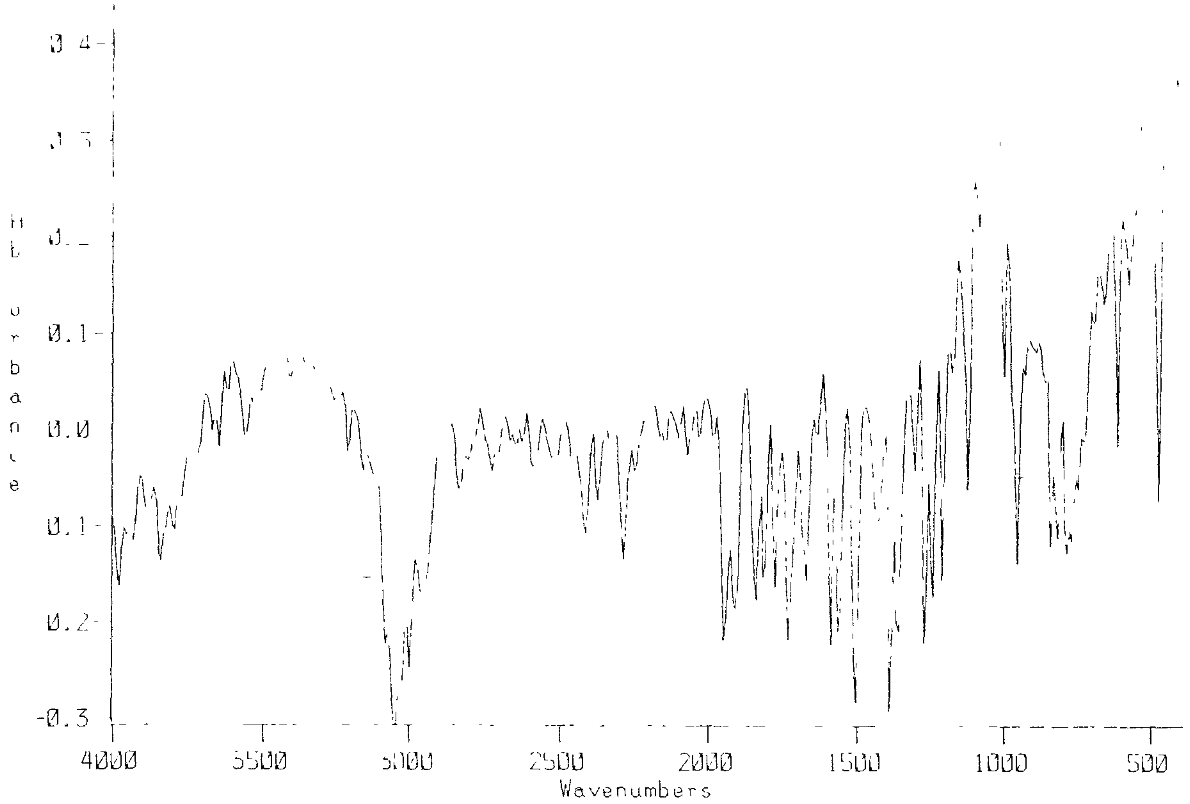


Figure 12.16 The Diffuse Reflectance Spectrum of the Sandy Soil Blank Extraction Residue in Absorbance Format without Microwave Treatment

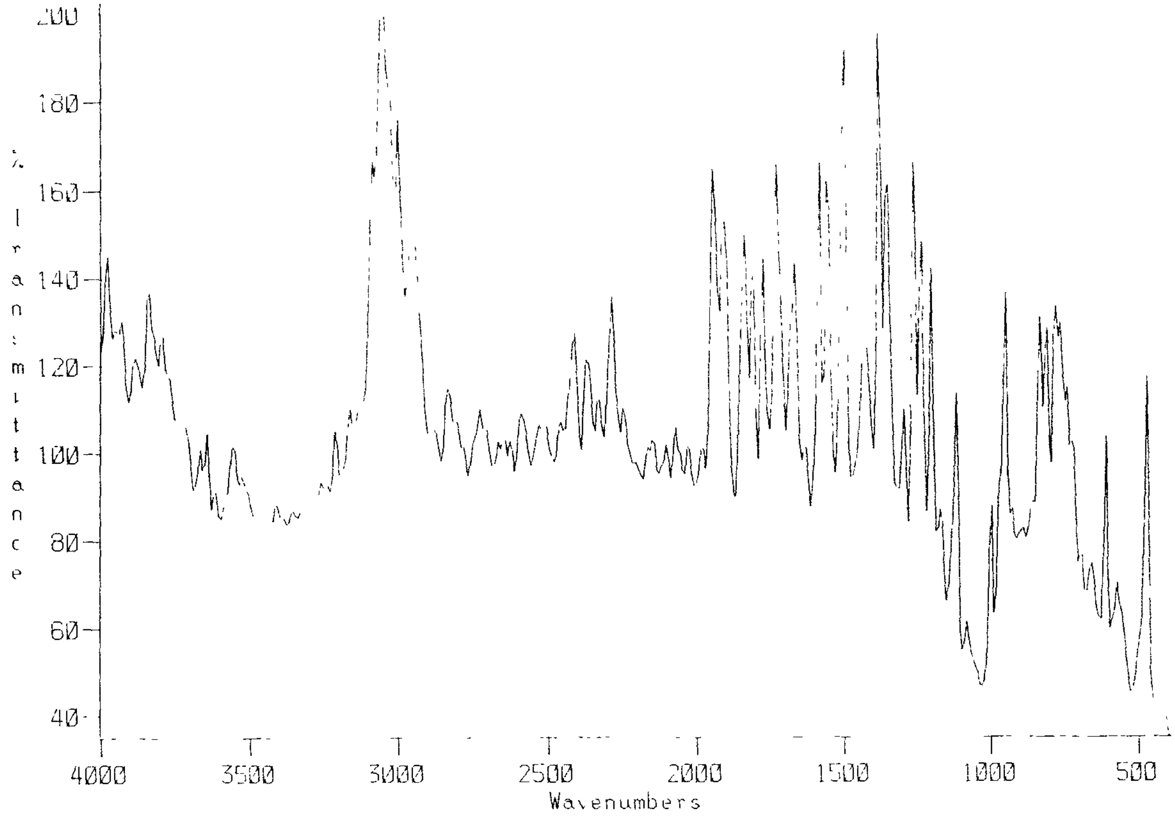


Figure 12.17 The Diffuse Reflectance Spectrum of the Sandy Soil Blank Extraction Residue in Transmittance Format without Microwave Treatment

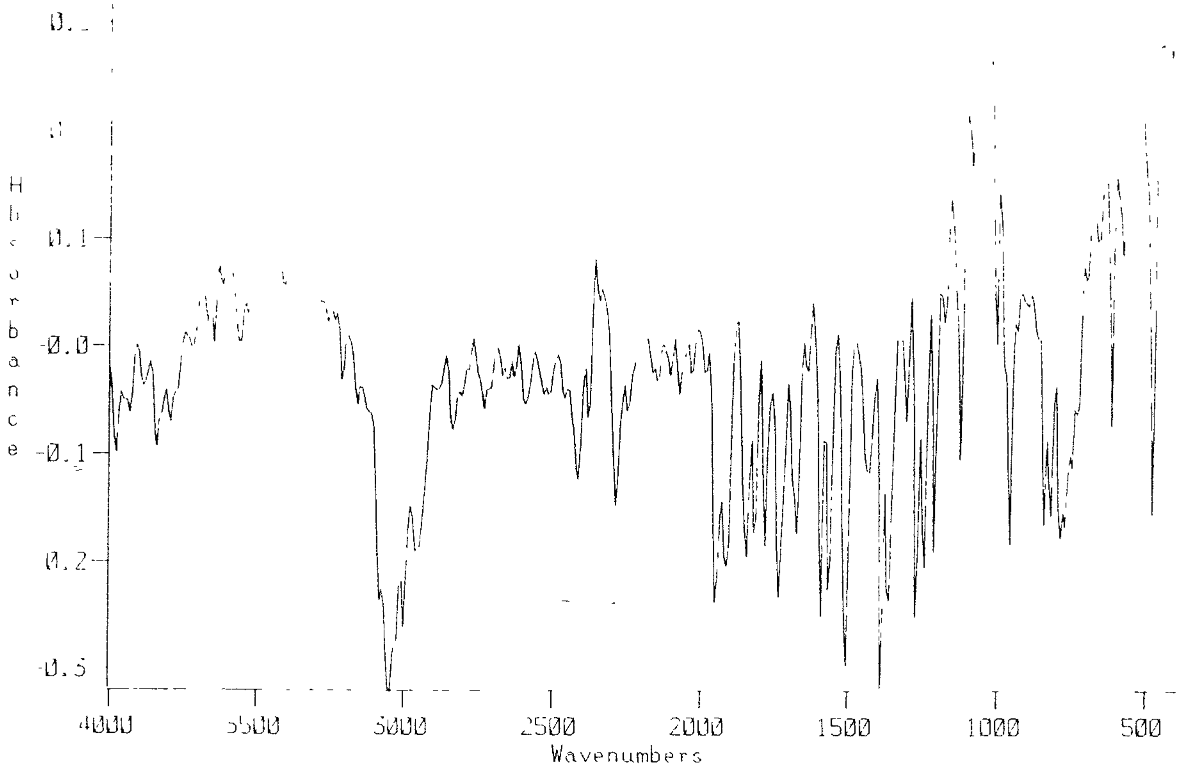


Figure 12.18 The Diffuse Reflectance Spectrum of the Sandy Soil Extraction Residue in Absorbance Format after Microwave Treatment

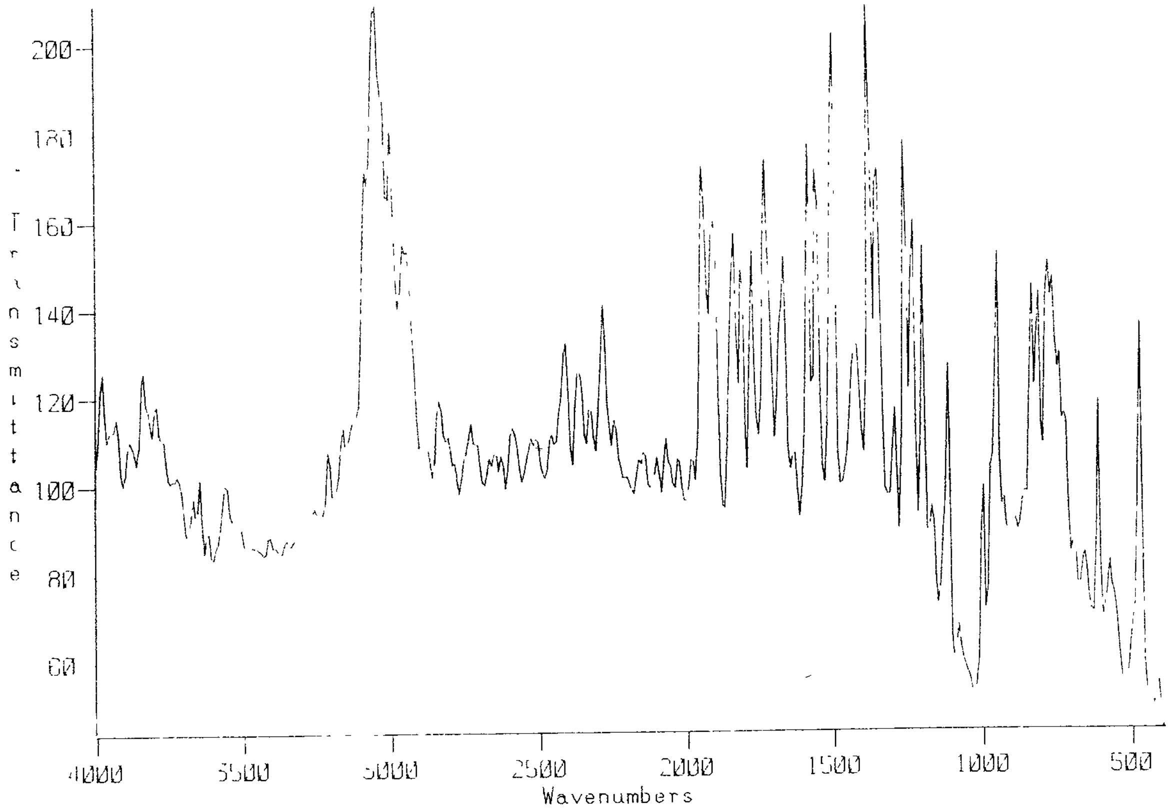


Figure 12.19 The Diffuse Reflectance Spectrum of the Sandy Soil Extraction Residue in Transmittance Format after Microwave Treatment

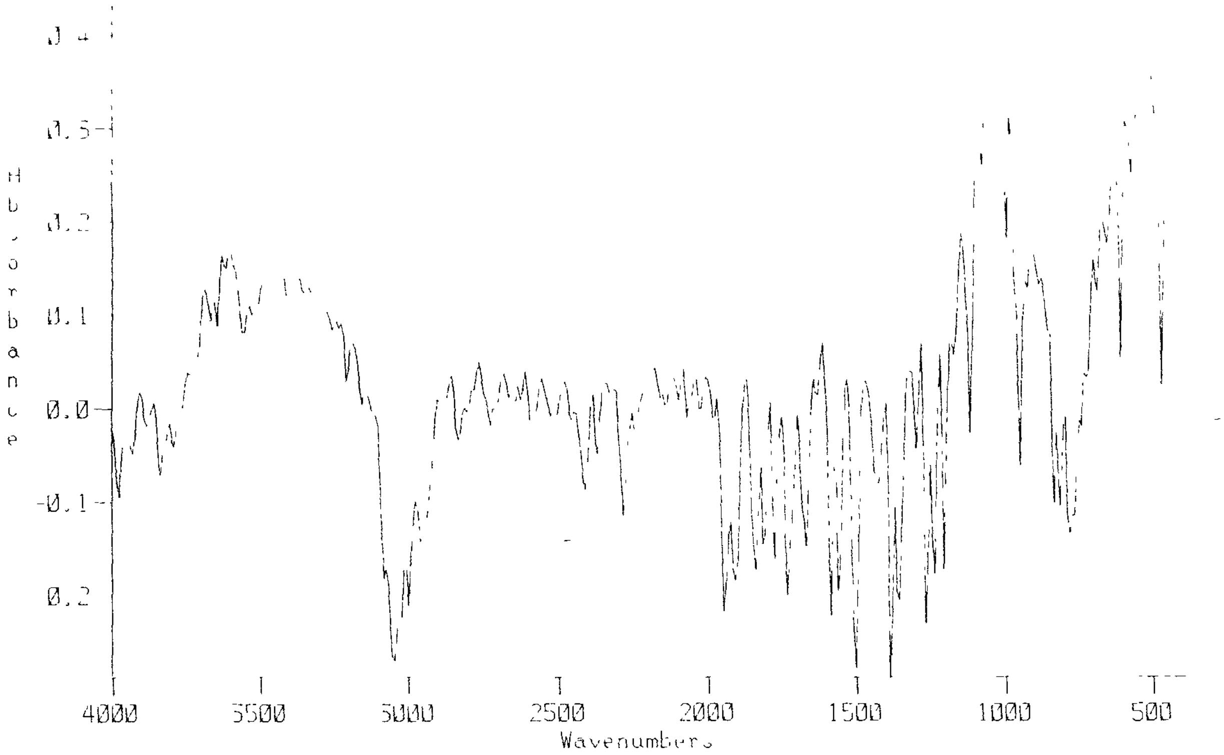


Figure 12.20 The Diffuse Reflectance Spectrum of the Clay Soil Extraction Residue in Absorbance Format after Microwave Treatment

