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Microwave treatment of hazardous wastes : feasibility studies - Operating costs

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ABSTRACT

Microwave Treatment of Hazardous Waste: Feasibility Studies-Operating Costs

by

Yongping Lu

Pilot plant studies have been carried out on a process for the remediation of soils contaminated with volatile organics (VOCs) and semi-volatile organics (SVOCs) by microwave-assisted steam distillation that had been developed in benchscale studies. The major concern had been that the process is based upon the use of electrical energy, and thus could not be competitive with fossil fuel based technologies like incineration. That concern was addressed in the pilot plant studies.

A pilot plant rated at 6 kW power and a cavity of approximately 60 cubic feet was used. In studies carried out on a water load it was found that the incident power was 4.3 kW. In those studies, the distribution of energy within the cavity was also studied.

Substrates studied were sand and soil, respectively. The total weights of the subtrates were in the 40-50 lb range. The substrates were impregnated with naphthalene. It was found that the remediation costs were of the order of $4/ton to effect 100% remediation. Even if total power operating costs are taken into consideration, the cost is less than $15/ton. That's an exceedingly low number. For incineration, costs are in the $200-$300/ton range, plus the ash problem and the public's dislike of

incineration processes.

The costs obtained in this study cannot be considered as a basis for making comparisons to existing processes. Comparable costs can only be obtained from field testing, now in the planning stage. Their significance is that it does not appear to be the case that the microwave process is prohibitively expensive because of the cost of electric power.

Other studies in the thesis related to analytical procedures: it was concluded that ultrasonic extraction was preferrable to Soxhlet extraction; also, normal needle injection into the GC/MS was as effective as hot needle injection.

MICROWAVE TREATMENT OF HAZARDOUS WASTES: FEASIBILITY STUDIES - OPERATING COSTS

by
Yongping Lu

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and Environmental Science
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APPROVAL PAGE
Microwave Treatment of Hazardous Waste: Fesibility Studies-Operating Costs

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TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

CHAPTER 1 INTRODUCTION

This thesis addresses the problem of remediating soils contaminated with hazardous wastes. This is an enormous problem: thousands of such sites exist within the United States. Many of them are classified as Superfund sites: sites which are remediated based upon federal laws and federal administrative regulations. There is a protocol followed in order to decide how to remediate such facilities: a. A Remediation Investigation (RI) is carried out: the hazardous wastes are identified, characterized, and located; b. A Feasibility Investigation (FI) report is issued which specifies recommended and alternative treatments and their associated costs; c. The United States Environmental Protection Agency (EPA) issues a Record of Decision (ROD) in which a specific treatment is recommended: Usually, in the case of organic contaminated soil, the recommended treatment is incineration on the site; d. A public hearing is held on the EPA recommendation: Usually, the recommendation is rejected by the local populace.

The response of the EPA is to seek alternate technologies which will be acceptable to the local community. Therefore there is a need for non-destructive alternate technologies to treat contaminated soil.

This process of rejection of the recommended technology of incineration at a Superfund site, and the call for alternative technology, is illustrated by the Superfund site called Southern Maryland Wood Treating Site in Hollywood, Maryland (1). This site is an abandoned wood treating facility which operated from 1965 to 1978. It was a pressure treatment facility for wood preservation using creosote and pentachlorophenol (PCP). The site covers 25 acres, surrounded by residential, agricultural, and wooded areas. It was an operated by L. A. Clarke and Sons from 1965 to 1978. In 1978, the operator went bankrupt and abandoned the site. Wastes generated on the site included retort and cylinder sludges, process wastes and spillage. Six unlined lagoons were used on-site for disposal. More specifically the hazardous wastes include: a) A total of 100,000 cubic yards of soil contaminated primarily with carcinogenic PAHs and PCP, also, octa and hecta dioxins. b) Shallow groundwater contains VOCs in the 10-100 ppm range. c) Surface soils (0-2ft) contain as much as 4.1 million micrograms per kilogram of PAHs.

This site was proposed for inclusion on National Priorities List (NPL) in October, 1984. Previously, in 1982, field investigations conducted by EPA Region III included sampling of domestic wells, monitoring wells, surface waters, soils, and sediments. Site assessment, sampling, identification, analysis, continued until January, 1985. Studies were carried out to characterize the damage to the groundwater and the air.

For the Feasibility Investigation, the following treatments were considered in detail: no action; on-site thermal; soil washing/extraction; in-situ soil flushing/biodegradation; in-situ vitrification; remove/off-site disposal and containment. Thermal (incineration) was recommended. The RI/FI was completed in May 1988.

In the EPA's Record of Decision dated June 29, 1988, incineration was recommended for remediation of the site. However, local opposition has caused the EPA to reevaluate its recommendation. And, developers of alternative technologies like the microwave processes being developed in this laboratory, were requested to propose on-site studies under the EPA Superfund Technical Assistance Response Team (START) program (2).

Thus there is a need for alternative technologies which are distinctly different from incineration. The major objective of this research is to develop a technology that will effect the remediation of organic contaminated soils at a relatively low temperature so that the process is cost-effective and the soil after treatment does not become a waste stream.

The technology that appears to have that capability is microwave technology. Microwave technology has unique characteristics: water is a strong absorber; air does not absorb microwave energy; materials that do not absorb microwave energy at ambient temperature can become strong absorbers at elevated temperatures; the penetration depth of the energy can be controlled by the frequency used; microwave energy can be applied in-situ; microwave energy is a non-ionizing energy. It is these properties which we have tried to take advantage of in developing appropriate technology. Those technologies are in different stages of development. They are discussed below individually.

First, the remediation of soils contaminated with VOCs and SVOCs: Water is a uniquely strong microwave absorber; the surrounding soil acts initially like a window with respect to the incident energy. Therefore steam distillation can effect the removal of VOCs and SVOCs. (In contrast, thermal treatments establish temperature gradients so that the water will diffuse from the soil into the air stream.) The resulting volatilized VOCs and SVOCs can either be recovered or passed through a microwave afterburner: a bed of SiC which heats rapidly to a 1000^0C in a microwave field.

Second, the remediation of soils contaminated with non-volatile organics is based upon the following considerations: Soils contain tens of thousands of organic chemicals, so many that a comprehensive characterization has never been accomplished. Yet these chemicals are not readily extracted. If, as might reasonably be presumed, there are many chemicals which are today considered hazardous, nevertheless, soil is not per se hazardous because such chemicals are "fixed" within the humic/clay soil fraction. In contrast, spilled chemicals do not readily enter this fraction of the soil. Instead they form multilayers on the outside of this fraction, held together by relatively weak Van der Waal's forces. Thus they are relatively speaking readily extractable. It is presumed that the barrier for the spilled chemical to enter this fraction is that the fraction is bound together by adhesion and cohesion water. Microwave treatment applied in-situ can remove this barrier resulting in the spilled organic being able to enter the fraction; the humic fraction being a strong microwave absorber can then chemically react and "fix" the organic. This model is consistent with studies which have shown that the organic after microwave treatment becomes non-extractable, and DRIFT-FTIR spectroscopy studies of the surface interactions between the organic and the clay and humic components which have shown that there are interactions, probably of a chemical nature.

Third, studies on the remediation of toxic metals in soil, centered on chromium, to complete the spectrum of generic hazardous wastes in soil studied: While the studies on the spilled organics have been aimed at keeping the operating temperature low, that is not the case in studies carried out on a a representative heavy metal contaminant, hexavalent chromium. In this case it was concluded that the treatment might be applicable only to soils which contained microwave absorbing minerals like hematite. Such minerals could incorporate the chromium into minerals which would not be considered hazardous. (Chromium ions make rubies red and emeralds green.) While such processes would take place at elevated temperatures, they would be lower than vitrification, a presently considered alternative treatment. A list of publications and presentations on the above-described microwave studies carried out in this laboratory is presented in Appendix 1.

The next stage is to go from the concept to practical realization. First, comes pilot plant studies. Those studies are underway to determine:

a) the economic feasibility of microwave treatment, based on pilot plant studies;

b) investigation of the treatment feasibility for soils that are contaminated with a wide variety of contaminants, using both bench scale and pilot plant scale.

Second, on-site testing: Planning is underway to develop a mobile unit to go on-site. This stage is being carried out in cooperation with the Raytheon Corporation, the largest vendor of microwave equipment.

The object of this thesis is to carry out studies on the operating costs for effecting the steam distillation of volatile organics (VOCs) and semi-volatile organics (SVOCs) from soil. Specifically, the operating cost of interest is the energy cost. That is generally considered the major cost of any process which utilizes electrical energy. In general, electrical costs are approximately three times the cost of using fossil fuels or natural gas. While such a cost may not be determinative as to whether or not a technology will be used, nevertheless, it has to be a seriously considered factor. These studies will be carried out in the pilot plant. The rated power from the microwave generators is 6 kw; the cavity is approximately 50 cubic feet. The approach that is taken is to first establish the incident power by measuring the power absorbed by a water load. This power will be less than the paid power. But this pilot plant system is much less efficient than the system that will be used on-site in terms of delivering the rated power of the microwave generator to the load. In the pilot plant the microwave generator operates at 2450 MHz. It consists of an array of eight magnetrons rated at 750 watts each. The efficiency of this system in terms of power delivery is of the order of 60 to 70%. On the other hand, in the on-site field investigations, the microwave generator will operate at 915 MHz and the rated power is 50 kW. Such systems have efficiencies over 90%. Then, sand

and soil, respectively, impregnated with naphthalene, will be subjected to microwave treatment. The degree of remediation will be determined by analyzing samples of the treated soil. The cost in terms of power will then be calculated for a given degree of remediation. Of course, it is recognized that this will be a rough estimate. Real costs will come from the field trials. But the magnitude of the cost obtained from the pilot plant studies will serve as a guide as to how improvements can be made in the process prior to going onto field testing.

Chapter 2 Interaction of Materials with Microwaves

Microwaves represent a portion of the electromagnetic spectrum. As such, they obey Maxwell's third and fourth equation. Namely, an alternately fluctuating magnetic field will produce an alternating electric field at right angles. And vice versa. It can be inferred that such waves will propagate in space at right angles to the electrical and magnetic field. This is true for electromagnetic radiation in general.

Differences in interaction with materials arise from the energy of the incident photon, as represented by its frequency, and associated wavelength. The frequency used in this study is 2400 MHz, the associated wavelength is The energy (h) is of the order of , corresponding to the rotational energy of molecules. Therefore, this energy when absorbed by a molecule can only effect changes in rotation (in contrast to electron excitation by UV-VIS and vibrational excitation by IR).

The major effects of the fields associated with microwave energy on materials are as follows(3):

The electrical field can cause dielectric materials to align by molecular rotation; charged particles to align by translation; effect high field intensities at points on conductors which contain sharp edges. The magnetic field can cause magnetic domains to align by rotation. Fluctuating electric and magnetic fields cause affected materials to heat because of frictional energy arising from collisions of affected materials in the course of alignment with the changing fields. High field intensities can cause ions in gas to stream toward the sharp edge causing arcing.

The fluctuating fields can not affect materials which either can not rotate with the field or rotate too rapidly with the field. Thus water is strong absorber in the liquid state but weak in the solid state, because fixed molecules cannot rotate, and in the gas state, because molecules rotate faster than the field. However, molecules which do not rotate at ambient temperature, may rotate sufficiently at higher temperatures to become strong absorbers. Metals are such strong absorbers that the fluctuating electrons reradiate the energy immediately, thus the metal acts as a reflector. On the other hand, a metal in which the surface area predominates over the volume acts as an absorber: the surface heated by absorption is not conducted away by the bulk metal. Thus metals are used as reflectors in microwave cavities but a light bulb placed in such a cavity rapidly glows white hot, reaching a temperature of approximately 1000^{0}C. Semiconductors will act as absorbers because the absorption is not sufficient at the surface to cause total reradiation.

While a magnetic field can be absorbed by magnetic domains ordinary iron magnets will not because the metal will act as a reflector. Ceramic magnets will act as absorbers, because ceramic materials are not absorbers.

The effect of microwave energy absorption on a system could be predicted if the distribution of absorbers were known, how they affect each other, and how temperature affects the absorption (4). Such a calculation involves parameters which can not be determined by present methods. Therefore, the role of theory is not analytical but to provide guidelines.

The type of microwave energy distribution system used in these studies is called a multimode applicator(5). The power source is vacuum electron tube called a magnetron. Electrons emitted from a heated filament are repelled into space by a negative cathode, confined to move in a circular path by a fixed magnetic field at right angles. This causes a circular gear-shaped anode to act as an LC circuit resonating at 2450 MHz. Radiation at this frequency is transmitted by an attached antenna into a waveguide, a rectangular-shaped metal duct, which conducts this radiation. A waveguide is rectangular duct made of metal, which by acting as a conductor shorts out the microwave radiation thereby preventing its escape through the walls. Additionally, it is sized large enough to allow the microwave fields to enter. The radiation then enters a cavity. The cavity is where the load is placed. In our studies, the load is placed upon a conveyor belt within the cavity. The load can be studied in motion or at rest. This is not a sealed system so the leakage of radiation must be contained. 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 approaches used for preventing leakage are apertures of less than a 1/4 of a wavelength; microwave absorbing materials like carbon-filled polyurethane; and shorting stubs, rectangular ducts in which reflected radiation travels a half a wavelength out of phase with the incoming radiation, thus causing destructive interference.

