A NEW HAZARDOUS WASTE TREATMENT TECHNOLOGY UTILIZING LOW POWER DENSITY MICROWAVE ENERGY

by
Gabriele Windgasse

Thesis submitted to the Faculty of the Graduate School of
the New Jersey Institute of Technology in partial fullfillment of
the requirements for the degree of
Master of Science
1988

APPROVAL SHEET

Title of Thesis: A new Hazardous Waste Treatment Technology utilizing low Power Density Microwave Energy

Name of Candidate: Gabriele Windgasse
Master of Science, 1988

Thesis and Abstract Approved: ______________________ 4/29/88
Dr.Leonard Dauerman Date
Associate Professor
Dept. of Chemical Eng.,
Chemistry and Environm.
Science

______________________ 27th April '88
Date

______________________ April 29, 1988
Date

VITA

Name: Gabriele Else Windgasse

Permanent address:

Degree and date to be conferred: Master of Science, 1988

Date of birth:

Place of birth:

Secondary education: Clara-Schumann-Gymnasium, Bonn,
"Abitur" June 1981.

Collegiate institutions attended	Dates	Degree	Date of Degree
Technische Universität Berlin	9/82-7/86	Equivalent of B.S.	1986
New Jersey Institute of Technology	9/86-5/88	Master of Science	May 1988

Major: Environmental Science/Toxicology Option.

Positions held: Research Assistant, NJIT 9/86-present.

To

L.D. and A.B.R.

ACKNOWLEDGMENTS

I wish to thank Dr. L. Dauerman and Dr. A. B. Ray for the attention and support I received, for sharing their knowledge with me, and for the time they spent answering numerous questions.
Further I want to thank Dr. R. Magee, Executive Director of the Center for Hazardous and Toxic Substance Management, NJIT, for providing us with funding;
and Chih-Ju Jou (Master of Science Candidate) for analyzing part of the experiments described in this thesis.

TABLE OF CONTENTS

Chapter Page

A. ABSTRACT

LIST OF TABLES

LIST OF FIGURES

Figure Page

ABSTRACT

Title of Thesis: A new Hazardous Waste Treatment Technology
utilizing low Power Density Microwave Energy
Gabriele Windgasse, Master of Science, 1988
Thesis directed by: Leonard Dauerman, Associate Professor of
Chemical Engineering, Chemistry and
Environmental Science

Two major applications of a new hazardous waste treatment technology using low power density microwave energy have been characterized: 1) Desorption of organic materials such as: trichloro-ethylene, para-xylene, naphthalene and gasoline hydrocarbons from substrates such as: sand and granulated activated carbon was achieved by microwave induced steam distillation and the application of a new phenomenon: arcing between GAC particles when they are exposed to microwave radiation. All contaminants could be removed to 100% (non-detectable with GC and GC-MS). 2) Decomposition of organic contaminants such as: trichloro-ethylene and trichloro-ethane in arcing/heating GAC beds. A new fluidized bed reactor ("RDW-reactor", after Ray, Dauerman, Windgasse) is described, where microwaves cause heating and arcing in a GAC bed, fluidized with argon or compressed air containing volatilized organic compounds.

Up to 100% decomposition of trichloro-ethylene was achieved. Only hydrogen chloride and carbon dioxide could be detected as products; specifically no other organics could be found in the gas stream analysed by a GC-MS data system.

B) INTRODUCTION

Hazardous and toxic wastes are of major concern of the public, the industry and many governmental agencies. The best approach to the solution of this problem is the prevention or minimization of the production of these wastes.

However, we have to find safe and lasting solutions for the toxic materials already produced and dispersed in the environment. Enclosing and burying of hazardous wastes, either in landfills or on site, increasingly become non-acceptable solutions. The problem is merely being transformed to one which is even more ominous: Enclosure in drums does not prevent leakage or other contamination of soils, surface waters, aquifers and tidal waters. Where that happens the impact on the remediation - if it is possible - is very costly and time consuming. To the affected industry Federal regulations make it increasingly difficult to landfill wastes, plus the number of available landfills is declining, due to Federal regulations. The cost of using landfills will rise tremendously, up to the point where it becomes prohibitive to use this solution for the hazardous waste problem. The following laws resulted in the detrimental impact to the "landfill solution":

1. the Resource Conservation and Recovery Act of 1976 (RCRA)
2. the Hazardous and Solid Waste Amendments of 1984 (HSWA)
3. the Superfund Amendments and Reauthorization Act of 1986 (SARA)

The combined impact of RCRA and HSWA was to cut down on the number of available landfills. Landfills, given interim permit status under RCRA, had to establish means to assure that funds would be available to remedy post-closure problems; also, wells had to be installed to monitor the impact of leaching from the landfill. Under HSWA, a deadline was set (November 1985) for compliance with these RCRA requirements. When that deadline arrived many landfills closed. Not only the number of landfills was reduced, but there has been a drastic curtailment on the materials that can be landfilled. Under RCRA, "...approximately two-thirds of the concentrated solvents...previously land disposed will now require treatment by incineration or an equivalent method." The impact of HSWA will be a further cut down on the use of landfills: HSWA requires that hazardous wastes must be treated with the best demonstrated available technology (BDAT) before it can be disposed on land. A list of available technologies is now being prepared from EPA.

SARA also strikes a blow at the use of landfills: the cost analysis for determining how to dispose waste must now take into account "...all short- and long-term costs, including operations, maintenance and future remedial actions..." in contrast to the prior situation in which only immediate costs had to be factored. Since each Superfund clean-up is treated uniquely the effect of this rule will be to curtail the use of landfills: anticipated future costs like post-closure remediation will be astronomical. There are alternate technologies available: recycling, incineration, biodegradation, vapor extraction, soil washing, carbon adsorption, filtration, precipitation of metals and stabilization. However, given the range of hazardous waste problems, their uniqueness and the staggering costs, new technologies are urgently needed. The goal is to have many options available, so that one can choose the most cost effective procedure for every specific situation. The need for alternative technologies is recognized by EPA's Superfund Innovative Technology Evaluation (SITE) program: EPA evaluates promising technologies in demonstration studies. If they are adopted, they are added to the list of Best Demonstrated Available Technologies. The technologies under investigation as of august 1987 are the following (Environment Reporter 8-21-87, p.1121):

1. Infrared incinerator produced by Shirco Infrared Systems
2. High-temperature plasma pyrolysis produced by New York DEC and Plasma Systems
3. Circulating fluidized bed incinerator produced by Ogden Environmental Services (GA Technologies)
4. Pure oxygen burner by Advanced Combustion Technololgies
5. High-temperature pyroplasma by Westinghouse
6. Solidification process by Hazcon
7. Fixation process by IWT Corp.
8. In-situ vapor extraction by Taravac
9. Basic-extraction sludge treatment by Resource Conservation Co.
10. Biological soil treatment by Detox Industries.

11. Electric pyrolysizer by Westinghouse

This laboratory has developed a comprehensive innovative hazardous waste treatment technology utilizing low density power microwave (MW) energy, that is, power below the levels which effect the formation of continous plasmas. Further, a new type of fluidized bed reactor has been developed. It was termed RDW-reactor, which stands for the names of the inventors and patent applicants Dr. A. B. Ray, Dr. L. Dauerman and G. Windgasse. The reactor has broad application in the chemical processing industry and in in-plant effluent emission control systems. In addition a new physical phenomenon has been characterized: arcing among granulated activated charcoal (GAC) particles in a microwave field.

The technology consists of the following processes, all carried out in a micowave field:

1) Desorption of volatiles from substrates (sand, soil, GAC, molecular sieves, sludge):
   a) Steam distillation - fixed bed
   b) RDW-reactor - fluidized bed
2) Destruction of organics:
   a) Arcing/heating in RDW-reactor - fluidized bed
3) Resource recovery of organics:
   a) Chemical reactions effected in the RDW reactor
4) Regeneration of spent GAC beds:
   a) Steam distillation - fixed bed

  b) RDW reactor - fluidized bed

5) Demobilization of heavy metals in soils:

  a) Vitrification with scrap iron to form non-conductive magnetic ferrites

6) Treatment of recalcitrant (non-biodegradable) organics:

  a) OH radicals (from persulfates, limed bleach ect.) react with recalcitrant organics adsorbed on substrates or in solution

7) In-situ (no excavation) treatment of contaminated soil:

  a) modification of existing technology

8) Encapsulation of metals by spraying a mist of calcined ceramics onto a fluidized bed

This thesis will focus upon the first two processes, namely the desorption of organics from substrates and the destruction of the resulting organic vapors. The other processes will be subjects of future reports issued by this reseach group.

C) THEORY OF MICROWAVES

Microwave energy is a form of electromagnetic radiation, with frequencies ranging from 100MHz (wavelength = 3m) to 300GHz (wavelength = 1mm). The frequencies available for industrial use are 915MHz (wavelength = 32.8cm) and 2450MHz (wavelength = 12.2cm). Usually household MW-ovens operate at 2450MHz. In a magnetron oscillating electrons within a magnetic field produce electromagnetic radiation, which is transmitted through a waveguide into the cavity of the oven (fig. 1)

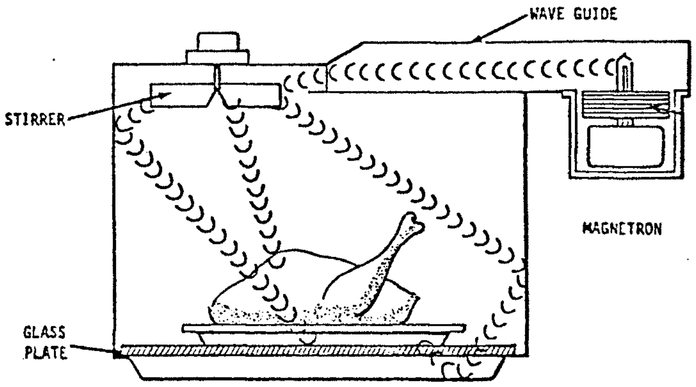


Fig. 1. Microwave oven

MW energy is composed of an electric field and a magnetic field at right angles to each other. The electric field interacts with charged or polar particles, or molecules with dipole moments. The magnetic field interacts with magnetic matter (i.e. ferrite) or charged particles in motion. The adsorption of one component leads to the collapse of the other. From main interest in dealing with dielectric materials is the electric field.

Objects (the load) placed in the oven interact with the radiation in several ways: The radiation is reflected, diffracted and adsorbed. The extent to which a given object interacts with the radiation in each of these ways is dependent upon the physical and chemical nature and the shape of the object as well.

1) Reflection of the microwave radiation by the object is undesirable. One obvious reason is that all available energy isn't being utilized. But there is a far more important reason: reflected radiation damages the magnetron. Note, that such radiation, in addition to being reflected, can be transmitted or diffracted. Also, it is of importance that the object does not draw extra power from the magnetron - thus creating a short circuit.

2) Diffraction occurs if the object and the wavelength of the radiation are of comparable magnitude. Then the radiation is bent around the load. This is the case in a household MW-oven, where the objects are in the decimeter range. It explains why it is very difficult to predict the field strength in a MW-oven: if any load is placed within the cavity, the size and shape of an object must be taken into account to define the field. Very small objects will adsorb MW energy very inefficiently.

3) The adsorbtion of MW energy is more complex: The depth of penetration - DoP - is sometimes defined as the depth at which the power level of the incident wave is decreased by 50%. This means, that 50% of the power is absorbed between the surface of the object and the penetation depth.

The degree of reflection and penetration of a particular material depend on its dielectric properties. There are three important parameters: The real part of the dielectric constant (ε'), the imaginary part of the dielectric constant (ε'') which is called "loss factor". These two parameters determine the incident radiation which is adsorbed. The loss tangent (tan d) is defined as the ratio of $\varepsilon''/\varepsilon'$, and determines the penetration depth: the larger the tan d, the smaller is the DoP (from W.R. Tinga, Dept. of Electr. Engineering, University of Alberta, Canada: Interactions of MW with materials, IMPI-Canada 1970):

$$\text{DoP} = \frac{0.269 \times \text{wavelength in vacuum(cm)} \times (\varepsilon')^{1/2}}{(\varepsilon'')}$$

or

$$\text{DoP} = \frac{0.269 \times \text{wavelength in vacuum(cm)}}{(\varepsilon')^{1/2} \times \tan d}$$

The third parameter is the relaxation time. It is a measure of the ability of a molecule to synchronize its rotation with that of the oscillating field of the MW radiation.

All three parameters are temperature dependent. The DoP for several materials at 20°C, at 2450MHz and 915MHz is (from R. Schiffmann: Microwave heating for the Food Industry, IMPI-Europe 1975):

Material	(ε')	tan d	DoP(m) 915MHz	DoP(m) 2450MHz
Al-ceramics	8 - 11	.0001-.001	311.9- 26.6	116.0 - 9.9
most plastics	2 - 4.5	.001-.02	62.4 - 2.1	23.2 - .7
pyrex glass	4.0	.001-.005	44.1 - 8.8	16.4 - 3.3
H_2O	78	.16	.64	.23

This table explains the transparency of MW energy for some materials. Note that at low frequencies the DoP is geater.

MW energy belongs to the non-ionizing radiation category, and can only cause changes in rotational energy of the molecules. Heating is caused by the friction of rotating molecules. Another way of looking at this is to visulize the dipoles lining up with the electrical field. The field changes direction 2450 million times per second. As the field is reversed the dipoles rotate to realign with the field and in the process intermolecular collisions cause heating. The size of a molecule determines how fast the dipole can realign. This property is called relaxation time. Large molecules usually have long relaxation times which decrease as the temperatures rise. Then the rate of energy absorption is increased as the molecules become more mobile (this can cause "runaway heating"). Small molecules like water tend to absorb less energy if the temperatue rises: the relaxation time is decreased further, the molecules move faster than the oscillating field.

Adsorption of energy can take place only where molecular rotation is possible (not in such covalently linked molecules as plastics). Ionic species adsorb only if they are in liquid state or in solution. The effects of adding a salt to water are: a) an increase in energy adsorption and b) a decrease in DoP.

Metals are weak adsorbers of MW energy, having a DoP much smaller than 1mm. They mainly act as reflectors (for example the steel cavity in a MW oven). However, the magnetic component of the MW radiation will also induce currents on the surface of metals. All materials with magnetic domains (metallic and ionic species) will adsorb MW energy leading to heating. Magnetic materials cease to adsorb MW energy at their Curie points, since they loose their magnetism at that temperature.

To prevent leakage of MW radiation, a perforated metal sheet bonded to the glass or plastic window is placed in the oven door. The wavelength of the MWs is too large to penetrate the small holes. In the laboratory metal window-screen was used to prevent MW leakage.

D) STEAM DISTILLATION STUDIES

1) Theory

A multiphase system of immiscible liquids will boil when the sum of the partial pressures of the respective liquids is equal to the ambient pressure, in accordance with Dalton's Law. The partial pressure will be equal to the vpor pressure of the respective liquid at the boiling temperature. If one of the components is water, then, the maximum temperature of the system is 100°C, assuming, that the ambient pressure is 760mmHg. This is the basis for the widely used chemical engineering unit operation called steam distillation. It is used to seperate small amounts of volatile organics from large amounts of non-volatile tars. Analogously, traces of organic contaminants on substrates such as sand, soil, GAC, molecular sieves and sludge represent volatile organics adsorbed on non-volatile substrates. It would appear, that desorption of these contaminants should be effected by steam distillation.

Heating the substrates thermally can not effect rapid steam distillation since the heat transfer from gas and container to the substrate, to water and contaminants is too slow to make that system feasible. In addition to the high energy costs associated with thermal treatment, there are substantial costs for heat resistant materials, plus the nature of thermal treatment units makes them unsuitable for on-site use.

In contrast to thermal treatment, microwave energy is <u>directly</u>

adsorbed by chemicals with dipole moments and low relaxation times. These are characteristics of water and many other organics. Since many substrates such as sand, soil, molecular sieves ect. do not adsorb MW energy it can be used to achieve steam distillation in these systems. Thus one utilizes the optimum method to effect heat transfer to the water and additional savings in installation and maintenance costs are foreseeable.

It was the purpose of the following studies to determine if, in fact, MW energy can effect a desorption of organics adsorbed on substrates of interest in the treatment of hazardous waste. The following organics were used, either on Granulated Activated Carbon (GAC) or pure sand:

a) p-Xylene representing a non-polar, highly volatile liquid soil contaminant

b) Naphthalene representing a non-polar solid with low vapor pressure

c) a mixture of gasoline hydrocarbons adsorbed on GAC.

a) and b) were added seperately to sand; c) was an actual industrial sample.

The experiments prove that it was possible to steamdistill organics, completely, from sand as well as from GAC. The percent-removal of organics is dependent on the amount of water available for steam distillation. For the experiments with sand this is the total amount of H_2O in the system; for GAC it is the amount of water already present in the pores of the GAC particles. Control experiments were carried out, to prove the effectiveness of the MW heating over conventional thermal heating.

2) Studies on sand

Experimental

Two organics were used in the experiments: para-xylene and naphthalene. p-Xylene, or 1,4-dimethyl benzene, is a nonpolar, highly volatile and flammable organic liquid. It is present in gasoline and used in the solvent industry as well as for making dyes, paints and insecticides. The vapor can be irritating to the eyes and the respiratory tract. Naphthalene is a solid, non-polar organic, with a very low vapor pressure. It is used for dyes, explosives and as a moth repellant. Naphthalene can be irritating to eyes, nose, throat and skin.

	para-xylene	naphthalene
Formula:	C_8H_{10}	$C_{10}H_8$
Mol.Wt:	106.17g	128.17g
Density:	0.8611g/ml	0.9625g/ml $^{100/4}$
Melting point:	13.3°C	80.5°C
Boiling point:	138.3°C	218.0°C
Dipole moment:	0 debyes (gasphase)	0 debyes
Vapor pressure:	10mmHg at 27.3°C	0.032mmHg at 25°C
OSHA limit:	100ppm over 8 hours	10ppm over 8 hours
Organic used:	Aldrich#13,444-9 "high purity"	Fisher Scientific, mp range 79.6-80.8°C

Sand used: Kiddies Fun Play Sand, Quikrete Co., washed, dried at 325°C

10g pure and clean sand in a 100ml glass beaker was uniformly mixed with one of the organic compounds. In the para-xylene experiments, 0.5ml (0.43055g or 4.055×10^{-3}moles) of the liquid was added to the sand sample. For the naphthalene experiments 5g of the solid was dissolved in about 120ml of hexane (HPLC-grade) and added to 200g sand. The mixture was stirred to dryness, and it was assumed that only the hexane evaporated. 10g sand contain theoretically 1.9505×10^{-3}mole naphthalene. Diffrent amounts of water were added to the naphthalene contaminated sand sample. The mixtures were exposed either to MW radiation (setting: "high"), or heated to diffrent temperatures in a thermal-convection oven; both exposures lasting 5 minutes.
The beaker containing the sand was then covered with a watchglass and cooled to room temperature. The sand was transfered, completely, into a fritted glass thimble, and extracted with 50ml hexane (HPLC-grade) for 3 hours in a Soxhlet-extractor. A gas chromatograph, external standards and the peak area calculation method were used for quantitative analysis.

Equipments used:

- SHARP carousel II convection microwave oven; output 700W, 2450MHz, serial no: 19763
- Gas-chromatograph, GOW-MAC, series 580-FID, model 169-560-FID
- Column: 5% OV-101 Chromasorb P, AW DMSC 80/100 mesh
- Printer: GOW-MAC 70-990
- Syringe: Hamilton Co., 10ul #801

GC-parameters:

- volume injected: 1.ul
- helium-flowrate: 30ml/min
- hydrogen-flowrate: 30ml/min
- air-flowrate: 200ml/min
- paper speed: 2.5cm/min
- Area calculation:

  peakheight x peakwidth at half-height

  The calculated area was multiplied with the attenuation, to adjust all areas to the range 10^{-11}.
- temperatures:

	para-xylene	naphthalene
detector temp.°C	200	270
column temp.°C	140	205
injector temp.°C	190	250

A calibration curve for p-xylene was developed using 5 hexane standards (51ppm to 5105ppm). Regression analysis produced the following formula:

$$ppm_{px} = \frac{\text{adj. area} + 2.97}{0.19657}$$

Five naphthalene standards in hexane were used (75ppm to 7572ppm) to obtain the following two equations:

at attenuation of 256×10^{-11}: 7572ppm, 1514ppm, 757ppm

(high concentrations)

$$ppm_{na} = \frac{\text{adj. area} - 39.6}{0.1658}$$

at attenuation 32 x 10^{-11}: 757ppm, 151ppm, 75ppm

(low concentrations)

$$ppm_{na} = \frac{\text{adj. area} + 1.68}{0.1797}$$

Two blank experiments were conducted (extraction of contaminated sand). The concentrations of the organics found after extraction and GC analysis, and the calculated concentration are given below

	p-xylene	naphthalene
calculated	13,041ppm	7,387ppm
experimental	13,477ppm	7,538ppm

The amounts of steam-distilled organics can be calculated using the Ideal Gas Law (1) and by Dalton's Law (2); it gives the mole fraction of the steamdistilled organic in the gasphase.

$$p\ V = n\ R\ T \tag{1}$$

$$X_{org.} = \frac{n_{org.}}{n_{water} + n_{org.}} = \frac{VP_{org}}{VP_{water} + VP_{org.}} \tag{2}$$

The ratio of the vapor pressures (VP_{water}/VP_{org}) gives the amount of H_2O necessary to steamdistill 1 mole of organic from the mixture.

Equation (3) is deduced directly from Eq. (2).

$$\frac{VP_{water}}{VP_{org.}} = \frac{\text{moles water}}{\text{moles organic}} \qquad (3)$$

To solve equations (2) and (3) the vapor pressures of water and the organic are needed. The vapor pressure for water was taken from CRC handbook p.D-189. Two formulas were adapted from CRC handbook 86/87, D-204,206 to calculate the vapor pressures for p-xylene and naphthalene at diffrent temperatures:

$$VP_{px} = 1.1618 \times 10^{-3} \times (\text{Temp.}^{\circ}\text{C})^{2.6747} \qquad (4)$$

$$VP_{na} = 1.099 \times 10^{-8} \times (\text{Temp.}^{\circ}\text{C})^{4.6203} \qquad (5)$$

Following are the calculated vapor pressures (mmHg) at temperatures used in the experiments:

temp°C	vp water	vp p-xylene	vp naphthalene	vp sum
65	187.54	82.06	-	269.60
65	187.54	-	2.61	190.15
91.4	554.35	204.21	-	758.56
99.2	738.53	-	18.43	756.96

The temperature in the thermal experiments was controlled by a sensor. Three p-xylene experiments were carried out at 110°C. It was assumed, that steam distillation takes place, as soon as the system reached 91.4°C - the same conditions as in the MW experiments.

From the vapor pressures, the molefraction X in the gasphase can be calculated from Eq.(2), and the number of moles H_2O necessary to steamdistill 1 mole of organic at that temperature by Eq.(3):

temp.°C	X_{px}	X_{na}	$\frac{\text{moles water}}{\text{moles org.}}$
65	0.304	-	2.29
65	-	0.0137	71.85
91.4	0.2692	-	2.71
99.2	-	0.0244	40.07

Table I gives a summary of both experiments, Table II and III give details for the p-xylene, and naphthalene resp., experiments. The GC-graphs for the experiments are attached in Appendix D-2.

Table I

Summary

Para-xylene and naphthalene experiments

exper.	ml H_2O	% removal MW	% removal 65°C	% removal 110°C
p-xylene	-	56.5	55.3	>99
p-xylene	1	>99	53.1	94.8
naphthal.	-	20.3	43.2	-
naphthal.	1	24.1	64.8	-
naphthal.	2	59.5	-	-
naphthal.	4	>99	(21.7)*	-

* It is possible, that the Soxhlet-Extraction was not complete, since water was found in the sand after the experiments. This may have clogged the thimble (hexane and water are immiscible).

Table II

Para-xylene experiments

10g sand containing 13,477ppm p-xylene,
exposed to 5 min MW or Thermal Heating

exp.#	ml H_2O	heating	temp. ^oC	ppm p-x found	% removal
1	-	-	20.0	13,477	-
2	-	MW	-	6,632	50.8
3	-	MW	-	5,101	62.2
4	-	Thermal	65	6,026	55.3
5	-	Thermal	110	traces	>99
6	1	MW	91.5	traces	>99
7	1	MW	91.5	traces	>99
8	1	Thermal	65	6,327	53.1
9	1	Thermal	110	1,293	90.0
10	1	thermal	110	traces	>99

Table III

Naphthalene experiments

10g sand containing 7,538ppm naphthalene,
exposed to 5 min MW or Thermal Heating

exp.#	ml H_2O	heating	temp. ^oC	ppm p-x found	% removal
1	-	-	20	7,538	-
2	-	MW	-	6,010	20.3
3	-	Thermal	65	4,283	43.2
4	1	MW	99.2	5,724	24.1
5	1	Thermal	65	2,657	64.8
6	2	MW	99.2	3,050	59.5
7	4	MW	99.2	traces	>99
8	4	Thermal	65	7,233	(4.0)*
9	4	Thermal	65	4,575	(39.3)*

* It is possible, that the Soxhlet-Extraction was not complete, since water was found in the sand after the experiments. This may have clogged the thimble (hexane and water are immiscible).