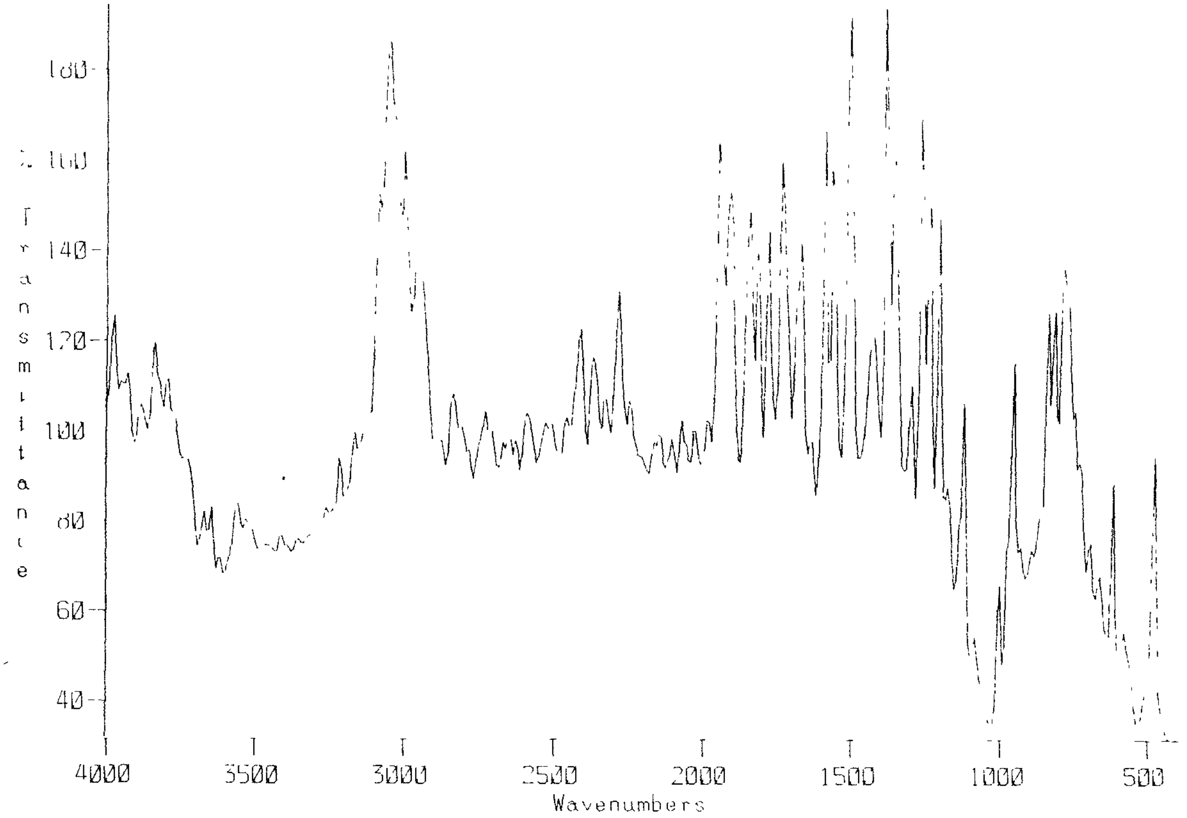


Figure 12.21 The Diffuse Reflectance Spectrum of the Clay Soil Extraction Residue in Transmittance Format after Microwave Treatment

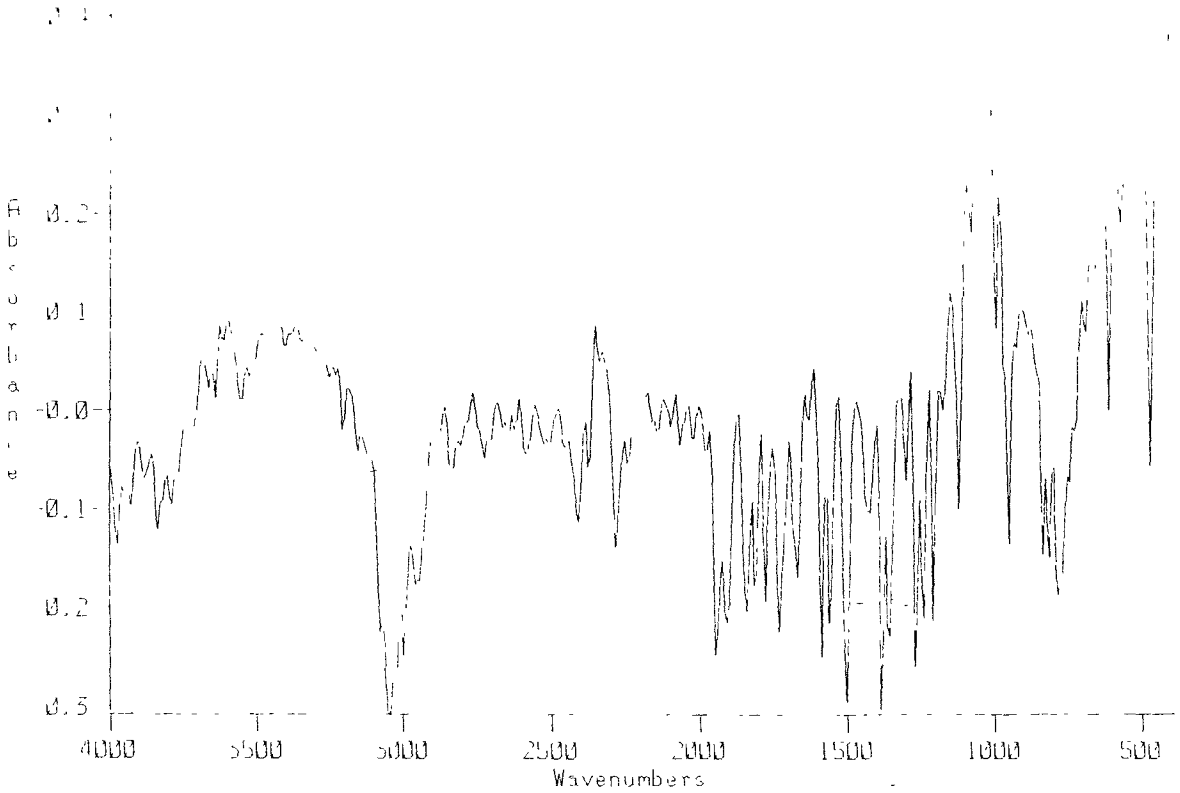


Figure 12.22 The Diffuse Reflectance Spectrum of the Clay Soil Blank Extraction Residue in Absorbance Format without Microwave Treatment

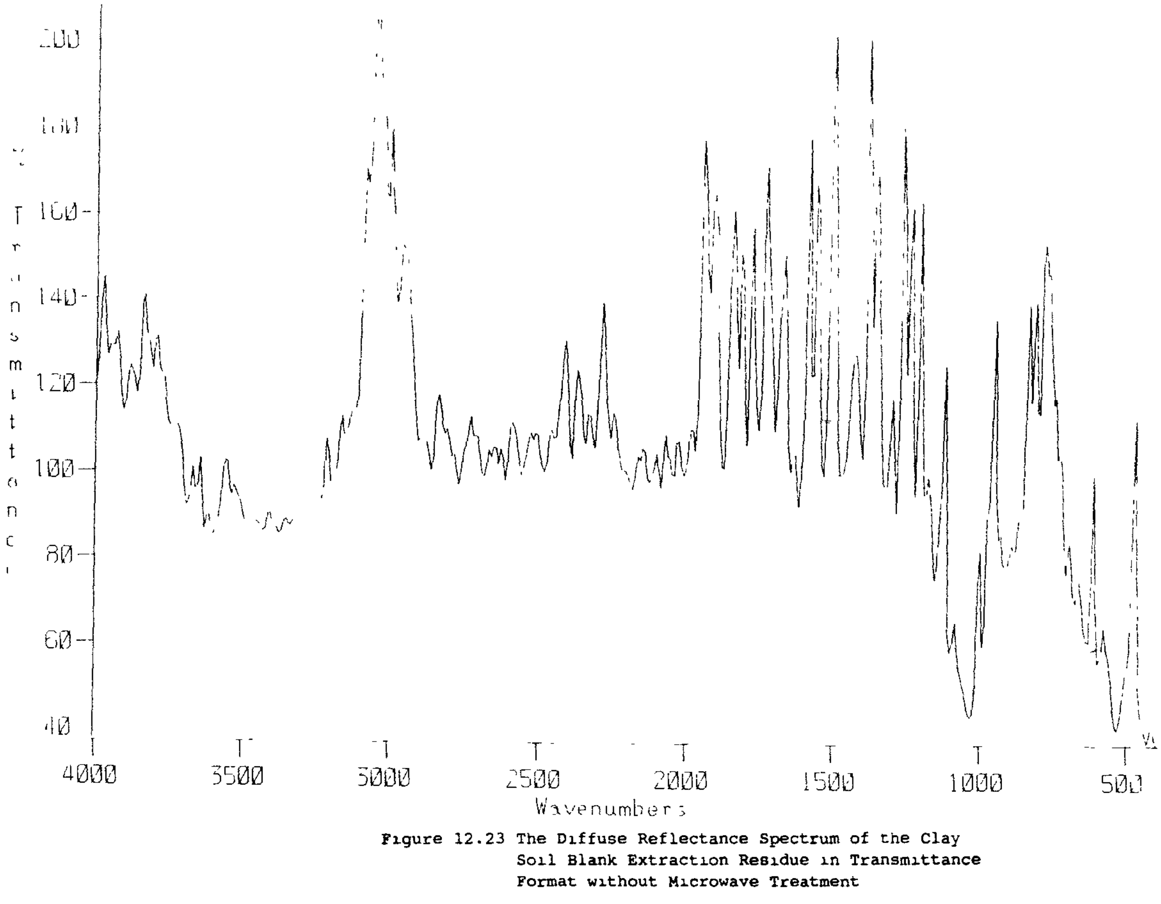


Figure 12.23 The Diffuse Reflectance Spectrum of the Clay Soil Blank Extraction Residue in Transmittance Format without Microwave Treatment

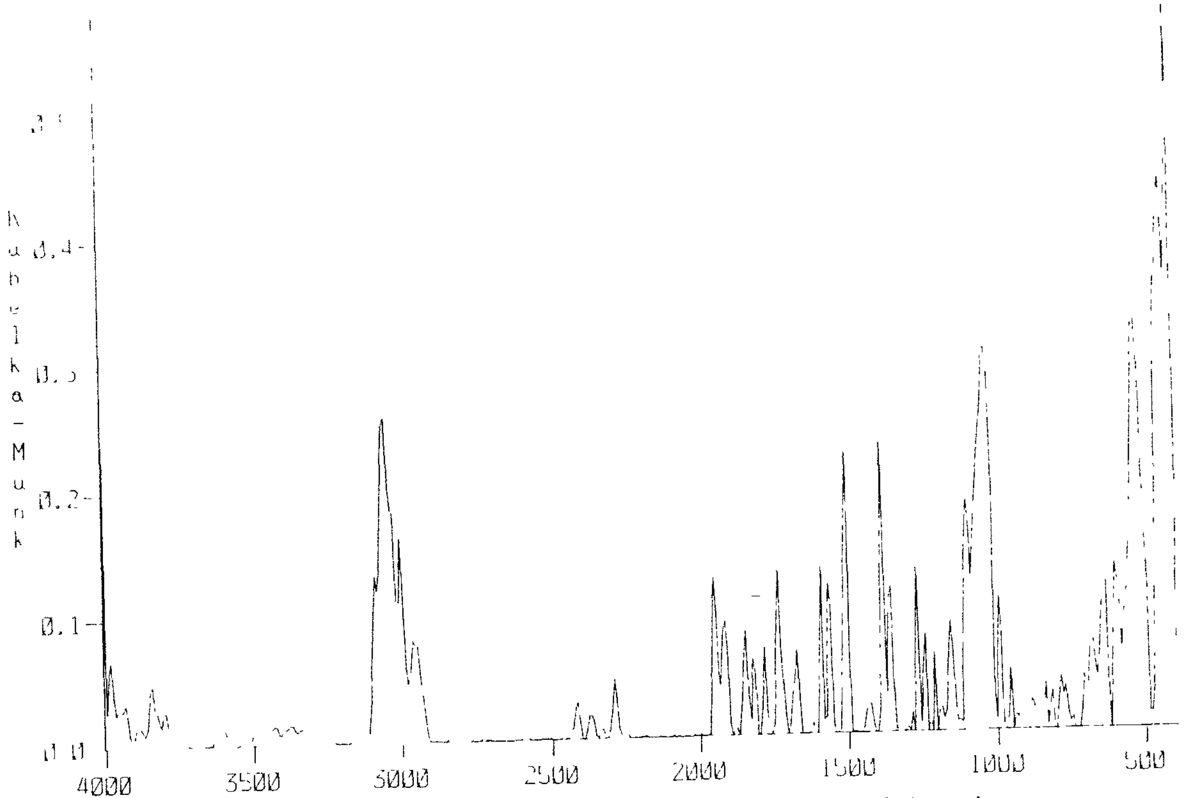


**Figure 12.24** The Diffuse Reflectance Spectrum of the Sandy Soil Blank Extraction Residue in Kubelka-Munk without Microwave Treatment

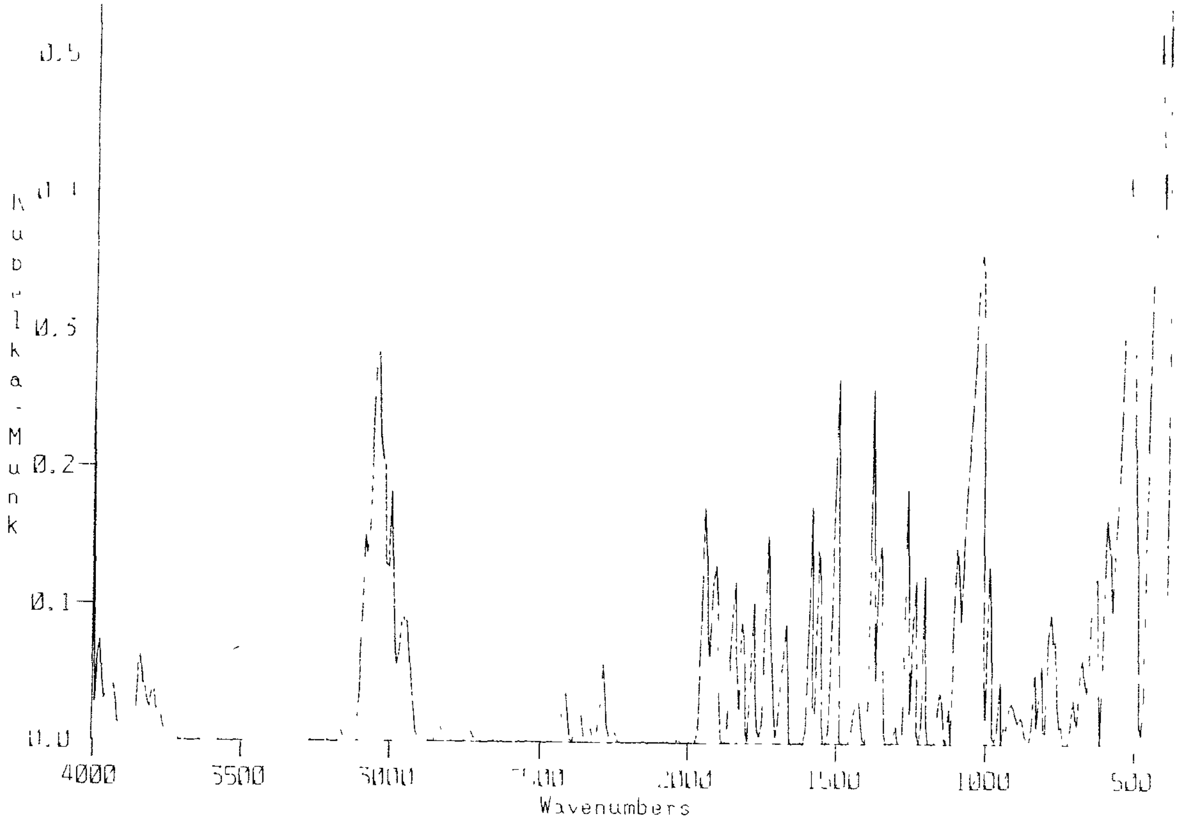


**Figure 12.25** The Diffuse Reflectance Spectrum of the Clay Soil Blank Extraction Residue in Kubelka-Munk without Microwave Treatment