There are variations in the setup. Some of these will now be described.

In the pilot plant an array of eight (8) 750 watt magnetrons are spaced above the cavity. The antenna of each magnetron extends into the cavity, thus there is no need for a waveguide to conduct the radiation into the cavity. In contrast, there would be a separate power unit containing a 6 kW magnetron, and the power would be conducted by a waveguide into the cavity. One advantage of the array is that each of the magnetrons is relatively cheap in cost, also, the system can be operated even if not all of them are functioning. Two, with the array it should be easier to obtain a more uniform distribution of radiation in the cavity. Three, it is possible to put a similar array in the bottom of the cavity, increasing the power, and, also, the uniformity of distribution of energy. There is a drawback. It is not possible to measure the energy reflected back to the magnetron, which would be a measure of the efficiency of the delivery of power, or to intercept the reflected power, which has the effect of destroying the magnetron by causing oscillations of the fields that are not the resonant frequencies.

The incident frequency could be 915 MHz, instead of 2450 MHz. The available frequencies for non-communication uses are limited to 2450 MHz and 915 MHz, respectively, by the United States Federal Communications Commission (FCC). The lower frequency can not be used if the power is less than 30 kW because such units are not available commercially. The low frequency radiation has a higher depth of penetration (one measure, is the depth at which the incident power drops off by a factor of 50%), but at the expense of less absorption by microwave-absorbing substances. Also, the lower frequency radiation is of longer wavelength, thus it will not leak through larger apertures than the high frequency radiation. Practically this means that if the load passes through the cavity on a conveyor belt, the aperture for entry can be larger, and, also, the throughput. For the on-site field trials now being planned with Raytheon Corporation. the largest vendor of microwave systems in the world and the fabricator of the pilot plant used in this study, a 915 KW unit will be used with a power of 50 kW.

In these studies, the radiation pattern is called multi-mode. A mode is the field configuration (magnetic and electric fields). In a multi-mode operation, the object is to have these fields distributed uniformly in the cavity to the greatest degree possible. However, a single travelling wave mode is advantageous because the cavity (or applicator) is the waveguide itself. The load passes through the waveguide through slots in the waveguide. The load has to be small so as to not distort the mode of the travelling wave; also, the slot must have its long dimension of the order of 1/4 of the incident radiation to prevent leakage of radiation through the slots. If the travelling wave is shorted by placing a metal in its path which is a conductor, and the reflected waves can be shorted by a reflector placed an integral number of wavelengths away from the short, then, a standing wave is set up. This is called a resonant applicator because as a result of reflections the amplitude of the wave increases, thus, in that part of the waveguide the energy will be intense. Again, the load has to be small, otherwise, the mode is distorted and so is the resonance.

The size of the cavity is fixed in these studies. Cavities have been operated in which the size of the cavity changes to optimize the delivery of power to the load. An example is the vitrification of spent radioactive materials. The optimum rate of power delivered is a function of the degree of vitrification of the material.

The power does not have to delivered into a cavity (or as it is also called an applicator). For example, this laboratory is planning to do on-site field studies on contaminated soil. It would be preferable to effect remediation in-situ. The equivalent of the cavity would be the soil. Two possible ways are being considered. One, waveguides would be placed over the soil containing slots through which the radiation enters the soil ("leaky waveguides"). Two, antennae would be placed in the soil to effect delivery. There are advantages to use disposable antennae made of scrap iron. Such antennae in addition to acting as radiators heat up rapidly to high temperatures, and thus will result in heating of the soil by conduction. In this manner their function is that of susceptor, a material which acts as a microwave absorber and delivers heat to the non-microwave absorbing material of interest..

The power that is delivered in these studies is varied in the most common way: the power is pulsed, the longer the off period, the smaller the power that's delivered. High power is when the delivery is continuous. The advantage of the pulsing approach is that the energy is most intense below the surface of the load; during the off period of the pulse there is time for the heat to be distributed more evenly in the load. In contrast, there are eight magnetrons within the pilot plant used in these studies. The power could be varied by changing the number of magnetrons operating.

In this study the microwaves heat the load. Also, the microwaves can be used to sustain a gas plasma. The plasma can be used to effect the destruction of volatile toxic substances(6).

Another type of applicator (or cavity) of considerable commercial interest is a teflon cavity which can be operated at high pressures. Teflon is a weak absorber of microwaves, therefore, the radiation will heat up the absorbing substances within the vessel. In contrast, if thermal heating were used, the vessel would have to be heated directly to a high temperature to effect a thermal conduction of heat to the contents within the pressure vessel.

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.

In the radioactive waste treatment industry: for calcination of wastes (10), and volume reduction (11).

For the disposal of household wastes: destruction in the home(12).

To destroy volatile hazardous wastes: fluidized bed reactors(13).

Chapter 3 Determination of Power Absorption and the Optimum Condition of Water Load in Microwave Pilot Plant

3.1 Introduction

The overall objective of these studies is to determine the operating costs and conditions for effecting the steam distillation of a volatile organic from sand and soil by microwave treatment. However, it is necessary to carry out studies on water first. There are two reasons. One, it is necessary to determine the power transferred to a water load because that value is used in the microwave technology field to characterize the microwave applicator. Two, the incident power is needed to estimate an operating cost. Also, studies on water can be used to determine the distribution of energy within the microwave cavity which is important in determining how loads are situated within the cavity: while the process will be continuous, initial studies are being carried out batchwise for simplicity; thus it is important that the uniformity of energy be determined so that the batchwise studies approximate the continuous mode conditions.

Two studies were carried out. One, in which the water load was contained in 1 liter beakers; the second, in pans. The first study involved reaching temperatures so that the water volatilized by boiling. In the pans, the temperature reached was below the boiling point. Additionally, these were the vessels used for the impregnated-substrate experiments, therefore, it was believed that this data would be more directly applicable to the interpreting those data. The rate of heat absorbed by the water load was calculated from measurements of the amount of water lost over a measured time. It is assumed, as is common in the microwave technology field, that the calculated value represents the maximum power which will be incident upon any load because water is a strong common absorber, and other absorbers can not lead to measurements which are easily made or interpreted.

3.2 Equipment and parameters

a. Microwave pilot plant (see Figure 3a): the frequency of the power generated is 2450 MHz; the cavity is approximately 82 scuff. in size: the dimensions are 65.75" x 37.25".

b. Microwave Survey Meter: HOLIDAY INDUSTRIES INC.

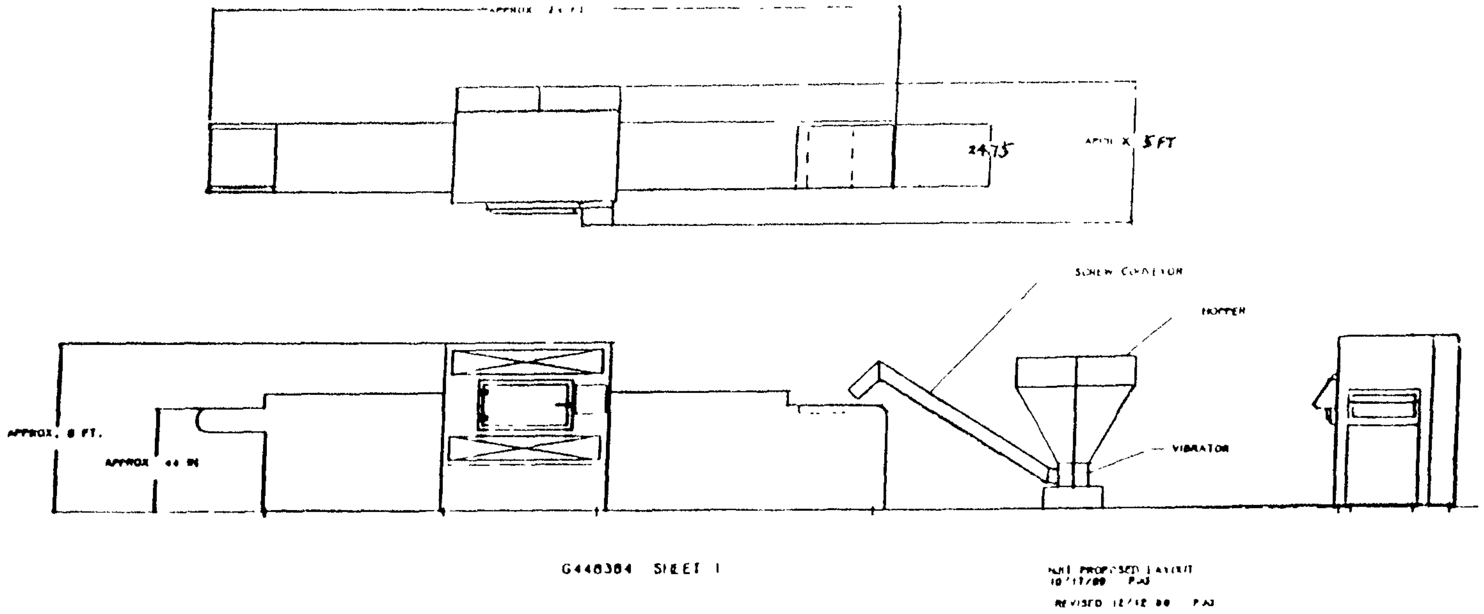
c. Tap water and six 1000 ml beakers.

d. Thermocouple:

e. Microcomputer Thermometer: Model # 7002H JENCO ELECTRONIC LTD.

f. Room temperature 22.5 °C; initial water temp. 20.9 °C.

FIGURE 3a **The Sketch of the Pilot Plant**



3.3 Experimental Procedure

3.3.1 Determination of heating power using water as test load:

One 1000 ml beaker containing 500 ml water was placed in the center of the cavity; the initial temperature was measured. The load were exposed to microwave radiation for 5 minutes, 10 minutes and 15 minutes, respectively: the dial settings for the heating cycles, which determine the output of the power from the magnetrons, were 80%, 100%, and 130%, respectively. The final volume of water were measured; the volume lost and average volume lost were calculated.

The above procedures were repeated except that the position of the load was changed.

3.3.2 Determination of power absorbed and optimum load pattern

The purpose of these studies is to determine how much power is absorbed by the soil and sand loads exposed to microwave radiation. It is assumed that water is a perfect absorber so that when water is used as a surrogate for soil and sand, respectively, the calculated incident power represents the power incident upon the soil and sand loads.

a. Water Load in Beakers

Each sample was prepared by filling 1000 ml beaker with 500 ml water. Six sample were put into the microwave pilot plant cavity (which was prewarmed about 10 minutes) in the following patterns:

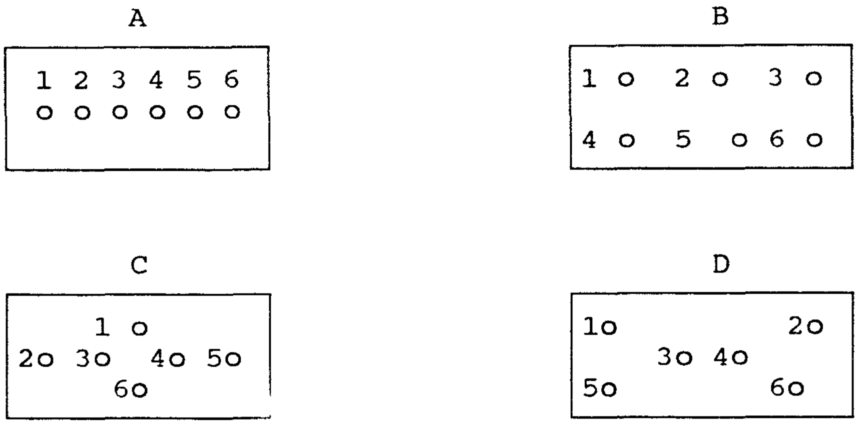


Figure 3b **Six Beaker Water Patterns**

After 10 minutes of exposure at the 130% dial setting, the beakers were removed, and each beaker was covered with parafilm to cool the water to ambient temperature, approximately 21 °C. Then the volume of the water after microwave exposure was measured. It was assumed that the density of water was 1.00 at the temperatures at which measurements were made, therefore, the volume in ml was equal to the weight in grams.