Results and discussion

To achieve steam distillation conditions, the sum of the vapor pressures of the organic and H_2O has to equal ambient pressure, that is 760mmHg. This is the case if the system is heated to 91.4^{o} (para-xylene) or 99.2^{o}C (naphthalene), no matter whether the heating is achieved thermally or by MW irradiation. MW selectively heat water molecules, so that the temperatures necessary for steam distillation are reached very rapidly, contrary to thermal heating, which is dependant on the heat transfer through sand and air.

In Tables I and II, the para-xylene experiments where no water was added do show a significant removal of p-xylene. The nearly 100% removal at 110^{o}C are presumably due to evaporation of p-xylene (bp 138.3^{o}C) on the heated sand. After MW heating under similar conditions the removal was 56.5%. It implies that the sand contained some water (room moisture) which caused steam distillation.

The temperatures in the MW experiments could not be determined. Most of the MW energy is directly adsorbed by H_2O molecules heating the water and generating steam. It was assumed, that the temperature of the organic and the water are about the same. The sand and the glass beaker are heated from the hot vapors (water and organics) but very slowly. Ultimately the whole system will reach the temperature of the vapors (91.4 and 99.2^{o}C).

To steamdistill 0.5ml para-xylene (4.055 x 10^{-3}mole) from sand

1ml water (5.55×10^{-2}mole) is sufficient. The theoretical amount of water necessary is calculated by equ.(3):

$$\frac{\text{moles water}}{\text{1 mole px}} \times \text{moles px on sand} = 2.71 \times 4.055 \times 10^{-3}$$

$$= 0.01099\text{moles } H_2O$$

$$= 0.1978\text{ml } H_2O$$

The room moisture plus the water added (1ml) supply more than five times the amount of water necessary to steamdistill 0.5ml p-xylene. Thus, complete removal is easily achieved.

In the thermal experiments, the added water decreases the removal efficiency (from 99% to 95% and 55% to 53% resp.): the energy is used to evaporate water in addition to p-xylene.

From equation (3) one can understand that contaminants with a low boiling point, like naphthalene, need a large amount of water for complete steam distillation from sand. Examining Tables I and III, it is clear, that the amount of water necessary to steamdistill naphthalene in the experiments is approximately four times that needed for p-xylene. This can be explained by the smaller mole fraction of naphthalene distilled at the boiling temperature (X_{px} 0.2692 vs. X_{na} 0.0244). If one compares the number of moles water necessary to steamdistill 1 mole of organic the diffence is nearly 20fold: for p-xylene 2.71moles H_2O and 40.07moles H_2O for naphthalene, at the corresponding steam distillation temperatures. The calculated amount of H_2O necessary to steamdistill 1.9505×10^{-3}mole naphthalene present in 10g sand at 99.2°C:

$\frac{\underline{\text{moles}}\ \underline{\text{water}}}{\text{1mole napht.}} \times \text{moles napht. present} = 40.07 \times 1.9505 \times 10^{-3}$

$= 0.0782$ mole H_2O

$= 1.4$ ml H_2O

Complete removal of naphthalene is achieved, in the MW experiments, only after the addition of 4ml water - 2ml H_2O, more than the calculated amount give, only 59% removal. The reason for that is not clear.

The experiments in which naphthalene was thermally heated showed incomplete removal. In experiments 8 and 9 not all of the water that was added evaporated, and the sand remained moist. It is possible that this resulted in an incomplete Soxhlet extraction; the solvent used (hexane) is immiscible with water, and the moist sand clogged the extraction thimble.

The experiments showed that both p-xylene and naphthalene can be steam distilled from sand by adding water and using MW irradiation. The conclusion is, that contaminated moist sand can be completely decontaminated from organics by MW induced steam distillation.

Future experiments:

Will the same results occur, when organic soil is treated?

Effects of high molecular weight organics (tar ect.).

Is it possible to recover the steamdistilled vapors?

3) Studies on GAC

Experimental

Two studies were conducted on an industrial petroleum loaded GAC sample. In one series diffrent volumes of water were added to the GAC sample with subsequent MW heating (single stage steam distillation): 10ml,MS-1; 20ml,MS-2; 30ml,MS-5; 40ml,MS-6; 50ml,MS-7.

In the second series 10ml water was repeatedly added to the same GAC sample, which was heated with MW after each addition (multiple stage heating): 1x10ml,SD-1; 2x10ml,SD-2; 3x10ml,SD-3; 4x10ml,SD-4.

The water was added to 10g GAC sample in a 150ml glassbeaker, and then exposed to MW radiation (setting "High") for 3-10min, depending on the volume of H_2O present. At the end of each exposure the GAC was found to be dry. In all multiple stage experiments and in MS-1 and MS-2 the GAC started to glow red and/or to arc. The SD-3 experiment was interrupted several times to avoid overheating of the beaker. For the multistage experiments the GAC was cooled before each new addition of water. After cooling down the GAC was transfered to a glass thimble, and extracted in a Soxhlet extractor for 3 hours using 50ml methanol. 2.0ul of the extract was injected in a gas chromatograph. The peak areas for the two biggest peaks were calculated by the same method as in the steam distillation experiments in section 2. To identify the compounds on the GAC and to confirm the GC results, 1.0ul of the extracts was injected in a GC-MS (gas chomatograph with a mass spectrometer detector). For all raw data material (GC-MS parameters, graphs ect.) see Appendix D-3.

Two blank experiments were conducted to obtain the amount of hydrocarbons on 10g GAC, without steam distillation treatment: HP-1 and HP-2 were extracted for 3 hours; the average numbers are given in Table IV and V. The removal due to steam distillation is given in % relative to the blanks. Tables IV and V show the GC results for single stage heating and multistage heating, respectively, Table VI shows the GC-MS results of the multiple stage experiments.

Equipment and Parameters:

- SHARP carousel II convection microwave oven; serial nr. 19763
- GC-MS: Hewlett-Packard: GC 5890 serial # 2738A10309
  MSD 5970B serial # 2716A10 472
  Chemstation computer system 8725 K 59784
  Column: PONA 50m x 0.2mm
- Syringe: Hamilton 10.0ul, #801
- Methanol: FLUKA 275409-687 HPLC grade
- GC: GOW-MAC, series 580, model 169-560-FID
  Column: 5% OV-101 Chromasorb P, AW DMSC 80/100 mesh
  parameters:
    - range x attenuation: 10^{-10} x 32
    - helium (carrier gas): 30ml/min @ 40psi
    - hydrogen: 25ml/min @ 40psi

- air: 200ml/min @ 26psi
- detector temp.: 200°C
- column temp.: 100°C
- injector temp.: 175°C
- paper speed: 5.0cm/min

Table IV

Single stage steam distillation of GAC

Experiments with 10g hydrocarbon loaded GAC
exposed to MW heating, after adding various volumes of H_2O.

Exp.	total H_2O ml	peak Area		% removal		average % removal
		peak 1	peak 2	peak 1	peak 2	
blank	-	193.6	355.9	-	-	-
MS-1	10	79.7	174.4	58.8	51.0	54.9
MS-2	20	114.4	256.0	40.9	28.0	34.5
MS-5	30	37.4	74.9	80.7	79.0	79.9
MS-6	40	127.7	290.4	34.0	18.4	26.2
MS-7	50	103.8	208.3	46.4	41.5	44.0

Table V

Multiple stage steam distillation of GAC

Experiments with 10g hydrocarbon loaded GAC
after every addition of 10ml H_2O the system was heated with
microwaves for 3 min.

Exp.	total H_2O ml	peak Area		% removal		average
		peak 1	peak 2	peak 1	peak 2	% removal
blank	-	193.6	355.9	-	-	-
SD-1	10	17.6	37.4	91.0	89.6	90.3
SD-2	20	14.1	29.9	92.7	91.6	92.2
SD-3	30	n.d.	n.d.	100	100	100
SD-4	40	n.d.	n.d.	100	100	100

Table VI

GC-MS analysis of multiple stage steam distillation

Exp.	total H_2O ml	peak Area		% removal		average % removal
		peak 1	peak 2	peak 1	peak 2	
blank	-	$13.44x10^{8}$	$6.87x10^{8}$	-	-	-
SD-1	10	$9.60x10^{7}$	$4.52x10^{7}$	92.85	93.43	93.14
SD-2	20	$8.89x10^{7}$	$4.12x10^{7}$	93.38	94.01	93.70
SD-3	30	no peaks detected		100	100	100
SD-4	40	no peaks detected		100	100	100

Results and discussion

GC-MS analysis yields more information than any other analytical method to date. The 50m capillary column used gave excellent separation of peaks, even isomers can be distinguished. The MS gives for every compound a characteristic pattern of charged molecule fractions. In other words: every molecule is ionized via an electron source, and ultimately broken into smaller parts, which are positively charged. These cations are accelerated and guided into a quadropole. The quadropole is tuned to let only one ionic species at a time reach the detector at the end of the quadropole. However, the MS can scan a wide range of masses in a short time. For every mass scanned, the number of ions detected is listed. The abundance of detected masses in one scan give the characteristic spectrum for a compound.

For a run the extracted GAC sample is injected into the GC, the separated compounds leave the column one after another, and enter the MS. One compound after another is broken into its characteristic masses, which are detected and counted. The sum of all ions counted gives the Total Ion Chromatogram (TIC) at that time. The TIC over the whole run is equivalent to the graph of a GC. Figure 2 shows the TIC for the blank experiment M-1 (10g contaminated GAC were extracted for 4 hours).

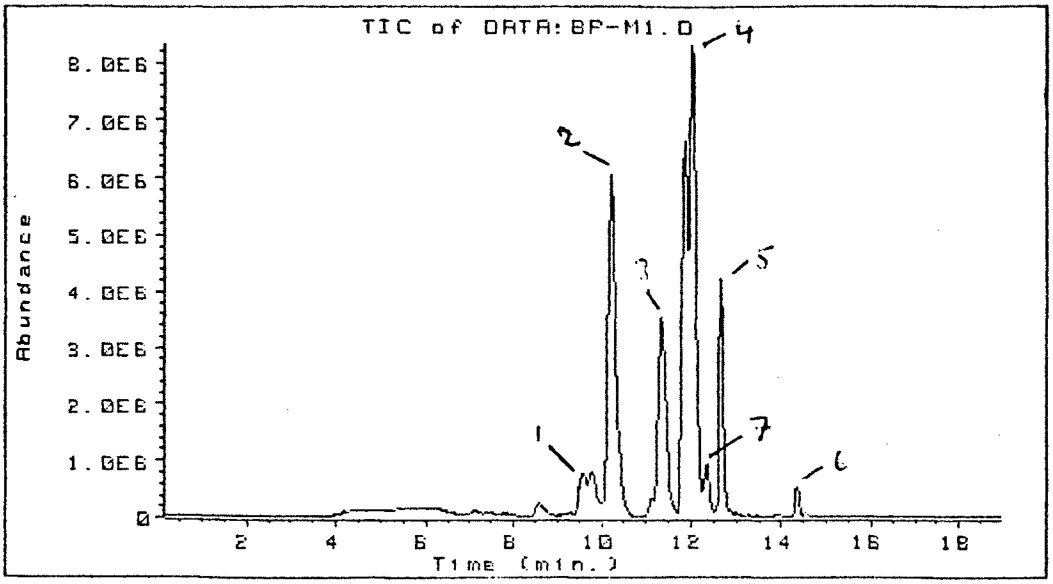
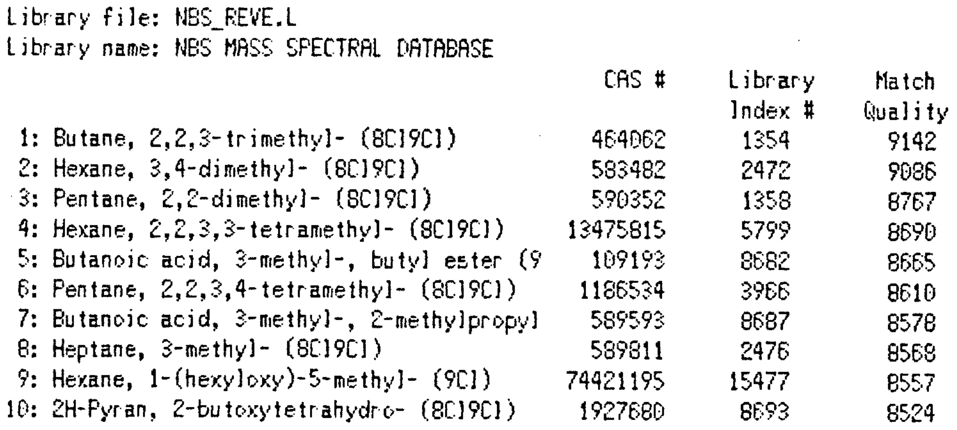


Fig.2 TIC of Blank run

The data for every run is digitally stored, and can be manipulated in many ways to obtain other information. For example a spectrum of the masses detected at a specific time during the run can be shown. This spectrum (for instance at a peak in the TIC) can be compared to the 38,000 spectra stored in the NBS library files. The library search gives the 10 best matches found, and the goodness of fit, compared to the spectrum from the TIC. See fig.3 for an example.



```
Library file: NBS_REVE.L
Library name: NBS MASS SPECTRAL DATABASE
                                               CAS #     Library    Match
                                                         Index #    Quality
 1: Butane, 2,2,3-trimethyl- (8CI9CI)          464062      1354       9142
 2: Hexane, 3,4-dimethyl- (8CI9CI)             583482      2472       9086
 3: Pentane, 2,2-dimethyl- (8CI9CI)            590352      1358       8767
 4: Hexane, 2,2,3,3-tetramethyl- (8CI9CI)    13475815      5799       8690
 5: Butanoic acid, 3-methyl-, butyl ester (9   109193      8682       8665
 6: Pentane, 2,2,3,4-tetramethyl- (8CI9CI)    1186534      3966       8610
 7: Butanoic acid, 3-methyl-, 2-methylpropyl   589593      8687       8578
 8: Heptane, 3-methyl- (8CI9CI)                589811      2476       8568
 9: Hexane, 1-(hexyloxy)-5-methyl- (9CI)     74421195     15477       8557
10: 2H-Pyran, 2-butoxytetrahydro- (8CI9CI)    1927680      8693       8524
```

Fig.3 NBS library search results

As one can see, the identification is not always unambiguous.

This is partly due to the fact, that the NBS library takes into account only the 10 highest peaks in the spectrum and their relative abundances. Since identification was not the purpose of these experiments, we did not make efforts to come to a clearer understanding of the nature of the compounds. Following are the best match for peak 1 to 7 from figure 2:

1) 2-methyl-hexane
2) 2,2,3,3-tetramethyl-butane
3) 4-methyl-heptadecane
4) 2,10-dimethyl-undecane
5) Ethyl-benzene
6) 2,2,5,5-tetramethyl-hexane
7) 2,2,3-trimethyl-butane

The parameters for the GC-MSD runs and integrations are listed in Appendix D-4. It is assumed, that peaks 2 and 4 (2,2,3,3-tetramethyl-butane and 2,10-dimethyl-heptadecane) in the TIC correspond to the 2 biggest peaks in the GC graphs. These are the peaks used to calculate the areas in Table VI.

Going back to Table IV, - the single stage steam distillation experiments - the highest loss of organics was observed in the 10ml and 30ml experiments (MS-1, MS-5; 55.1% and 81.5%, resp.). It is possible, that this is due to the observed arcing/red glowing of the GAC at the end of these experiments. Although there is significant loss of organics in all experiments, this procedure did not result in complete removal of these organics. Another variation of steam distillation procedure was then tried: multiple stage steam distillation of the GAC sample. Tables V and VI list the results.

It is surprising how well the GC and GC-MS analyses match: SD-1 and SD-2 show only slight differences in the % removal: 90.3% and 92.2% for the GC analysis, and 93.1% and 93.7% in the GC-MS runs. SD-3 and SD-4 are alltogether consistant: no peaks detected either by the GC or GC-MS. It was expected to find a larger difference in percent removal between the stages, but the experiments do show a very high initial removal (90.3 - 93.1% removal with adding 1x10ml). The removal seemed not to be increased by adding another 10ml volume of H_2O (92.2 -93.7%). It is possible, that this is due to the arcing in the GAC bed observed during all runs.

The most remarkable result is that the steam distillation with MW irradiation can remove 100% of the adsorbed organics on GAC when carried out in stages. After the third addition complete removal was achieved. Even when the sensitivity of the GC was increased four fold (10^{-10} x 8) no peak was detected (SD-3 and SD-4)!

The removal of organics from GAC appears to follow these principles:

1) The removal is higher if arcing/red glowing GAC occurs. This is not surprising, as the very high temperatures attained during the process cause evaporation of high boiling hydrocarbons (one probable contaminant, heptadecane, has a

b.p. of 301.8^oC)

2) The removal is higher when the same volume of water is added in small portions rather than in one step (MS-6 in Table IV and SD-4 in Table IV and Table V and VI).
3) The evaporation rate is highest when water is added in stages and arcing/red glowing is allowed to occur.

During steam distillation the following steps occur:
Water surrounding GAC particles will probably cause

- diffusion of hydrocarbons into the water (small masstransfer stream) and
- diffusion of H_2O molecules into the GAC (large masstransfer stream); water replaces the air present in the pores of GAC; the air is saturated with hydrocarbon vapors.

If the removal of organics was only a diffusion problem, one could overcome the concentration gradient by adding more and more water (leaching approach). Table IV shows that this does not give complete removal. The heating process itself plays an important role in the complete removal of organics:
MW radiation will initiate two heating processes: it heats the water and also the GAC. First, GAC is a strong MW adsober: 30g GAC are heated to 95^oC from room temperature in less than 20 seconds; second, the H_2O molecules in the GAC pores are heated directly by the MW as well as indirectly (convection) by the hot GAC. Due to these two heating effects the water in the GAC is transformed faster into steam than the surrounding water in the

beaker. Hence, H_2O molecules can no longer diffuse into the hot, "steaming" GAC. The temperature of the particle surface does not exceed 100°C, since it is constantly cooled by the surrounding water. It is the steam generated inside the GAC pores that causes the steam distillation of the organics and not the hot water outside the GAC particles.

As soon as no water is left inside the GAC steam distillation ceases and the surface of the GAC remains cooled to 100°C so long as water boils outside. Finally, when all the outside water is evaporated the GAC starts to heat up to the red-glowing temperature. (Arcing is a phenomenon not related to the temperature and will be discussed later). Since only a limited amount of water can enter the pores of GAC particles, this quantity may not be sufficient to remove all hydrocarbons by steam distillation. Some possiblities to solve the problem of limited amount of available water:

a) allow the GAC to soak as much water as possible - very useful appoach for GAC used to filter liquid waste streams;

b) adding water several times to the GAC, with or without cooling periods in between (the water added cools the GAC down);

c) combination of a) and b).

E) Arcing/Heating studies

1) Theory

The previously discussed unit operation, MW induced steam distillation of organic contaminants from substrates, causes the volatilization of organics in a water saturated atmosphere. A technology that aims at the complete treatment of hazardous wastes has also to destroy the volatilized organics.

We developed a new type of fluidized bed reactor, using MW radiation in the process. This method will not only be of significance to the problem of treating hazardous wastes but also of potential general importance for the processing in the chemical industries.

During our studies with Granulated Activated Carbon (GAC) we observed a new phenomenon, termed "arcing": 1g dry virgin GAC on a watchglass was irradiated with microwaves in a regular household MW-oven (700W output). Small white, intermittent arcs were observed in the small heap and on the surface of the GAC, as soon as the oven was turned on. The intensity of the arcing lessens after a short time but does not cease. The same phenomena were observed by a research group at Argonne National Laboratory: R. Varma et al. Argonne National Laboratory, Microwave assisted chemical process for treatment of hazardous waste, annual report, Oct. 1987.

Different types of activated carbon were tried (coconut shell based, coal based) with similar results. On agitation of the GAC bed in a rotating tube or a fluidized bed the arcing instead of tapering off became more intense. We realized that the arcs create optimal conditions for the destruction of organics thus our incentive to use this phenomenon. A device that uses arcing of materials in a MW field was termed "RDW-reactor" (after the inventors and patent applicants: Dr. Asim B. Ray, Dr. Leonard Dauerman, Gabriele Windgasse).

GAC suits very well for a MW reactor: it adsorbs MW radiation strongly, leading to heating and arcing of the bed. In addition GAC has catalytic properties and strongly adsorbs organics. The influence of the last two properties on the destruction process is not clear. However, GAC is not the only material that leads to arcing: diffrent kinds of metal shots (aluminium, copper, tin etc.) were tried out and also produced arcing.

Arcs normally occur between two isolated conductors, separated by a non-conducting medium, air, for example. It is common knowledge that when one puts metals in a MW oven and power is turned on, arcing takes place. Following is the most probable explanation of arcing between two conductors in a MW field:

Mobile (conducting) electrons of conducting materials couple with the oscillating MW field of 2.45Ghz - a frequency of 2450 million cycles per second. Under these conditions the electrons gain enough energy to leave the suface of the material (metals, for example) causing ionization. The positively charged particle experiences a separation of charges on the surface (fig.4), and a potential diffence develops between adjacent particles. When this potential becomes high enough arcing occurs. In addition to the adsorption of the electrical component charged particles in motion will also adsorb the magnetic component of the electromagnetic field.

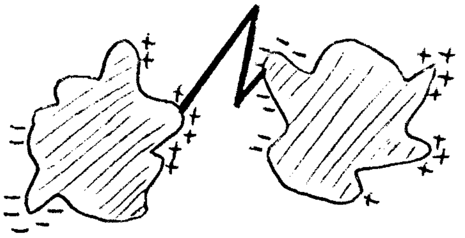


Fig.4 Discharge between GAC particles

In support of this hypothesis it may be pointed out that arcing does not occur when a conducting medium, such as salt water, is present between the two particles. A conducting medium apparently prevents the development of a potential difference. GAC, like metals, is a conductor since it contains graphite. It should behave in a similar way as metals under MW radiation. The following observations regarding GAC justify this hypothesis:

- GAC particles in insulating media, such as: distilled water, silicone oil or air arced when irradiated with MW
- when sodium chloride was added to distilled water and was used as the medium, arcing ceased immediately
- powdered activated carbon either does not produce arcing or only very few arcs: the intimate contact of the particles prevents a potential build up.

- large and irregular shaped particles produce stonger arcing than smaller GAC granules: higher potentials can build up, plus the fact that the electro-magnetic field is much stronger at edges; this is called field concentration (see fig.5)
- fluidization of GAC produces stronger arcing in the RDW-reactor, which does not lessen with time. This is mainly due to the constant motion of the GAC bed, which prevents the particles from coming in contact with each other, providing optimum separation between them for the arcing to occur.

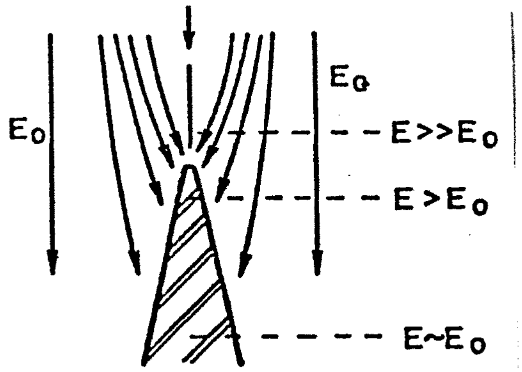


Fig.5 Field concentration

The possibility, that an adsorbed substance (for example a volatile organic) causes the arcing of GAC was also considered. However, this possibility was rejected: Due to arcing and heating of the GAC the temperature of the particles is very high (the bed can reach red-glowing temperatures in a few minutes). The majority of organic compounds volatilizes or is destroyed at about 600 - 800°C. The temperatures of the GAC should be sufficient to free these adsorbed organics. So the arcing - if it was due to the adsorbed substances - should cease very soon after

MW exposure. Since the arcing process continues undiminished when the bed is in constant motion (rotating tube or fluidized bed) we discount the above possibility. It is concluded that the sparking phenomenon is a property of GAC conforming well with known principles. It is dependent on:

a) the strength of the applied electric field
b) the particle size and shape
c) the presence of conducting or non-conducting environment.

The critical fact is that the GAC particles have to be isolated from each other. This can best be achieved in a fluidized bed reactor where the carrier gas could also supply the necessary cooling of the reactor (RDW-reactor). The electrical field strength in oven cavity varies with time and cannot be kept constant.