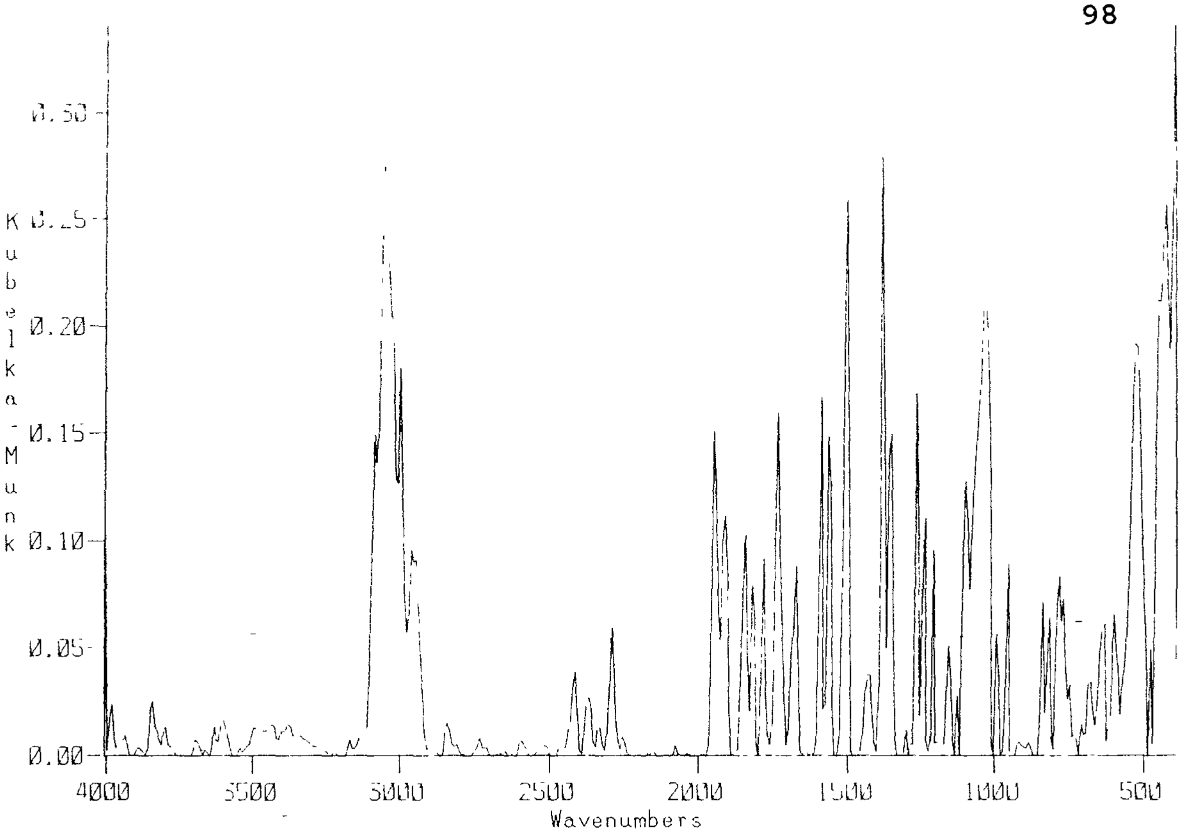


**Figure 12.26** The Diffuse Reflectance Spectrum of the Sandy Soil Extraction Residue in Kubelka-Munk after Microwave Treatment

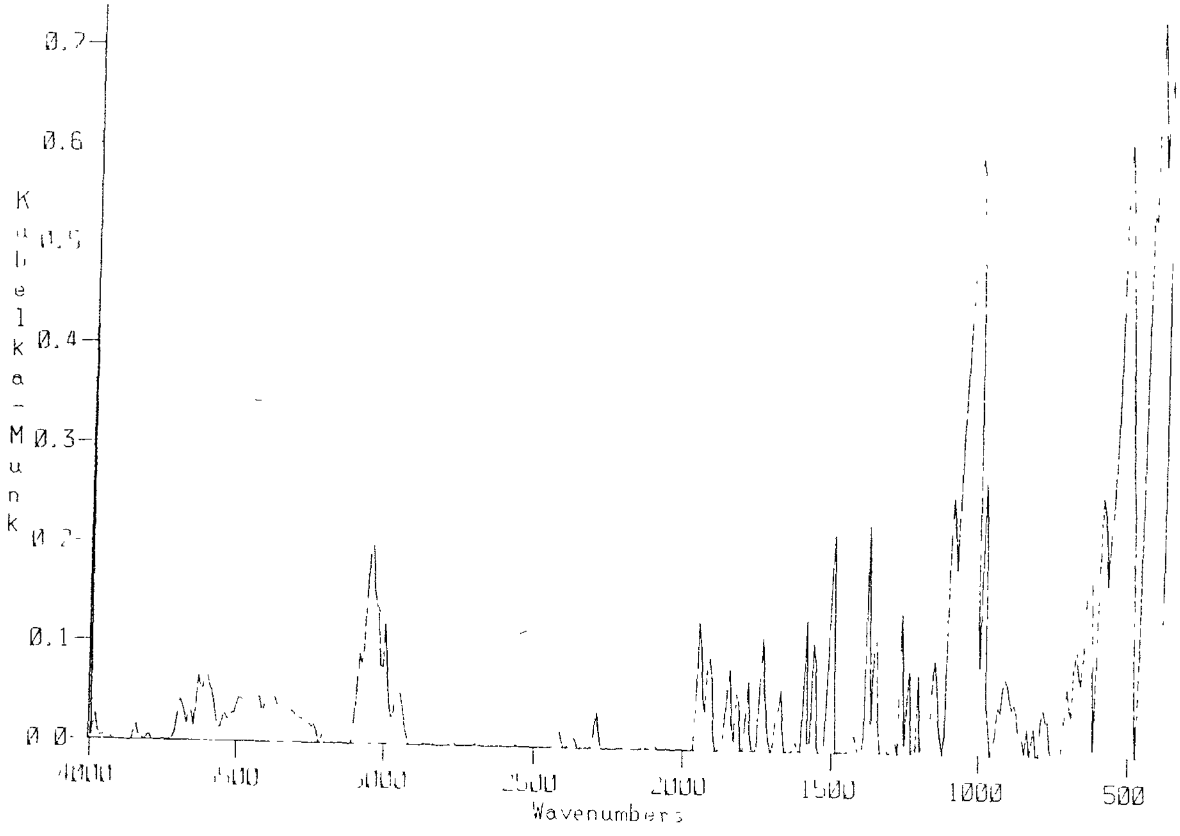


**Figure 12.27** The Diffuse Reflectance Spectrum of the Clay Soil Extraction Residue in Kubelka-Munk after Microwave Treatment.

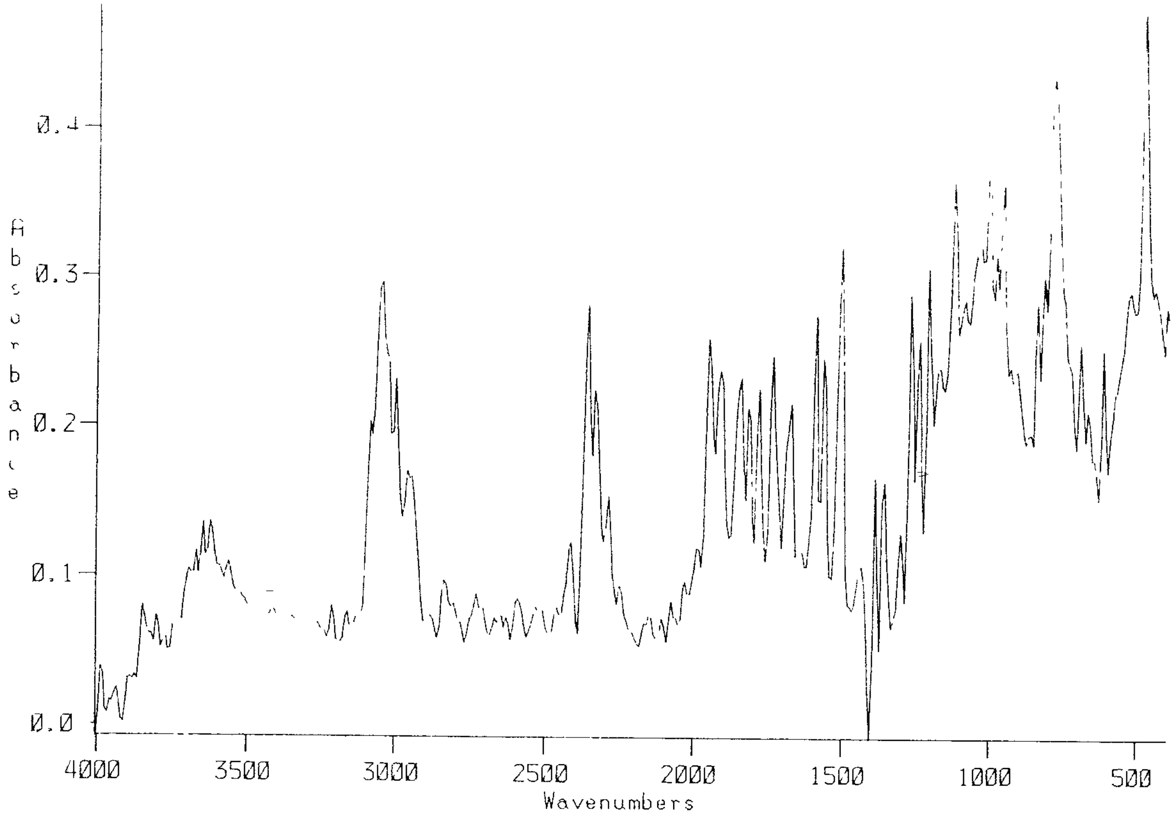


Figure 12.28 The Diffuse Reflectance Spectrum of the Mixture of Pure Sandy Soil and Pure Solid Naphthalene in Absorbance Format without Microwave Treatment

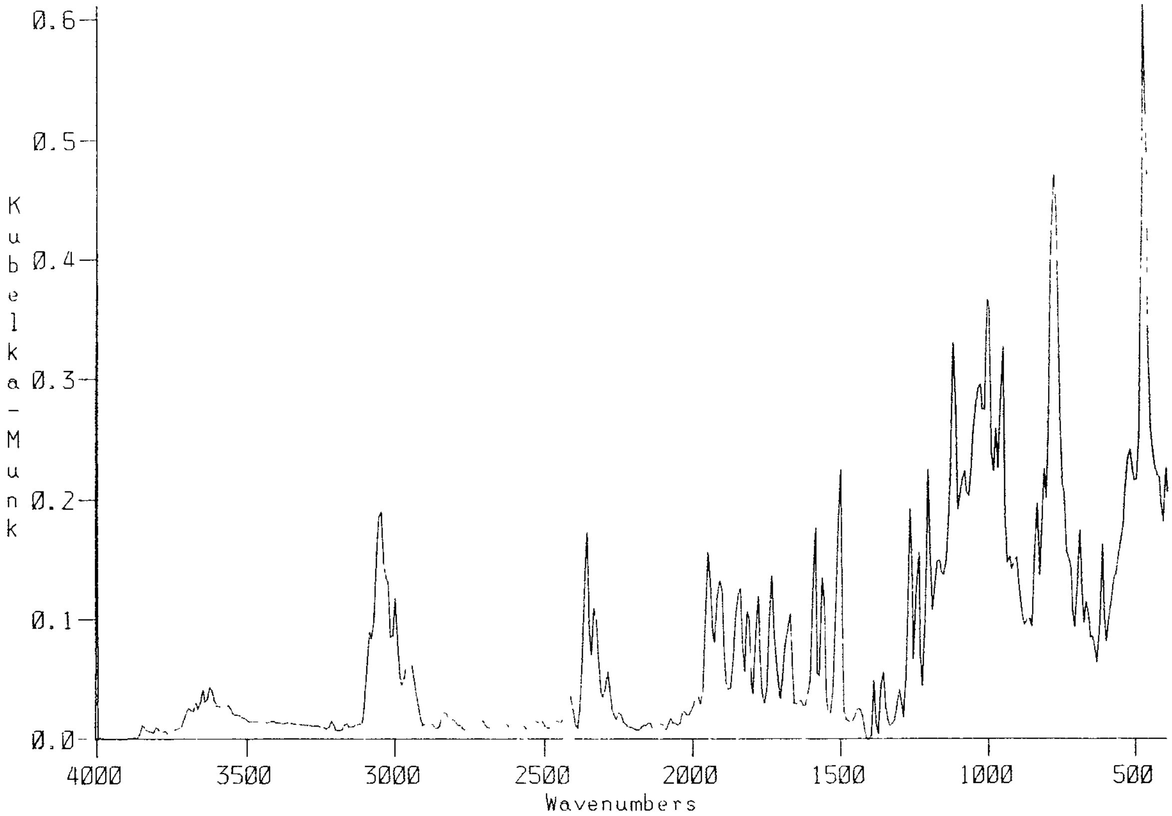


Figure 12.29 The Diffuse Reflectance Spectrum of the Mixture of Pure Sandy Soil and Pure Solid Naphthalene in Kubelka-Munk Format without Microwave Treatment