The same procedure was carried out by placing five beakers of water and four beakers of water in the following different patterns:

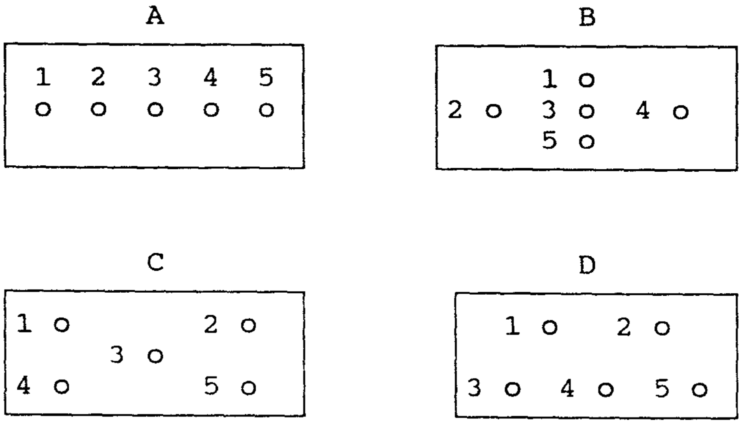


Figure 3c Five Beaker Water Patterns

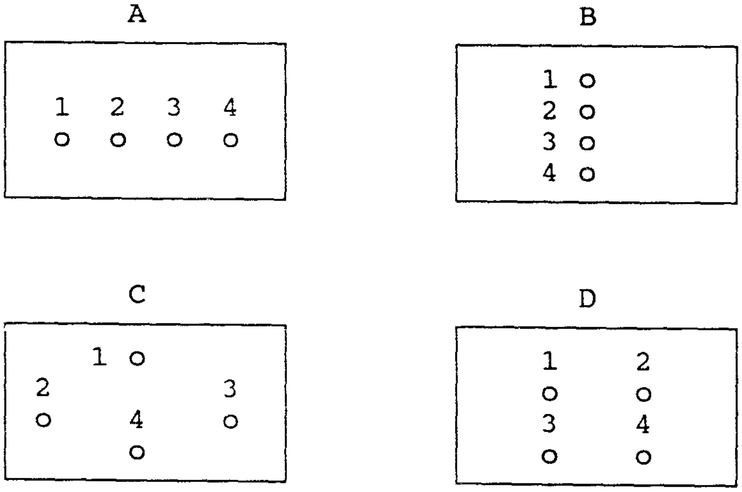


Figure 3d Four Beaker Water Patterns

b. Water Load in Pyrex Rectangular Pans

The pans used in the soil and sand studies were filled with water to a depth of approximately one inch. It was assumed that the power incident upon the water loads was dissipated in four different ways: a) to heat the water; b) to evaporate the water; c) by conduction from the water to heat the pans; d) by conduction from the pans to heat the air and the conveyor belt upon which the pans rested, respectively. It was assumed that the latter heating effects, namely, conduction to the air and the conveyor belt, were negligible. Thus the following measurements were carried out to obtain the data to make the necessary calculations: a) the weight of the water before and after treatment; b) the temperature of the water before and after treatment; c) the weight of the pans; d) the external temperature of the pans after heating; e) the air temperature. It was assumed that the temperature of the pan after heating was the average of the external surface temperature and that of the internal surface: the internal surface temperature was assumed to be the same as that of the water after treatment; the external, the air temperature.

3.4 Results and Discussion

3.4.1 Determination of heating power using water as test load:

The data relating the incident power to the heating time for different power settings is presented in Table 3a.

Table 3a Incident Power Related to Heating Time and Power Settings

	Power	80%			100%			130%		
	Time(min)	5	10	15	5	10	15	5	10	15
1	Vf (ml)	452	314	180	386	220	85	418	232	86
	Vl (ml)	48	186	320	114	280	415	82	268	414
2	Vf (ml)	444	296	176	390	240	90	402	208	70
	Vl (ml)	56	204	324	110	260	410	98	292	430
3	Vf (ml)	431	316	186	432	272	120	398	242	88
	Vl (ml)	69	184	314	68	228	380	102	258	412
Vl_a (ml)		58	191	319	97	256	402	94	273	419
SD (ml)		8.7	9.0	4.1	20.8	21.4	15.5	8.6	14.3	8.1
RSD (%)		15	4.7	1.3	21	8.4	3.9	9.1	5.2	1.9
95% C.L.(ml)		58+/-22	191+/-22	319+/-10	97+/-52	256+/-53	402+/-38	94+/-21	273+/-35	419 +/-20

* Vf is final volume of water
Vl is volume lost of water after microwave heating
Vl_a is the average of volume lost
SD is standard deviation
RSD is relative standard deviation

Referring to Table 3a, the highest average volume lost (419 ml) during microwave treatment is when both the treatment time and magnetron power were the highest: 15 minutes, and 130% dial setting; the 95% confidence limits is 419+/-20 ml. However, this is similar to the results of 100% dial setting. Thus the highest dial setting is 100%; higher values do not affect the incident power.

3.4.2 Determination of power absorbed and optimum load pattern

a. Water load in beakers

The results of the load patterns test are listed on Tables 3b, 3c, and 3d. For the calculation of heat absorbed and the rate of heat absorbed by water, the following equations were used:

$$Q = M\,C\,(Te - To) + M'\,H$$

M is total mass of water (50 g for each beaker)
C is specific heat of water (4.212 $J/g.{}^{0}C$)
Te is the final temperature of the water (100 ^{O}C)
To is the initial temperature of the water (20.9 ^{O}C)
M' is the mass of total water lost due to boiling
H is the heat of vaporization of water (2.313 KJ/g)

The rate of heat absorbed by the water is:

$$R_Q = \frac{Q}{t}$$

t is heating time (10 minutes = 1/6 hr)

1 kw = 3600 kJ/hr

Table 3b Water Load: Incident Power as Function of Configuration and Position (6 Beakers)

POSITION	V(ml)	CONFIGURATION				
		A	B	C	D	Average
1	Vf(ml)	419	410	428	422	
	Vl(ml)	81	90	72	78	
2	VF(ml)	416	427	418	425	
	Vl(ml)	84	73	82	75	
3	Vf(ml)	397	442	424	402	
	Vl(ml)	103	58	76	98	
4	Vf(ml)	402	414	426	415	
	Vl(ml)	98	86	74	85	
5	Vf(ml)	428	409	419	414	
	Vl(ml)	72	91	81	86	
6	Vf(ml)	416	431	426	436	
	Vl(ml)	84	69	74	64	
Vl_{av} (ml)		87	78	77	81	81
SD		11.5	13.3	4.1	11.5	10.1
RSD (%)		13	17	5	14	12
95% C.L.		87+/-12	78+/-14	77+/-4	81+/-12	81+/-11
Q (kJ)		2207	2082	2076	2124	2122
R_Q (kw)		3.7	3.5	3.5	3.5	3.6

Referring to Table 3b, the highest average water loss is 87 ml, which is found for configuration A. The standard deviation is 11.5 ml; but in configuration C, the standard deviation is 4.1. However, the water loss was the lowest, 77 ml.

The average rate of heat absorbed by the water was 3.6 kw.

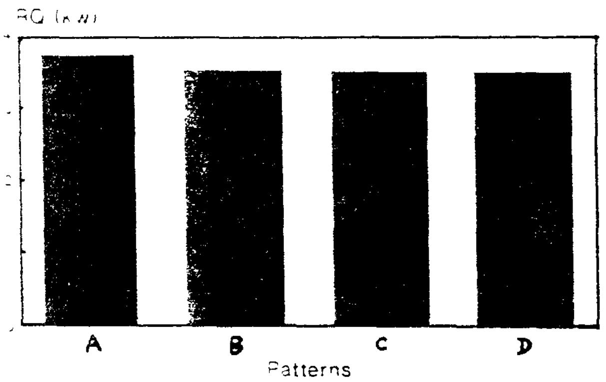


Figure 3e <u>**Six Beakers Containing Water Load: Rate of Heat Absorbed**</u>

In Table 3c, the highest average water loss is 96 ml which is not very high. It is found for configuration C. The standard deviation is 8.7 ml. But in configuration D, the standard deviation is 6.5. But the water loss is 94 ml, a little less than in C.

The average rate of heat absorbed by water is 3.2 kw.

Table 3c **Water Load Studies: Incident Power as a Function of Configuration and Position (five beaker patterns)**

POSITION	V(ml)	CONFIGURATION				
		A	B	C	D	Average
1	Vf(ml)	401	406	414	412	
	Vl(ml)	99	94	86	88	
2	Vf(ml)	426	408	392	400	
	Vl(ml)	74	92	108	100	
3	Vf(ml)	429	400	401	402	
	Vl(ml)	71	100	99	98	
4	Vf(ml)	382	417	411	402	
	Vl(ml)	118	83	89	98	
5	Vf(ml)	409	419	403	414	
	Vl(ml)	91	81	97	86	
Vl_{av} (ml)		91	90	96	94	93
SD		19.2	7.9	8.7	6.5	10.6
RSD (%)		21	9	9	7	12
95% C.L.		91+/-24	90+/-10	96+/-11	94+/-8	93+/-13
Q (KJ)		1885	1874	1943	1920	1906
R_Q (kw)		3.1	3.1	3.2	3.2	3.2

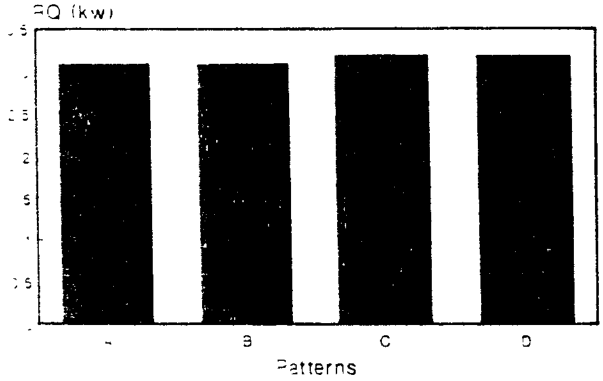


Figure 3f <u>Five Beakers Containing Water Load:
Rate of heat absorbed</u>

In Table 3d, the highest water loss is 119 ml which is found for configuration D. The standard deviation is 8.2 ml. But in configuration B, the standard deviation is 2.6, which is the lowest value among the above three tables. However, the water loss is 97 ml, among the lowest values.

Table 3d __Water Load Studies: Incident Power as a Function of Configuration and Position (four beaker patterns)__

POSITION	V(ml)	CONFIGURATION				
		A	B	C	D	Average
1	Vf(ml)	402	406	392	389	
	Vl(ml)	98	94	108	111	
2	Vf(ml)	410	404	395	370	
	Vl(ml)	90	96	105	130	
3	Vf(ml)	375	402	372	385	
	Vl(ml)	125	98	128	115	
4	Vf(ml)	368	390	370	381	
	Vl(ml)	132	100	130	119	
Vl_{av} (ml)		111	97	118	119	111
SD		20.4	2.6	13.1	8.2	11.1
RSD (%)		18	3	11	7	10
95% C.L.		111+/-32	97+/-4	118+/-21	119+/-13	111+/-18
Q (kJ)		1693	1564	1758	1767	1696
R_Q (kw)		2.8	2.6	2.9	2.9	2.8

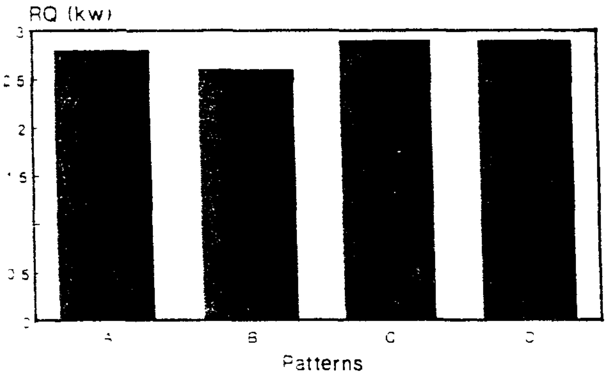


Figure 3g __Four Beakers Containing Water Load: Rate of Heat absorbed__

3.5 Conclusions:

The power absorbed does not change significantly as the mass of the water loads is increased.

The optimum distribution of the loads is based upon the following considerations: the incident power, measured by water loss, is to be maximized; the uniformity, measured by the standard deviation, to be minimized. However, if both factors can not be maximized, it is believed that uniformity is a more important factor. However, too low a power should be avoided because then the sample might be in a region in which the incident power is annihilated. It appears that a value within 25% of the maximum incident power would be acceptable. In Table 3b, configuration A leads to the greatest incident power; C, to the minimum standard deviation. The 95% confidence limits for A is 12, therefore, 77 could be a possible true value. Since that value could lie within the spread of the experimental error in A, it is possible that A does not give the optimum power configuration. Therefore configuration C is chosen because the uniformity is greatest.

Considering all of the configurations represented in the three tables(Table 3b,3c,3d), the minimal standard deviation is 2.6, which is shown for configuration B of Table 3d. So finally, this is the biggest uniform heating pattern. This pattern will be chosen for the following experiment to determine repeatability, that is, four beakers of water in the longitudinal order in the center of the pilot cavity.

3.6 To determine the repeatability of the measurements of configuration B in Table 3d, three more runs were carried out and the results are as follow:

1 o
2 o
3 o
4 o

Referring to Table 3e, the repeatability of this experiment was good; this pattern was chosen for the following experiment.

Table 3e Reproducibility Studies of Water Load: Incident Power as a Function of Configuration and Position (Four Beakers)

POSITION	V(ml)	CONFIGURATION				
		A	B	C	D	Average
1	Vf(ml)	403	410	413	406	
	Vl(ml)	97	90	87	94	
2	Vf(ml)	403	411	413	404	
	Vl(ml)	97	89	87	96	
3	Vf(ml)	396	405	404	402	
	Vl(ml)	104	95	96	98	
4	Vf(ml)	385	396	386	390	
	Vl(ml)	115	104	104	100	
Vl_{av} (ml)		103	95	94	97	97
SD		8.5	5.9	7.1	2.6	6.0
RSD (%)		8	6	8	3	6
95% C.L.		103+/-14	95+/-9	94+/-11	97+/-4	97+/-10
Q (kJ)		1619	1545	1536	1564	1566
R_Q (kw)		2.7	2.6	2.6	2.6	2.6

b. Water Load Studies: Pyrex Rectangular Pans

The evaporation of water, in the absence of heating, in the cavity of the pilot plant was measured at a water temperature of 51 ^{o}C. The weight loss of water after 10 minutes was 0.1 lb, from 9.2 lb (pan+H_2O) initially to 9.1 lb (pan+H_2O) finally. Also, at a water temperature of 40 ^{0}C, the natural evaporation of water was measured. Similar results were obtained at this temperature.