In the experiments both air and argon were used for creating a fluidized GAC bed. In addition to the GAC-arcing one could also observe strong and stable gas discharges in the experiments where argon was the carrier gas. The "small" arcs originating from the GAC particles seem to trigger the breakdown of argon: they supply the necessary electrons which are accelerated in the electric field until they gain sufficient kinetic energy to cause the ionization of argon atoms. These ions create more electrons starting a chain reaction. The breakdown of the argon gas is visible in "vein-like" arcs which grow rapidly along the glass walls of the reactor. The color of these "veins" changes during an experiment from red-violet in the beginning to green-blue after a few minutes (probably as a function of temperature). The temperature in the arcs is very high but the electrons, which contribute the most energy, can tavel only a very short distance: the system is operated under atmospheric pressure where the mean free path of electrons is very short and collisions with other molecules are highly probable, resulting in their ionization. Argon ions may travel further colliding with other molecules and transfering energy, ultimately leading to the decomposition of these molecules.

The presence of large amounts of water molecules in the argon gas supresses its breakdown: the electrons produced in the GAC arcs ionize the water molecules rather than the argon as the ionization energy of water (12.61eV) is less than that of Argon (15.06eV). The lowest ionization energies of several gases and vapors used in the experiments are given in Table VII.

To determine whether or not arcing can cause decomposition of organics and to which metabolites, three series of experiments were conducted:

a) pure TCE was added to a fixed GAC bed and exposed to MW; the vapors were collected in alkaline solution and analysed for hydrochloric acid;

b) GAC loaded with hydrocarbons was exposed to MW in a fluidized bed (RDW-reactor), after treatment the GAC was extracted in a Soxhlet-extractor and analysed by GC for hydrocarbons;

c) water-saturated TCE vapor in a carrier gas was passed through a GAC bed (simulating a fluidized bed) which was exposed to MW radiation (RDW-reactor). Gas samples before and after the MW oven were analysed by GC-MS for TCE and other organics.

Table VII

Lowest ionization energies for molecules present in Arcing/Heating experiments

(Electron Impact Phenomena, F. Field, J. Franklin, 1957, p.243f)

Reactant	Products	Ionization Potenial (eV)
Ar	Ar+	15.7
Ar* + Ar	Ar_2+	15.06
H_2O	H_2O+	12.61
	H+,OH	19.6 +/- 0.2
	OH+,H	18.0
N_2	N_2+	15.55
NO	NO+	9.25 +/- 0.02
NO_2	NO_2+	12.3 +/- 0.2
O_2	O_2+	12.2 +/- 0.2
	O+,O-	16.9 +/- 0.2
CO	CO+	14.009
CO_2	CO_2+	13.79
TCE C_2HCl_3	TCE+ C_2HCl_3+	8.8

2) Studies with pure TCE and GAC

Experimental

In the following experiments the major parameter studied was the effect of arcing on the decomposition of TCE. As described before such arcing is brought about by the presence of GAC in a MW field. The arcing is enhanced when the GAC particles are in motion and it is inhibited when the GAC is coated with an ionic compound like sodium carbonate (both these observations, enhancement and inhibition, were first reported by this laboratory). No arcing is observed if convectional thermal heating is used. The set-up for the fixed bed experiments is described below.

0.5ml TCE (CMS, ACS grade, 86.4-87.4^{o}C bp.) was added to 1g GAC (Calgon F-200) in a 125ml Erlenmeyer flask (fig.6) and shaken until the mixture appeared dry. This flask (A) was connected to an empty flask B to prevent back flow from flask C to flask A (B and C were 250ml Erlenmeyer flasks). Flask C - connected to B - contained 100ml 10% Na_2CO_3, to adsorb hydrogen chloride molecules produced in flask A. The system was placed inside a convection/MW oven and heated either thermally (oven preheated to 230^{o}C, exposure time 3-5min) or by MW energy (2min, setting "High"). During experiments with thermal heating the rubber tubing started to melt at ca. 225^{o}C. These experiments were interrupted at that point.

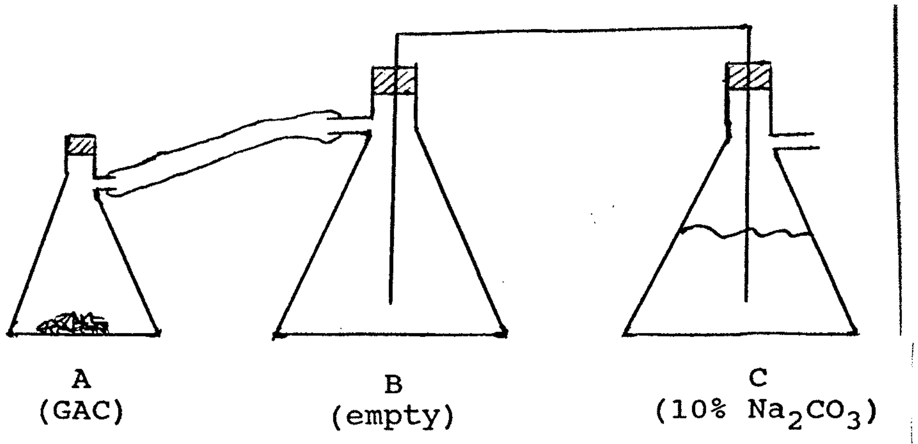


Fig. 6 Set-up for fixed-bed experiments

To agitate the GAC particles a "rotating tube" was used (see fig.7). The oven model used was equipped with a rotating plate at the bottom (carousel) in order to expose the load to an uniform MW field. The plate was removed and a connection from the rotating center to the glasstube was installed. As the center rotated slowly (ca. 10s for one revolution), the GAC was in constant motion. This set-up did not involve a flask B. It was difficult to keep the experimental conditions constant: the rotation was not uniform in all experiments. The amount and strength of the arcing varied throughout the experiments (possibly due to the changing MW field in the cavity). The rating in Table VIII and IX - "many, some, few, none arcs" - is subjective.

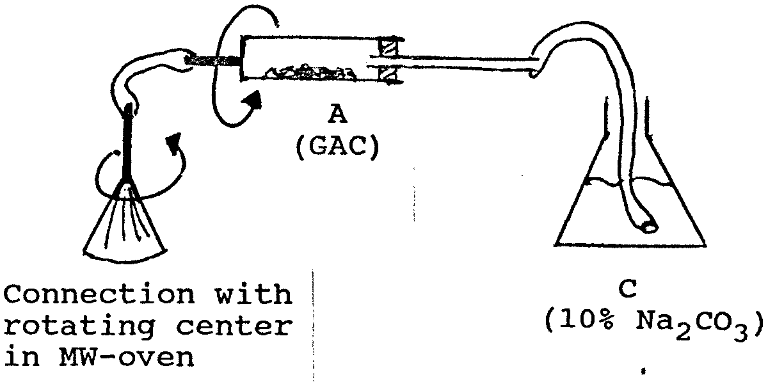


Fig. 7 Set-up for rotating tube experiments

In all of the experiments bubbling in flask C started immediately after its insertion into the oven. After heating, residual hydrochloric acid was removed as follows: The flasks were disconnected (exept experiment #13) and 100ml of alkaline sodium carbonate (Na_2CO_3) were added to flask A. This mixture was shaken for two minutes, filtered, neutralized with 2M nitric acid (HNO_3) and diluted to 250ml volume. Any liquid in B was combined with C, neutralized with conc. HNO_3 and also diluted to 250ml. Both samples were then analysed for the chloride ion concentration (which directly represented the hydrogen chloride concentration) with a chloride ion electrode as follows: to a 25ml sample 25ml 0.05M $KClO_4$ - an ionic strength buffer - were added, the mixture was stirred in a glass beaker. The electrodes were immersed and the voltage measured.

The voltage obtained is proportional to the activity of the chloride-ions. The activity of chloide-ions is dependent on the concentration of all ions present in the solution. An ionic strength buffer keeps this number constant, without interfering with the activity of the chloride-ions. The voltage measured is proportional to the chloride-ion concentration. A calibration curve with standards between 10 and 100ppm [Cl-] gave the following equation:

$$\text{ppm}[\text{Cl}^-] = \text{inv.log} \frac{302-(\text{mV})}{51}$$

The chloride-ion mass (in mg) in a 250ml solution is calculated by dividing the ppm amount found by 4. The masses found for flask A and C were added, and the % decomposition calculated as follows:

0.5ml TCE = 0.016691 moles [Cl-] = 591.7mg [Cl-] = 100%

$$\%\ \text{Decompos.} = \frac{(\text{mg } [\text{Cl}^-] \text{ found x } 100)}{591.7}$$

Table VIII summarizes the results; the details and conditions of the experiments are presented in Table IX.

Table VIII

Summary of results

(Experiments with GAC and pure TCE)

Experiments	Agitation of GAC	Arcing	Average % Decomposition
Thermal	no	none	0.16%
MW	no	some	3.12%
MW	rotating tube	many	37.71%

In oder to determine whether or not the TCE decomposition is due to arcing or due to MW heating, the GAC was coated with solid Na_2CO_3 (#3,7) or Na_2SO_4 (#4,8): 1g GAC was heated with 50ml solution (10%) of the salts in the MW until all water evaporated and the salt coated the GAC particles. Only in experiment #7 very few arcs were observed, the other experiments with coated GAC showed no arcing.

In one case (#10) TCE was not added directly to the GAC, but the GAC was saturated with TCE vapors. The total amount of chloride-ions present (corresponding to the adsobed TCE) in that experiment was 5.353mg.

In the last 3 experiments on Table IX (#11,12,13) another possible route of TCE decomposition was studied: Flask C contained 50ml 0.15M $K_2S_2O_8$ plus 50ml 1M KOH, rather than 100ml Na_2CO_3. If TCE is vaporized in the MW reactor, and only a small

portion of it is destroyed by arcing, the remaining TCE vapors pass untreated through the solution in flask C. In the presence of strong alkaline oxidizing agents such as $K_2S_2O_8$ TCE, and its derivatives could be decomposed to hydrochloric acid, and then trapped as an alkaline salt. A solution of $K_2S_2O_8$ is activated by heating (MW, in this case) and decomposes to H_2O_2, thus providing the oxidizing species necessary (I. Kolthoff, I. Miller: J. Am. Chem. Soc., July 1951, p.3055f.)
Two blank experiments were conducted without TCE (#1,5).

The following instruments were used:

- reference electrode: Ag/AgCl double junction, Corning # 476067
- chloride electrode: solid state, Corning # 080895
- pH-meter: 140 pH-meter, Corning # 211458

Table IX

Experiments with GAC and pure TCE

Decomposition determined by HCl analysis

#	GAC coated with:	TCE	Heating	GAC in movement	Arcing	mg Cl found	% Decompos.
1	-	-	thermal	no	none	0.81mg	-
2	-	0.5ml	thermal	no	none	0.98mg	0.16%
3	Na2CO3	0.5ml	thermal	no	none	1.10mg	0.19%
4	Na2SO4	0.5ml	thermal	no	none	0.72mg	0.12%
5	-	-	MW	no	some	0.79mg	-
6	-	0.5ml	MW	no	some	52.6mg	8.9%
7	Na2CO3	0.5ml	MW	no	few	1.9mg	0.33%
8	Na2SO4	0.5ml	MW	no	none	0.7mg	0.12%
9	-	0.5ml	MW	rotating tube	many	96.7mg	16.35%
10	GAC sat. with TCE vapor		MW	rotating tube	many	1.16mg	21.47%
11	-	0.5ml	MW	rotating tube	some	195.73mg	34.79% (*)
12	-	0.5ml	MW	rotating tube	many	167.8mg	29.8% (*)
13	-	0.5ml	MW	rotating tube	many	364.4mg	64.79% (*) (**)

(*) Flask C contained a mixture of KOH and $K_2S_2O_8$ solution

(**) After the run, some of the liquid that was used to catch the HCl-vapors was soaked into the reactor tube where it reacted violently as soon as it came in contact with the GAC. The vapors produced were caught in the liquid.

Results and Discussion

Refering to Table IX it is apparent that decomposition is effected by combined MW heating and arcing. The increased decomposition in experiments with the agitated GAC bed is associated with the stronger arcing observed. It appears reasonable to conclude, that arcing causes the decomposition of TCE, and that the rate of decomposition depends on the abundance and strength of the arcs.

In Table IX the thermal experiments and the experiments with coated GAC show very low chloride-concentrations in the liquid: 0.7mgCl - 1.9mgCl indicating a very low decomposition rate of TCE (less than 0.2%). All results are close to the background values 0.81mgCl and 0.79mgCl. This indicates, that there is no significant decomposition of TCE due to heating caused thermally or by microwaves.

Significant decompositions were achieved in experiments in which arcing was observed (#6,9,10,11,12,13). Arcing in unagitated GAC gives 8.9% decomposition (#6); whereas agitated GAC beds (#9,10,11,12,13) which produce more and stonger arcs yield an average decomposition of 37.7%. It is probable that the actual decomposition achieved was higher than 37.7%: experiment #13 was the only experiment in which <u>all</u> gases evolving from the GAC bed were caught in flask C. In all other experiments the flasks were disconnected after the run and the gas developing from the GAC bed when alkaline solution was added escaped. Experiment #13 shows, that hydrogen chloride is adsorbed on the surface of the GAC. The remaining TCE is thought to evaporate from the GAC bed, since it is not adsorbed by alkaline solutions.

To determine whether or not the decomposition to HCl is limited by the presence of the single hydrogen in the TCE molecule, experiment #9 and #11 were repeated with Trichloroethane - $C_2H_3Cl_3$ - rather than TCE (C_2HCl_3). A 10% solution of Na_2CO_3 and 1M KOH, resp., were used in flask C. The % decomposition was found to be 33.9% and 35.13% respectively, which is very close to the average decomposition found with TCE. This confirms our conclusion that the limiting parameter for decomposition is the arcing.

No higher decomposition could be achieved because many TCE molecules evaporate from the hot GAC without coming into contact with an arc or electrons produced in arcs. As stated earlier these electrons gain energy in the MW field and may ionize a molecule with which they collide. Table VII shows, that TCE has an ionization energy of 8.8eV; N_2 and O_2 have higher ionization potentials: 15.55eV and 12.2eV, resp. This indicates that TCE is the easiest molecule to be ionized by electrons or indirectly by reactive species formed in the arcs. One possibility to increase the % removal from substrates and/or the decomposition % is to increase the abundance and strength of arcs in the bed. This can be best achieved by fluidizing a GAC bed with a gas stream. These experiments are described below.

3) Studies with hydrocarbon loaded GAC in a fluidized bed

Experimental

The purpose of these experiments was to regenerate spent GAC, that is, remove adsorbed species by either volatization or destruction in a fluidized arcing/heating bed. The industrial sample used in the steam distillation experiments (section D-3) was studied.

10g hydrocarbon loaded GAC were placed in a 500ml glass separatory funnel fitted with a Roto-Flo Teflon-valve. Carrier gas was blown through the GAC from the bottom creating a fluidized GAC bed (RDW-reactor). The whole system was placed in a MW oven (fig.8).

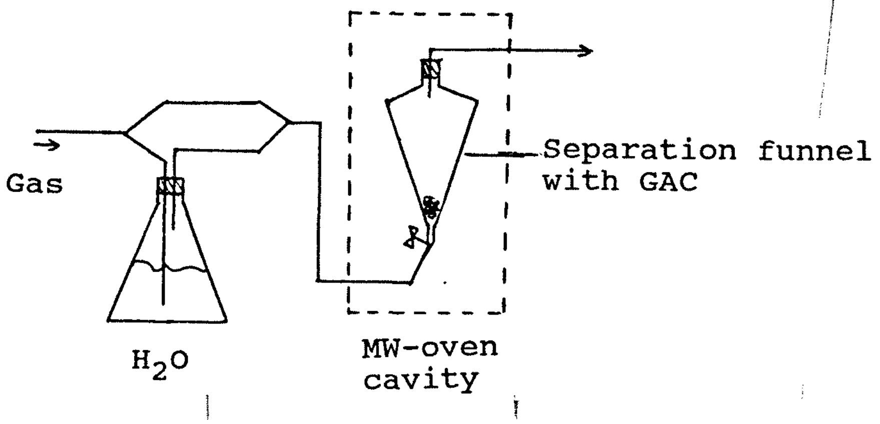


Fig.8 Set-up for RDW-reactor (hydrocarbon loaded GAC)

Two gases were used for fluidization: compressed air and argon. To effect water vapor saturation of the gases, the gas stream was split, and one part was passed through water. Five minutes was the exposure time to MW during the air experiment and 2.5 min for the argon run. After irradiation, the GAC was extracted for 3 hours in a Soxhlet extractor with methanol and analysed in a GC (same conditions as in the steam distillation experiments, see D-3 for details, and Appendix E-3 for raw data). The same blank experiments were used and the three highest peaks were taken into account for area and removal percent calculations. The parameters for blanks and samples were kept the same. Table X gives a summary of the results. In addition a GC-MS analysis for the argon experiment (MS-4) was conducted. The blank run in this case was M-1. The Total Ion Chromatograms for these runs are attached in the Appendix.

Table X

Experiments with hydrocarbon loaded GAC in a fluidized bed

Exp.	Gas	area peak 1	area peak 2	area peak 3	Average Removal %
GC-analysis					
blanks	-	193.6	75.08	355.85	-
MS-3	air	27.04	10.4	59.2	85.2%
MS-4	argon	23.04	9.6	50.16	87.1%
GC/MS-analysis					
blank	-	6.87×10^8	4.74×10^8	13.44×10^8	-
MS-4	argon	3.70×10^7	9.15×10^7	31.68×10^7	83.9%

Results and Discussion

The results in Table X show, that over 80% of the adsorbed compounds could be removed: An exposure of 2.5 minutes with argon as a carrier gas one can remove 83.9-87.1% of the hydrocarbons present. The experiment with compressed air as a carrier gas (5 min exposure) results in 85.2% removal. Further experiments are needed to determine the effect of exposure time and the nature of the carrier gas on the regeneration process.

Two effects, alone or in combination, are believed to be responsible for the removal of the hydocarbons:

1) the GAC is heated with Microwaves very quickly to high temperatures,
2) the arcs between GAC particles.

Steam distillation may also be a factor in this removal but it is assumed that it only plays a minor role. Moisture adsorbed by the GAC from the room air is the only source of water, since the hot GAC particles do not adsorb any water present in the carrier gas. In all experiments strong white arcing was observed between GAC particles. Since the carrier gases are saturated with water, no argon breakdown as described in the theory section (E-1) could occur. The arcs may heat a small portion of the particle surface and cause volatile compounds in that region to be vaporized. However, this heating is limited to a small area only and could not account for the 80% removal observed. It is more likely that the temperature of the GAC is so high that most of the hydrocarbons are volatilized. In the fluidized bed experiments only a small part of the GAC bed is heated to red hot temperatures, as the incoming gas stream constantly cools the particles. The temperature can be controlled by changing the flowrate of the carrier gas. Destruction of the hydrocarbons will only take place if the molecule encounters a reactive species in the gas.

We conclude that a RDW-reactor can be used to regenerate spent GAC. Unlike technologies used pesently, the fluidizing gas stream is not heated. The carrier gas can be inert (like argon or carbon dioxide) preventing the loss of GAC due to combustion or the formation of toxic hydrocarbons. Some GAC is lost due to the friction of the particles: a dust trap after the reactor has to be installed.

Steam distillation of GAC alone, or in combination with an arcing/heating fluidized bed reactor are promising possibilities for GAC regeneration.

4) Studies with a fluidized GAC bed and TCE vapors

Experimental

The purpose of this study is to determine, whether or not an arcing/heating fluidized GAC bed can decompose chlorinated organics in the vapor phase, to what extent and to which products. The following experimental set-up was used:

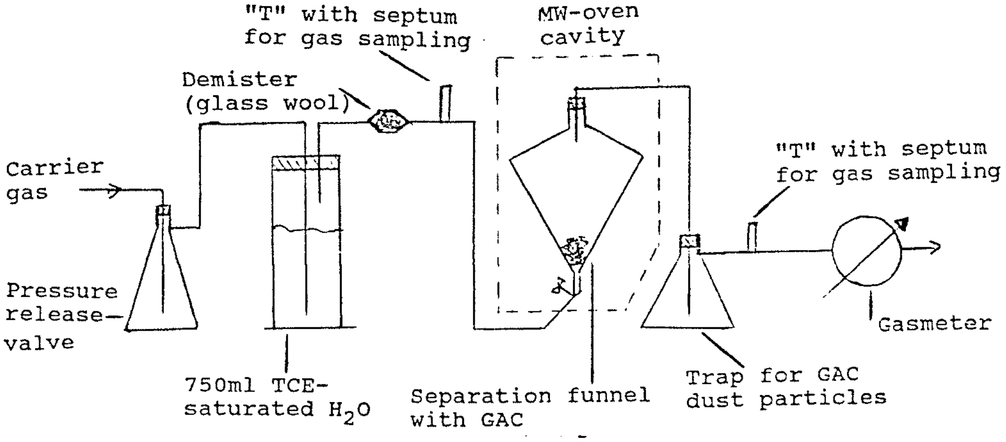


Fig.9 Set-up for RDW-reactor (TCE vapors in carrier gas)

Initially the condensables in the gas streams were collected before and after treatment, over a time, in a dry-ice trap or in a liquid nitrogen trap. This approach was not feasible. Among the problems encountered were the following:

- the flowrate needed for fluidizing the GAC bed was too great to collect the organics in the traps;
- by passing the gas stream through methanol (which was cooled in isopropyl-alcohole and dry ice), the back pressure affected the

flowrate in the reactor which could not be kept constant during the experiments. The flowrates for the blanks and the actual runs could not be compared;

- bubbling the gas stream through methanol seemed to "airstrip" the organics already trapped;
- splitting the gas stream before the MW-reactor was not feasible (one stream was collected as a "blank" before the reactor, the other stream was collected after the reactor): the flowrates of each stream could not be determined seperately.

From this it was clear that a method was needed in which sampling could be effected without disturbing the gas streams. This was accomplished by sampling the gas streams before and after MW treatment: Gastight syringes (Hamilton #1701, 10ul) were used for sampling the gas through septa that sealed the experimental system from the outside (see fig.9). To compensate for deviations from steady-state conditions and for possibly leaking syringes, internal reference compounds were chosen: Argon and nitrogen (in the experiments with compressed air). The samples obtained were analysed using the GC-MS. It would not have been feasible to use only GC because of the need for a multiplicity of detectors and columns to separate and detect a mixture of gases and organics.

In the gas samples before and after the MW reactor, the concentration of TCE changes relative to the internal reference gas. Other organics which were possibly formed in the reactor can also be detected - in relation to the reference gas. Although any definite statements about the absolute concentration of the reactants and products cannot be made, one can obtain a relative decomposition rate for TCE.

The arcing/heating fluidized bed process is not a steady-state system: the arcs are transient and in addition the concentration of TCE in the gas phase is not constant over the total period of the experiment: The TCE saturated water is "air-stripped" with the carrier gas, to provide a gas stream that has a certain TCE concentration and is saturated with water vapor. In long runs, the concentration of TCE in water and in gas phase will change. In all our experiments fresh TCE-saturated water was used and since the runs were only of 3-4min duration it was assumed that the TCE concentration did not change significantly during the course of experiment. However, the initial ratios of TCE vs. reference gas differed greatly indicating that the water was not always saturated with TCE (see Table XI). The theoretical concentration in the gasphase was calculated using Henry's constant (H'): assuming the water is nearly saturated with TCE (ie. 1000ppm = 1mg/l), H' for TCE at 20°C is 0.42.

$$H' = \frac{\text{conc. in gasphase}}{\text{conc. in liquid phase}} = \frac{\text{420mg TCE}}{\text{1l } H_2O \text{ liquid}}$$

Note, that 1l H_2O refers to in the liquid phase.

The concentration of TCE in the gasphase in ppm (mol/mol) is calculated by

$$\frac{0.42\text{g TCE} \times 10^6}{131.39\text{gTCE/mol} \times 55.556\text{mol}H_2O} = 57.5\text{ppm}$$

For GC-MS parameters, TICs, integration and events files: see appendix E-4.

From the ratio of areas (TCE/inert gas) before and after the MW oven the % decomposition was calculated:

$$\% \text{ decomposition} = 100 - \frac{100 \times \text{ratio after MW}}{\text{ratio before MW}}$$

Before any sample was taken the reactor was run for ca. 2 minutes, to establish a quasi-steady state. The volumetric flow for each valve setting of the carrier gas was determined in ft^3/min with a gasmeter.

In all experiments the sample after the MW reactor was taken first and injected immediately into the GC-MS. After that the air sample before the MW was taken and the tip of the syringe was stuck into a septum to prevent leakage. Immediately after finishing the GC-MS run for the first sample the second sample was injected.