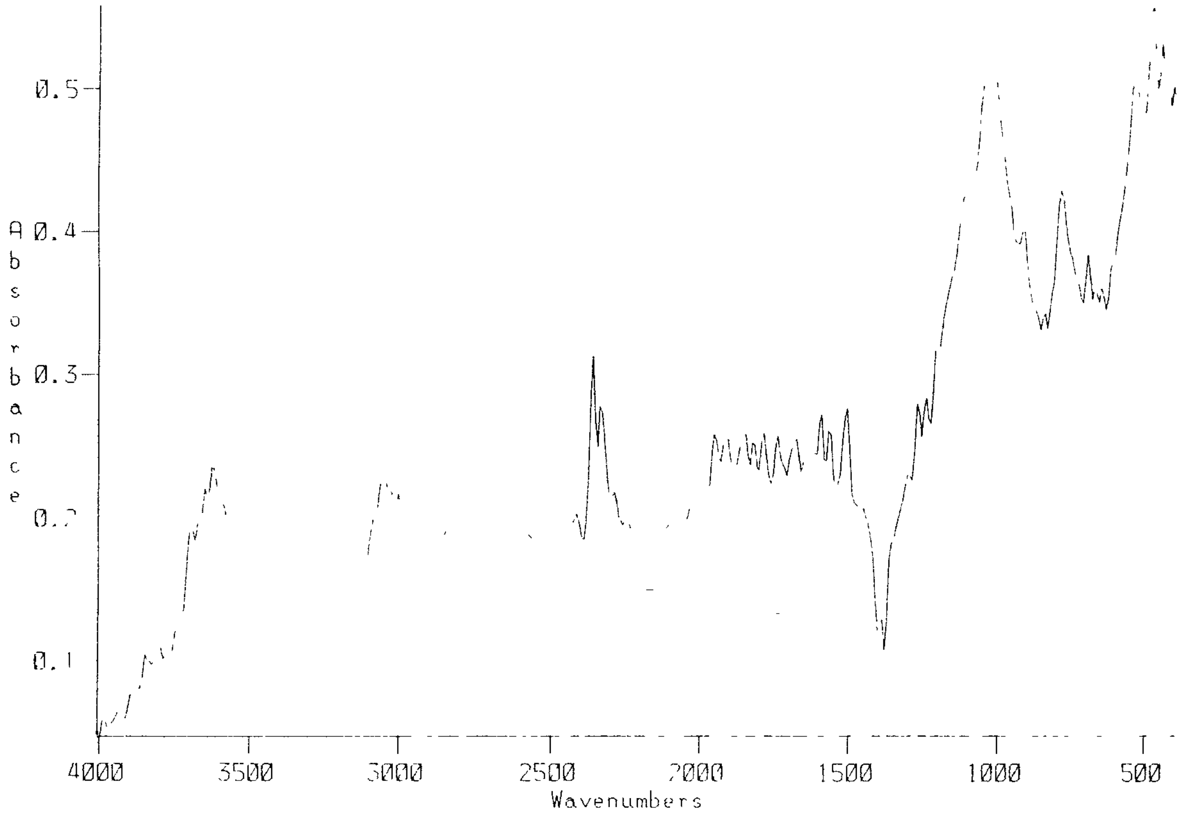


Figure 12.30 The Diffuse Reflectance Spectrum of the Mixture of Pure Clay Soil and Pure Solid Naphthalene in Absorbance Format without Microwave Treatment

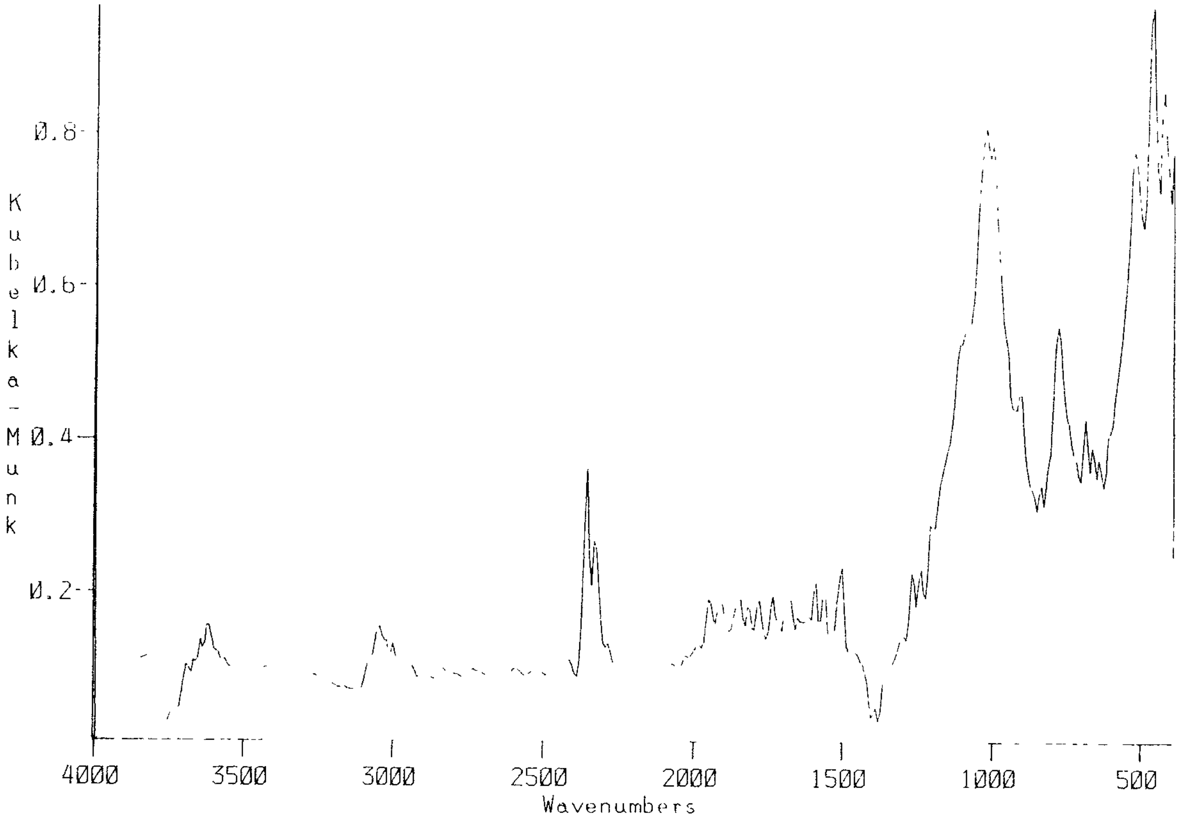


Figure 12.31 The Diffuse Reflectance Spectrum of the Mixture of Pure Clay Soil and Pure Solid Naphthalene in Kubelka-Munk Format without Microwave Treatment

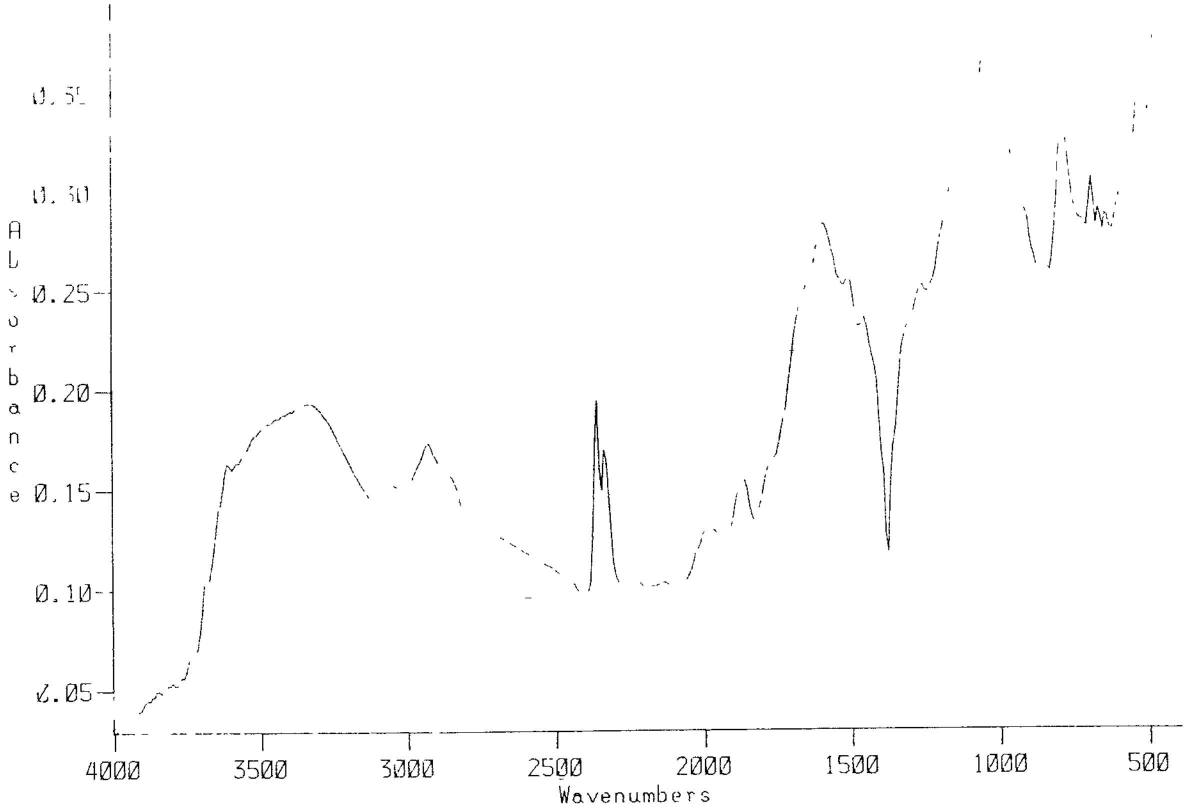


Figure 12.32 The Diffuse Reflectance Spectrum of the Pure Humus in Absorbance Format without Microwave Treatment

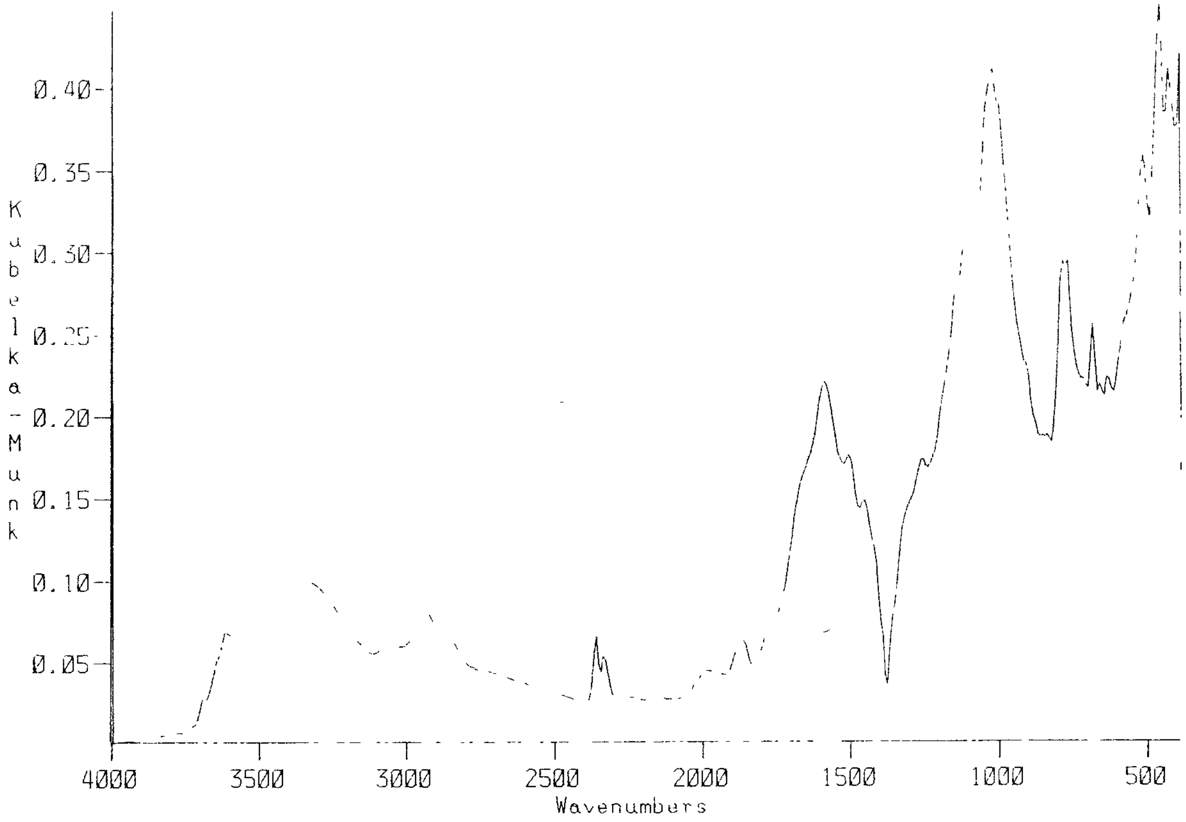


Figure 12.33 The Diffuse Reflectance Spectrum of the Pure Humus in Transmittance Format without Microwave Treatment

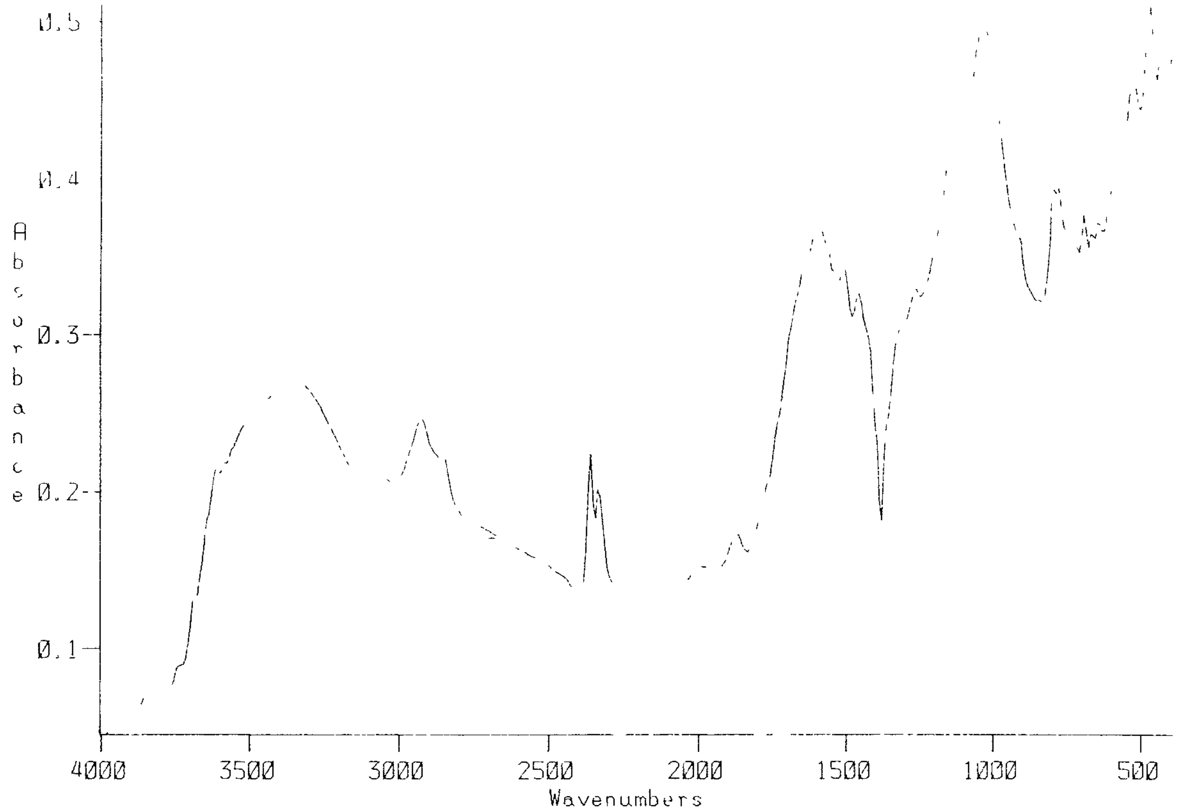


Figure 12.34 The Diffuse Reflectance Spectrum of the Humus Blank Extraction Residue in Absorbance Format without Microwave Treatment