The heat incident upon the load was assumed to be absorbed as follows:

$$Q = M_{(H2O)}\ C_{(H2O)}\ T_{(H2O)} + M_{(H2O\ lost)}\ H_{(glass)} + M_{(pan)}\ C_{(glass)}\ T_{(pan)}$$

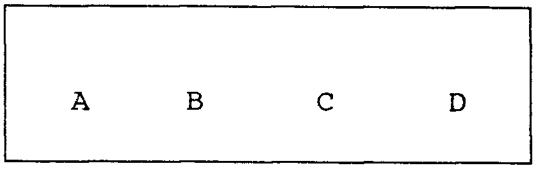
Q is the heat absorbed by the load (kJ)
$M_{(H2O)}$ is the mass of water before microwave heating (g)
$C_{(H2O)}$ is the specific heat of water (4.212×10^{-3} kJ/g.^{o}C)
$T_{(H2O)}$ is the temperature difference of water before and after microwave heating
$M_{(H2O\ lost)}$ is the mass of water lost after microwave heating (g)
$H_{(glass)}$ is the heat of vaporization of water (2.313 kJ/g)
$M_{(pan)}$ is the mass of Pyrex pan (g)
$C_{(glass)}$ is the specific heat of Pyrex pan (0.00077 kJ/g.K)
$T_{(pan)}$ is the temperature difference of Pyrex pan before and after microwave heating

The microwave heating of water in the four Pyrex rectangular pans is shown in Table 3f.

Table 3f <u>**Microwave Heating: Four Pyrex Pans of Water Load**</u>

	PARAMETERS	POSITION			
		A	B	C	D
Before MW Treatment	$Wt_{(pan)}$ (lb)	4.9	4.9	4.9	4.9
	$Wt_{(pan+H2O)}$ (lb)	9.3	9.3	9.3	9.3
	$Wt_{(H2O)}$ (lb)	4.4	4.4	4.4	4.4
	$Temp_{(H2O)}$ (^{o}C)	20	20	20	20
	$Temp_{(pan)}$ (^{o}C)	20	20	20	20
After 10 min. MW Treatment	$Wt_{(pan+H2O)}$ (lb)	9.1	9.1	9.1	9.1
	$Wt_{(H2O\ lost)}$ (lb)	0.2	0.2	0.2	0.2
	$Temp_{(H2O)}$ (^{o}C)	72	75	73	70
	$Temp_{(cavity)}$ (^{o}C)	38	38	38	38
	$Temp_{(pan)}$ (^{o}C)	55	57	56	54
Q (kJ) per pan		602	630	612	584
R_Q(kw) per pan		1.00	1.05	1.02	0.97
SD		0.03			
$Q_{(total)}$ (kJ)		2428			
$R_{Q(total)}$ (kw)		4.0			

* The pattern of load was as following:



Refer to Table 3f, the microwave heating of the water in the four Pyrex rectangular pans, it is seen that incident power is 4.0 kW: also, the difference in power absorbed as a function of position is approximately 5%, which is considered insignificant.

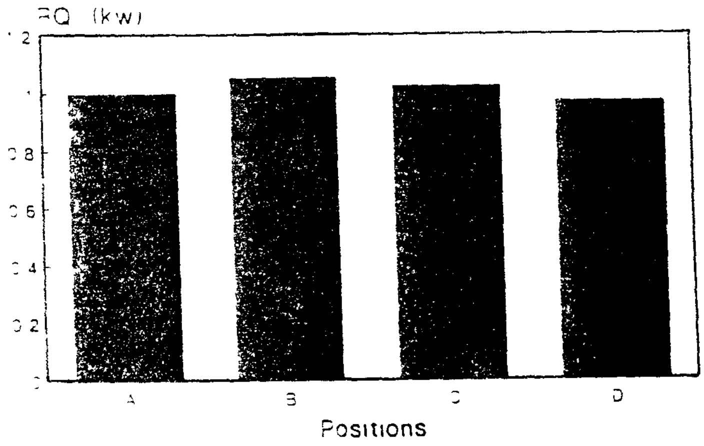


Figure 3h <u>Four Pyrex Pans Containing Water Load: Rate of Heat Absorbed</u>

Table 3g **Microwave Heating of Six Pyrex Pans of Water Load**

	PARAMETER	POSITION					
		A	B	C	D	E	F
Before MW Treatment	Wt$_{(\text{pan})}$	4.9	4.9	4.9	4.9	4.9	4.9
	Wt$_{(\text{P+W})}$	9.3	9.3	9.3	9.3	9.3	9.3
	Wt$_{(\text{H2O})}$	4.4	4.4	4.4	4.4	4.4	4.4
	Temp$_{(\text{H2O})}$	20	20	20	20	20	20
	Temp$_{(\text{Pan})}$	20	20	20	20	20	20
After 10 min MW Treatment	Wt$_{(\text{P+W})}$	9.2	9.1	9.1	9.2	9.2	9.2
	Wt$_{1(\text{H2O})}$	0.1	0.2	0.2	0.1	0.1	0.1
	Temp$_{(\text{H2O})}$	57	61	65	67	61	58
	Temp$_{(\text{cav})}$	41	42	42	42	42	42
	Temp$_{(\text{pan})}$	50	52	54	55	52	50
Q (kJ) per pan		362.7	504.8	541.9	455.4	367.8	371.1
R_Q(kw) per pan		0.60	0.84	0.90	0.76	0.61	0.62
SD		0.12					
Q$_{(\text{total})}$ (kJ)		2269.7					
$R_{Q(\text{total})}$ (kw)		4.3					

* The pattern of the six Pyrex pans was as following:

A B C D E F

Turning next to the six Pyrex rectangular pan configuration, Table 3g, it is seen that the incident power is 4.3 kW. The incident power appears to vary with the position. The water in the middle positions, namely, B, C, and D, respectively, received incident power of the order of 15 to 40% higher than the other positions.

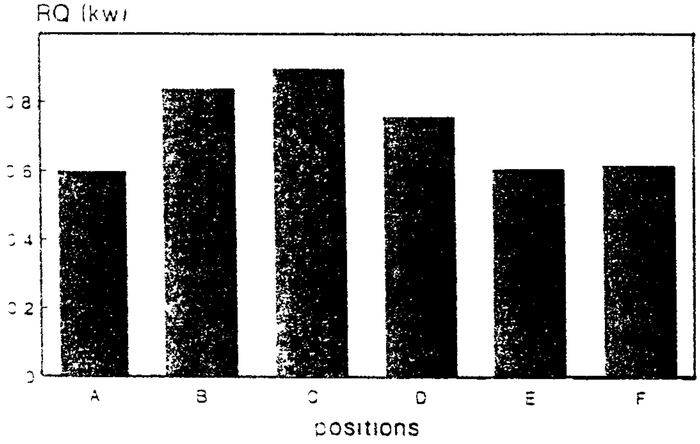


Figure 3i __Six Pyrex Pans Containing Water Load: Rate of Heat Absorbed__

Table 3h Microwave Heating of Eight Pyrex Pans of Water Load

	PARAMETER	POSITION							
		A	B	C	D	E	F	G	H
	Wt(pan) (lb)	4.9	4.9	4.9	4.9	3.4	3.4	4.9	4.9
Before	Wt(p+w) (lb)	9.3	9.3	9.3	9.3	5.6	5.6	9.3	9.3
MW	Wt(H2O)(lb)	4.4	4.4	4.4	4.4	2.2	2.2	4.4	4 4
Treatment	Temp(H2O) C	20	20	20	20	20	20	20	20
	Temp(pan) C	20	20	20	20	20	20	20	20
	Wt(p+w)(lb)	9.2	9.1	9.1	9.1	5.5	5.4	9.2	9 3
After 10 min	Wt(w lost)(lb)	0.1	0.2	0.2	0.2	0.1	0.2	0.1	0
MW	Temp(H2O) C	50	52	57	57	56	57	50	50
Treatment	Temp(cav) C	35	35	35	35	35	35	35	35
	Temp(pan) C	43	44	46	46	46	46	43	43
Q(kJ) per pan		291.8	415.4	460.9	460.9	182	188	291.8	291 8
Rq(kw) per pan		0.49	0.69	0.77	0.77	0.3	0.31	0.49	0.49
SD		0.15							
Q(total) (kj)		2583							
Rq(total) kw		4.3							

* The pattern of the eight Pyrex pans of water was as following:

A	C	E	G
B	D	F	H

For the eight Pyrex pans configuration, it is seen in Table 3h, that the incident power is similar to that found in the six pan configuration, namely, 4.3 kW. There is a variation in the power: the water in positions B, C, and D, respectively, received incident power levels of approximately twice as high as the other positions.

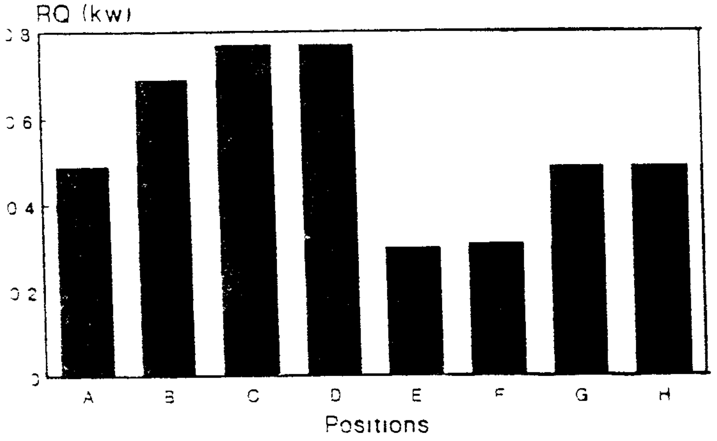


Figure 3j Eight Pyrex Pans Containing Water Load: Rate of Heat Absorbed

3.7 Conclusions(pans experiments)

The power absorbed plateaus out with six pans at 4.3 kW as evidenced by the fact that there was no increase with 8 pans. Thus this is assumed to be the maximum incident power in the impregnated-substrate studies in which 8 pans were used. There is evidence in the Pyrex rectangular pan studies that the power is distributed inhomogeneously in the cavity. Referring back to the beaker experiments, extrapolation of the incident power calculations leads to an incident power of 4.3 kW, like that found in the pan experiments. Therefore, 4.3 kW is considered a reasonable value to report in the literature to characterize the microwave system, and to estimate the power incident upon the impregnated-substrates. Because there appears to be inhomogeneities in the distribution of energy in the cavity, the eight pan configuration will be used in the remediation experiments to minimize those effects.

Chapter 4 Analytical Procedures: Extraction and Sample Injection into the GC/MS

4.1 Introduction

The analysis of the impregnated substrate involves two procedures: first, sample preparation; second, GC/MS analysis.

The purpose of this study is to determine the optimum extraction procedure to use in sample preparation, and to determine the optimum way to inject samples into the GC/MS.

4.2 Sample Preparation (Extraction Studies)

The sample preparation procedure is required so that the sample can be introduced into the GC/MS. For the analysis of semivolatile organics (e.g. naphthalene) in sand or soil, the sample preparation procedure is as follows: extraction of the impregnated substrate; dilution; and concentration. This chapter will focus on the sample extraction procedure.

Two methods are appropriate for extracting naphthalene from substrata such as sand and soil: Soxhlet and ultrasonic extraction. On the basis of equilibrium stages, the Soxhlet method is clearly superior to ultrasonic extraction provided that more than one stage is needed for extraction:

ultrasonic extraction is limited to a single equilibrium stage whereas with the Soxhlet method it is possible to reach thousands of stages of extraction.

During ultrasonic extraction, the substrate and the solvent are mixed and subjected to ultrasonic vibration. Since they are mixed and agitated only once, it is possible to have but one equilibrium stage. In Soxhlet extraction, the solvent(methanol) is evaporated, and condensed, the resulting stream of solvent then mixes with the naphthalene and substrate in the extraction thimble. Since the solvent is naphthalene free, a succession of equilibrium stages occurs because the solvent and the substrate will be out of equilibrium: naphthalene can dissolve in methanol but the entering methanol is naphthalene free. So the longer time of Soxhlet extraction, the more naphthalene dissolved in the methanol. However, in the ultrasonic extraction, when the equilibration is reached, the maximum extraction efficiency does not increase with time.

It is assumed that equilibrium can be reached with the Soxhlet method. In the ultrasonic method each particle of substrate with adsorbed naphthalene is subject to agitation by vibration. But in the Soxhlet thimble, channels of least flow resistance may exist so that the solvent flows through those channels without mixing with the bulk of the substrate.

On the one hand, if there were no channeling, the Soxhlet method would be clearly superior provided that more than one stage of equilibrium were needed. But since the possibility of channeling can not be eliminated, experimental data is needed to determine which method provides the clearest advantage.

To make the comparison, it is necessary to compare each method under optimum conditions. It is necessary to extract sufficient amounts of naphthalene so that the measurement error is minimized. That means using as large a possible a sample of substrate and a minimum amount of solvent. But it is also necessary to reach equilibration in a reasonable time. To achieve optimum conditions, the above parameters, namely, the amount of substrate and volume of solvent, will be varied as a function of vibration time to determine the time that the extraction plateaus: that's the optimum condition. Also, the effect of the amount of naphthalene on the substrate will be considered.