Table XI

Experiments with a fluidized arcing/heating bed and TCE vapors in the carrier gas

Exp.	Gas	GAC	flowrate ft3/min	before MW: area TCE / area gas x 10^{-3}	after MW: area TCE / area gas x 10^{-3}	% Decomposition
#40	Ar	4g	-	2.610	2.202	15.6%
#41	Ar	4g	0.035	16.133	12.655	21.6%
#42	Ar	8g	0.18	1.118	0.747	33.2%
#44	Ar	8g	0.05	10.116	1.406	86.1%
#45	Ar	8g	0.08	4.129	no TCE peak detected	100%
#46	Ar	8g	0.08	4.159	1.160	72.1%
#48	Air	4g	0.075	7.557	5.228	30.8%
#54	Air	4g	0.0225	42.741	11.346	73.5%

Results and discussion

Refering to Table XI, it is evident that TCE can be decomposed in the gasphase. The percent decompositions observed range from 15.6% to 100%. This is significant because another research group at the Argonne National Laboratory using other approaches, concluded that it was not possible to decompose TCE in the gasphase in presence of a MW field and GAC (page 8 in R.Varma, S.Nandi, D.Cleaveland: Microwave-Assisted Chemical Process for Treatment of Hazardous Waste, Annual Report Oct. 1987, Project Number 23310, Argonne National Laboratory, Ill.). Varma et al. report sparking in the GAC bed, upon irradiation with MW, throughout the experiments but their objective was to eliminate or reduce this phenomenon (page 6 in the report).

Another question to determine in our experiments was whether or not GAC reacted under these conditions to produce other halogenated species which would presumably be toxic. If that were the case, then other beds like copper shots would have been used, since arcing/heating is not limited to GAC beds. All air samples were checked for the presence of other organics than TCE, none were found.

The gas samples were injected into a GC-MS, for detection of other reaction products and to calculate the relative decomposition of TCE. One typical TIC is shown below (experiment #44A before the reactor, #44B after the reactor)

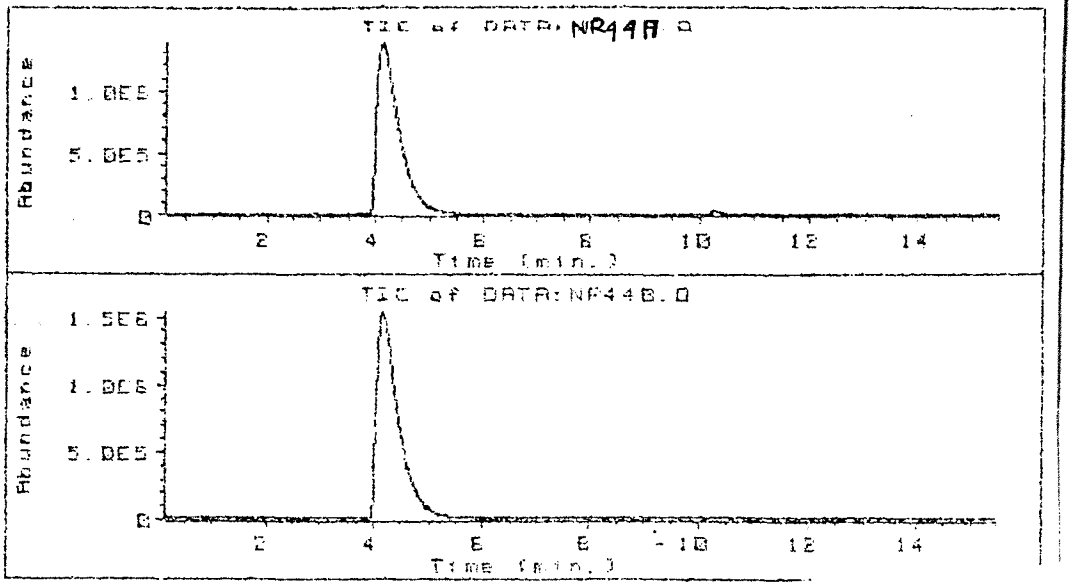


Fig. 10 TIC of gas samples

The carrier gas peak (argon) is clearly recognizable (retention time 4.0-5.5min). All other peaks are much smaller. The following TICs show the portion after the argon peak in more detail (fig.11).

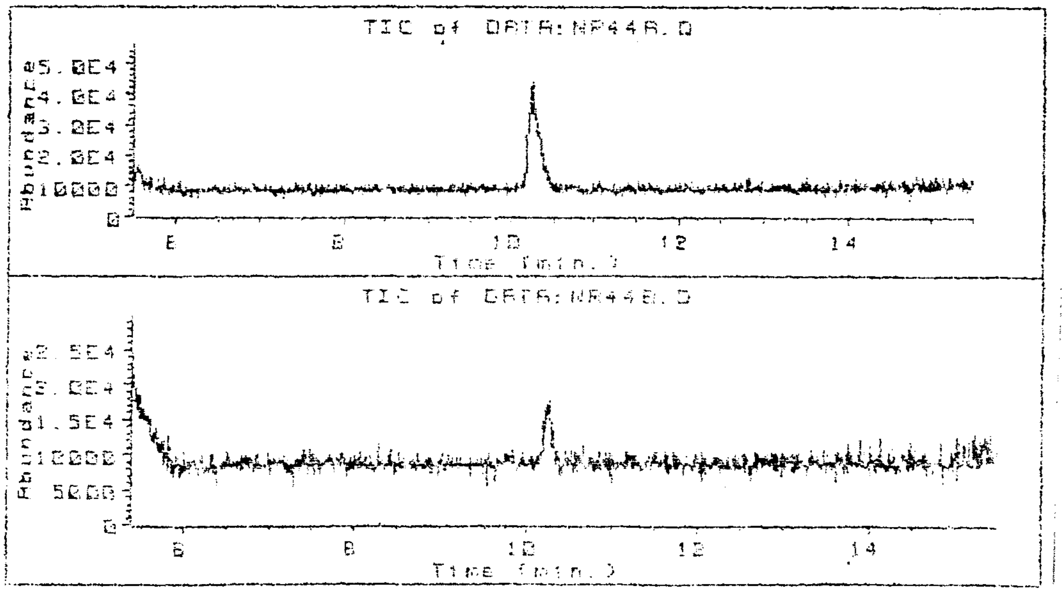


Fig.11 TIC details

The peak at 10.2min was identified as TCE. The difference in abundance is not an indication of the decomposition of TCE: it is the ratio of the argon peak area over the TCE peak area that shows, whether the TCE concentration changed or not. The integration for the area calculation was done with the Selective Ion Chromatogram (SIC): not all the detected ions are shown in the chromatogram but only of a certain range. The range of masses for the nitrogen SIC was 26-29 amu, for the argon SIC 38-41 amu and for the TCE SIC 130-135 amu. This takes into account the fact that the molecular peak has the highest abundance in the spectrum of a molecule. It is important that no other molecules should have ions in that region. Figure 12 shows the SIC for argon and TCE in #44B.

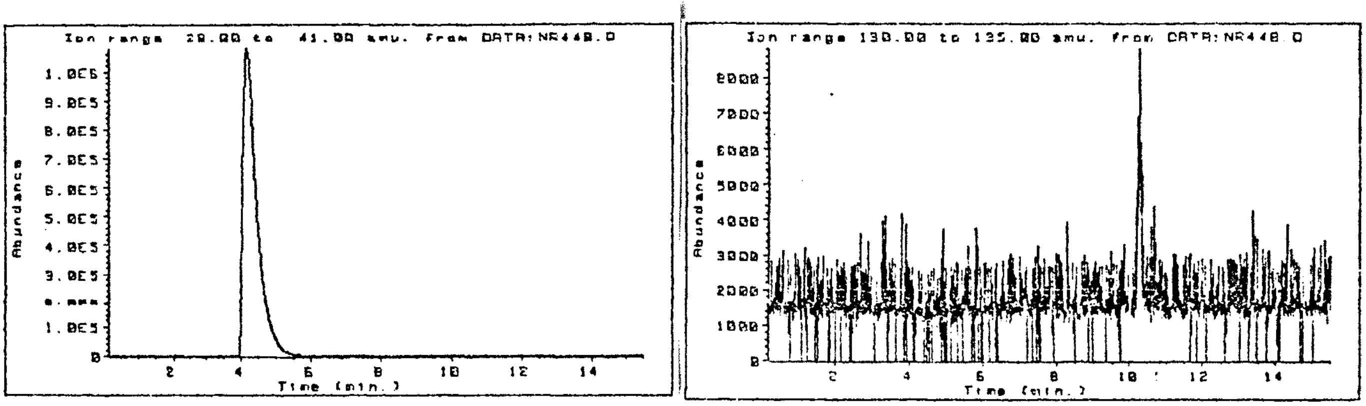


Fig.12 SIC for Argon and TCE

Note the difference in abundances in the SICs. The SIC has the advantage that background noise from other compounds is automatically eliminated. The TCE-SIC shows that there are small and varying amounts of ions in that mass range throughout the chromatogram; this is interpreted as background noise of ions in the range 130-135 amu. The only significant peak in that SIC is from TCE at retention time 10.2 min. See Appendix E-4 for the integration parameters and the TICs of the other runs. The calculated areas are also listed; the ratios can be found in Table XI.

Referring to the data in Table XI, consider first the experiments in which argon was used as a carrier gas. In experiments #45 and #46, in which the gas flowrate and the amount of GAC were nearly the same, the decompostion ranged from 72.1 to 100%. We assume that this variation is due to the fact that in a non-steady-state reactor - in which gas flowrate and temperature fluctuations occur due to arcing - the contact time of the carrier gas with the GAC bed vary to a great extend. The gasmeter values were based upon steady-state flow conditions throughout the system. It is assumed, that the error is in the order of 25%. The results of experiment #44 are consistant with the above arguments and data: The gas flowrate is slightly less (0.05 vs. 0.08ft^3/min). Assuming the same uncertainty of ca. 25%, the decomposition of 86.1% lies within the range. Turning to #42, the measured gas flowrate is about three times the previous ones, and the percent decomposition is within 1/2 to 2/3 less than the above mentioned ones. In #40 and #41 the amount of GAC was halved and the average percent decomposition drops to approximately 18%. This effect is perhaps due to the fact that the concentration of arcs in the GAC bed drops exponentially rather than linearly. Then the decomposition falls by a factor of four. This is consistent with the results. Following is a summary of the experiments with

Argon, and 8g GAC:

Experiment	Flowrate ft3/min	% Decomposition
#42	0.18	33.2
#44	0.05	86.1
Aver. of #45,#46	0.08	86.05

Two regression equations were calculated with these values, which show a linear relationship between the flowrate of the carriergas and the decomposition of TCE vapors (the goodness to fit for both equations is 0.9518):

$$\text{Flowrate (ft}^3\text{/min)} = 0.2522 - 0.00217 \times (\%\ \text{TCE decomposed})$$

$$\%\ \text{TCE decomposed} = 113.66 - 437.54 \times (\text{Flowrate ft}^3\text{/min})$$

Turning to the studies in which air was used, it seems that the air behaves somewhat diffrent than Argon, but the general pattern seems to be the same: lowering the flowrate increases the percent decomposition. However, the reasons for this difference in behavior remains to be investigated in more detail.

Taking into account the special nature of this reactor, some general rules can be pointed out:

The lower the flowrate of the carrier gas and the greater the GAC amount in the reactor, the higher the probabiltity of a TCE molecule to encounter an arc or any other reactive species (electrons, ions, excited atoms, radicals etc.) in the reactor, resulting in the decomposition of the TCE molecule. The carrier gas flow cannot be reduced to very low settings since the gas has also a cooling function. In all runs but #48 at least part of the GAC was red-glowing hot. The use of argon as a carrier gas has the advantage, that the GAC cannot burn, although burning was not observed in experiments with air. As a matter of fact the GAC is regenerated in every run. CO_2 could also be used as a carrier gas. The use of air has the advantage that O_2+ is an easily formed reactive species in the MW reactor (see Table XII). The destruction of a TCE molecule can be due to:

1) the energy transferation from excited molecules to TCE, with a subsequent reaction of the TCE molecule: $TCE + Y^* \longrightarrow TCE^* + Y$

2 the ionization of a TCE molecule by a reactive species; for example electrons or cations: $TCE + (e-)^* \longrightarrow TCE+ + (e-)$ or $TCE + Y+ \longrightarrow TCE+ + Y$

3) MW heating of the GAC itself,

4) catalytic reactions on the GAC surface.

Dr. Varma's studies show no TCE decompostion due to contact with the GAC surface: TCE vapors were led over a GAC bed during MW irradiation. Our studies with thermal heating of TCE and GAC indicate, that no decomposition takes place, only desorption (section D-3). This leaves only the first two reactions: TCE+ or TCE* reacts with itself and/or any other molecules. Table XII shows the reactive species presumably present in the experiments and their ionization energies (adapted from Table VII). One can see that in argon and in air the TCE molecule is the first one to be ionized if it encounters a high energy species on the way through the reactor. The reactive species that are most likely to exist besides TCE+, are O_2+ in the air experiments and H_2O+ in the argon experiments.

From these results it is assumed that TCE is completely decomposed into HCl, CO and CO_2. CO and CO_2 spectra were buried under the carrier gas peak and could not be detected with the GC-MS. Two decomposition products of TCE could be found after the reactor: hydrochloric acid and carbon dioxide. Hydrochloric acid was found to be adsorbed on the GAC bed and in the condensate in the tubing after the reactor (analysis by silver-chloride precipitation). Carbon dioxide was identified in the experiments with argon (analysed by carbon dioxide electrode method). These two analyses were qualitative, not quantitative. It was impossible to determine whether or not the carbon originates from GAC or TCE.

It is concluded, that TCE in the gasphase can be decomposed in a fluidized, arcing GAC bed up to non-detectable levels (with GC-MS). No derivates of TCE other than HCl and CO_2 were found in the Total Ion Chromatograms (TIC).

Table XII

Reactive species present in arcing/heating reactor with carrier gases argon and compressed air

Argon experiments	ionization energy	air experiments	ionization energy
C_2HCl_3+	8.8eV	C_2HCl_3+	8.8eV
		O_2+	12.2eV
H_2O+	12.61eV	H_2O+	12.61eV
CO_2+	13.79eV	CO_2+	13.79eV
CO+	14.009eV	CO+	14.009eV
Ar_2+	15.06eV		
		N_2+	15.55eV
Ar+	15.7eV		
		O+,O-	16.9eV
OH+,H	18.0eV	OH+,H	18.0eV
H+,OH	19.6eV	H+,OH	19.6eV

F) CONCLUSION

Experiments with para-xylene and naphthalene showed that organics can be completeley removed from sand using MW induced steam distillation, depending on the mole fraction X_{org} in the gasphase (equ.2). This favors compounds with high vapor pressures such as p-xylene. But low vapor pressure compounds like naphthalene can also be steam distilled with a large enough volume of water. GAC in contrast to sand is a porous material that adsorbs water, in addition to other organic compounds. The steam developed in the pores results in the steam distillation of adsorbed compounds. Experiments showed that 100% desorption of all contaminants can be achieved, that is, the GAC can be completely regenerated. The most effective method was multiple stage heating: to a GAC sample water was repeatedly added, followed by MW irradiation of the sample (to dryness) between each addition of water. After three stages none of the adsorbed hydrocarbons was detected either in GC or in GC/MS. In addition to the steam distillation also GAC-arcing seems to have an effect on the removal rate: in experiments where arcing was observed between particles the desorption was greater.

The phenomenon of arcing GAC beds for decomposition of organic materials was first used from this research group. R. Varma et al. reported arcing in GAC beds during MW radiation but failed to acknowledge its significance for the decomposition of organics. Varma et al. claim that there is no destruction of TCE due to irradiation with MW if GAC is present. Our experiments, in fixed and fluidized GAC beds show that TCE can be decomposed - up to 100% - and that the decomposition is due to arcing. The most effective process is achieved when a GAC bed is fluidized with a gas that contained water and TCE vapors. This reactor was termed "RDW-reactor", after the inventors and patent applicants Dr. Asim B. Ray, Dr. Leonard Dauerman, Gabriele Windgasse.

It is assumed, that the arcing is a property of the GAC itself: graphitic structures on the particle surface accomodate loose electrons which are "boiled off" by the high frequency MW field. Between charged GAC particles a potential builds up and a discharge occurs which is observed as an arc. Free electrons - from arcs as well as from graphite - cause ionization of other molecules in the reactor, namely TCE+, O_2+ and H_2O+. This will provide a very reactive environment in which TCE can be easily decomposed. The only decomposition products found after the MW reactor were HCl and CO_2. No other organics could be detected in the gas by GC-MS analysis.

The wide range of % decomposition (15-100%) is assumed to be due to the many variables the system is dependent on, but mainly on the contact time of the carrier gas with the GAC particles. The decomposition of TCE depends on the probability of a TCE molecule encountering an arc or a reactive species in the reactor. Thus an increase in the contact time should also increase the rate of decomposition. The MW field in the oven cavity is constantly changing therefore the arcing/heating of the bed is not uniform.

The arcs themselfs are transient. Considering a short time period the system is not in a steady state. However, with several reactors in a row these constantly changing parameters should level out. This would lead to a system that is capable of decomposing organic contaminants uniformly over a long time period.

In this thesis only two possible application of this new technology are described. So far the desorption via steam distillation and the decomposition in the RDW-reactor enable one to handle many types of organic wastes:

- solid waste streams, such as soil, sludge, GAC, molecular sieves can be cleaned by steam distillation;
- liquid waste streams by adsorbing the caontaminants on substrates such as GAC, molecular sieves etc., which are then handled as solid wastes;
- gasous waste streams which can be decomposed directly in the RDW-reactor.

The technology established from this research group needs to be investigated in much greater detail. The following reseach topics are suggested:

- the nature and origin of the arcs in GAC beds,
- how well GAC can be regenerated by MW induced steam distillation (adsorption rate before and after steam distillation),
- recycling of the vapors developed during steam distillation

- the importance of the temperature of the GAC in the RDW-reactor for decomposition of organic vapors,
- the importance of the catalytic properties of GAC in the RDW-reactor,
- whether or not arcing provided by metal shots (aluminium, copper etc.) be sufficient to cause decomposition of organic vapors in the RDW-reactor.

G) LITERATURE CITED

CRC Handbook 86/87

Environment Reporter, 8-21-87, p.1121

F. Field, J. Franklin: Electron Impact Phenomena, 1957

I. Kolthoff, I. Miller: J. of American Chemical Society, July1951

W.R. Tinga, Dept. of Electr. Engineering, University of Alberta, Canada: Interactions of MW with materials, IMPI-Canada 1970

R. Schiffmann: Microwave heating for the Food Industry, IMPI-Europe 1975

R. Varma, S. Nandi, D. Cleaveland: Microwave-assisted Chemical Process for Treatment of Hazardous Waste, Annual Report Oct. 1987, Project number 23310, Argonne National Laboratory, Ill.

H) APPENDIX

D-2

Steam distillation studies on sand

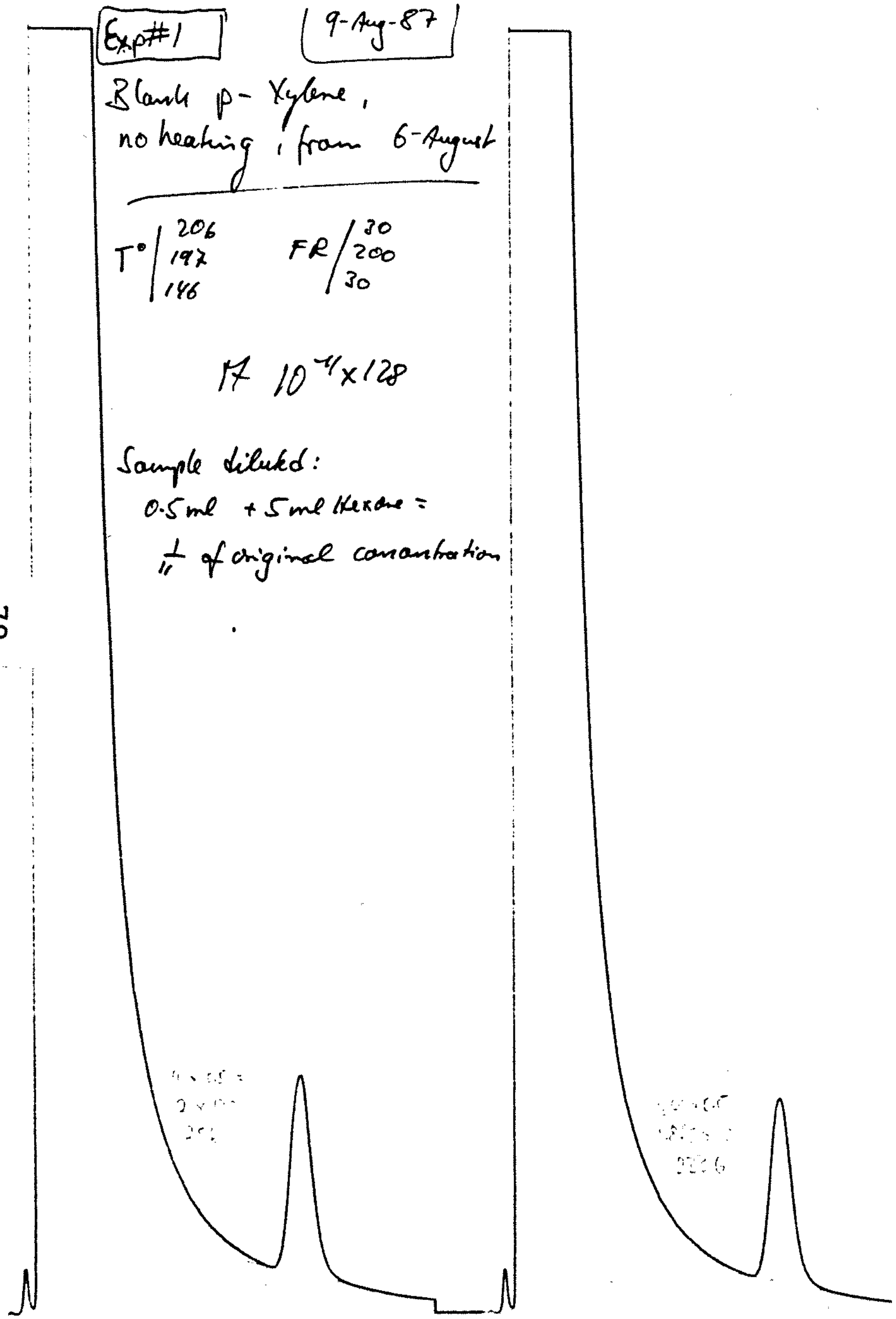
GC graphs for experiments described in chapter D-2:

Para-xylene

#1 #2 #3 #4 #5 #6 #7 #8 #9 #10

Naphthalene

#1 #2 #3 # #5 #6 #7 #8 #9



Exp#1

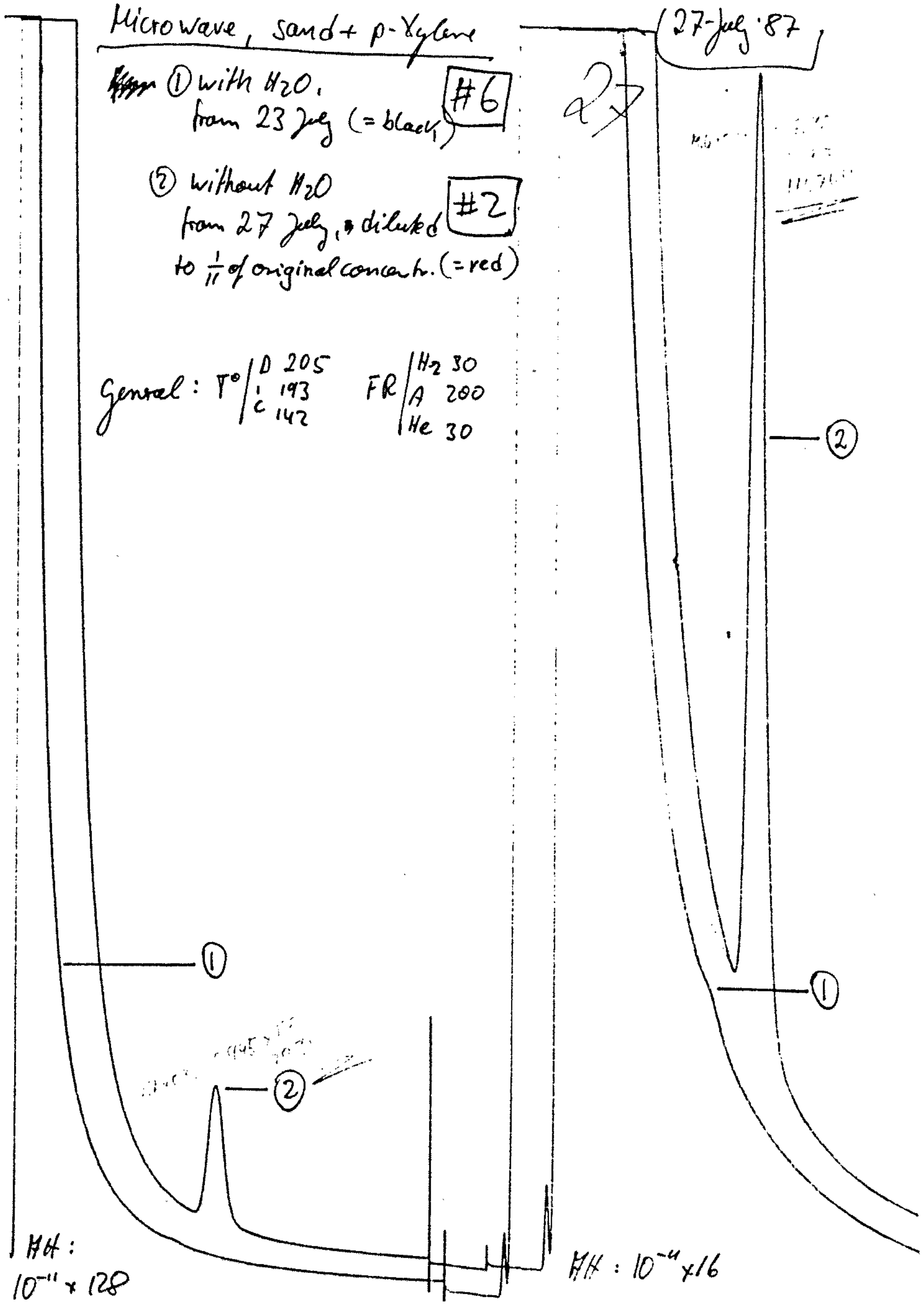
9-Aug-87

Blank p-Xylene, no heating, from 6-August

T° | 206 / 197 / 146   FR | 30 / 200 / 30

HH $10^{-4} \times 128$

Sample diluted:
0.5 ml + 5 ml Hexane = $\frac{1}{11}$ of original concentration



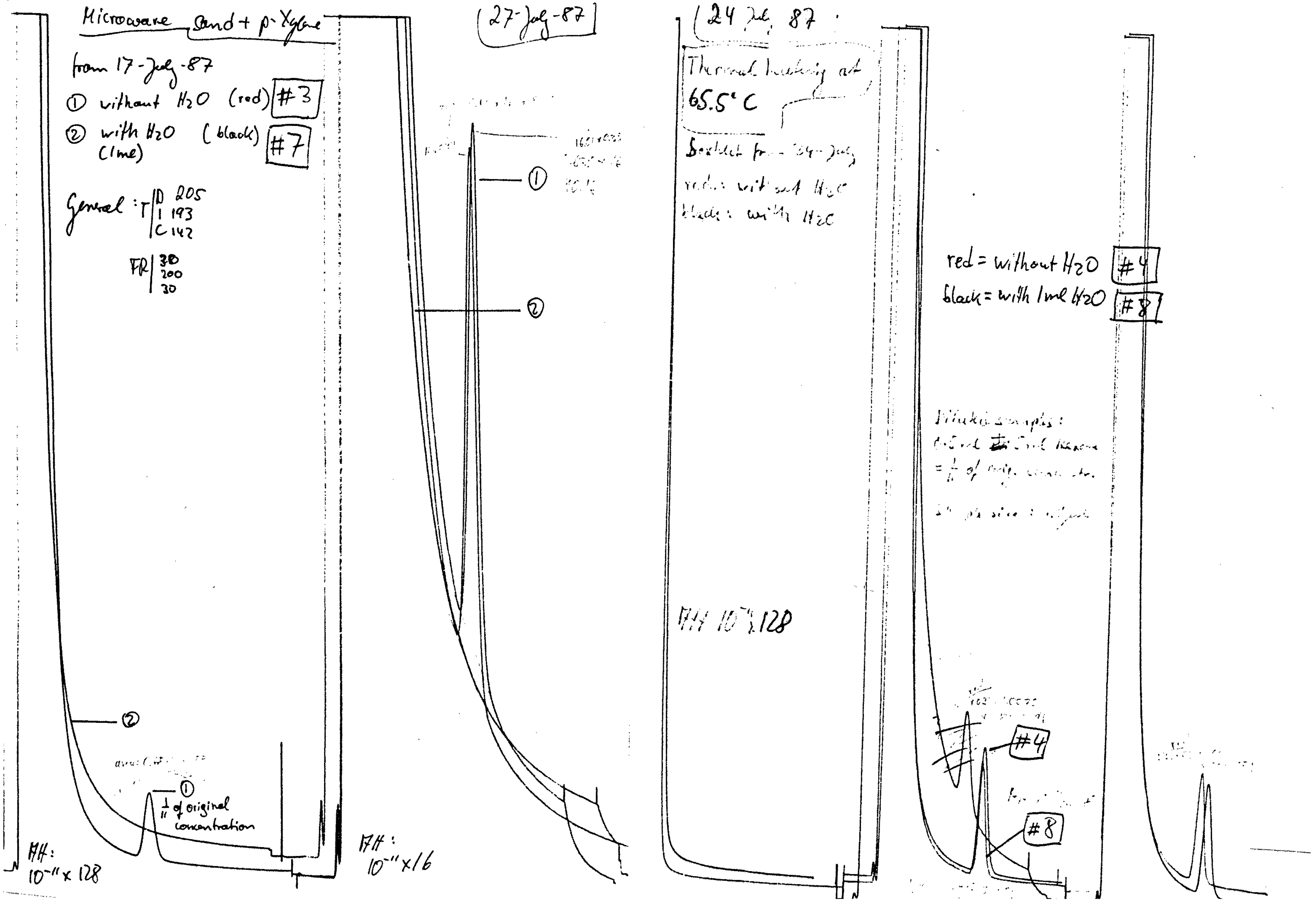
Microwave, sand + p-Xylene

① with H_2O, from 23 July (= black) #6

② without H_2O from 27 July, diluted to $\frac{1}{11}$ of original concentr. (= red) #2

General: T° | D 205 / I 193 / C 142   FR | H_2 30 / A 200 / He 30

27-July '87



Microwave sand + p-Xylene

from 17-July-87
① without H_2O (red) #3
② with H_2O (1ml) (black) #7

General : T | D 205, I 193, C 142
FR | 30, 200, 30

(27-July-87)

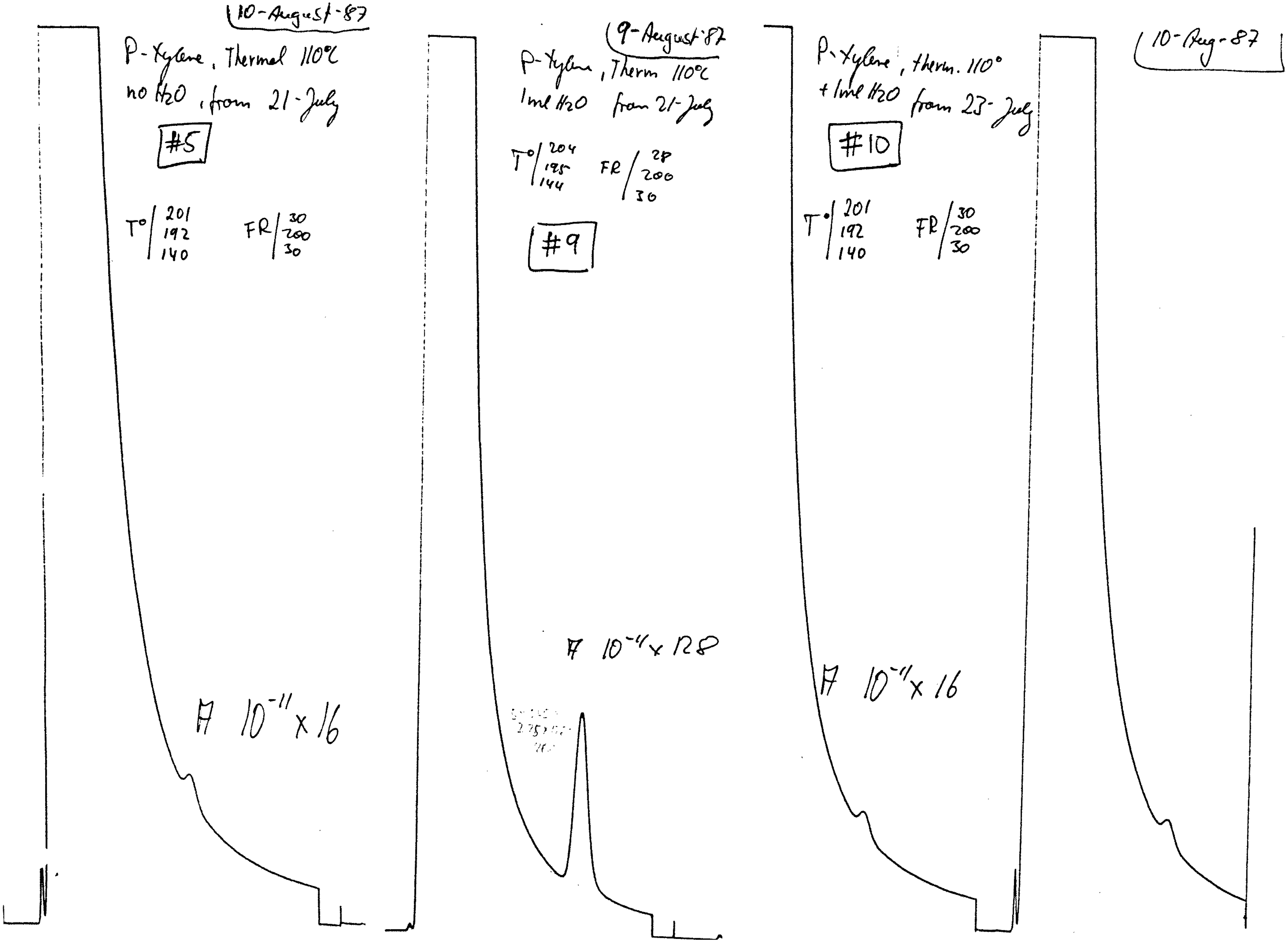
(24 July 87)

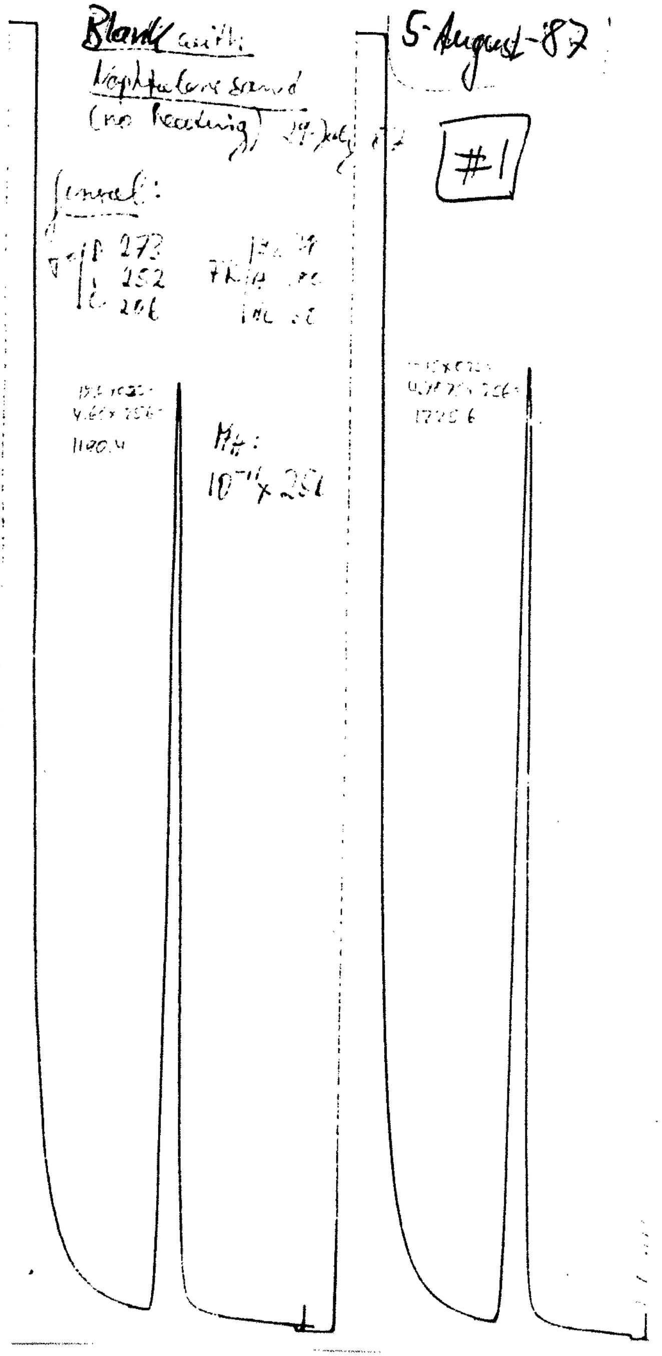
Thermal heating at 65.5°C

Soxhlet from 24-July
red: without H_2O
black: with H_2O

red = without H_2O #4
black = with 1ml H_2O #8

Diluted samples:
0.5 ml ~~[illegible]~~ 5 ml hexane
= $\frac{1}{11}$ of orig. concentr.
[illegible]


10-August-87
P-Xylene, Thermal 110°C
no H2O, from 21-July
#5
T° 201 / 192 / 140
FR 30 / 200 / 30
A 10^-11 x 16
9-August-87
P-Xylene, Therm 110°C
1ml H2O from 21-July
T° 204 / 195 / 144
FR 28 / 200 / 30
#9
A 10^-11 x 128
P-Xylene, therm. 110°
+1ml H2O from 23-July
#10
T° 201 / 192 / 140
FR 30 / 200 / 30
A 10^-11 x 16
10-Aug-87



Blank with:
Naphthalene sand
(no heating) 29-July-87

Jennel:

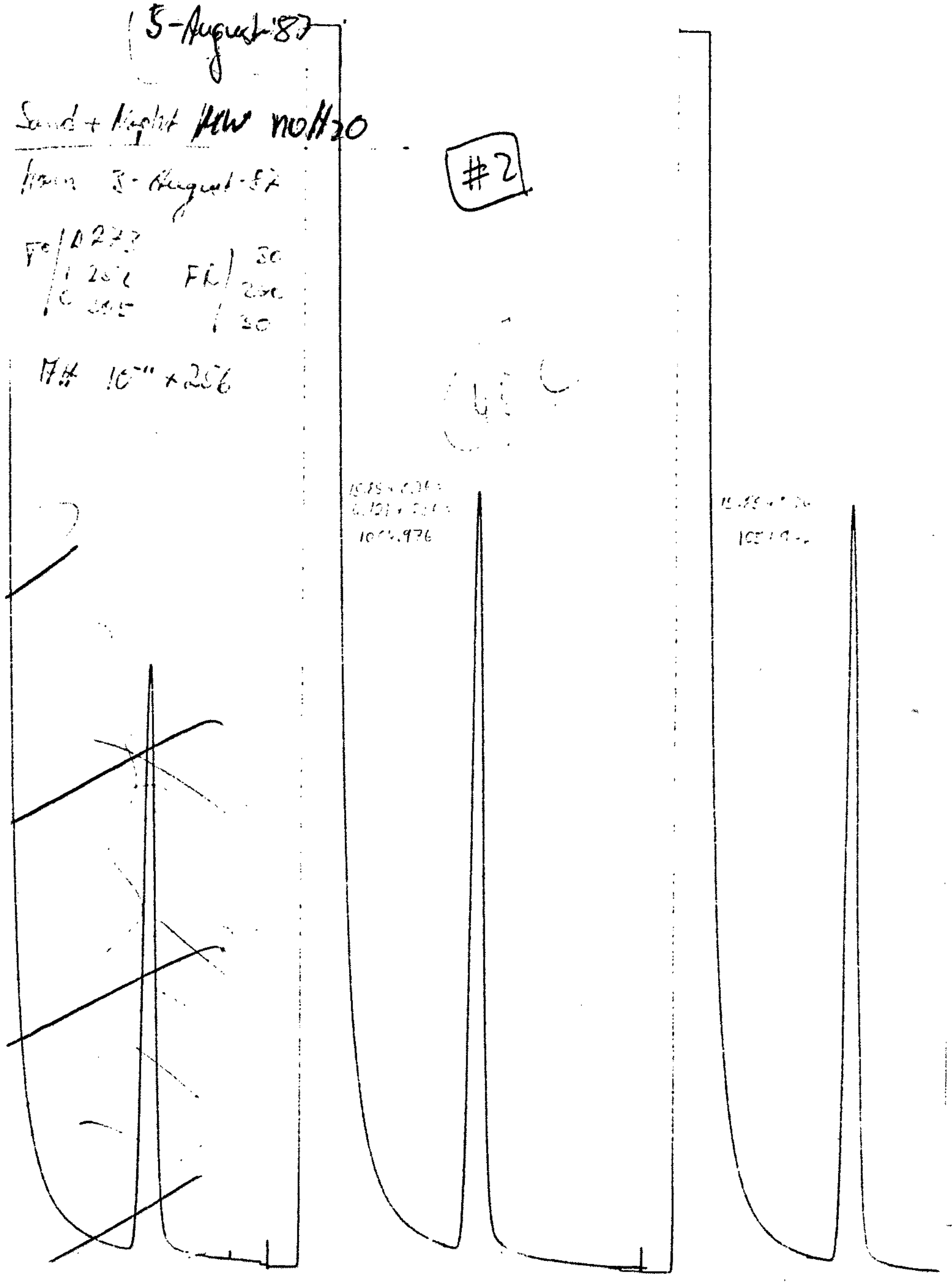
T° | D 273 | 252 | C 206

FR | [illegible]

H#: 10⁻¹¹ x 256

5-August-87

#1



5-August-87

Sand + Napht new no H2O

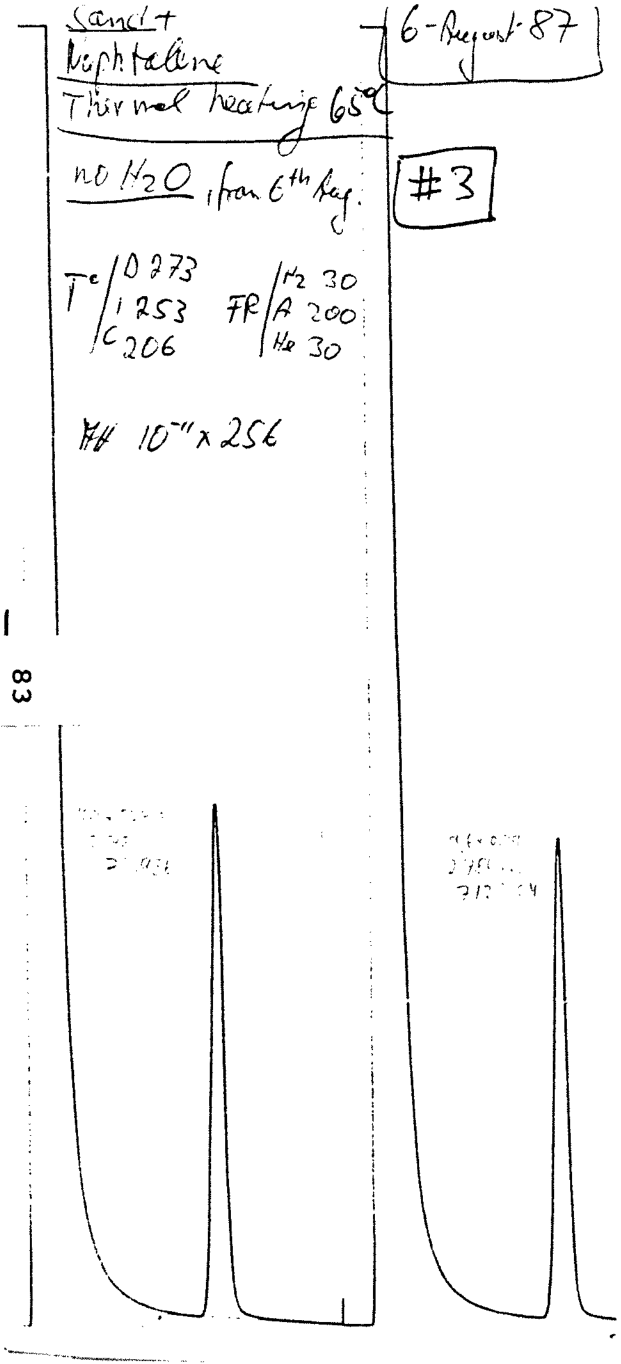
from 3-August-87

T° | D 273 | 256 | C 205

FR | 30 | 250 | 30

H# 10⁻¹¹ x 256

#2



Sand + Naphtaline
Thermal heating 65°C
no H_2O, from 6th Aug.