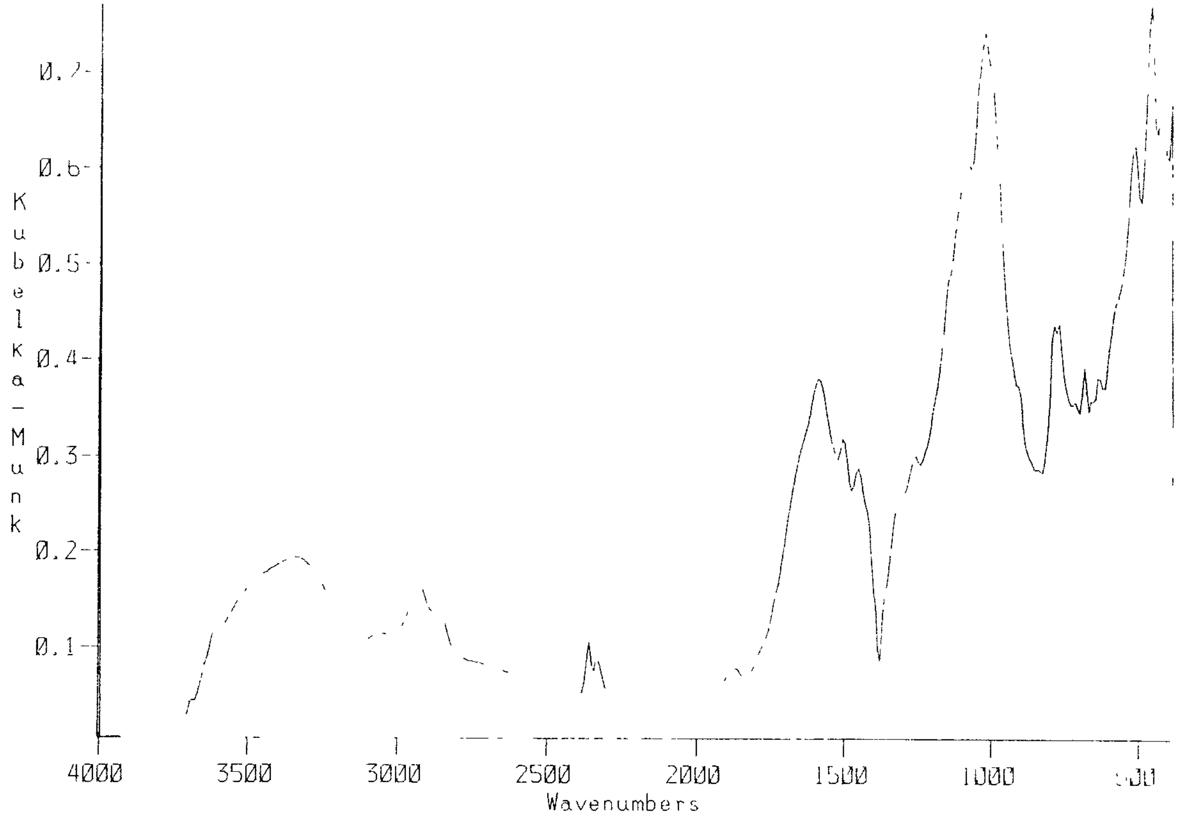


Figure 12.35 The Diffuse Reflectance Spectrum of the Humus Blank Extraction Residue in Kubelka-Munk Format without Microwave Treatment

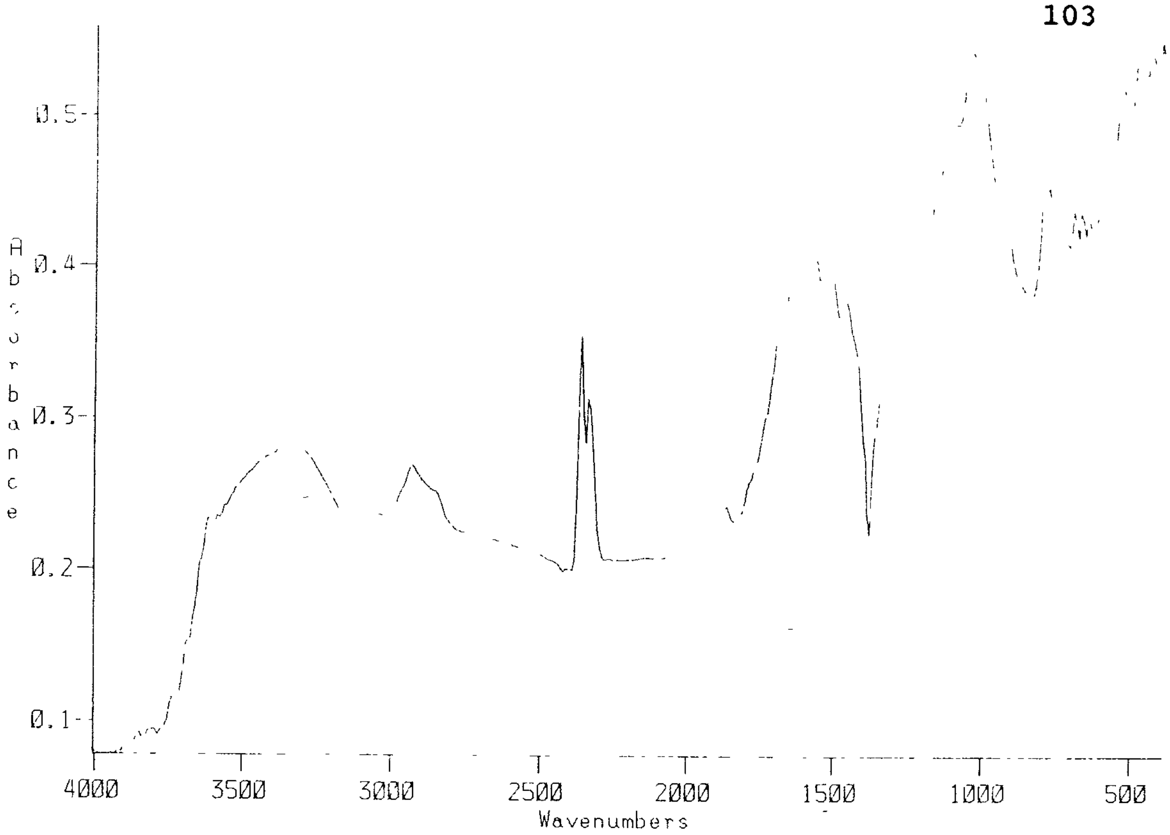


Figure 12.36 The Diffuse Reflectance Spectrum of the Humus Extraction Residue in Absorbance Format after Microwave Treatment

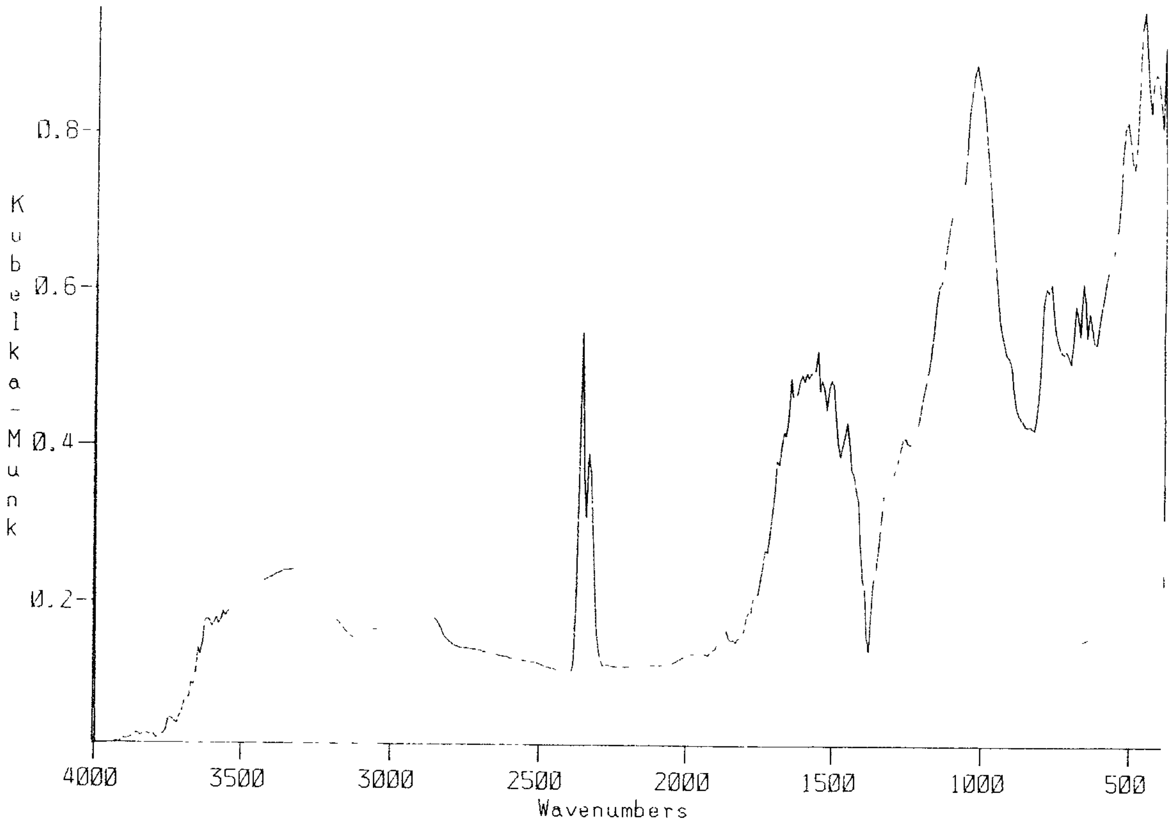


Figure 12.37 The Diffuse Reflectance Spectrum of the Humus Extraction Residue in Kubelka-Munk Format after Microwave Treatment

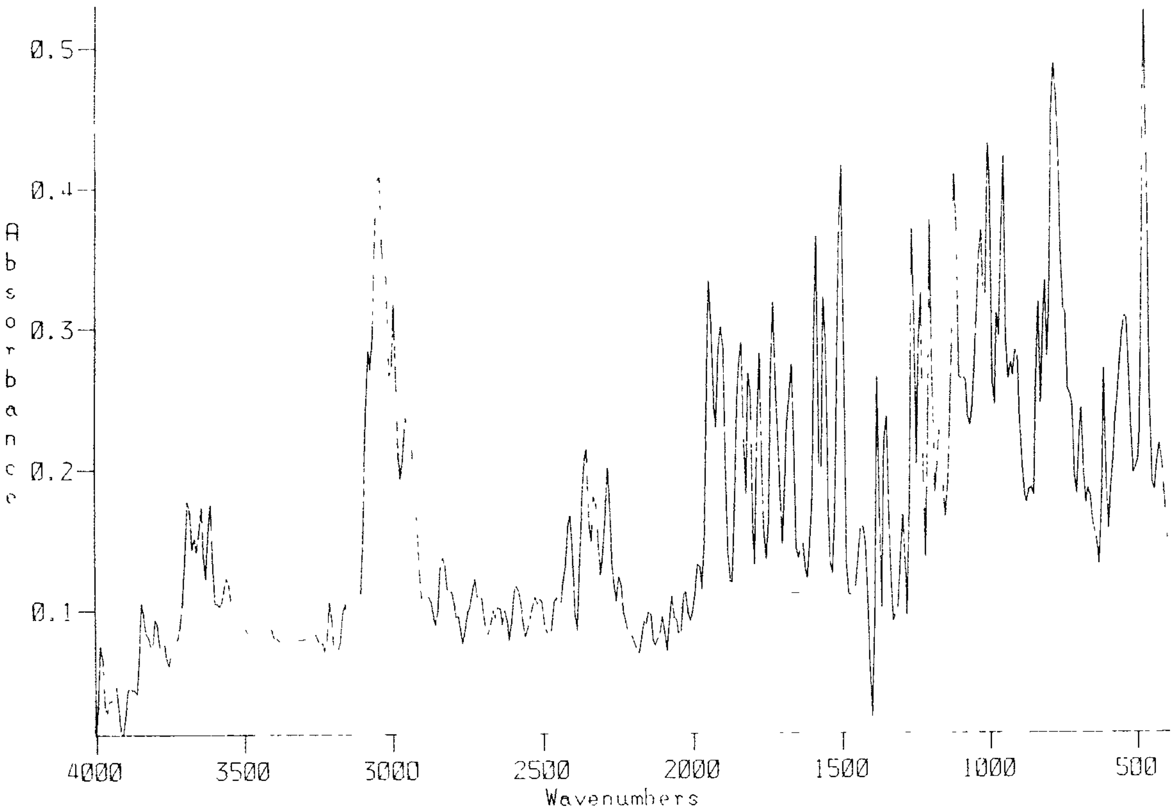


Figure 12.38 The Diffuse Reflectance Spectrum of the Mixture of Pure Humus and Pure Solid Naphthalene in Absorbance Format without Microwave Treatment

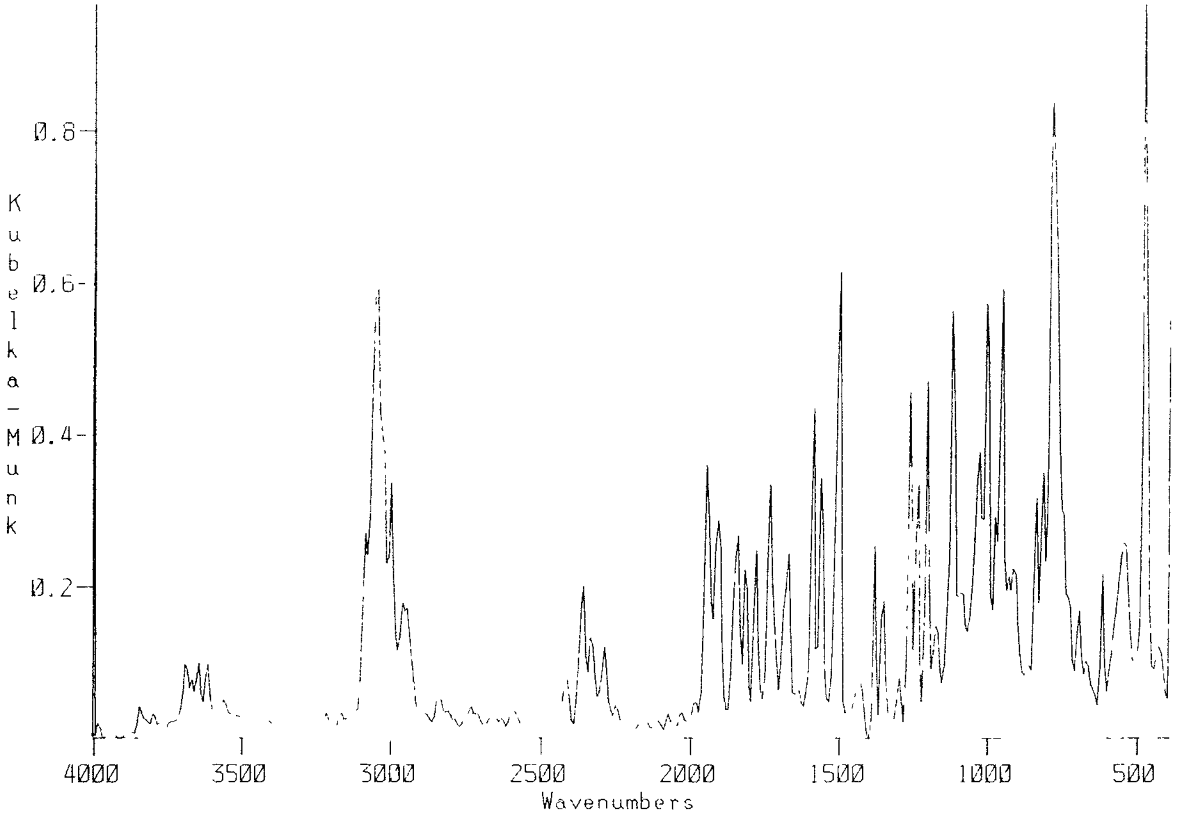


Figure 12.39 The Diffuse Reflectance Spectrum of the Mixture of Pure Humus and Pure Solid Naphthalene in Kubelka-Munk Format without Microwave Treatment