One of the advantages of ultrasonic is that each molecule of sample is vibrated by the ultrasonic radiation, the solvent can go through the sample completely. While in Soxhlet extraction, the solvent dissolves the naphthalene by dropping through the sample. This method of dissolution cannot be complete.

4.2.1 Experimental Section

a. Soxhlet extraction test

Each of five samples were prepared by adding 5 ml of a solution of 20.0 mg naphthalene/ml methanol to 50 g sand. In each run, 80 ml of methanol was used as solvent. The Soxhlet extraction was done for 24 hr, 46 hr, 51 hr, 72 hr and 96 hr, respectively. After extraction, the extracts were first diluted to 100 ml with methanol, then 1.0 ml of this solution was further diluted to 10 ml with methanol. Finally, 1.0 ul of this solution was injected to the GC column for GC/MS analyses. The concentration corresponding to 100% extraction efficiency should be 100 ng/ul.

b. Ultrasonic extraction test

1). Time vs extraction efficiency(E%)

Each sample was prepared by adding 5 ml of 20 mg naphthalene/ml methanol to 50 g sand, and then mixed well in a 150 ml beaker; 45 ml methanol was added as solvent to extract naphthalene from the sand, and mixed well; parafilm was used to cover the beakers. The samples were ultrasonically extracted for different times. The samples were filtered, then cooled down to room temperature; 1 ml of filtrate was diluted to 10 ml. 1.0 ul was injected into the GC/MS, compared to calibration curve "lucy1.Q" to get the concentration of the injected sample. The extraction efficiency could then be calculated as follows:

If the extraction efficiency were 100%, the concentration of injection sample should be 200 ng/ul. The equation for the actual extraction efficiency is:

$$Ea\% = \frac{\text{Ca (actual concentration ng/ul)}}{200 \text{ (ng/ul)}} \times 100\%$$

2). The Relationship between Extraction Efficiency and the Ratio of Substrate to Solvent

The concentration of naphthalene in sand (2000 ppm by weight) was kept constant. Also, the amount of sand (50 g). The ratio of sand to methanol was varied.

Add 5 ml of 20 mg naphthalene/ml methanol into 50 g sand, then mix the sample well in 150 ml beaker; add different volumes of methanol; carry out ultrasonic extraction for 20 minutes. Filter the sample, and then cool down the sample to room temperature. Take 1.0 ml of filtrate, dilute to 10 ml, inject 1.0 ul into the GC/MS. Calculate the extraction efficiency of each sample.

3). Height to diameter of substrate (H/D of sand) vs E%:

Use the same amount of naphthalene and sand and methanol, just change the size of beakers.

The extraction and analyses procedures are as above described. The concentration of injected sample should be 200 ng/ul if extraction efficiency were 100%.

Additionally, extractions with 10% of water (based upon the weight of sand) was also carried out. The purpose was to determine whether the addition of water affected the desorption of the naphthalene from the substrate.

4.2.2 Results and Discussion

In Table 4a, the efficiency of Soxhlet extraction as a function of time is tabulated.

Table 4a Soxhlet Extraction

Sample #	1	2	3	4	5
Time(hr)	24	46	51	72	96
Con. (ng/ul)	30.23	29.49	95.85	98.70	67.98
	35.68	29.94	91.70	86.23	50.95
	24.18	25.05	79.69	98.31	59.48
Cav(ng/ul)	30.03	28.16	89.08	96.08	59.47
E %	30.0	28.1	89.1	96.1	59.5
E_a %	60.6				
SD	28.5				
RSD %	47.1				
95% C.L.	60.6 +/- 35.4				

* E_a Average extraction efficiency
SD, RSD and 95% C.L. is mentioned to the extraction efficiency
Cav is the average concentration.

The results in table 4a show that for Soxhlet extraction, the highest extraction efficiency for naphthalene impregnated sand is 96.1%; the corresponding time for extraction is 72 hours. However the lowest is only 28.1% at the extraction time of 46 hours. The difference is 68%. But after 96 hours, the efficiency drops to 59.5%. Thus the extraction efficiency did not increase with extraction time. Probably it is due to the fact that in some samples there is channeling that causes poor extraction efficiency.

The ultrasonic extraction efficiencies are presented in Table 4b.

Table 4b <u>Ultrasonic Extraction</u>

Sample #	1	2	3	4	5	6
time(min)	5	10	15	20	25	30
C (ng/ul)	86.19	149.7	109.2	128.6	115.3	147.1
E%	43.1	74.9	54.6	64.3	57.7	73.6
E_a%	61.4					
SD	11.1					
RSD %	18.0					
95% C.L.	61.4 +/- 11.6					

It is seen that the maximum extraction efficiency is 74.9% obtained after 10 minutes. After 30 minutes, 73.6%. The range of extractions from 5 to 30 minutes was from 43.1 to 73.6%. Presumably, in a single extraction if some of the sand forms clumps which don't break up, this could lead to variable extractions independent of the time.

The effect of added water on ultrasonic extraction efficiency is shown in Table 4c.

Table 4c Ultrasonic Extraction:(with 10% water)

Sample No.	1	2	3	4
Time (min.)	5	10	15	25
Con.(ng/ul)	150.0	192.6	142.8	130.2
E%	75.0	96.3	71.4	65.1
E_a%	75.3			
SD	11.0			
RSD %	14.6			
95% C.L.	75.3 +/- 13.6			

The extraction efficiency varies from 75.0 to 96.3%, compared to 43.1 to 73.6% in the absence of water. It would appear that the addition of water increases the extraction efficiency.

In Table 4d the efficiency of ultrasonic extraction efficiency as a function of the substrate to solvent ratio is shown.

Table 4d **Ultrasonic Extraction: Ratio of Substrate to Solvent (without water)**

Sample #	1	2	3	4	5
Sand(g)/ solvent(ml)	50/100	50/50	50/33	50/25	50/20
R=S(g)/M(ml)	0.5	1.0	1.5	2.0	2.5
C(ng/ul if100%E)	100	200	300	400	500
Ca(ng/ul actual)	83.7	128.6	232.3	283.1	356.6
E%	83.7	64.3	77.4	71.0	71.3
E_a%	73.5				
SD	6.6				
RSD %	8.9				
95% C.L.	73.5 +/- 8.2				

It is seen that when the sand/solvent ratio is varied from 0.5 to 2.5 that the extraction efficiency varies from 83.7 to 71.3%; but there is no trend. It would appear that within this range, the sand/solvent ratio is not significant.

The data in the following series of experiments presented in Table 4e shows how the addition of water effects the relationship between the substrate/solvent ratio and the extraction efficiency.

Table 4e <u>**The ratio of substrate to solvent vs E%**</u>

<u>**(with 10% water)**</u>

Sample No.	1	2	3	4	5
Sand(g)/ Methanol(ml)	50/70	50/60	50/50	50/30	50/20
R=S(g)/M(ml)	0.7	0.8	1.0	1.7	2.5
C(ng/ul if 100%E)	142.9	166.7	200.0	333.3	500.0
Ca(ng/ul actual)	124.6	127.0	174.1	213.4	379.5
E%	87.2	76.2	87.1	64.0	75.9
E_a%	78.1				
SD	8.6				
RSD	11.0				
95% C.L.	78.1 +/- 10.7				

The range of extraction efficiencies is from 64.0 to 87.2%; as was the case when water was not added, there is no trend.
Also, the range of extraction efficiencies is similar to that found when water was not added.

In Table 4f, data on the effect of the height to diameter ratio of the extraction vessel upon extraction efficiency is presented.

Table 4f The Effect of the Height to Diameter Ratiof of Extraction Vessel upon Extraction Efficiency

Sample No.	1	2	3	4
Beaker size(ml)	50	150	250	400
H/D (mm/mm)	19/	15/	11/	5/
Con.(ng/ul)	100.3	128.6	133.7	127.2
E%	50.1	64.3	66.9	63.6
E_a%	61.2			
SD	6.5			
RSD %	10.7			
95% C.L.	61.2 +/- 10.3			

The H/D ratio varied from 19 to 5, the extraction efficiency from 50.1 to 63.6%. It would appear that between a ratio of 19 to 15, the extraction efficiency reaches a plateau.

The extraction of naphthalene impregnated sand after microwave treatment in the pilot plant was carried out using both the Soxhlet and ultrasonic methods. The results are shown in Table 4.7.

Table 4g Removal of naphthalene(ng/ul) from sand vs treatment time

	Soxhlet extraction (4 days)		Ultrasonic extraction (20 minutes)	
min(MW)	Blank	10min(MW)	Blank	10
# 1	55.35	ND	72.87	3.439
# 2	63.60	ND	71.46	2.322
# 3	62.28	ND	74.25	3.409
Ca (ng/ul)	60.41	———	72.86	3.057
SD(ng/ul)	3.62	———	1.14	0.524
RSD (%)	6.0	-- ---	1.6	17.1
95% C.L.	60.41 +/- 8.98	———	72.86 +/- 2.83	3.057 +/- 1.30
E%	60.4	———	72.9	-----

* ND means not detectable.
Ca is average concentration.

It is seen that greater extraction in both the blank and the treated sample is effected by ultrasonic extraction. Also, that microwave treatment either renders the naphthalene non-extractable or effects its volatilization. Presumably it volatilizes because sand, which is mainly covalently-bonded silica, does not bond organics strongly or chemically react with organics.

4.2.3 **Conclusions** (Sample Preparation:Extraction)

It is concluded that ultrasonic extraction is as efficient as Soxhlet extraction. Ultrasonic extraction is preferable because it is easier to carry out. Also, the effect of adding water is questionable, so it does not appear to be necessary. Also, the ratio of H/D for the container vessel does not appear to be significant within the range that was studied.

4.3 GC/MS Analysis

Quantitative analysis requires that measurements should be reproducible. Although many factors can affect the reproducibility of the measurement, the following study will be limited to those now enumerated: first, the effect of sample injection volume; second, concentration; third, sample injection procedure.

4.3.1 Experimental Section

The following specific programs were used: The tuning method that was used is AUTOTUNE. The parameter file is NAPH-LU.A. The DATA ACQUISITION form, the TEMPERATURE PROGRAM & HEATED ZONES, and the SCAN ACQUISITION form is listed in appendix .

The reproducibility of the responses was tested as a function of the volume of the sample injected and the concentration of the sample. The response was determined from the area associated with the total ion chromatographic (TIC) peak. That area was compared for the following volumes of injected samples of naphthalene/methanol standard solution. The injection volumes used were 2.0 ul, 3.0 ul, and 5.0 ul, respectively. The variations in the concentration of the standard were 2 ng/ul, 50 ng/ul, and 200 ng/ul, respectively..

Additionally, two injection techniques were compared. The first was normal injection, and the second was hot needle injection.

a. **Hot needle injection technique**

The following procedure was used in testing the hot needle method:

1). Draw up sample in syringe barrel without leaving an air plug between the sample and plunger.

2). Draw up the sample leaving 2-3 ul air gap in the needle volume.

3). After insertion into the injection zone, allow the needle to heat up for 3-5 seconds.

4). Inject the sample rapidly and withdraw the needle from the inlet within one second.

5). The samples injected varied both in volume and concentration.

b. **Normal injection method:**

1). Draw up sample in syringe barrel without leaving an air plug between the sample and plunger.

2). Inject the sample rapidly and withdraw the needle from the inlet within one second.

3). The sample injected varied both in volume and concentration.

4.3.2 Results and Discussion

The data for the normal injections are presented in Table 4h; for the hot needle injections, Table 4i. For the normal injections, the variation in standard deviations does not appear to vary with the injection volumes, from 1.0 to 5.0 uL; nor, with respect to concentration, varying from 20 to 200 ng/uL. Looking at the comparable hot needle injection data in Table 4i, again, there appears to be no trend with respect to injection volume: for example, the 2.0 uL and 5.0 uL data are similar, but the 3.0 uL data is not. With respect to concentration, again, there is no trend: for example, 20 uL, has the highest standard deviation at 1.0 uL injection, namely, 21.2, and the lowest at 5.0 uL injection, 4.2. Comparing the two injection methods, The standard deviation for the normal injection is less in 7 out of the 12 comparable cases. This is not considered to be a significant difference.

4.3.3 Conclusions (GC/MS Analyses)

There does appear to be any advantage in using hot needle injection as opposed to normal injection. Nor any advantage to using a specific injection volume in the 1.0 to 5.0 uL range. Likewise, there is no advantage to using a specific concentration in the 20 to 200 ng/uL range.