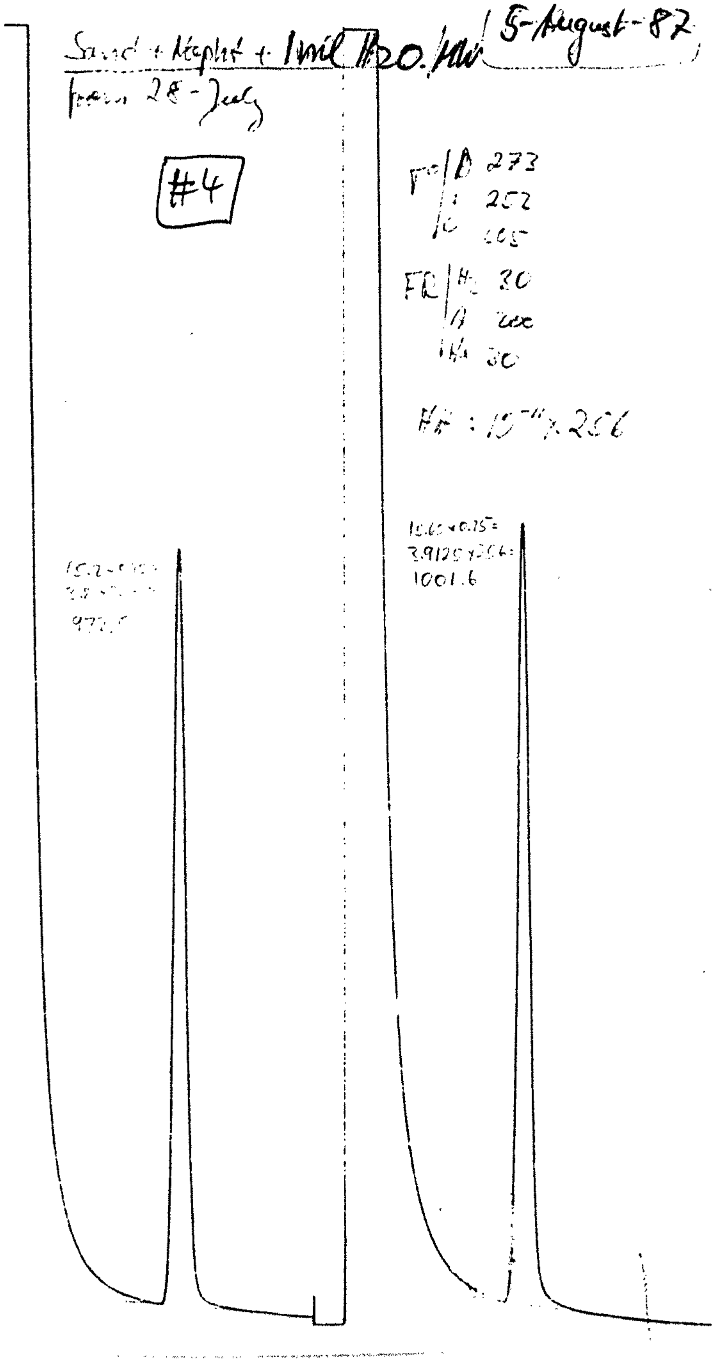
6-August-87

#3

T° D 273 / I 253 / C 206

FR H_2 30 / A 200 / He 30

A# 10^{-11} x 256



Sand + Naphth + 1ml H_2O /ml
from 28-July

5-August-87

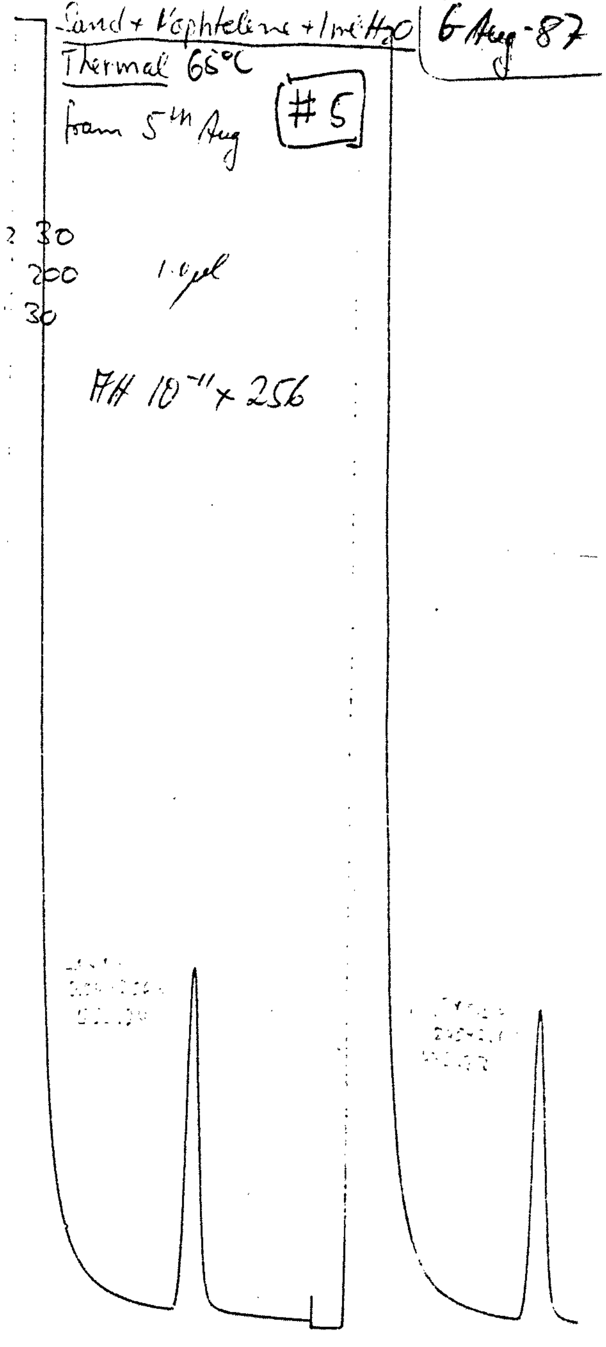
#4

T° D 273 / I 252 / C 205

FR H_2 30 / A 200 / He 30

A# : 10^{-11} x 256

15.65 × 0.25 =
3.9125 × 256 =
1001.6



Sand + Naphtaline + 1ml H_2O
Thermal 65°C
from 5th Aug

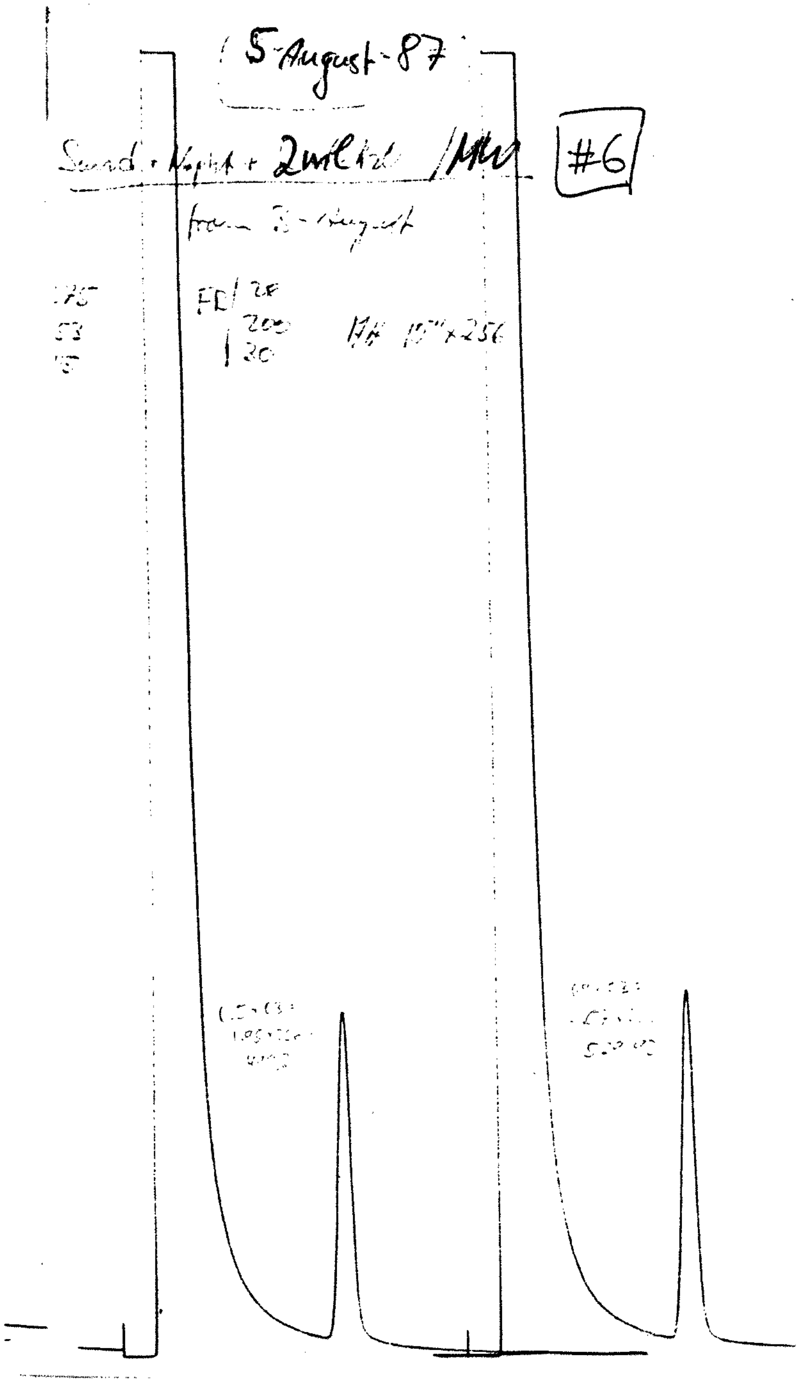
6-Aug-87

#5

30
200
30

1.0 µl

A# 10^{-11} x 256



5-August-87

Sand + Napht + 2ml H_2O /MW

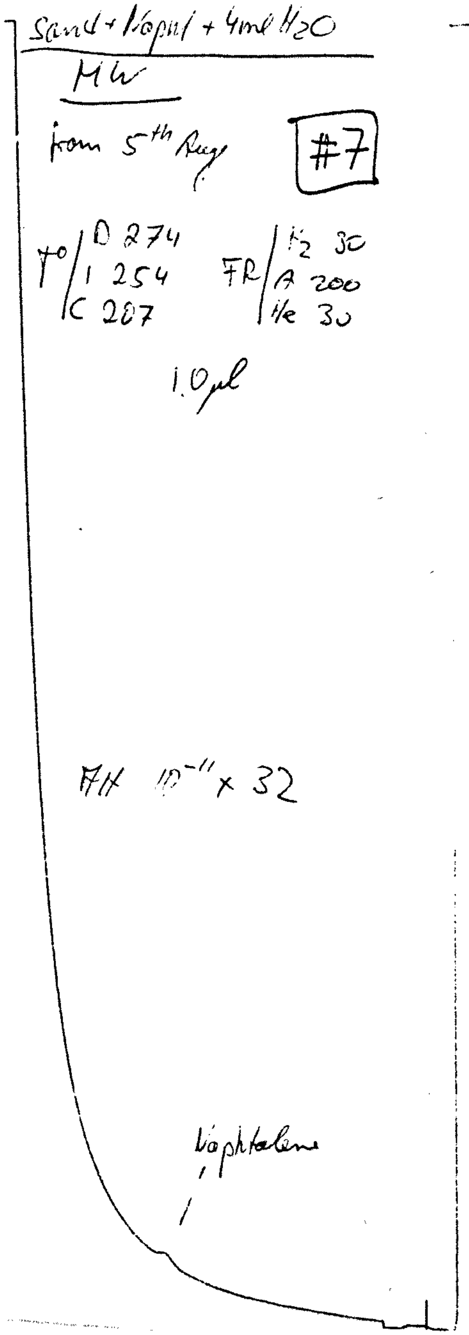
#6

from 3-August

175
53
15

FD/ 28
200
30

AH 10^{-11} × 256



Sand + Napht + 4ml H_2O

MW

from 5th Aug

#7

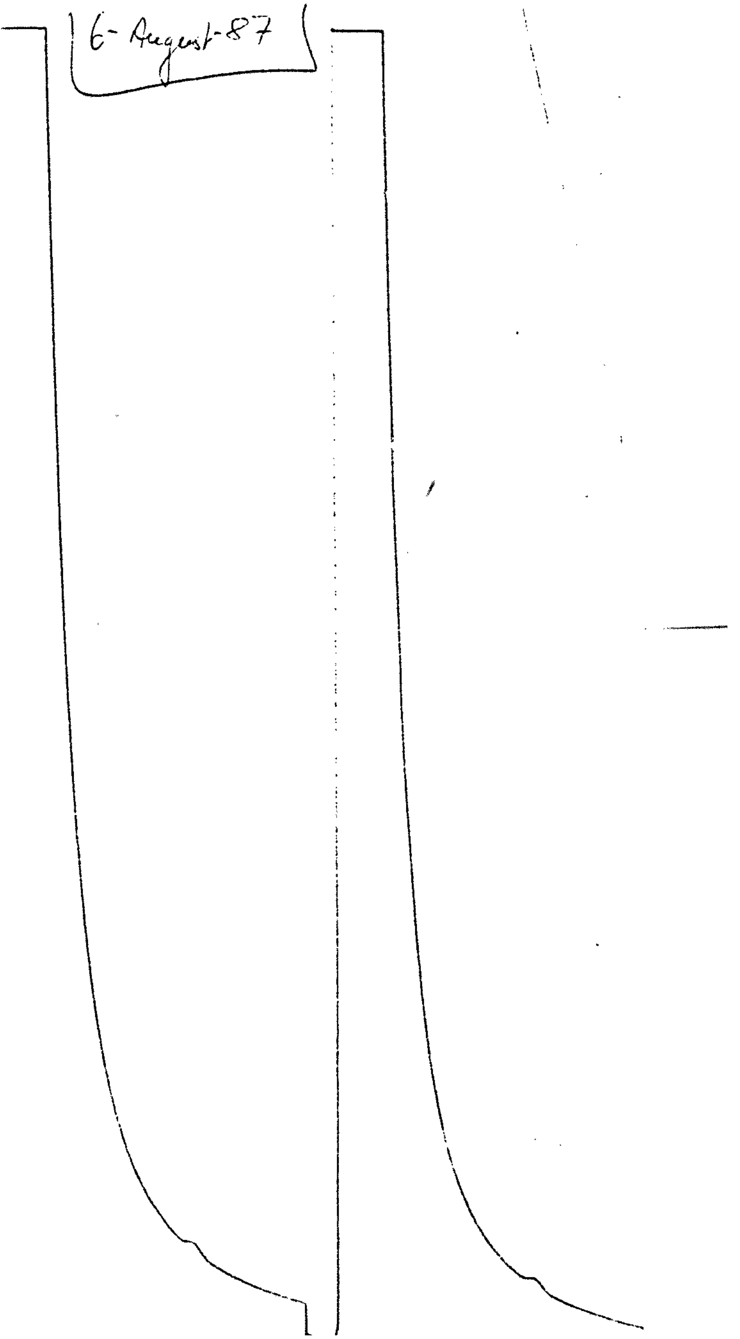
T°/ D 274
I 254
C 207

FR/ H_2 30
A 200
He 30

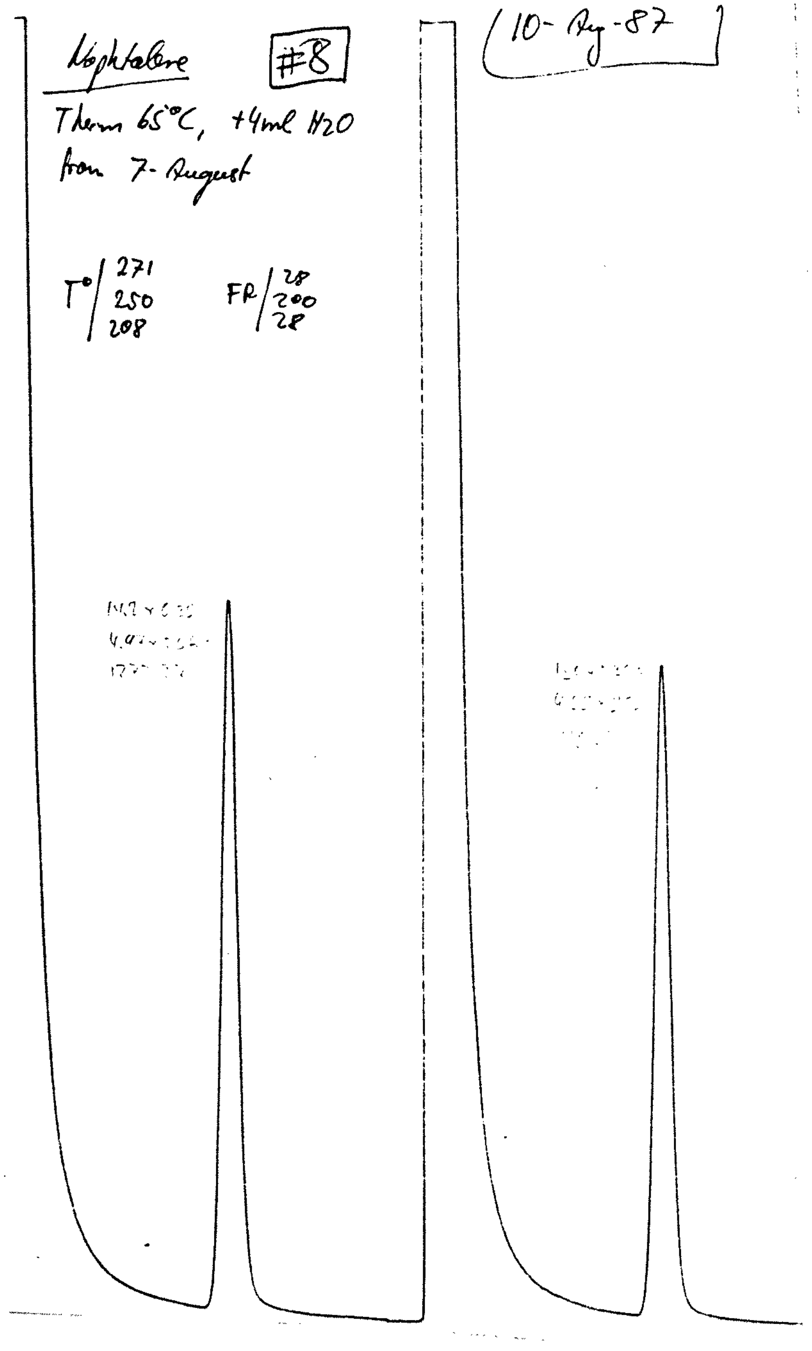
1.0 μl

AH 10^{-11} × 32

Naphtalene



6-August-87

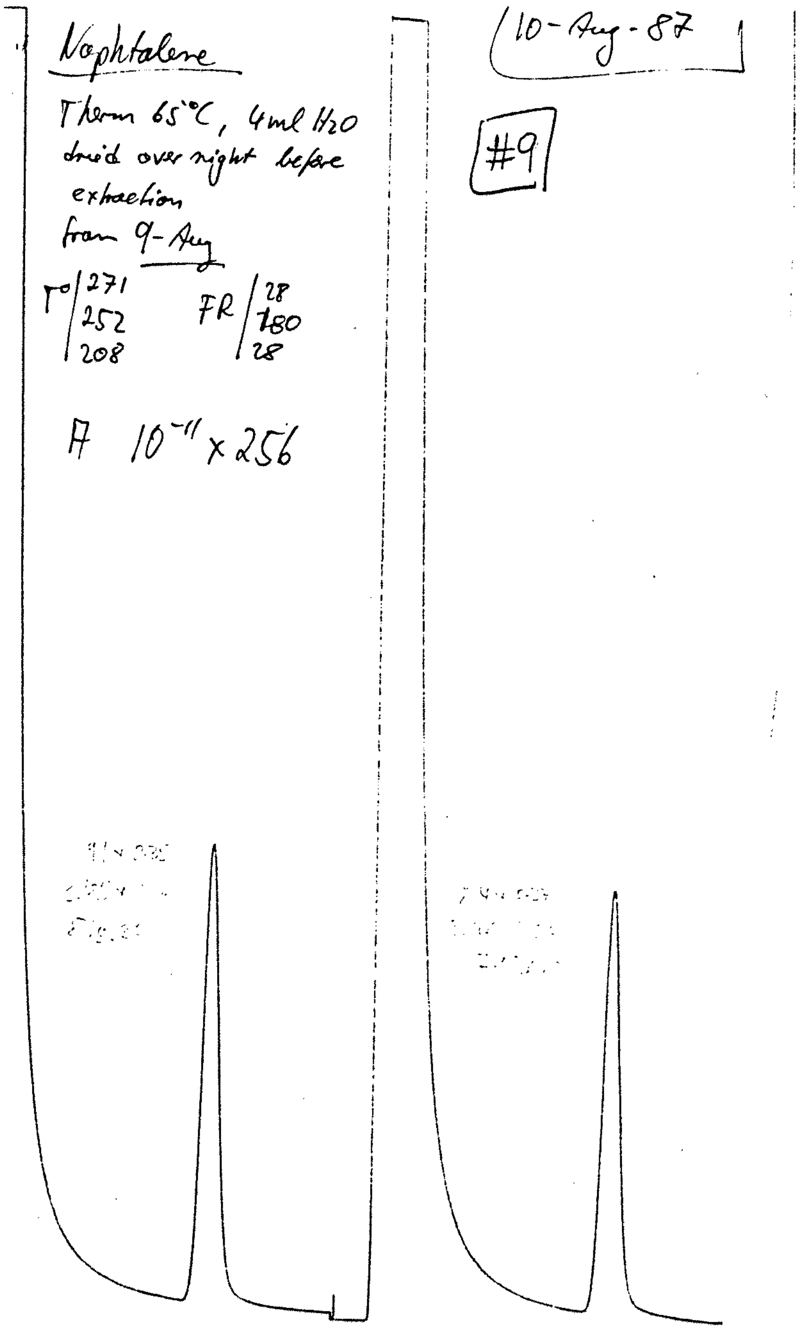


Naphtalene #8

Therm 65°C, +4ml H_2O
from 7-August

T° | 271 250 208
FR | 28 200 28

10-Aug-87



Naphtalene

Therm 65°C, 4ml H_2O
dried over night before
extraction
from 9-Aug

T° | 271 252 208
FR | 28 180 28

A $10^{-11} \times 256$

10-Aug-87

#9

D-3

Steam distillation studies on GAC

Experiments described in chapter D-3

GC graphs for Blanks and single stage heating:

HP-1 HP-2 MS-1 MS-2 MS-5 MS-6 MS-7

GC graphs for multiple stage heating:

SD-1 SD-2 SD-3 SD-4

GC-MS parameters, graphs and calculated areas:

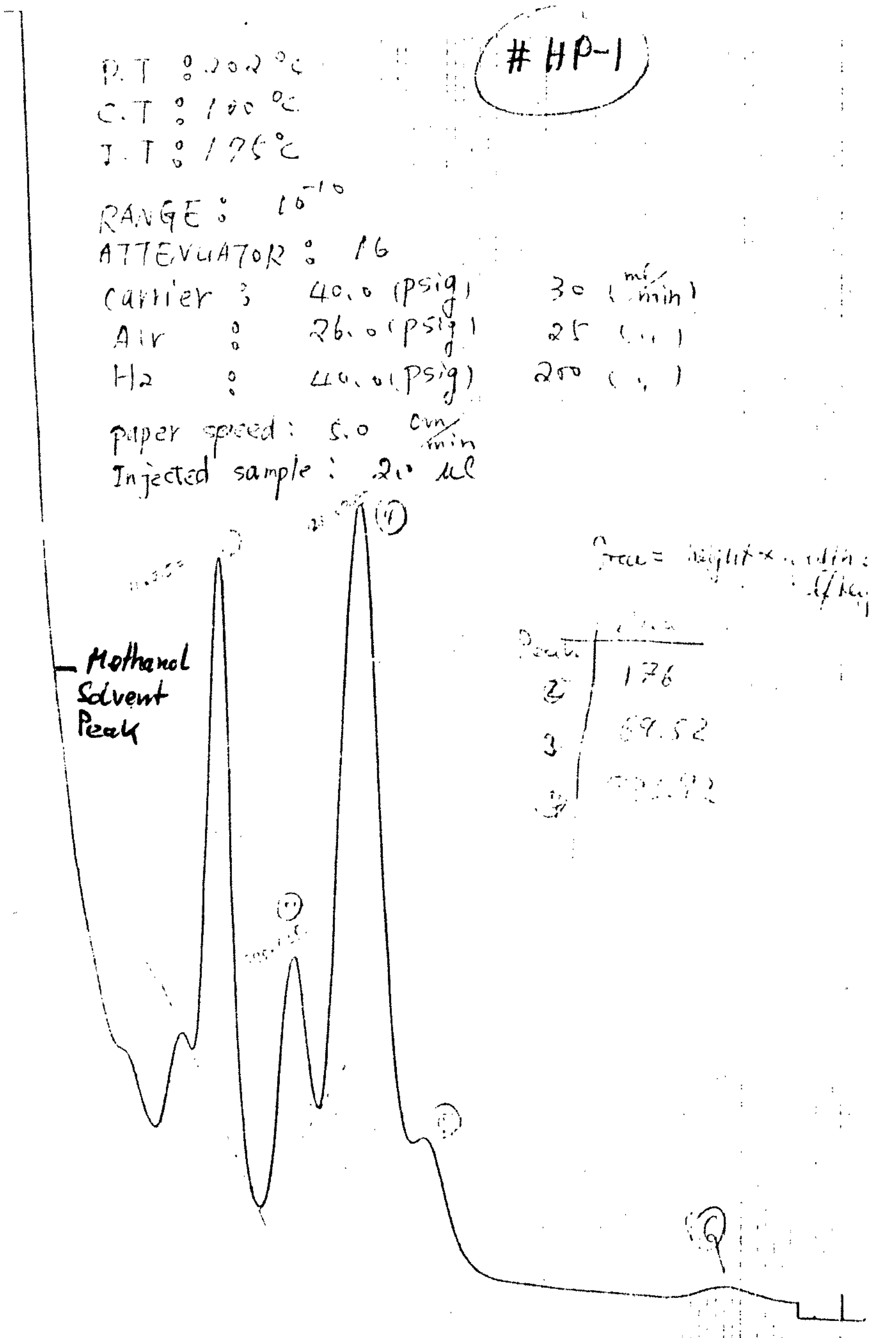
Data aquisition

TCE tune

TIC of pure solvent (methanol)