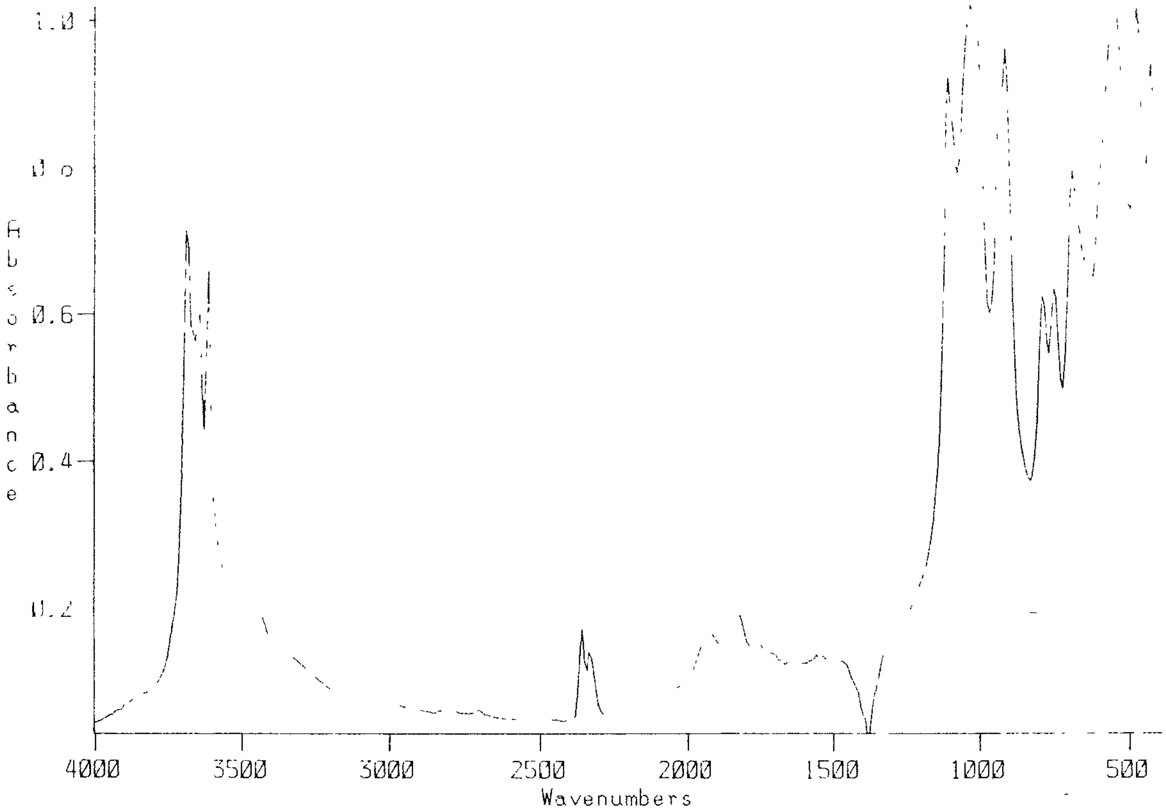


Figure 12.40 The Diffuse Reflectance Spectrum of the Pure Kaolin & Magnetite in Absorbance Format without Microwave Treatment

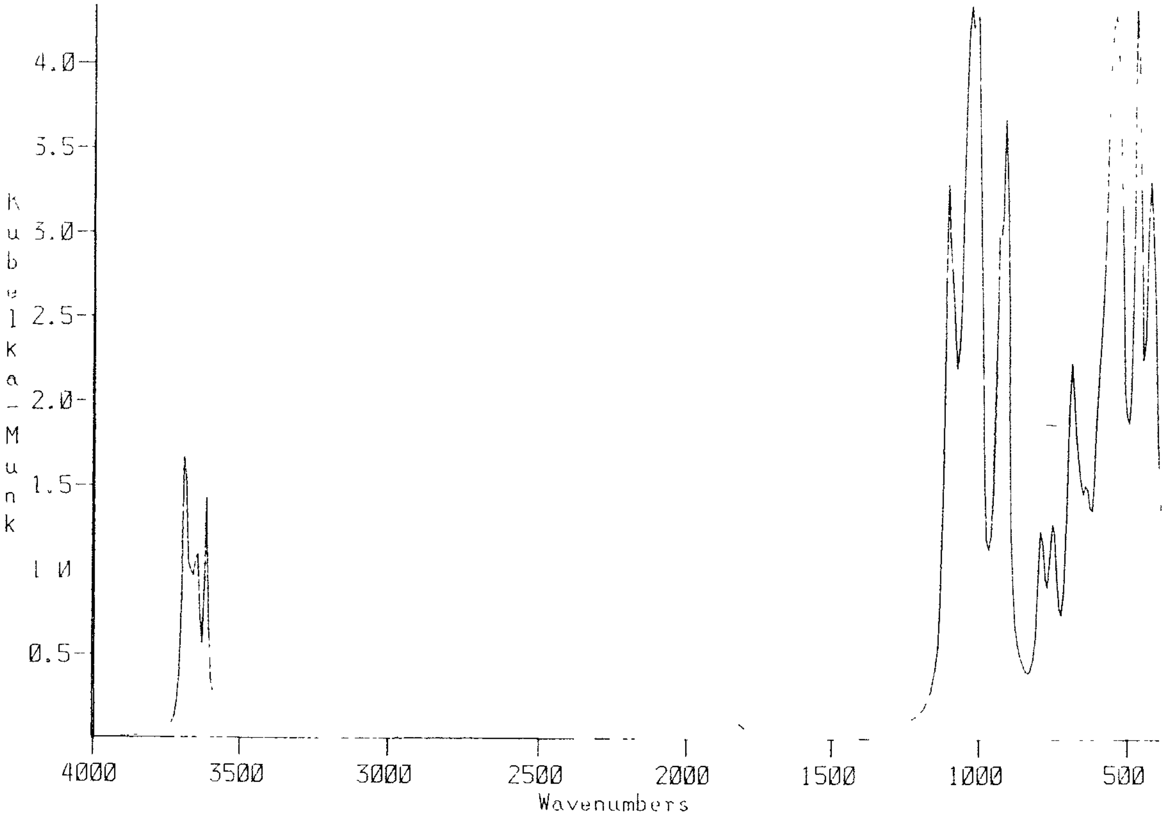


Figure 12.41 The Diffuse Reflectance Spectrum of the Pure Kaolin & Magnetite in Kubelka-Munk Format without Microwave Treatment

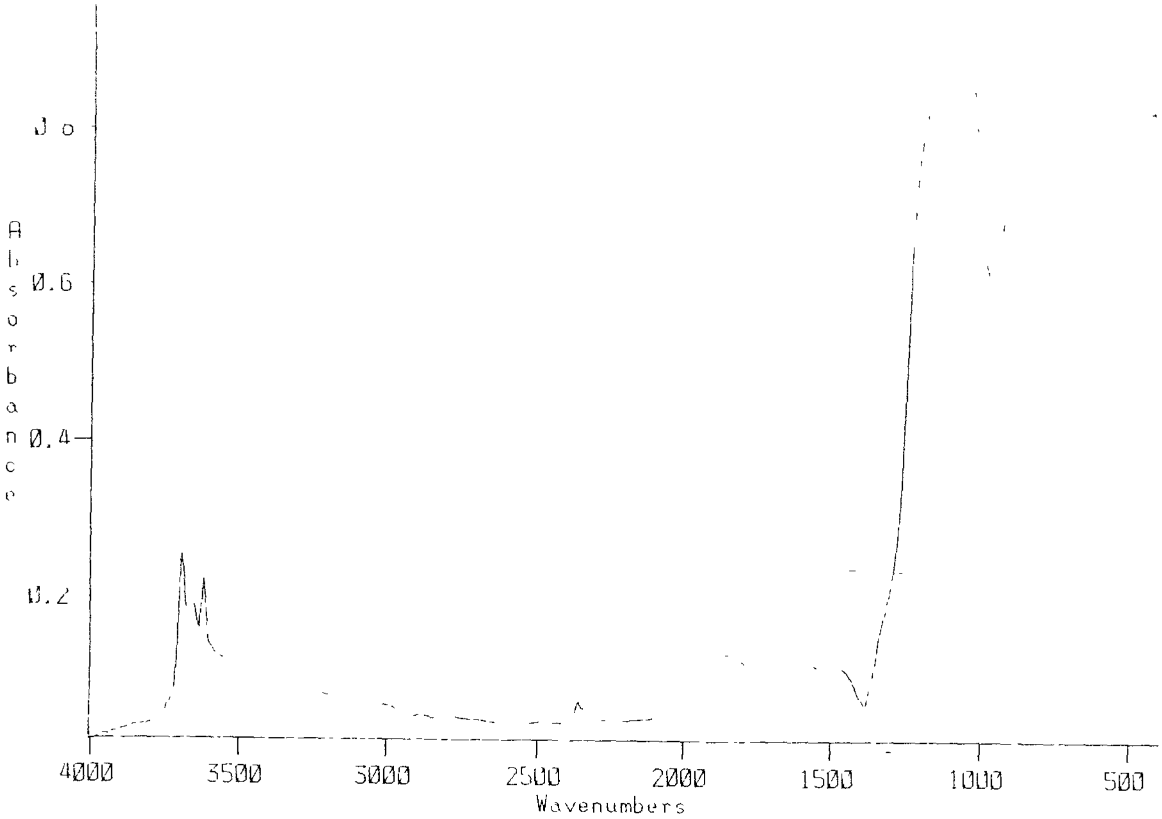


**Figure 12.42** The Diffuse Reflectance Spectrum of the Kaolin & Magnetite Blank Extraction Residue in Absorbance Format without Microwave Treatment

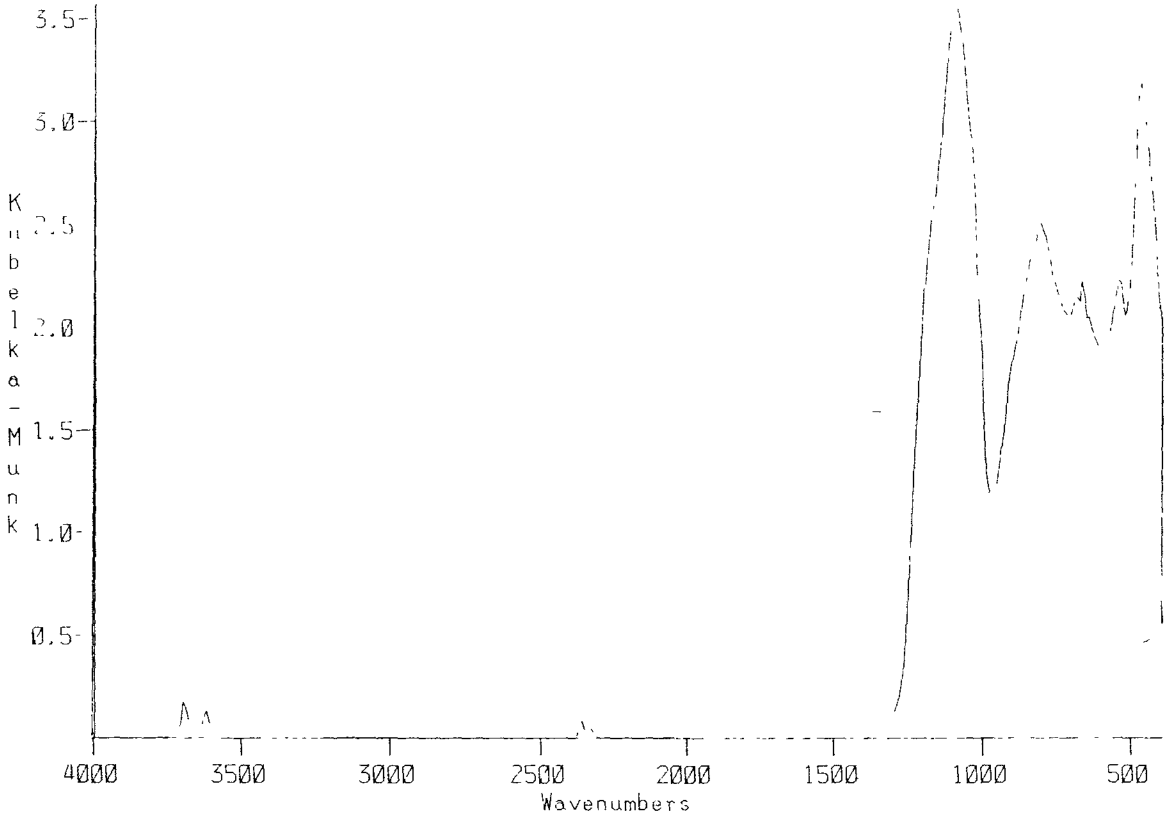


**Figure 12.43** The Diffuse Reflectance Spectrum of the Kaolin & Magnetite Blank Extraction Residue in Kubelka-Munk Format without Microwave Treatment

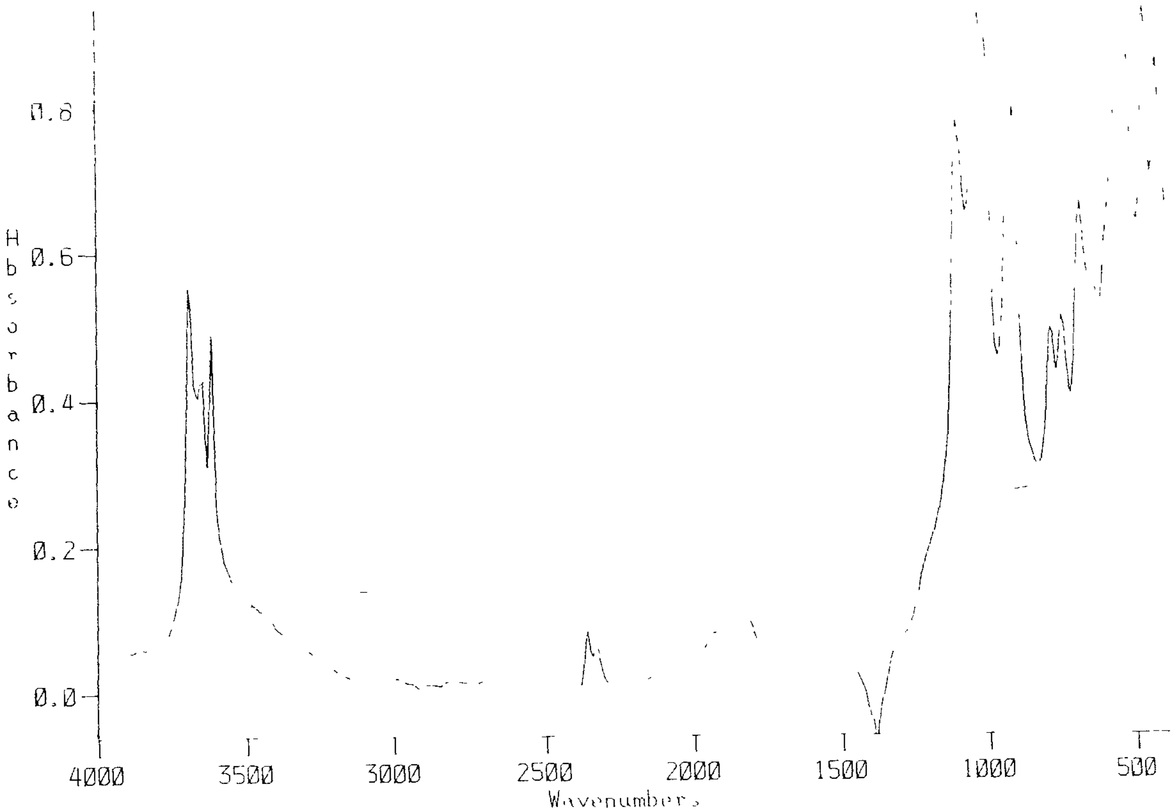


**Figure 12.44** The Diffuse Reflectance Spectrum of the Kaolin & Magnetite Extraction Residue in Absorbance Format after Microwave Treatment