Table 4h NORMAL INJECTION

Inj. Vol	1.0 ul			2.0 ul			3.0 ul			5.0 ul		
Con. ng/ul	20	50	200	20	50	200	20	50	200	20	50	200
Area	28407	1390643	5886206	47420	2552230	89755413	71649	3008752	10134895	134100	3556709	10023312
	354334	1538719	5941608	52549	2574744	9507821	73849	3145877	13545587	141598	3730434	15127779
	51508	1205659	6529023	63057	2616650	9920085	69762	3329839	13515063	160751	2792292	13142938
	41788	1258333	5612879	63415	2665771	10974640	67503	3163721	12244438	155705	3962719	12919613
$\bar{A}$	39284	1348339	5992429	56610	2602349	9844490	70691	3162047	12359996	148039	3510539	12803411
SD	8497	128931	333863	6871	43304	733416	2341	113927	1387825	10679	438985	1820743
RSD(%)	21.6	9.6	5.6	12.1	1.7	7.5	3.3	3.6	11.2	7.2	12.5	14.2

$\bar{A}$: average area

SD: standard diviation

RSD: relative standard diviation

Table 4i HOT NEEDLE INJECTION TECHNIQUE

Inj. Vol	1.0 ul			2.0 ul			3.0 ul			5.0 ul		
Con. ng/ul	20	50	200	20	50	200	20	50	200	20	50	200
Area	23012	1147086	7139385	28757	1585858	7521572	38504	2625440	14976155	80152	4777238	18821555
	22822	1201944	6405325	33134	1759260	6919721	37008	2488420	10307025	72099	3928531	16281974
	18658	1468994	5900401	32638	1600391	7749710	32292	2808154	11826338	73027	4101961	20064217
	32684	1453934	6066262	30553	1607473	8587983	34489	2773047	11416978	76768	4058281	19882267
$\bar{A}$	24294	1317990	6377845	31271	1638246	7694747	35573	2673765	12131624	75512	4216503	18762503
SD	5147	144877	475851	1745	70301	598236	2376	127088	1733814	3199	329964	1508712
RSD(%)	21.2	11.0	7.5	5.6	4.3	7.8	6.7	4.8	14.3	4.2	7.8	8.0

$\bar{A}$: average area

SD: standard diviation

RSD: relatival standard diviation

Chapter 5 Operating Costs (Incident Power): Remediation of Naphthalene Impregnated Substrates

5.1 Introduction

The purpose of these studies is to estimate the operating costs to remediate soils contaminated with volatile organics (VOCs) and semi-volatile organics (SVOCs). That aspect of the operating being studied is the cost of the power. Specifically, the power incident upon the substrates. That value was determined in the previously discussed water load studies. To get an estimate of this important factor, two substrates impregnated with naphthalene were studied, namely, sand and soil. By knowing the weight of the substrates, the incident power, and determining the degree of remediation analytically, the operating cost to effect a given degree of remediation of a ton of substrate can be estimated.

5.2 Experimental Section

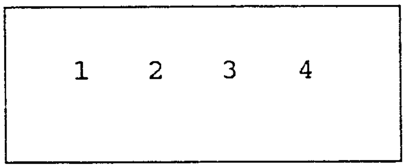
The substrates were treated in Pyrex rectangular pans: sizes (15" x 10" x 2") and (13" x 9" x 2"). The ultrasonic extractor used was Model . A Holloday microwave radiation leaking test apparatus was used to check the pilot plant for leaks. The GC/MS system used was the Hewlitt Packard 5890 GC/5970 MS.

Separate studies were carried out on two substrates: sand and soil, as described below.

5.2.1 Naphthalene-Impregnated Sand Studies

48.0 g naphthalene(99.9%) were dissolved in about 700 ml methanol in a 1000 ml Erlenmeyer flask; to assist in the dissolving of the naphthalene in the solvent, the flask was mildly heated in the fume hood (to minimize evaporation, the flask was covered by parafilm). Then, 52.9 lb (24.0 kg) sand were weighed, and impregnated by the naphthalene solution in a big tray under the hood. The sample was then mixed well. Assuming the mixing produced a homogeneous distribution of the naphthalene, the concentration of naphthalene in the sand was 2000 ppm (by weight). The sample was then allowed to stand in the tray overnight to let the solvent evaporate. It assumed that a small part of naphthalene was also evaporated.

Four batches of 50 g of this sand sample were taken as blank sample (without microwave treatment). 2.4 liter of tap water (10% water in sand by weight) was added to the samples to be microwave-treated, and mixed well. All the samples were then equally separated into the eight dishes (each about 3 kg of sand and about 1 inch high), and covered with aluminum foil. The microwave pilot plant, containing 2 liters of water, was pre-warmed for at least 10 minutes, and the microwave radiation leakage was checked during this time. The eight Pyrex baking dishes of sand sample were loaded into the microwave cavity with the pattern of four, lengthwise, and two, side by side. The aluminum foil was taken off. The load pattern was as follows:



The microwave pilot plant was first run for 1 minute, the sand in each pan was hand-mixed, and about 50 g sample was taken from each side by side baking dish and placed into eight 150 ml beakers. The beakers were then covered by parafilm. Then the microwave pilot plant was operated for an additional 2 minutes; the method of sampling was the same as that described above for the 1 minute treatment; after the additional 5 minutes, the sampling was repeated; likewise, for the additional 7 minutes run,, sampling was repeated; and similarly for the final additional 10 minutes.

A total of forty 150 ml beakers sand sample were taken and treated as follows: From each of the beakers, 50.0 g. samples were taken; 25 ml of methanol was added to each sample. Each sample was then extracted ultrasonically for 20 minutes, cooled down to room temperature, vacuum filtered and diluted to the volume of 25 ml with methanol.

The three blank samples were extracted the same way as samples, and diluted to 25 ml with methanol.

Before the GC/MS analysis of the samples, the calibration curve was checked by injecting a middle range concentration of the standard naphthalene/methanol solution: a new calibration curve should be created if the percent difference was over the range of 4%. Also, the concentration of one microwave-treated sample and a blank sample were run to determine if those concentrations were in the range of calibration curve.

In this experiment, the concentrations of samples from microwave treatment times of 1 minute to 15 minutes, and the blanks were above the highest of the calibration curve (2 ng/ul to 400 ng/ul). So, additional dilution was needed. 1 ml of each those samples was diluted to 10 ml with methanol (dilution factor was 10).

Finally, all blanks and samples were analyzed by the GC/MS. The blank recovery and the relationship between the naphthalene removal after microwave treatment and the treatment time can be calculated.

5.2.2 Naphthalene-Impregnated Soil Studies

These studies were similar to the previously described studies on naphthalene-impregnated sand (See 4.3.1). The sample preparation, treatment, and analytical procedures differed only in the following ways: The total weight of soil was 44.1 lb (20.0 kg); the microwave treatment times were: 5 minutes; additional 5 minutes; additional 5 minutes; additional 5 minutes; additional 10 minutes; three blank samples were used.

In this experiment, the concentrations of samples from microwave treatment time of 5 minutes, 10 minutes, and the blanks were so high that they were outside the range of the calibration curve (2 ng/ul to 400 ng/ul). So, additional dilution was needed. 1 ml of each those samples was diluted to 10 ml with methanol (dilution factor was 10 .

All blanks and samples were analyzed by GC/MS. The blank recovery and the relationship between the naphthalene removal after microwave treatment and the treatment time can be calculated.

5.3 Results and Discussion

5.3.1. Sand Studies

Referring to Table 5a, the degree of remediation of sand as a function of microwave treatment time, it is seen that analyses were carried out at five different treatment times at eight different positions. Four positions were serially related: these are referred to as positions 1-4; the side-by-side positions are referred to as A and B. It was assumed that the A and B position samples would correspond to duplicate sampling of a similarly treated substrate. First, the overall trend: remediation increases

Table 5a Naphthalene Impregnated Sand Pilot Plant Studies: Naphthalene Removed as a Function of Time

time \ No		Microwave Treatment Time																			
		1 min				3 min				8 min				15 min				25 min			
		1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
CON. ng/ul	A	225.0	146.3	149.5	150.9	184.0	175.7	158.2	152.3	98.9	143.8	105.4	137.6	81.9	61.2	36.7	95.2	5.7	10.1	6.9	21.3
	B	202.1	191.6	215.9	150.4	175.9	166.2	145.5	147.6	121.2	134.1	193.7	171.9	59.4	25.8	17.5	80.9	10.9	5.5	9.2	16.3
	Ave.	213.6	169.0	182.7	150.7	180.0	171.0	151.9	150.0	110.1	139.0	149.6	154.8	70.7	43.5	27.1	88.0	8.3	7.8	8.0	18.8
Naphthalene Removed(%)		15.0	32.8	27.3	40.1	28.4	32.0	39.6	40.3	56.2	44.7	40.5	38.4	71.9	82.7	89.2	65.0	99.7	98.7	99.7	99.3
SD		9.2				5.0				6.9				9.1				0.2			
Average Removed(%)		28.8				35.1				45.0				77.2				99.6			

Blank					
	No.	1	2	3	4
	Con. (ng/ul)	228.7	158.8	287.7	330.5
	Ave.Con. (ng/ul)	251.4			
	Recovery (%)	$\%(\text{Recovery}) = \frac{251.4\ (\text{ng/ul})}{400\ (\text{ng/ul})} \times 100\%$			

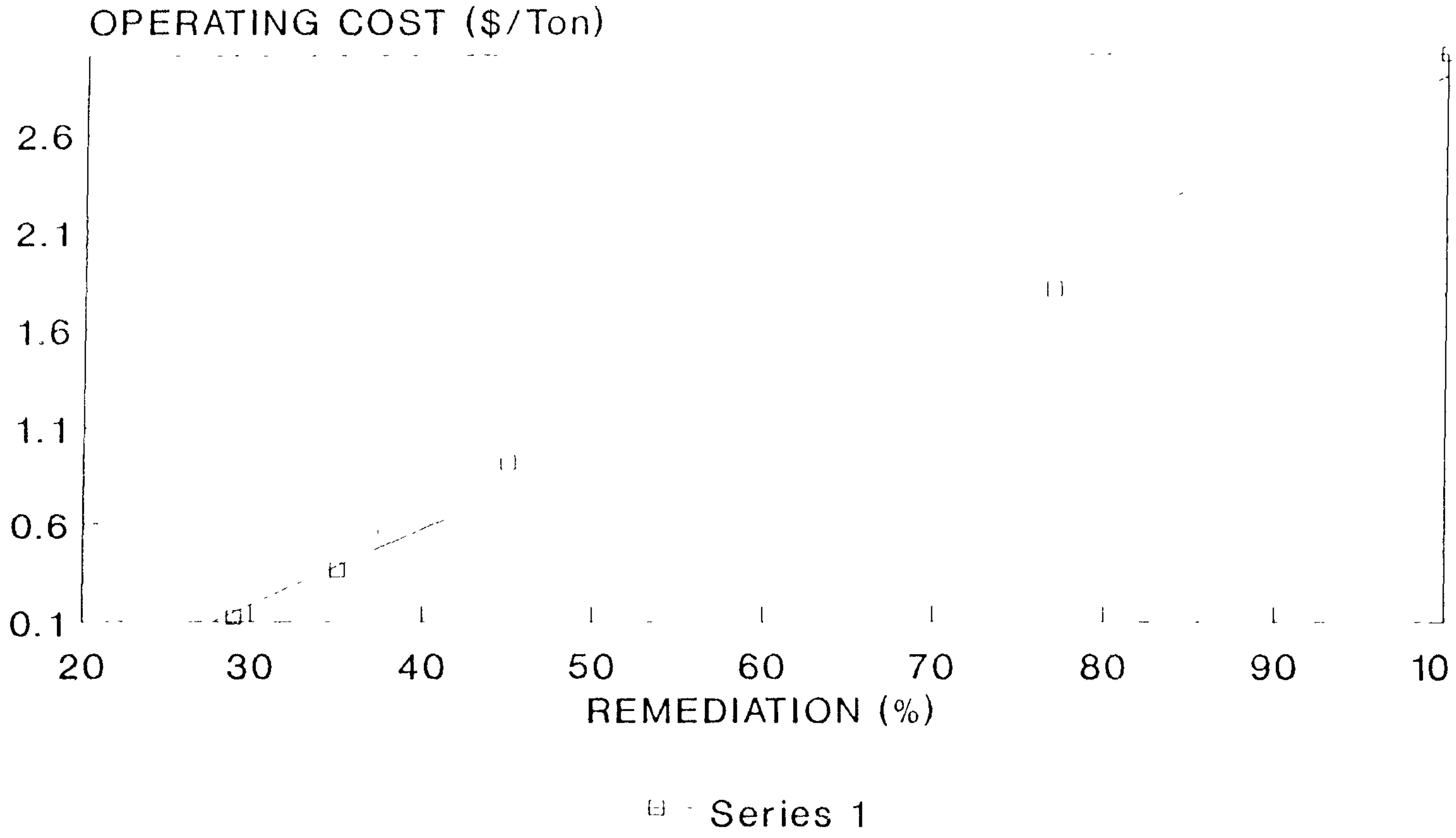
with treatment time, reaching approximately 100% between 15 and 25 minutes. There seems to be no trends with position, indicating that the power is distributed relatively uniformly. There are variations in the duplicates (A and B) but this is probably due to inhomogeneities in the distribution of naphthalene in the sand, leading to different results after sampling. However, it is the trend which is of most significance in this study in which we are trying to estimate the operating cost. That trend is as stated above clear.