Integator events

BP-M1 (Blank) SD-1 SD-2 SD-3 SD-4



P.T : 202 °C
C.T : 100 °C
I.T : 175 °C

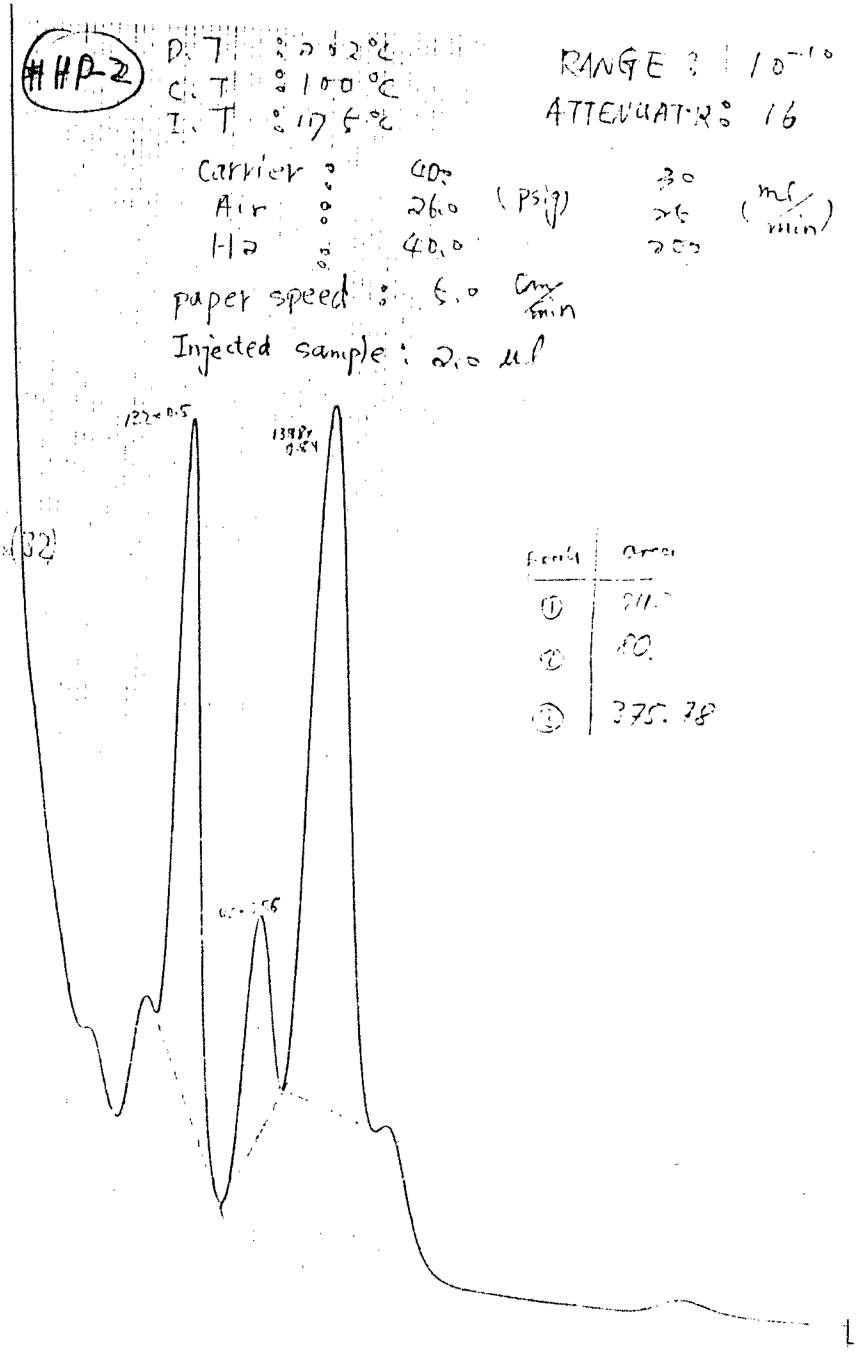
RANGE : 10^{-10}
ATTENUATOR : 16

Carrier :	40.0 (psig)	30 (ml/min)
Air :	26.0 (psig)	25 (")
H2 :	40.0 (psig)	250 (")

paper speed : 5.0 cm/min
Injected sample : 2.0 ul

Area = height × width [illegible]

Peak	[illegible]
②	176
3	69.52
③	[illegible]



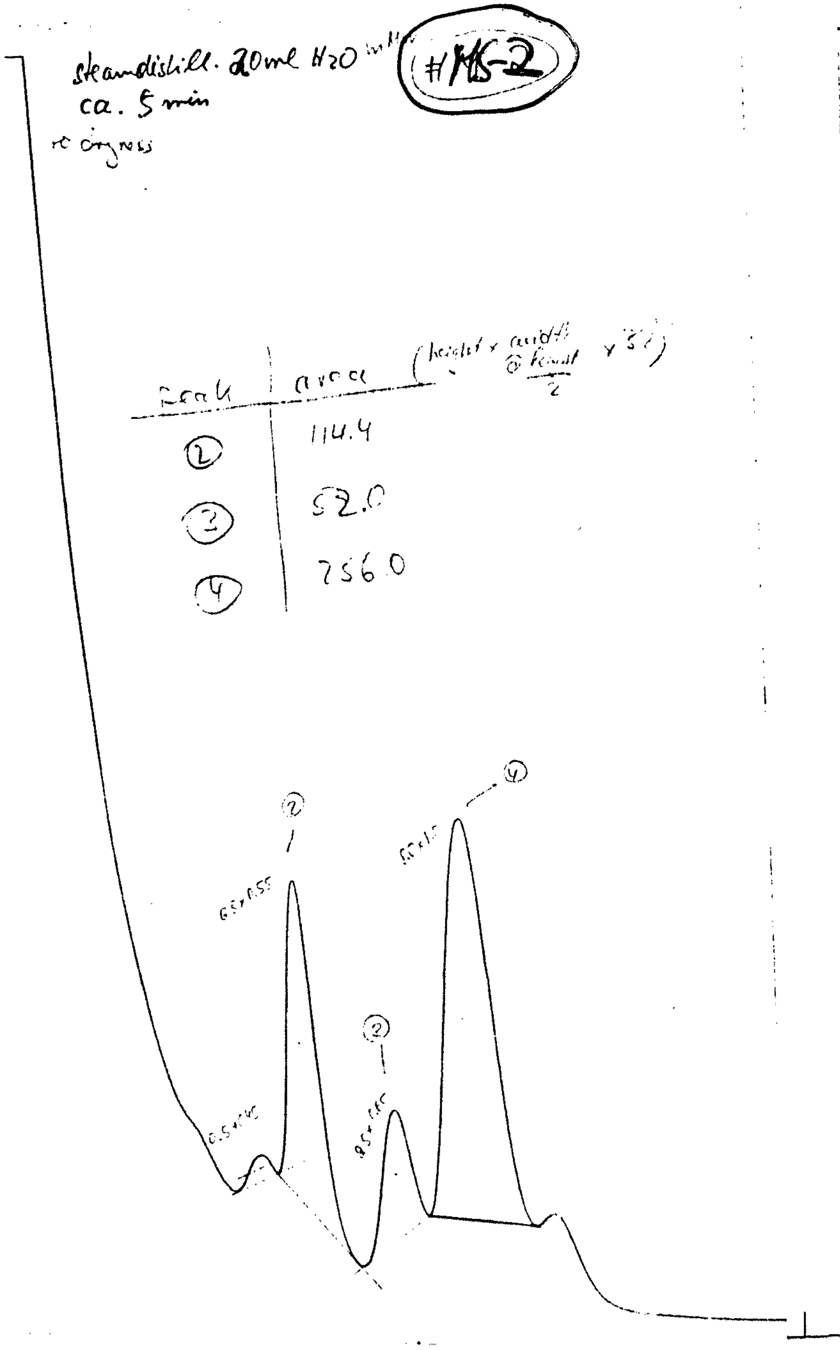
P.T : 202 °C
C.T : 100 °C
I.T : 175 °C

RANGE : 10^{-10}
ATTENUATOR : 16

Carrier :	40.0	(psig)	30 (ml/min)
Air :	26.0		25
H2 :	40.0		250

paper speed : 5.0 cm/min
Injected sample : 2.0 ul

Peak	area
①	211.[illegible]
②	80.
③	375.78



steamdistill. 20ml H2O in M

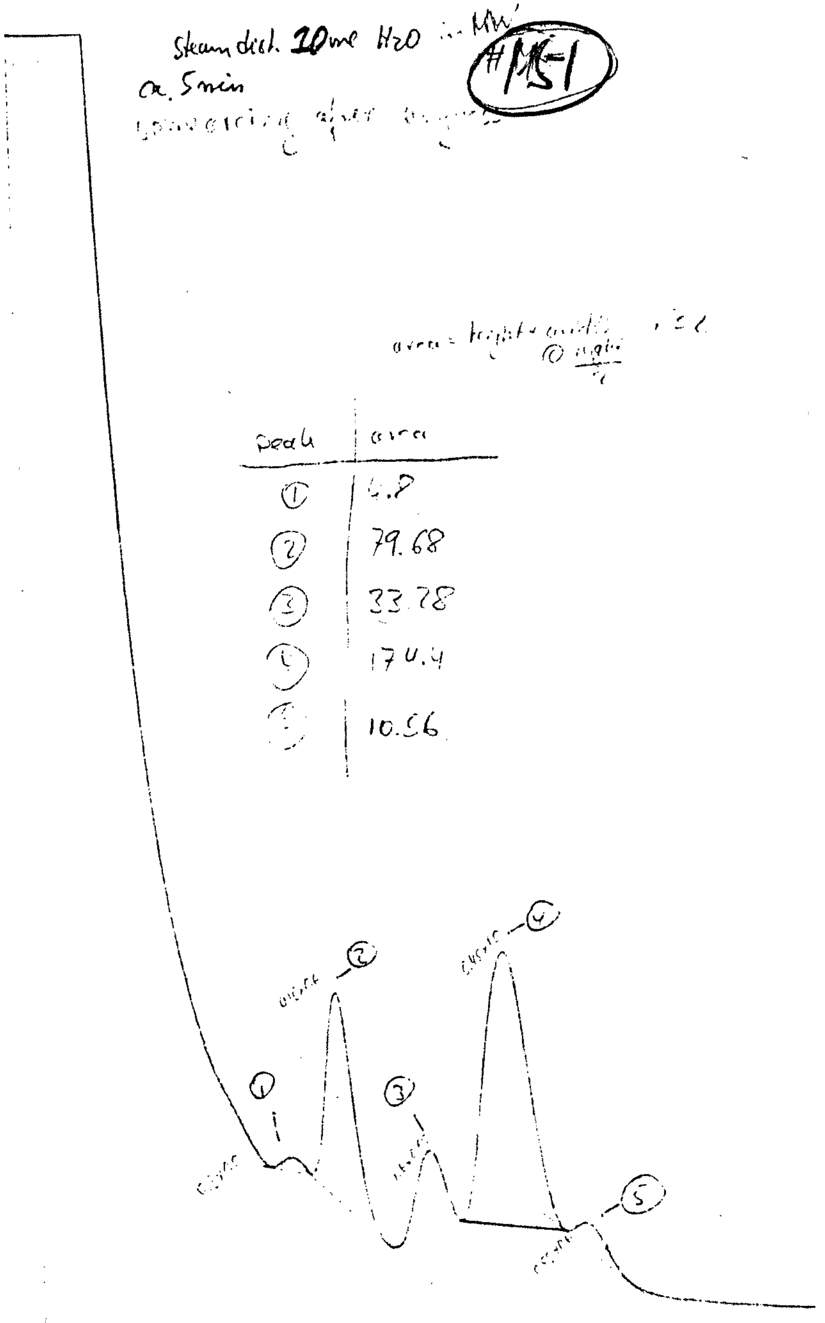
ca. 5 min

rc dryness

#MS-2

(height × width @ height/2 × 32)

peak	area
②	114.4
③	52.0
④	256.0



Steam dist. 20ml H2O in MW

ca. 5 min

[illegible]

#MS-1

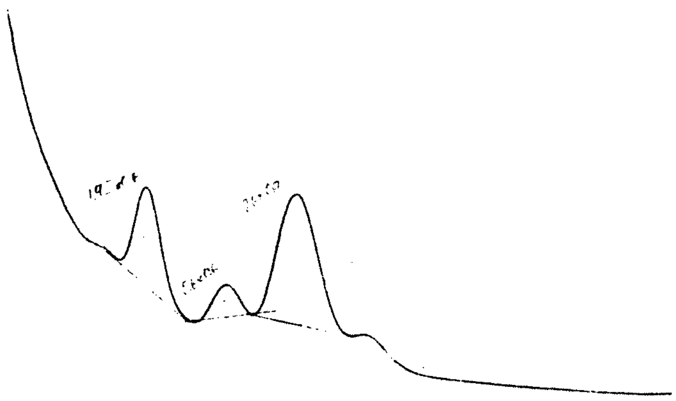
area = height × width @ height/2 × 32

peak	area
①	4.8
②	79.68
③	33.78
④	174.4
⑤	10.56

30 ml H2O
steamdistillation
to dryness, red glowing GAC

#MS-5

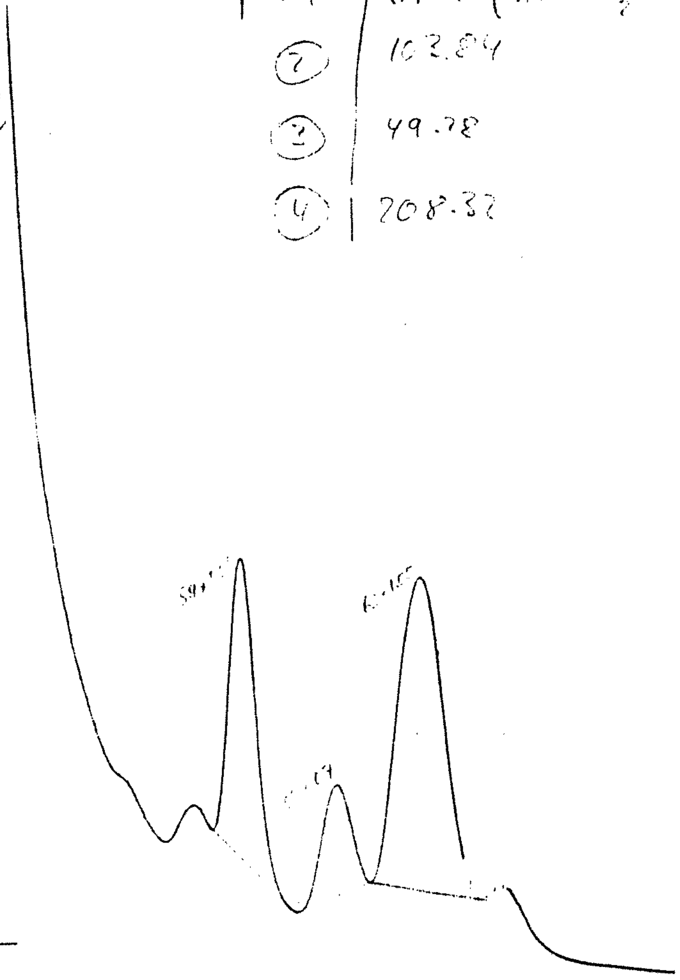
Peak	area (h × w at h/2 × 32)
②	37.44
③	11.52
④	74.58



steam dist.
50 ml H2O
10.0 min MW
to dryness

#MS-7

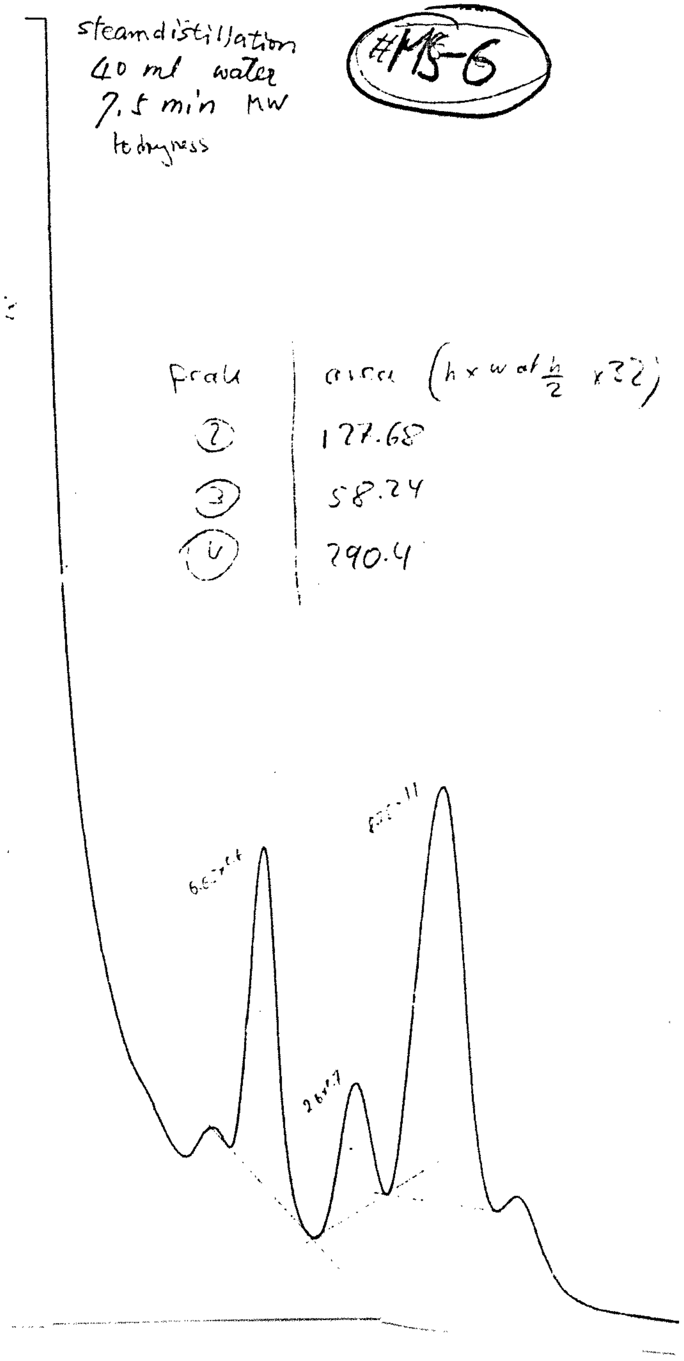
Peak	area (h × w at h/2 × 3
②	103.84
③	49.78
④	208.32