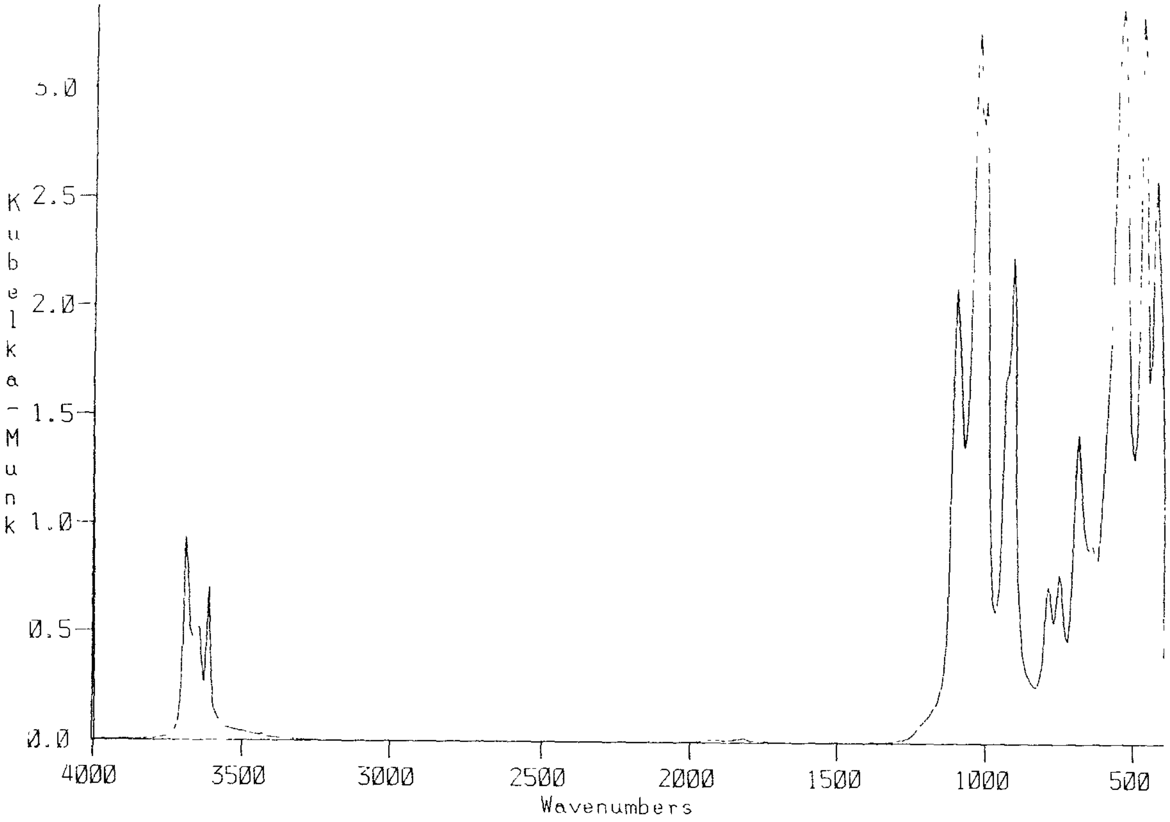


**Figure 12.45** The Diffuse Reflectance Spectrum of the Kaolin & Magnetite Extraction Residue in Kubelka-Munk Format after Microwave Treatment

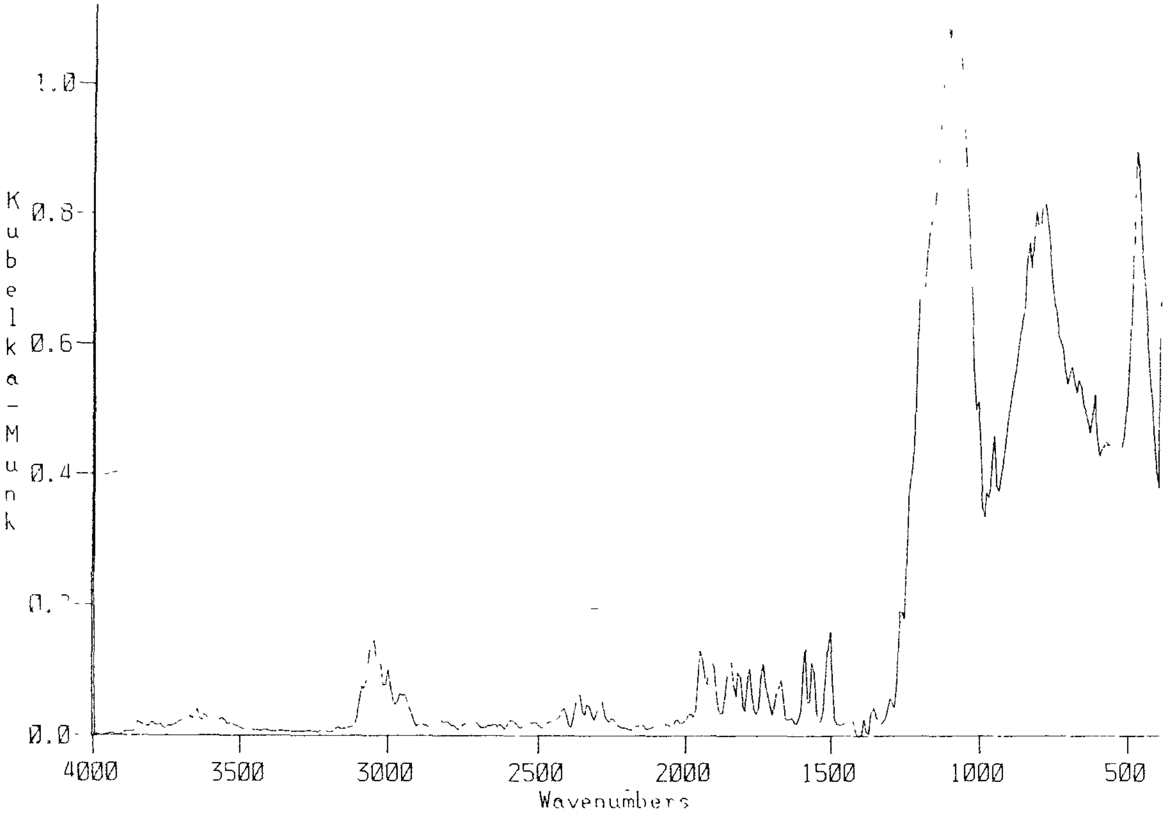


Figure 12.46 The Diffuse Reflectance Spectrum of the Mixture of Pure Kaolin with Magnetite and Pure Solid Naphthalene in Kubelka-Munk Format without Microwave Treatment

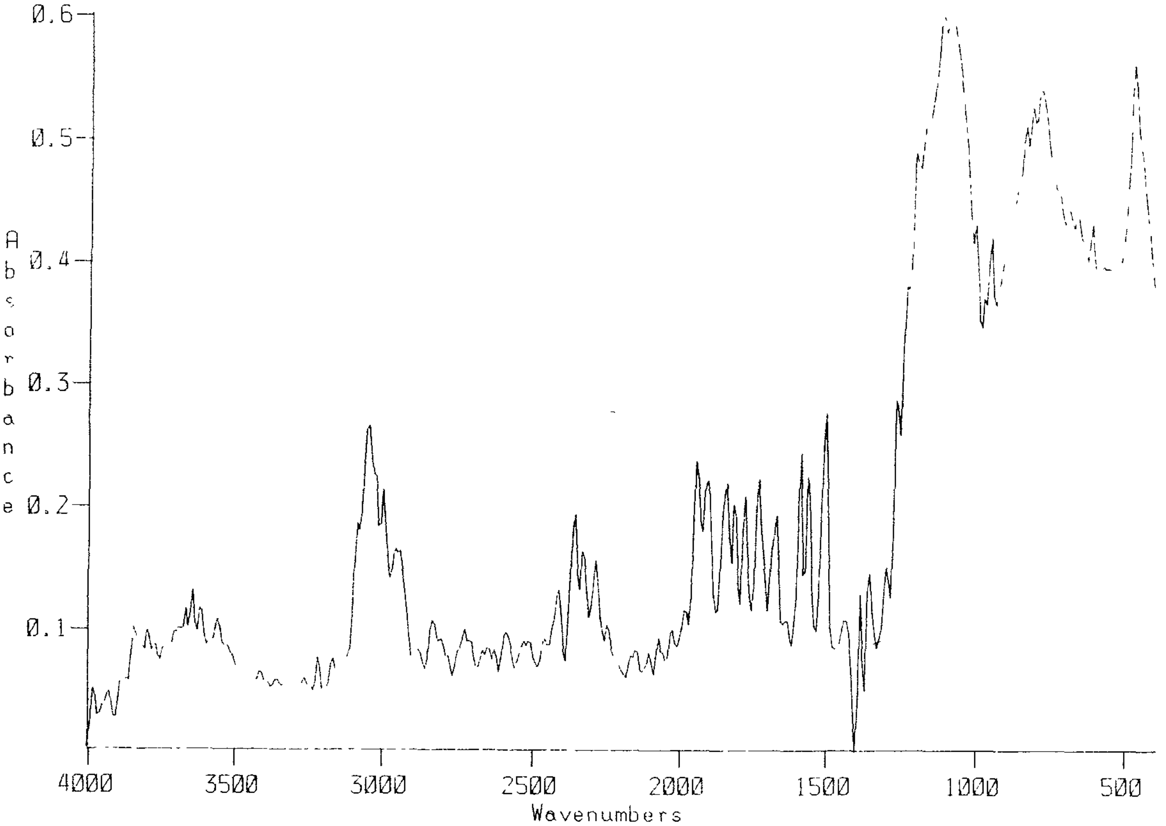


Figure 12.47 The Diffuse Reflectance Spectrum of the Mixture of Pure Kaolin with Magnetite and Pure Solid Naphthalene in Absorbance Format without Microwave Treatment

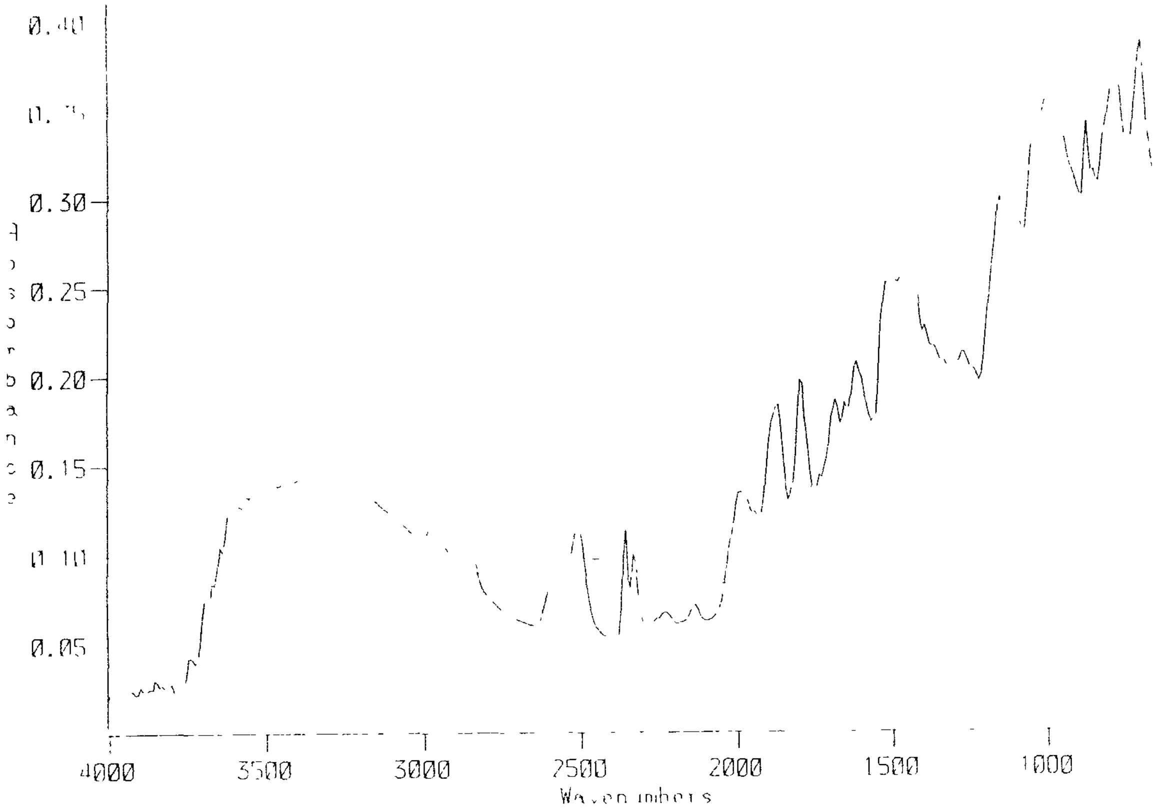


Figure 12.48 The Diffuse Reflectance Spectrum of the Mixture of Sand and Solid Naphthalene Dissolved by Methanol

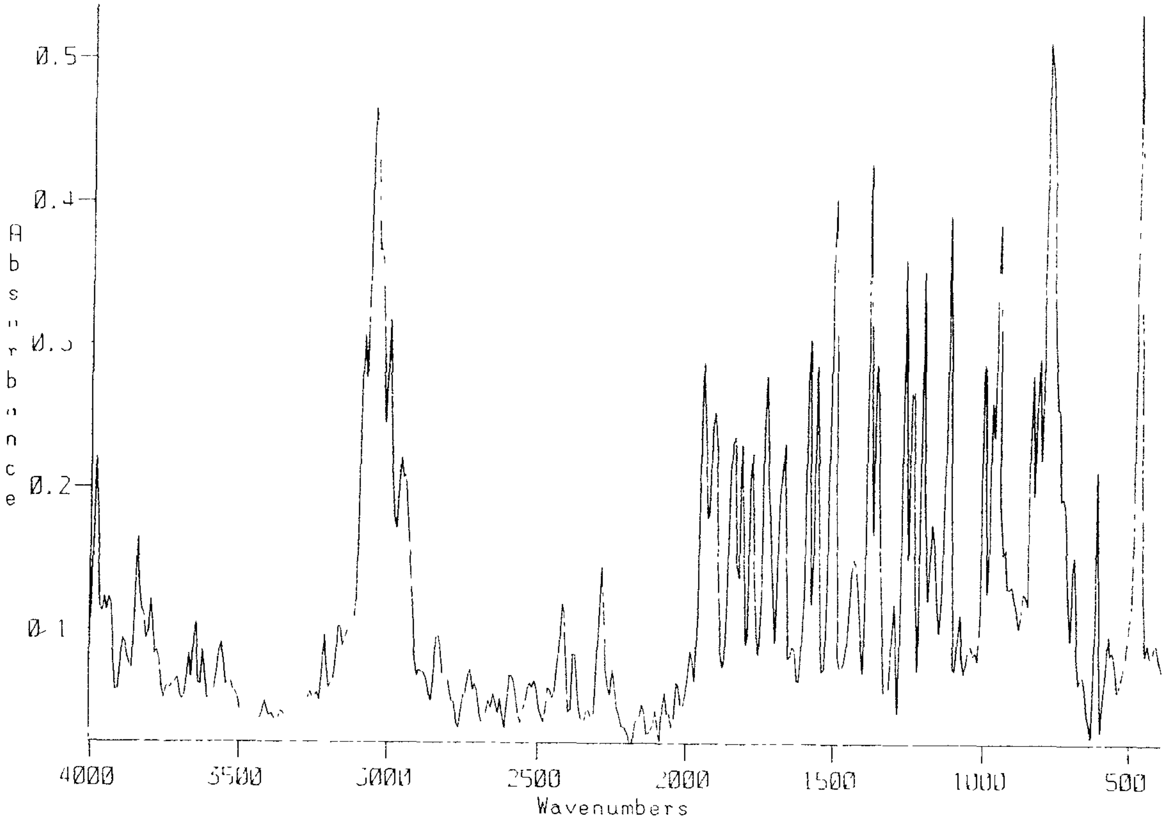


Figure 12.9 The Diffuse Reflectance Spectrum of the Mixture of the Pure Sand and Pure Naphthalene in Absorbance Format without Microwave Treatment

# CHAPTER 13. CONCLUSIONS

Mass balance studies were carried out on the microwave assisted steam distillation of volatile organic chemicals (VOCs) and semi-volatile organics (SVOCs), respectively, from substrates.