Table 5b **Naphthalene Impregnated Sand Pilot Plant Studies: Operating Cost (Incident Power) as a Function of Time and Degree of Remediation**

MW Treatment Time		kw-hr	$/kw-hr	Operating Cost ($/ton)	Remediation (%)
mins	hr				
1	0.017	0.073	0.0029	0.12	29
3	0.05	0.215	0.0086	0.36	35
8	0.13	0.559	0.022	0.92	45
15	0.25	1.075	0.043	1.79	77
25	0.42	1.806	0.072	3.00	100

* The total weight of naphthalene contaminated sand was 52.9 lb (0.024 tons)

Figure 5a Naphthalene Impregnated Sand Pilot Plant Studies: Operating Costs (Incident Power) and % of Remediation



Next, the operating costs were calculated. It is assumed that the incident power is 4.3 kW; and the cost of electricity is $0.04/kW-hour. The results are shown in Table 5b and plotted in Figure 5a. It is seen that for 100% remediation that cost is estimated to be less than $4/ton. While this figure may be in error, it is regarded only as an estimate, the fact that it is so low indicates that the belief is erroneous that the electricity cost will make microwave treatment a prohibitively costly remediation treatment.

5.3.2. Soil Studies

Referring to Table 5c, the degree of remediation of soil as function of microwave treatment time, it is seen that analyses were carried out at five different treatment times at eight different positions. Four positions were serially related: these are referred to as positions 1-4; the side-by-side positions are referred to as A and B. It was assumed that the A and B position samples would correspond to duplicate sampling of a similarly treated substrate. First, the overall trend: remediation increases with treatment time, reaching approximately 100% between 15 and 20 minutes. There seems to be no trends with position, indicating that the power is distributed relatively

Table 5c Naphthalene Impregnated Soil Pilot Plant Studies: Naphthalene Removed as a Function of Time

time / No		Microwave Treatment Time																			
		5 min				10 min				15 min				20 min				30 min			
		1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4	1	2	3	4
CON. ng/ul	A	179.1	134.7	173.6	160.8	50.4	186.9	159.0	194.7	149.0	13 37	145 2	124.0	21.0	10.6	23.5	18.5	10.9	31.3	24.5	27.8
	B	200.8	121.3	149.3	179.3	132.2	139.3	136.7	18 43	384 2	119 8	70.1	170.3	41.5	10.9	29 6	39.7	44 4	23 1	11.8	20.6
	Ave.	190.0	128.0	161.5	169.9	91.3	163.1	147.9	48.2	266 6	66.6	107.6	147.2	31.3	10.7	26.5	29 1	27.7	27.2	18.2	24.2
Naphthalene Removed(%)		7.7	37.8	21.6	17.5	55 7	20.8	28.2	18.2	87 1	96 8	91 8	92 9	98.5	99 5	98 7	98.6	98 7	98.7	99.1	98 8
SD		10.9				14 2				3.6				0 4				0.2			
Average Removed(%)		21.2				30.2				92.9				98.8				98.8			

Blank	No.	1	2	3
	Con. (ng/ul)	158.8	229.9	229.0
	Ave.Con. (ng/ul)	205.9		
	Recovery (%)	$\%(\text{Recovery}) = \frac{205.9\ (\text{ng/ul})}{400\ (\text{ng/ul})} \times 100\%$		

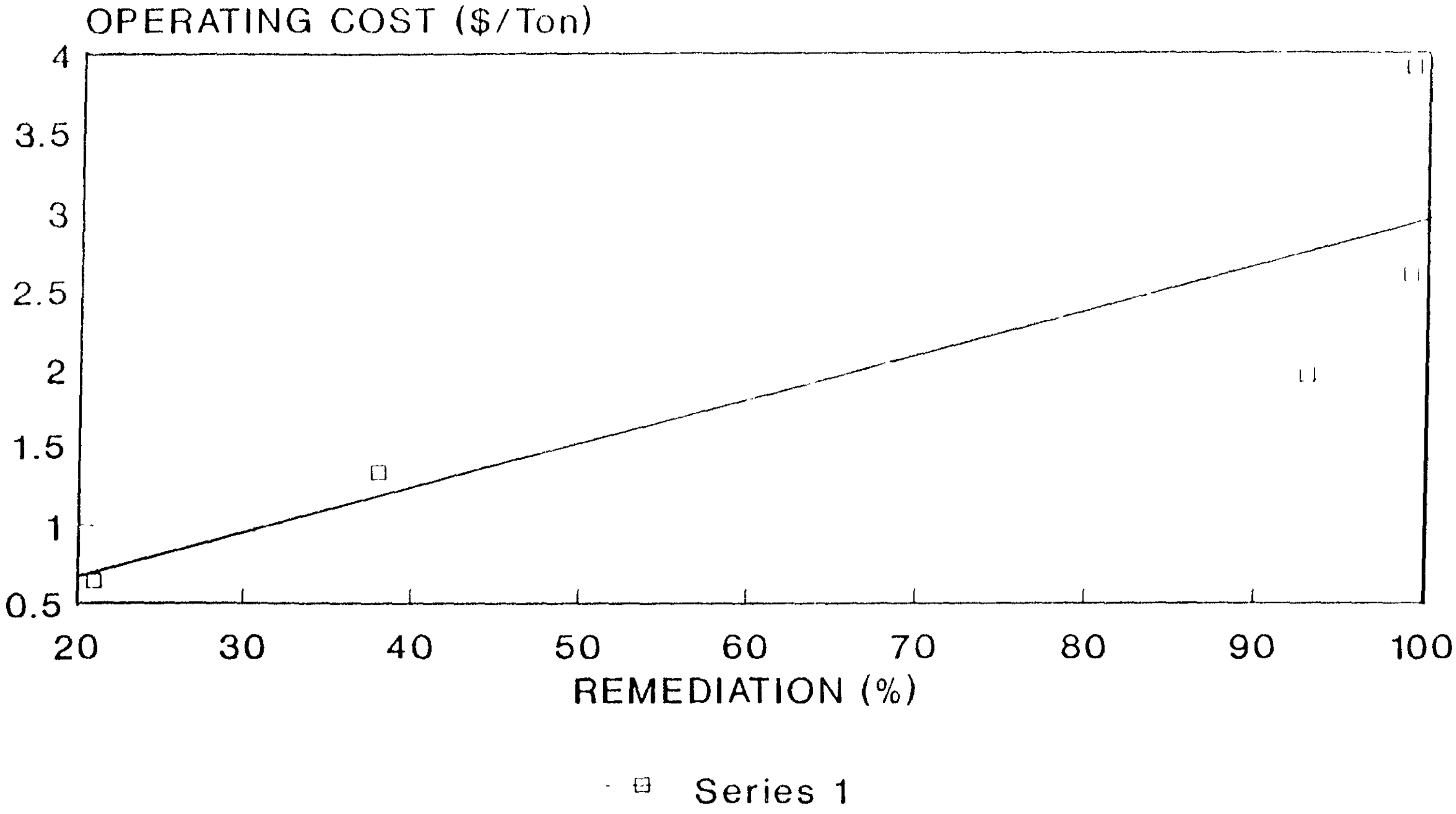
uniformly. There are variations in the duplicates (A and B) but this is probably due to inhomogeneities in the distribution of naphthalene in the sand, leading to different results after sampling. However, it is the trend which is of most significance in this study in which we are trying to estimate the operating cost. That trend is as stated above clear.

Table 5d Naphthalene Impregnated Soil Pilot Plant Studies: Operating Costs (Incident Power) as a Function of Time and Degree of Remediation

MW Treatment Time		kw-hr	$/kw-hr	Operating Cost ($/ton)	Remediation (%)
mins	hr				
5	0.083	0.357	0.014	0.64	21
10	0.17	0.731	0.029	1.32	38
15	0.25	1.075	0.043	1.95	93
20	0.33	1.419	0.057	2.59	99
30	0.50	2.150	0.086	3.91	99

* The total weight of naphthalene contaminated soil was 44.1 lb (0.022 tons)

Figure 5b Naphthalene Impregnated Soil Pilot Plant Studies:Operating Costs (Incident Power) and % of Remediation



the power costs has been made based upon pilot plant studies carried out on naphthalene-impregnated sand and soil, respectively. It has been found that the remediation cost is of the order of $4/ton, an extraordinarily low value. Even if the assumptions were modified for the worst possible scenario, for example, the total power is 400x the incident power, still, the operating cost is less than $15/ton, a remarkably low value. It is concluded that electric costs are not prohibitive, and that the feasibility of microwave treatment of hazardous wastes cannot be ruled out based upon the assumption that such costs will be prohibitive. Note that cost reported in this study is an estimate, and that it's sole purpose is provide a basis for drawing inferences about actual power costs. Such actual power costs will be determined in field testing, using a 50 kW generator operating at 915 Mhz, now being planned.

Conclusions

A process for the remediation of soils contaminated with volatile organics (VOCs) and semi-volatile organics (SVOCs) by microwave-assisted steam distillation had been developed in benchscale studies. But the major concern was that the process is necessarily based upon the use of electrical energy, and thus could not be competitive with fossil fuel based technologies like incineration. That concern was addressed in pilot plant studies.

Studies were carried out on naphthalene-impregnated sand and soil, respectively. A pilot plant rated at 6 kW power and a cavity of 60 cubic feet was used. In studies carried out on a water load it was found that the incident power was 4.3 kW. Using total weights of the substrates in the 40-50 lb range, it was found that the remediation costs were of the order of $4/ton to effect 100% remediation. Even if total power operating costs are taken into consideration, the cost is less than $15/ton. That's an exceedingly low number. For incineration, costs are in the $200-$300/ton range, plus the ash problem and the public's dislike of incineration processes.

The costs obtained in this study cannot be considered as a basis for making comparisons to existing processes. Comparable costs can only be obtained from field testing, now in the planning stage. Their significance is that it does not appear to be the case that the microwave process is prohibitively expensive because of the cost of electric power.

Other studies in the thesis related to analytical procedures: it was concluded that ultrasonic extraction was preferable to Soxhlet extraction; also, normal needle injection into the GC/MS was as effective as hot needle injection.

Future Studies

It has been found that the operating cost in terms of the cost for power to remediate contaminated soil by microwave-assisted steam distillation is not prohibitive. That being the case further pilot plant studies are needed to assist in the design of the scale up process.

One, equations need to be developed relating the following parameters: the relevant soil characteristics; the relevant organic characteristics; the effect of organic concentration and distribution; the depth of penetration of the incident radiation; the effect of the water concentration and distribution; the temperature distribution. All of these must be related to capital and operating costs. These variables must be embedded in dimensionless variables to facilitate scale up.

In the present study, the initial pilot plant studies, the relation between operating costs, specifically, power costs, to effect given degrees of remediation was studied. This work is a starting point. Other effects to be studied in this continuing investigation in the immediate future include: the effect of water; the effect of temperature; the effect of concentration.

Two, the handling of the off-gases. Initially, in the field testing, granulated activated charcoal (GAC) absorption is acceptable. But for actual operations, the probable courses are either recovery by condensation, or destruction in an afterburner. Furthermore, for these two options, it may be necessary to concentrate the organic in the effluent. Membrane separation represents a possible option. Also, if it may be cost-effective to operate above the lower explosion limit in the gas phase. For safety, nitrogen blanketing is needed. Again, membrane separation technology offers the possibility of separating the nitrogen from the air in-situ, rather than bringing in tank cars of liquid nitrogen.

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Appendix 1. <u>Publications and Presentations on Microwave Studies</u> (contributions from NJIT Microwave Treatment of Hazardous Wastes Laboratory)

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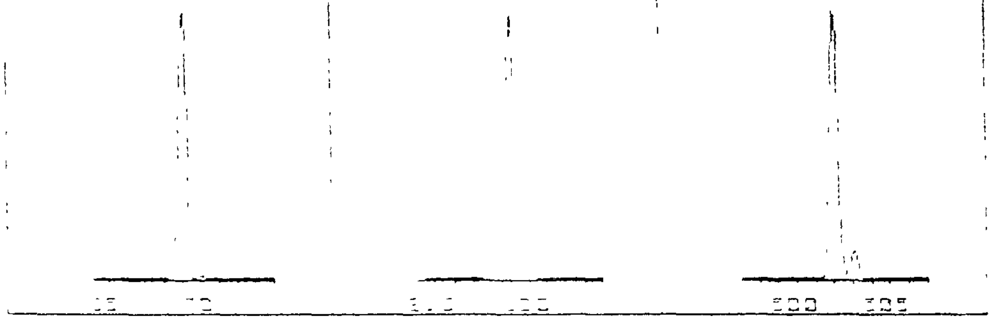
Appendix 2 GC/MS Operating Parameters

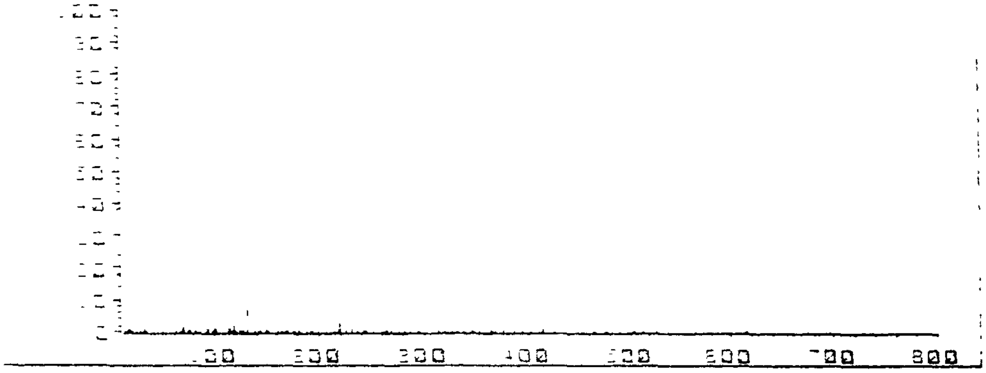
```
A U T O T U N E              ATUNE.U     11 Dec 91   8:32 am
Misc Info      Perfluorotributylamine (PFTBA)
Instrument :  5970
Multiplier   2000                                   Emission      ON
  AMU gain    137       AMU offset     59           Repeller   10.20
 Ion focus    4.0       Entr lens      05              X-ray     4.0
 Axis gain     -6                                  Axis offset    17
   Samples      4         Averages      .            Stepsize   0.10
```

```
 69.10 = 1545524    | 219.10 = 724970    | 502.00 = 147475
   PW = 0.51        |    PW = 0.50       |    PW = 0.46
```



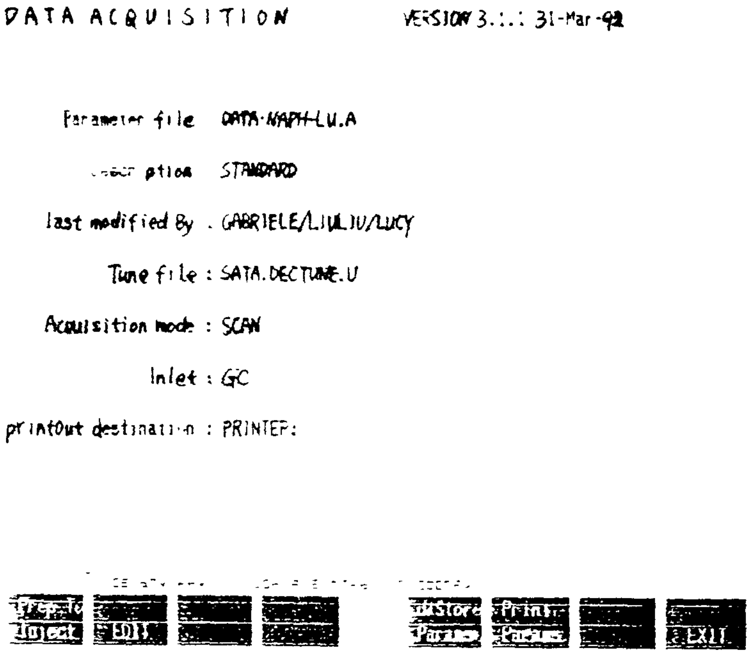
```
[GRAPHICS]
[ATUNE]
```

```
Scan:   10.00 - 800.00 Samp rt: 2   Thresh: 500
111 peaks        Base: 69.00 Abundance: 1156544
```



```
   Mass      Abund    Rel Abund   Iso Mass    Iso Abund    Iso Ratio

  69.00   1156544     100.00        70.00       11830         0.95
 219.00    646464      55.86       220.00       25704         4.03
 502.00    113392       9.48       503.00       11511        10.15
```

```
[GRAPHICS]
[ATUNE]
```



DATA ACQUISITION VERSION 3.1.1 31-Mar-92

Parameter file DATA·NAPH-LU.A

Description STANDARD

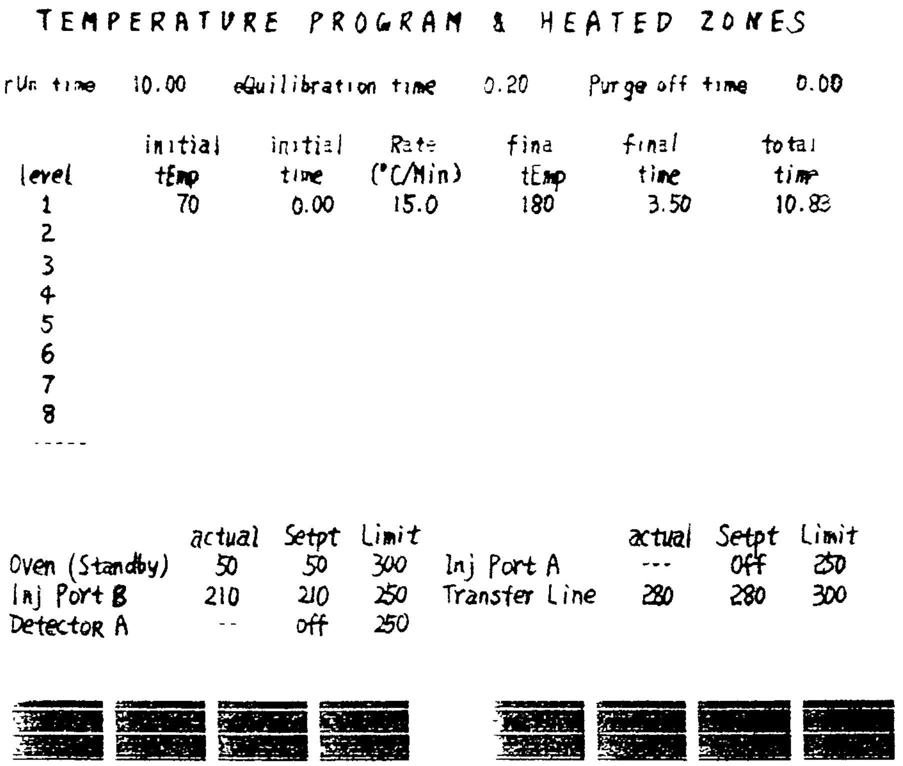
last modified By . GABRIELE/LIULIU/LUCY

Tune file : SATA.DECTUNE.U

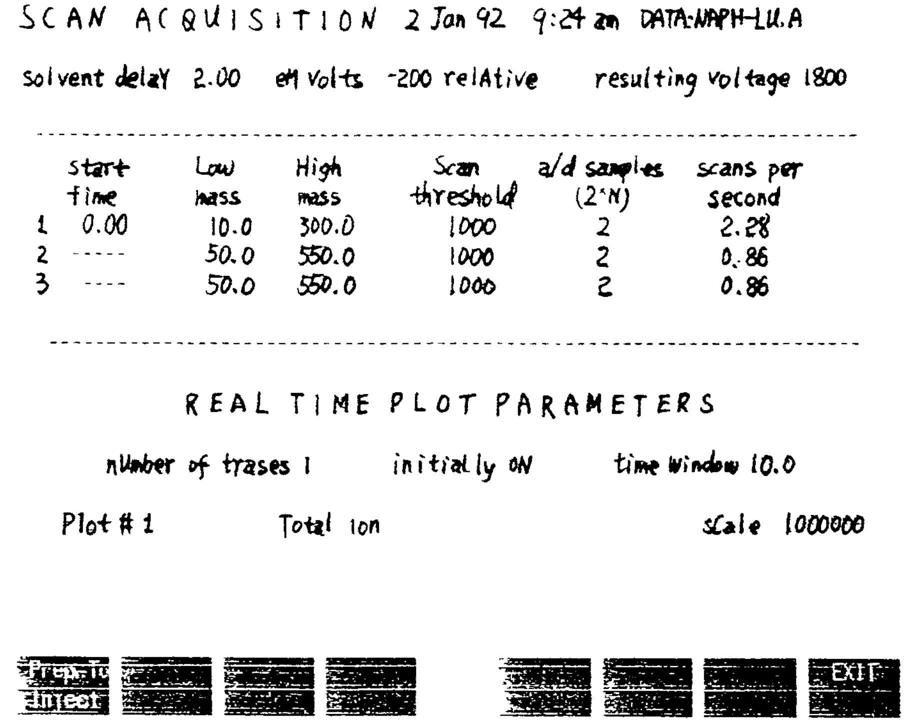
Acquisition mode : SCAN

Inlet : GC

printout destination : PRINTER:

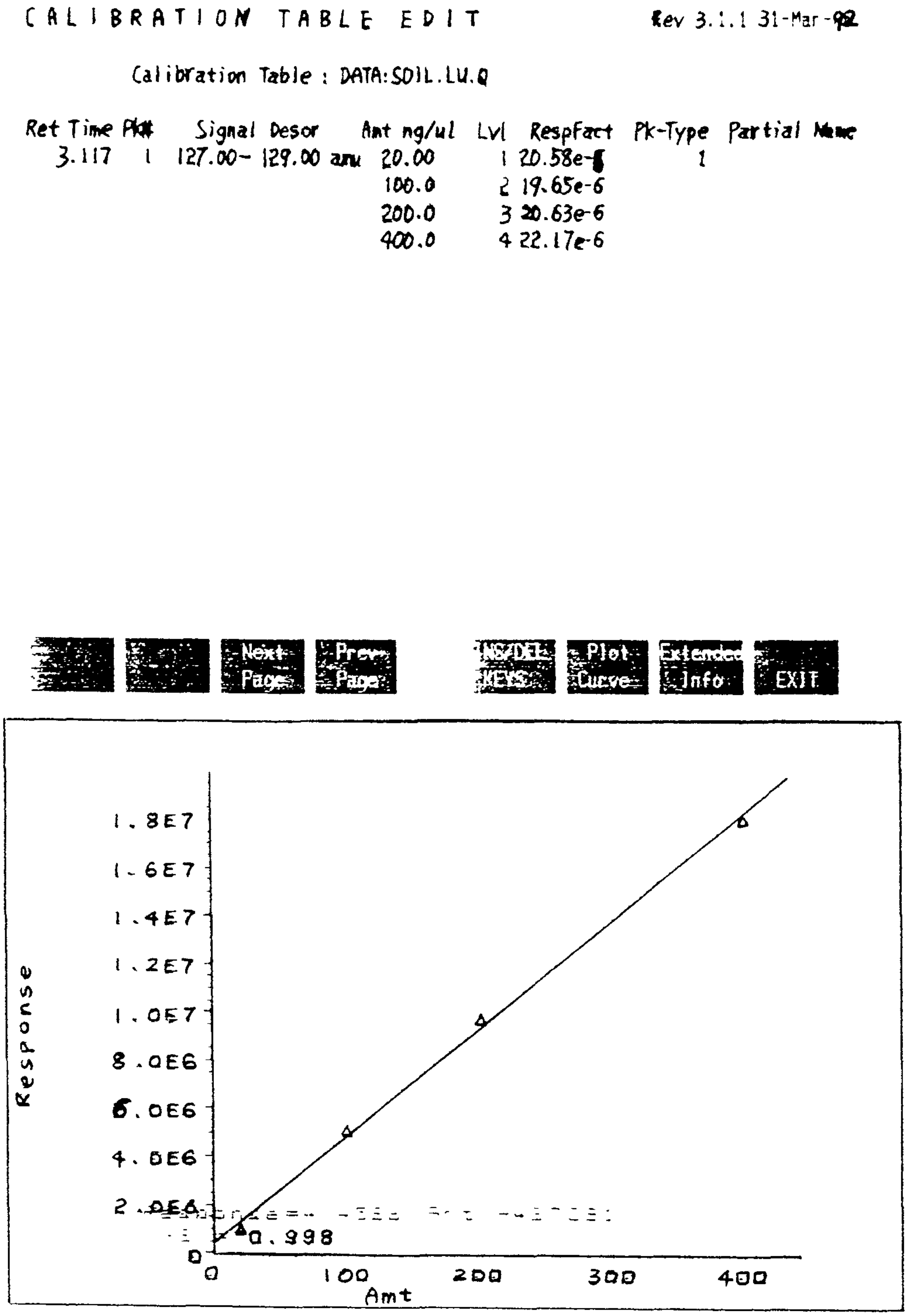


```
TEMPERATURE PROGRAM & HEATED ZONES

rUn time  10.00   eQuilibration time   0.20    Purge off time   0.00

          initial  initial   Rate     final   final    total
level      tEmp     time   (°C/Min)    tEmp    time     time
  1         70      0.00     15.0      180     3.50     10.83
  2
  3
  4
  5
  6
  7
  8
 -----

                  actual  Setpt  Limit                  actual  Setpt  Limit
Oven (Standby)      50      50    300   Inj Port A        ---    Off    250
Inj Port B         210     210    250   Transfer Line     280    280    300
Detector A          --     off    250
```



```
SCAN ACQUISITION  2 Jan 92  9:24 am  DATA:NAPH-LU.A

solvent delaY  2.00   eM Volts  -200 relAtive    resulting voltage 1800

 ------------------------------------------------------------------
    start    Low    High      Scan     a/d samples   scans per
    time     mass   mass    threshold    (2^N)        second
 1  0.00     10.0   300.0     1000         2           2.28
 2  -----    50.0   550.0     1000         2           0.86
 3  ----     50.0   550.0     1000         2           0.86
 ------------------------------------------------------------------

              REAL TIME PLOT PARAMETERS

     nUmber of trases 1      initially ON      time Window 10.0

   Plot # 1          Total ion                       sCale  1000000
```

```
          *** Integrator Events ***

Initial   Peak Width          0.010
initial   Threshold           9
Initial   Area Rejeot         1
            Shoulders  OFF

   0.000  Area Sum off
   0.000  Integ ON
  10.000  Area Sum OFF
  10.000  Integ OFF
```



```
CALIBRATION TABLE EDIT                    Rev 3.1.1 31-Mar-92

        Calibration Table : DATA:SOIL.LU.Q

Ret Time Pk#     Signal Desor    Amt ng/ul  Lvl  RespFact  Pk-Type  Partial Name
   3.117   1  127.00- 129.00 amu  20.00       1 20.58e-6      1
                                  100.0       2 19.65e-6
                                  200.0       3 20.63e-6
                                  400.0       4 22.17e-6
```