The substrates studied were sand and soil, respectively. These substrates were impregnated with naphthalene. The naphthalene concentration in the substrate was 2000 ppm: taking into account the sample size, the total amount of naphthalene was 0.1 gram.

It was assumed that the naphthalene, after treatment, would be in three possible states: a. In the substrate, and recoverable by extraction; b. Volatilized. c. In the substrate, but not extractable. For the first state, the substrate was subjected to Soxhlet extraction; for the second, the gases were trapped in methanol-containing wash bottles situated outside the microwave cavity; and for the potential non-extractables, the substrates were investigated by DRIFT (diifuse reflectance Fourier Transform spectroscopy).

It was found that approximately 85% of the naphthalene could be accounted for by extraction and trapping: no evidence for non-extractables in the substrates was found by DRIFT. Since the sample size was only 0.1 gram, the unaccounted material was approximately 0.015 grams. That amount could have easily been lost due to absorbption on the tubes from the reaction vessel to the wash bottles or by diffusion through connections. It is concluded that mass balnces can be carried out on this system in the manner developed in this study.

Table 13.1 Summary: Total Recovery (%) as a Function of Substrate, Treatment, Time, and Cavity Position

| Substrate | Treatment | Time min. | Position | Total Recovery % |
|---|---|---|---|---|
| sand | thermal | 1.5 | / | 91 +/- 2 |
| sand | microwave | 5 | 1 | 95 +/- 1 |
| sand | microwave | 7 | 1 | 84 +/- 2 |
| sand | microwave | 9 | 1 | 80 +/- 1 |
| sand | microwave | 5 | 2 | 90 +/- 3 |
| sand | microwave | 5 | 3 | 92 +/- 3 |
| sandy soil | microwave | 5 | 3 | 85 +/- 2 |
| Clay soil | microwave | 5 | 3 | 84 +/- 2 |
| Humus | microwave | 5 | 3 | 80 +/- 11 |
| clay with magnetite | microwave | 5 | 3 | 75 +/- 2 |

# CHAPTER 14. FUTURE STUDIES

The mass balance obtained was approximately 85%. It may be desirable to increase that value. To that end, larger sample sizes are needed. That's only practical if the pilot plant is used.

Naphthalene is not a good candidate for DRIFT: the infrared spectrum is not distinctive, basically, absorptions due to C-H bonds, like in soil. A more distinct infrared absorber should be used, like a bromine-containing organic.

## APPENDIX I. OPERATING PARAMETERS

### A. GC/MS ACQUISITION PARAMETER FILE

```
                         DATA:NAPH-LU.A



Miscellaneous
-------------

Description               : STANDARD
Operator                  : GABRIELE/LIULIU/LUCY
Date & time               : 21 Feb 92  1:23 pm
Inlet                     : GC
Configuration file        : DATA:DECTUNE.U
Acquisition mode          : Scan
Electron Multiplier       : -200.00
EM absolute               : FALSE



Temperature Zones
-----------------

Initial temperature       : 70.00
Initial time              : 0.00
Equilibration  time       : 0.20

                      Set Points       Soft Limits      Status
                      ----------       -----------      ------
Oven                      50               300            On
Inj Port A                 0               250            Off
Inj Port B               210               250            On
Transfer Line            220               300            On
Ion Source                 0               250            On
Mass Analyzer              0               300            On
Detector A                 0               250            Off
Detector B                 0                 0            On
```

```
                        ACQUISITION PARAMETER FILE

                              DATA:NAPH-LU.A



Plot Parameters
---------------

Plotting Active           : TRUE
Plot Start Time           : 0.00
Number of plots           : 1
Time Window               : 10.00

Display 1

Low mass      : 10.00
High mass     : 800.00
Scale         : 1000000.00
Plot type     : Total Ion



Als control
-----------

Number of Sample Pumps    : 1
Number of Sample Washes   : 1
Number of A washes        : 1
Number of B washes        : 1
Pre-wash bottle           : 1
Post-wash bottle          : 0
Stroke                    : Full
Viscosity                 : High
Injector mode             : On column
Injection mode            : MANUALLY
```

```
                         ACQUISITION PARAMETER FILE

                              DATA:NAPH-LL.A



Run Table entries
-----------------

Run table 1

Time          : 0.00
Class         : Oven program
Ramp Rate     : 150
Final Temp    : 180
Hold time     : 3.50

Run table 2

Time          : 0.00
Class         : Group
Number        : 1

Run table 3

Time          : 0.00
Class         : Mass Spec
State         : On

Run table 4

Time          : 10.00
Class         : Stop run
```

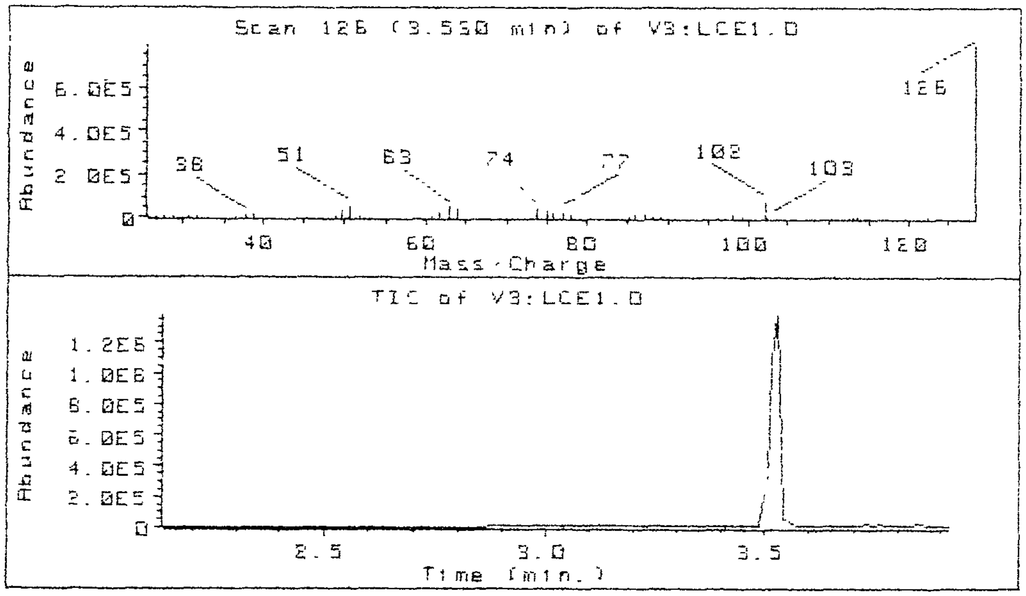
```
                         ACQUISITION PARAMETER FILE

                              DATA:NAPH-LO.A




Group Entries
-------------

Number of Groups : 1

Group 1


   Channel 1

      Low mass           : 10.00
      High mass          : 200.00
      Number of samples  : 4
      Peak threshold     : 1000
```

## B. DRIFT OPERATING PARAMETERS

DRIFT and ATR/FTIR Operating Parameters

```
<<< parameter set CURRENT.PV >>>
APT=OPEN           LEFT=3500.0        SAMP10=            UDR=2
APTYP=TRIANG       MENCOL=740b80b00b00SAMP2=AKK1T        XSB=0
BACK=KBR2          MICRONRES=0.01     SAMP3=             XSCALE=100
BANDEDGE1=0.2      MORE=N             SAMP4=             XSIZE=AUTO
BANDEDGE2=0.8      NEWSPEC=AB1T       SAMP5=             YMAX=AUTO
BEAM=INT           NLV=0.05           SAMP6=             YMIN=AUTO
DAPTYP=TRIANG      NPOINTS=AUTO       SAMP7=             YSCALE=100
DELAY=1.0          ORDER=2            SAMP8=             YSIZE=AUTO
DET=INT            ORIENT=NORMAL      SAMP9=             ZFF=2
DSPCOLOR=DIFFERENT PAPERSIZ=SM        SCANS=64
DSPMOVE=TOGETHER   PAXES=Y            SCANTO=TR
DSPOFFSET=NONE     PCOMM=NONE         SCBACK=1.000
ELWN=15800.8235    PEN=AUTO           SCNSTOR=256
ENP=AUTO           PKSENS=1           SCSAMP=1.000
FFP=4000.0         PKSOURCE=G/S       SEN=4
FGNULL=/usr/lib/fgnPKTAB=Y            SIGNAL=AUTO
FGREG=/usr/lib/fgrePLABEL=ATC 313 LAB.SPEC=SPEC40
FILTLO=1           PLOTPAGE=Y         SPEED=5
FLP=400.0          PLOTTER=AUTO       SSP=NO
FLTRTYP=BP         PLUNITS=CM         STP=AUTO
GCAP=N             PPARMS=RES         SUBFAC=0.0
GCDELAY=0          PSDESC=            SUBTYPE=H2O
GCNBACK=20         PXOFF=0.0          SUMAX=AUTO
GCNBASIS=20        PYOFF=0.0          SUMIN=AUTO
GCTIME=45          REF=POLYR          SVIG=N
GRR=40             RES=4              SVIM=N
HWIDTH=10.0        RIGHT=3300.0       SVMR=N
INTFACT=1          RUNCOMMENT=        SVSB=N
KMBASE=AUTO        RUNTITLE=          SYM=ASYM
KVAL=2.0           SAMP=AB1T          TRANSBW=0.05
```

## C. TOTAL ION CHROMATOGRAM AND MASS SPECTRUM OF NAPHTHALENE



```
                                      T: null.
                                      Z: TIC of V3:LCE1.D
DRAW done                             Y: null.
[DE]                                  X: Scan 128 (3.530 min) of V3
```

# APPENDIX II

## Publications and Presentations on Microwave Studies

(NJIT Microwave Treatment of Hazardous Wastes Laboratory)

Windgasse, G. and Dauerman, L. 1992. Microwave Treatment of Hazardous Wastes: Removal of Volatile and Semi-Volatile Organic Contaminants from Soil. Journal of Microwave Power and Electromagnetic Energy 27(1): 1992.

Zhu, N., Dauerman, L., Gu, H. 1992. Microwave Treatment of Hazardous Wastes: Remediation of Soils Contaminated by Non-Volatile Organic Chemicals Like Dioxins. Journal of Microwave Power and Electromagnetic Energy 27(1): 1992.

Sedhom,E., Dauerman,L., Ibrahim, N., and Windgasse,G. 1992. Microwave Treatment of Hazardous Wastes: 'Fixation' of Chromium in Soil. Journal of Microwave Power and Electromagnetic Energy 27(1): 1992.

Dauerman, L. and Windgasse, G. 1990. Microwave Treatment of Hazardous Wastes. Mikrowellen & HF Magazin 16(4) 329-331.

Dauerman L. and Windgasse G. 1990. Microwave Treatment of Hazardous Wastes. TIZ International 114: 7/8- 503 - 506.

Dauerman, L., Windgasse, G., Gu,H., Ibrahim, N., and Sedhom,E. 1991. Applications of Microwave Treatment of Hazardous Wastes: a) Non-Volatile Organics; b) Heavy Metals. in Microwave Processing of Materials II Materials Research Society pp 61-67.

Dauerman, L., Windgasse, G., and Zhu, N. 1991. Microwave Treatment of Hazardous Wastes: 'Chemical Fixation' of Organics Like Dioxins in Contaminated Soil. Proceedings of the International Congress on Microwaves and High Frequency Volume II, p. 283 Nice, France.

Dauerman, L. and Windgasse, G. 1990. Microwave Treatment of Hazardous Wastes: Chemical Mechanisms; Proceedings of the Industrial Microwave Processing Conference, Deakin University, Geelong, Australia, Section 6.

Dauerman, L. and Windgasse, G. 1989. Microwave Treatment of Hazardous Wastes. Proc. KEMA Intl. Conf. on High Frequency/Microwave Processing and Heating, Arnhem, The Netherlands. 6-6-1 to 6-6-5.

Dauerman, L., Windgasse, G., and Ray, A. B. 1988. Microwave Radiation Treatment of Hazardous Wastes A. Treatment of Substrates; Proceedings of the American Institute of Chemical Engineer's Annual Meeting, Denver, CO.

Windgasse, G., Dauerman, L., and Ray, A.B. 1988. Microwave Treatment of Hazardous Wastes: B. Treatment of Volatiles; Proceedings of the American Institute of Chemical Engineer's Annual Meeting, Denver, CO.

Dauerman,L. 1991. Microwave Treatment of Hazardous Wastes: Dioxin-Contaminated Soil. Givaudan, Inc., Clifton, NJ, June 3, 1991.

Dauerman, L. 1991. (invited panelist) Workshop: Electric-Driven Separation Technologies. Sponsored by Electrical Power and Research Institute (EPRI), AIChE Annual Meeting.

Dauerman, L. and Windgasse, G. Microwave Treatment of Hazardous Wastes: Physical Chemical Mechanisms. 1992. Materials Research Society, San Francisco, CA.

Dauerman, L. and Windgasse,G. Microwave Treatment of Hazardous Wastes. 1992. International Conference On

Hazardous Waste Management: Technology, Perception, and Reality. Atlantic City, New Jersey.

Dauerman, L. Microwave Treatment of Hazardous Wastes. 1991. EPA Science Advisory Board Meeting NJIT, April, 1991.

Dauerman,L. 1988. A Novel Flow Reactor: Kinetics of the Decomposition of Volatilized Trichloroethylene in a Fluidized Bed of GAC in a Microwave Field, seminar, Department of Chemical Engineering, Tulane University, New Orleans, La.

Dauerman, L. 1988. panelist, Workshop Session on Research Needs, International Conference on Physiochemical and Biological Detoxification of Hazardous Wastes. Atlantic City, New Jersey.

Fan, S. 1989. Microwave Treatment of Organic Contaminated Soil, MS Thesis. New Jersey Institute of Technology, Newark, N.J. 07102.

Gu, H. 1990. The Application of Microwave Technology to the Remediation of Non-Volatile Organic Contaminated Soil. MS Thesis, New Jersey Institute of Technology, Newark, N.J. 07102.

He, Y. 1990. Microwave Treatment of Hazardous Wastes: Benchscale and Pilot Plant Studies. MS Thesis. New Jersey Institute of Technology, Newark, N.J. 07102.

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