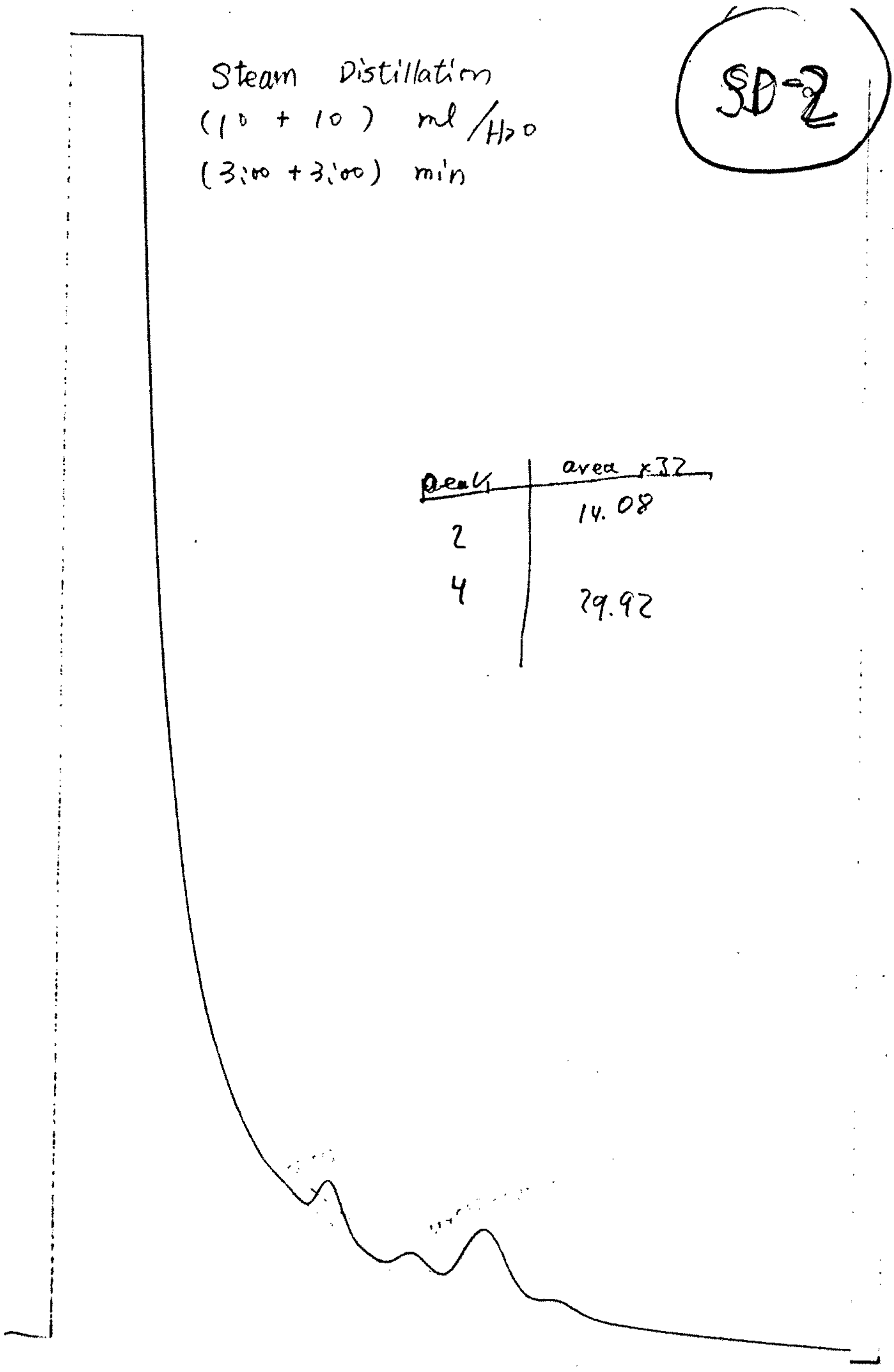


steamdistillation
40 ml water
7.5 min MW
to dryness

#MS-6

Peak	area (h × w at h/2 × 32)
②	127.68
③	58.24
④	290.4

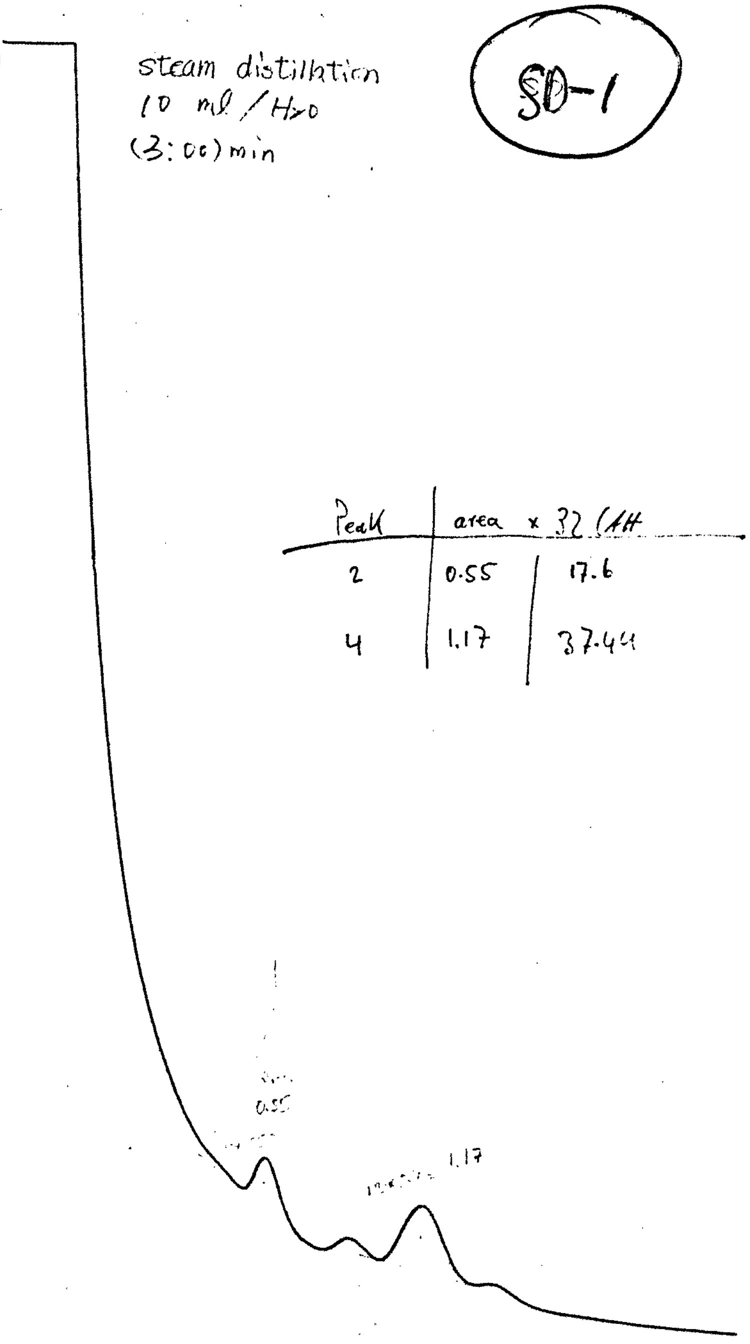




SD-2

Steam Distillation
(10 + 10) ml/H_2O
(3:00 + 3:00) min

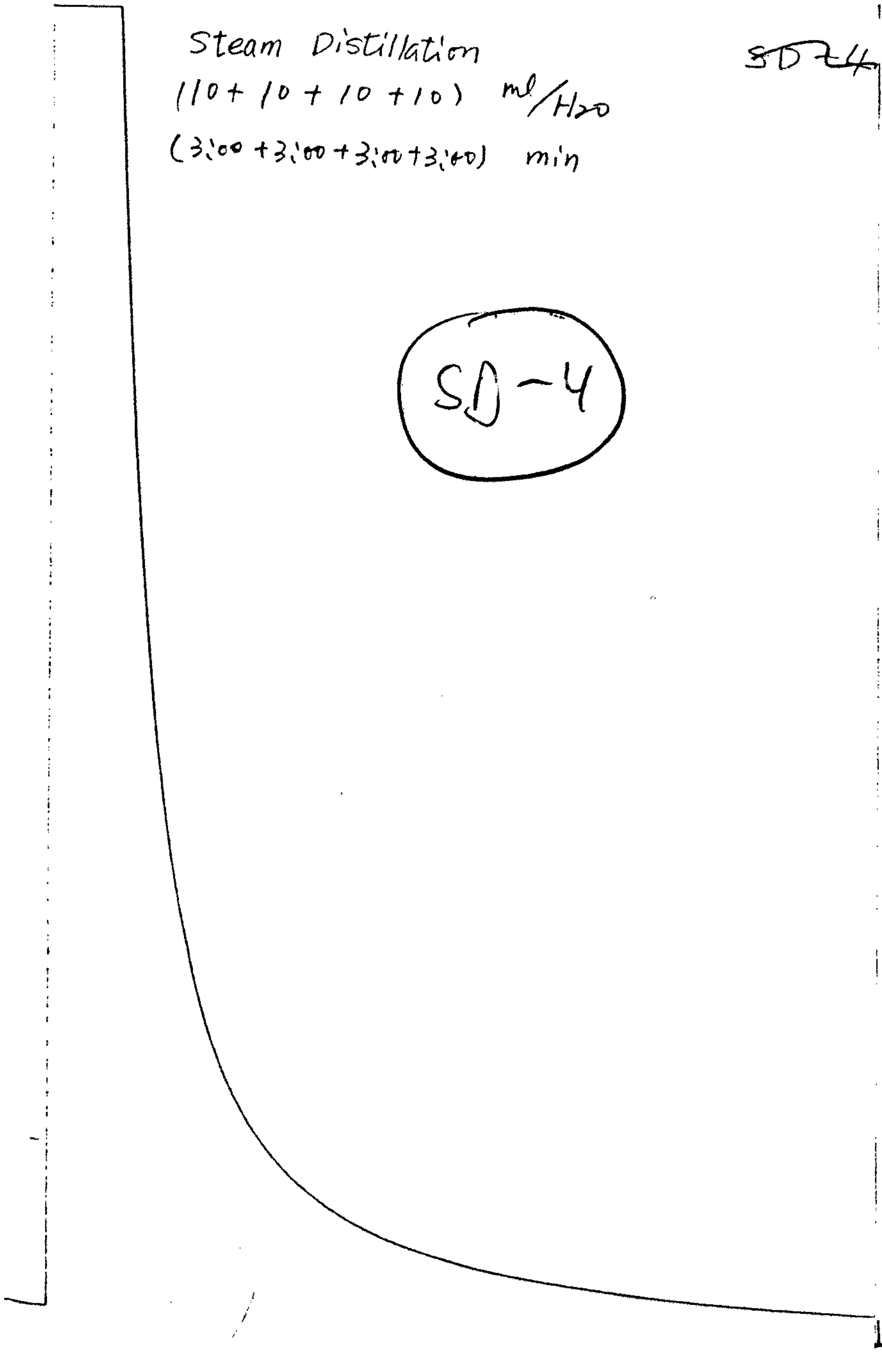
Peak	area x32
2	14.08
4	29.92

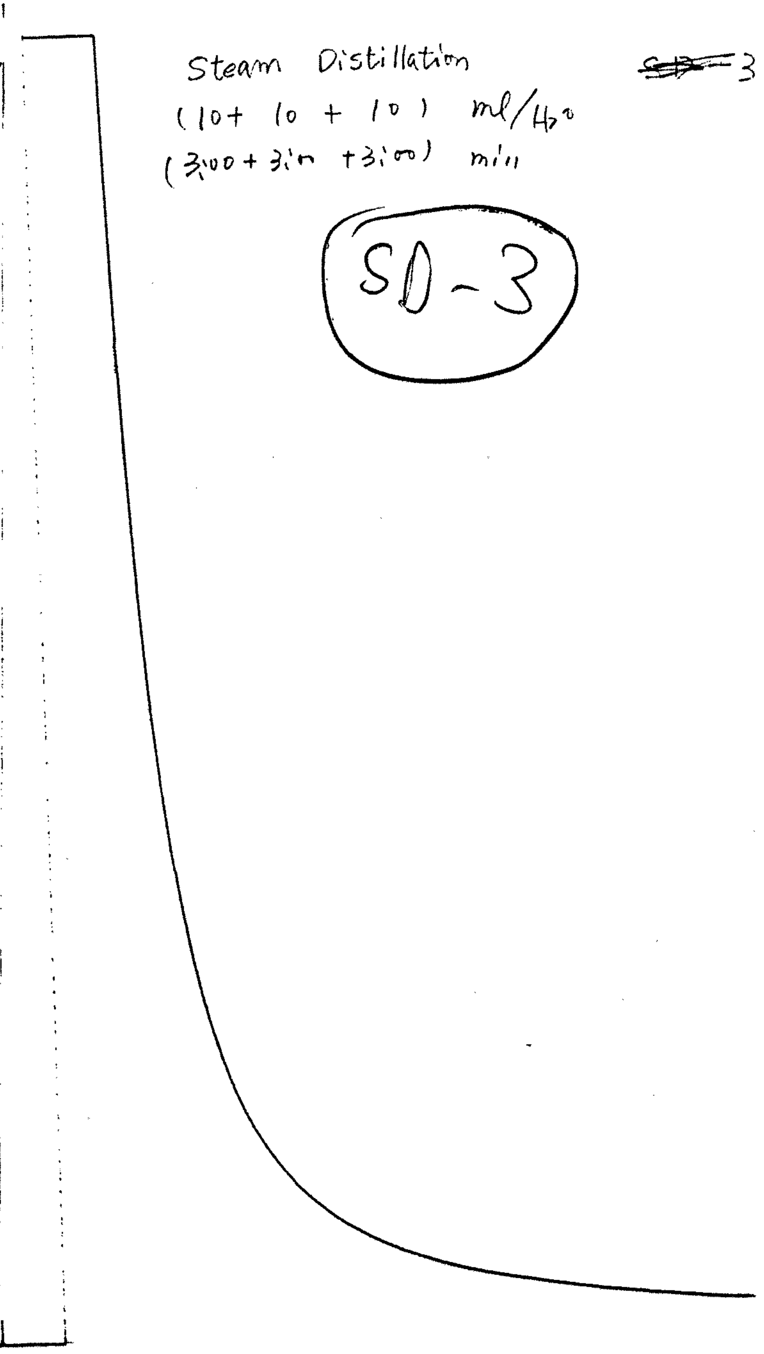


SD-1

steam distillation
10 ml/H_2O
(3:00) min

Peak	area	x 32 (AH
2	0.55	17.6
4	1.17	37.44


Steam Distillation
(10+10+10+10) ml/H2O
(3:00+3:00+3:00+3:00) min
SD-4
SD-4

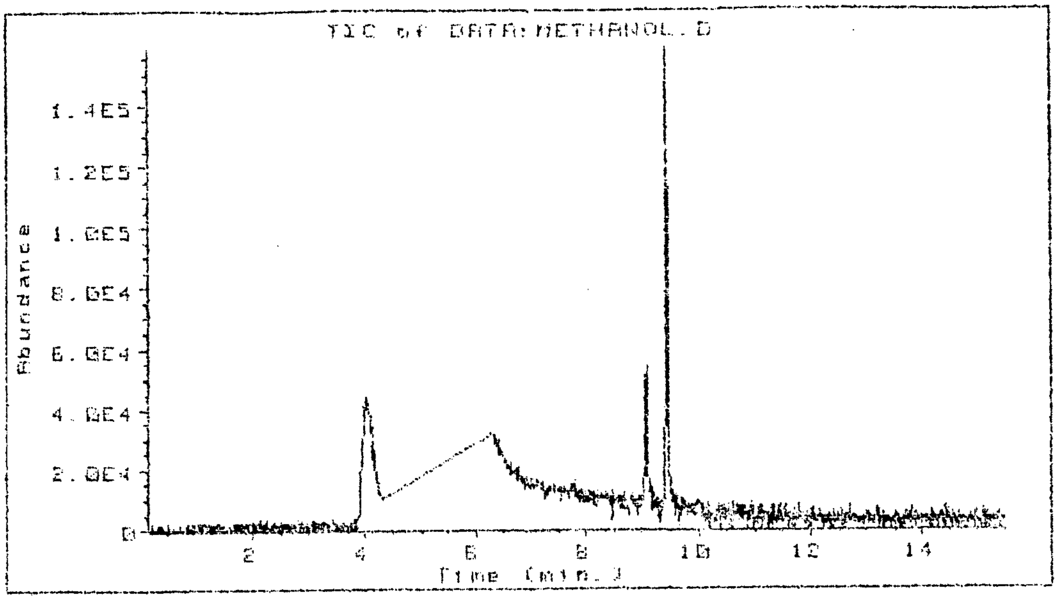

Steam Distillation
(10+ 10 + 10) ml/H2O
(3:00+3:00 +3:00) min
~~SD~~-3
SD-3

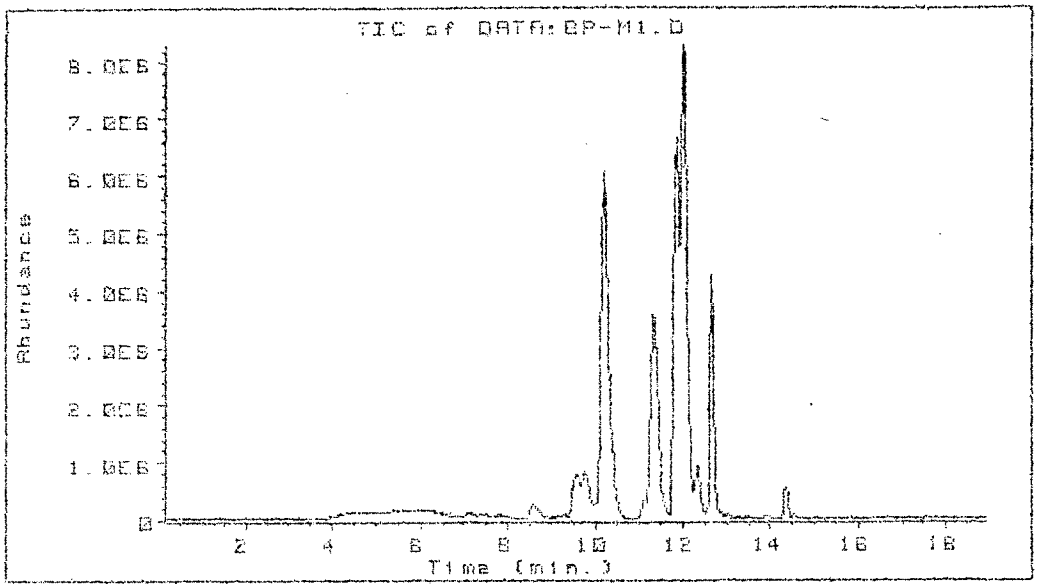
```
     Parameter file : DATA:BP-AQ.A

        Description : STANDARD

   last modified By : G

          Tune file : DATA:TCETUNE.U

   Acquisition mode : SCAN

              InJet : GC

printOut destination : PRINTER:


 solvent delaY  0.00   eM volts  -200 relAtive     resulting voltage 1600

 -----------------------------------------------------------------------
     start     Low      High       Scan     a/d samples   scans per
     Time      mass     mass     threshold     (2^N)       second
  1   0.00      10.0    500.0      1000          2          0.87
  2  -----      50.0    550.0      1000          2          0.86
  3  -----      50.0    550.0      1000          2          0.86


   T E M P E R A T U R E   P R O G R A M  &  H E A T E D  Z O N E S

rUn time  20.50    eQuilibration time    0.20    Purge off time    0.00

            initial    initial    Rate      final     final       total
 level        tEmp      time    (°C/Min)    tEmp      time        time
   1           40       0.00      0.0        40        3.00        3.00
   2                             10.0       150        0.00       14.00
   3                             20.0       180        0.00       15.50

                  actual  Setpt  Limit                  actual  Setpt  Limit
Oven (Standby)      73     40     300   Inj Port A        ---     Off    250
Inj Port B         185    180     250   Transfer Line     280     280    300
Detector A         ---    Off     250

                 Run Table Editor

                 Page  1                           Page  2
  0.00 Group  1
  0.00 Mass Sp On
  4.30 Mass Sp Off
  6.20 Mass Sp On
 20.50 Stop Run
```

TCE tune

```
MASS SPECTROMETER PARMS        FILE:  TCETUNE.U

      Multiplier: 1000                         Emission: ON

        amu Gain:   0       amu Offset:  65    Repeller: 10.2

       ion Focus: 204.        ent Lens: 200     X - ray:  0.0

       mass gaiN:   750                       mass offseT:     0


ACQUISITION & DISPLAY PARMS         FILE:  TCETUNE.U

     tune Mass1:  95.00      tune Mass2: 131.00      tune Mass3: 136.00

  misc Info : PFTBA TUNED FOR TCE RUNS

     Window: 5.00          Averages: 9            stepsiZe: 0.10

       Scale:    100     sCale mode: Autoset    mass3 Factor: 1.0

  scan range               Low mass: 10.0         High mass: 150.

   Threshold:   500                            samples (2^N): 2


NORMALIZATION FACTORS             FILE:  TCETUNE.U

         m/Z        Target %                m/Z        Target %
          50         100.0                   69          50.0
         131          50.0                   50         100.0
          50         100.0                   50         100.0
```

Methanol TIC





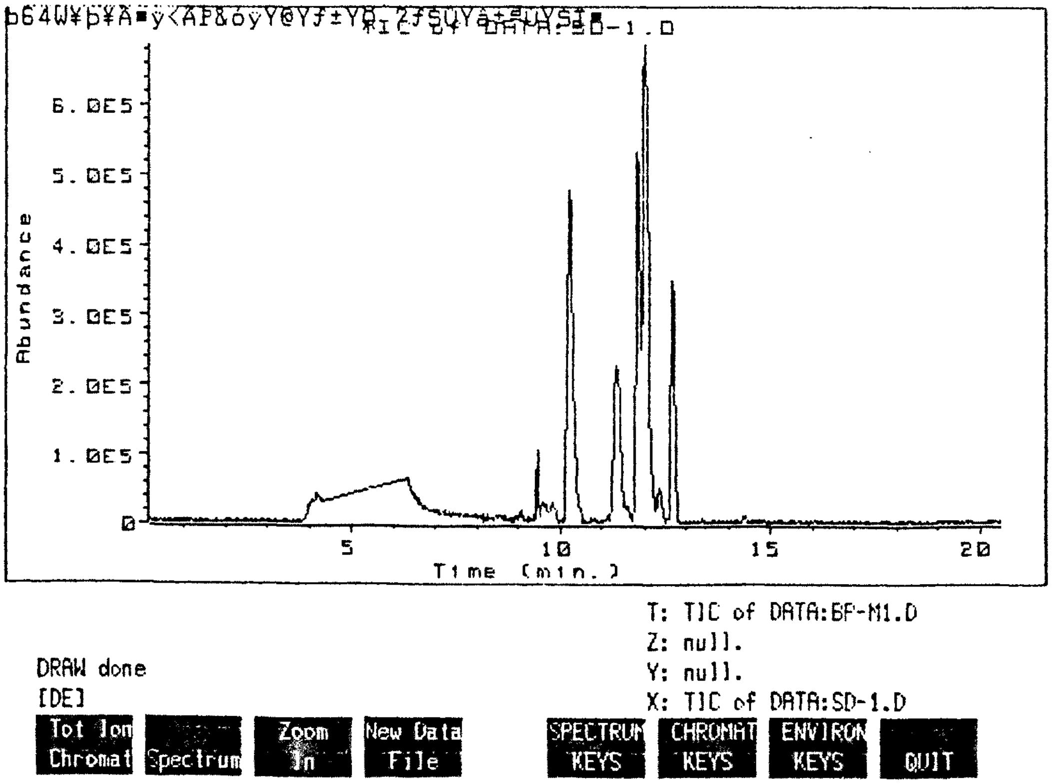
BP-M1 (Blank)

```
                                              T: null.
                                              Z: null.
DRAW done                                     Y: null.
[DE]                                          X: TIC of DATA:BP-M1.D
```

Integrator events

```
           *** Integrator Events ***

Initial    Peak Width          0.200
Initial    Threshold          16
Initial    Area Reject         1
             Shoulders   OFF

   0.000   Integ OFF
   9.600   Integ ON
  19.000   Integ OFF
TIC of DATA:BP-M1.D
GEORGE'S SOX-EXTRACTION, BP:SITE#9757, NO TREATMENT

Peak#  Ret Time   Type   Width        Area       Start Time    End Time
   1      9.776   BV     0.105    20283457          9.602       9.984
   2     10.214   PV     0.187   687241718          9.984      10.926
   3     11.329   PV     0.212   473772226         10.926      11.693
   4     11.853   VV     0.134   529932535         11.693      11.925
   5     12.020   VV     0.148   813670269         11.925      12.254
   6     12.348   VV     0.136    84282969         12.254      12.515
   7     12.656   VV     0.098   280467732         12.515      13.179
   8     13.258   VV     0.101     2719789         13.179      13.372
   9     13.950   PV     0.179     3629333         13.788      14.132
  10     14.350   VV     0.109    35373561         14.132      14.476
  11     14.540   VV     0.124     4541488         14.476      14.875
```

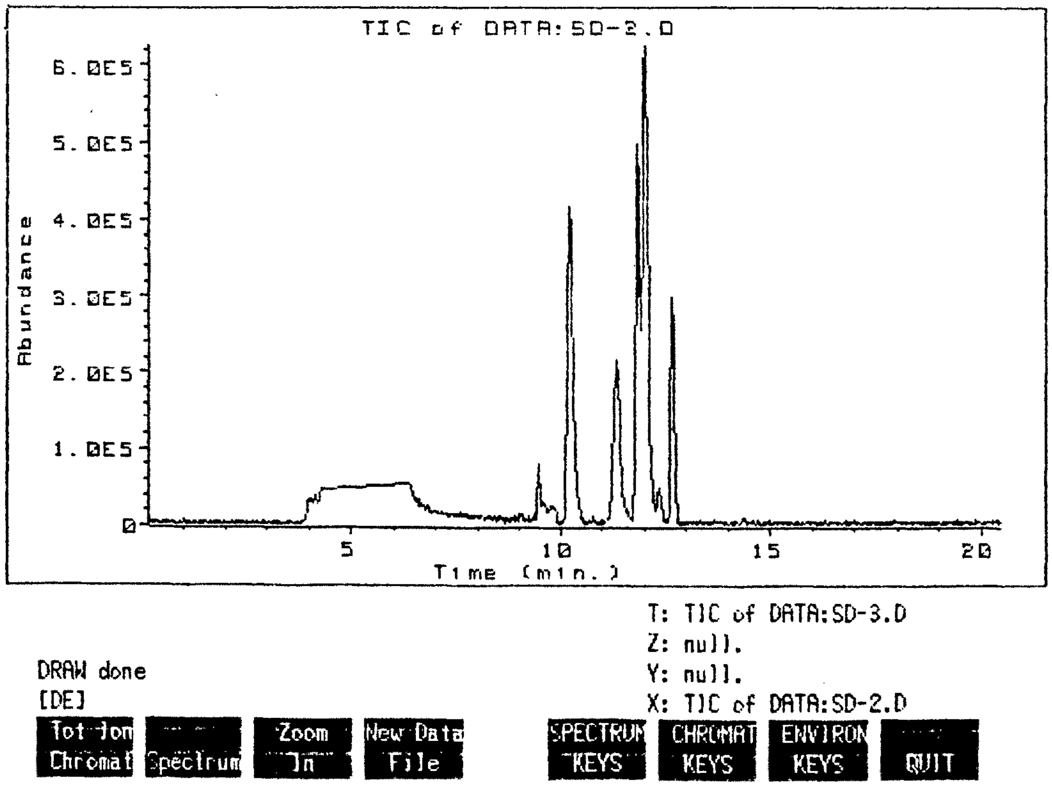
```
                         *** Area Percent   ***

                        Report by Retention Time
==========================================================================
Operator: G                                          15 Jan 88  12:54 pm
Sample Info : JOU'S EXTR.,1X10ML H20,1X3MIN MW,BP-AQ, JAN-15-88
Misc Info:
Integration File Name : DATA:SD-1.I
                           Bottle Number : 0

Ret Time   Signal Descr     Type      Area   Height    % Pk    % Sg  % LPk  % LSg
==========================================================================
 10.224       Total Ion     BV    45164571   466974 100.00   23.31 100.00   71.90
--------------------------------------------------------------------------
 11.355       Total Ion     PV    28732933   219277 100.00   14.83 100.00   45.74
--------------------------------------------------------------------------
 11.851       Total Ion     VV    33186633   519707 100.00   17.13 100.00   52.83
--------------------------------------------------------------------------
 12.014       Total Ion     VV    62819294   681453 100.00   32.42 100.00 100.00
--------------------------------------------------------------------------
 12.363       Total Ion     VV     4029025    47576 100.00    2.08 100.00    6.41
--------------------------------------------------------------------------
 12.672       Total Ion     VB    19827035   337463 100.00   10.23 100.00   31.56
--------------------------------------------------------------------------
```



```
T: TIC of DATA:BP-M1.D
Z: null.
Y: null.
X: TIC of DATA:SD-1.D
DRAW done
[DE]
```

SD-1

```
                          *** Area Percent   ***

                        Report by Retention Time
=======================================================================
Operator: G                                        15 Jan 88  12:05 pm
Sample Info : JOU'S EXTR.,2X10ML H2O,2X3MIN MW, BP-AQ, 15-JAN-88
Misc Info:
Integration File Name : DATA:SD-2.I
                                Bottle Number : 0

Ret Time   Signal Descr      Type      Area   Height    % Pk   % Sg  % LPk  % LSg
=======================================================================
 10.219       Total Ion      PV    41183176   410028  100.00  23.43 100.00  70.91
-----------------------------------------------------------------------
 11.344       Total Ion      BV    24786026   212643  100.00  14.10 100.00  42.68
-----------------------------------------------------------------------
 11.841       Total Ion      VV    30871148   485334  100.00  17.57 100.00  53.16
-----------------------------------------------------------------------
 12.006       Total Ion      VV    58074769   617933  100.00  33.05 100.00 100.00
-----------------------------------------------------------------------
 12.351       Total Ion      VV     3533173    46121  100.00   2.01 100.00   6.08
-----------------------------------------------------------------------
 12.664       Total Ion      VB    17287031   287991  100.00   9.84 100.00  29.77
-----------------------------------------------------------------------
```

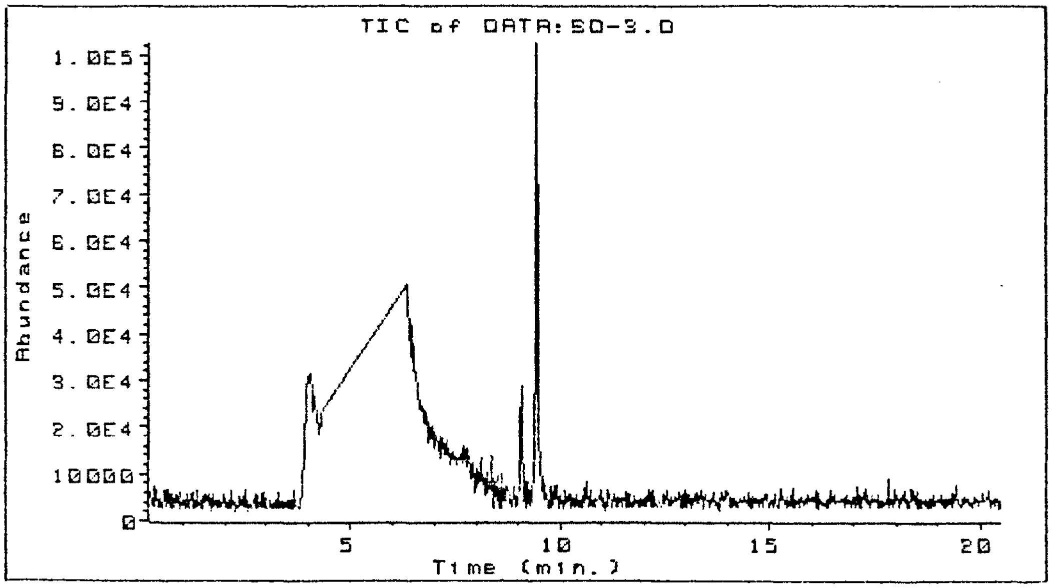


```
T: TIC of DATA:SD-3.D
Z: null.
Y: null.
X: TIC of DATA:SD-2.D
DRAW done
[DE]
```

SD-2

```
                              *** Area Percent  ***

                             Report by Retention Time
================================================================================
Operator:                                                    15 Jan 88  11:38 am
Sample Info : JOU'S EXTRACTION, 3X10ML H2O  3X3MIN MW, BP-AQ
Misc Info:  JAN 15,88
Integration File Name : DATA:SD-3.I
                              Bottle Number : 0
```

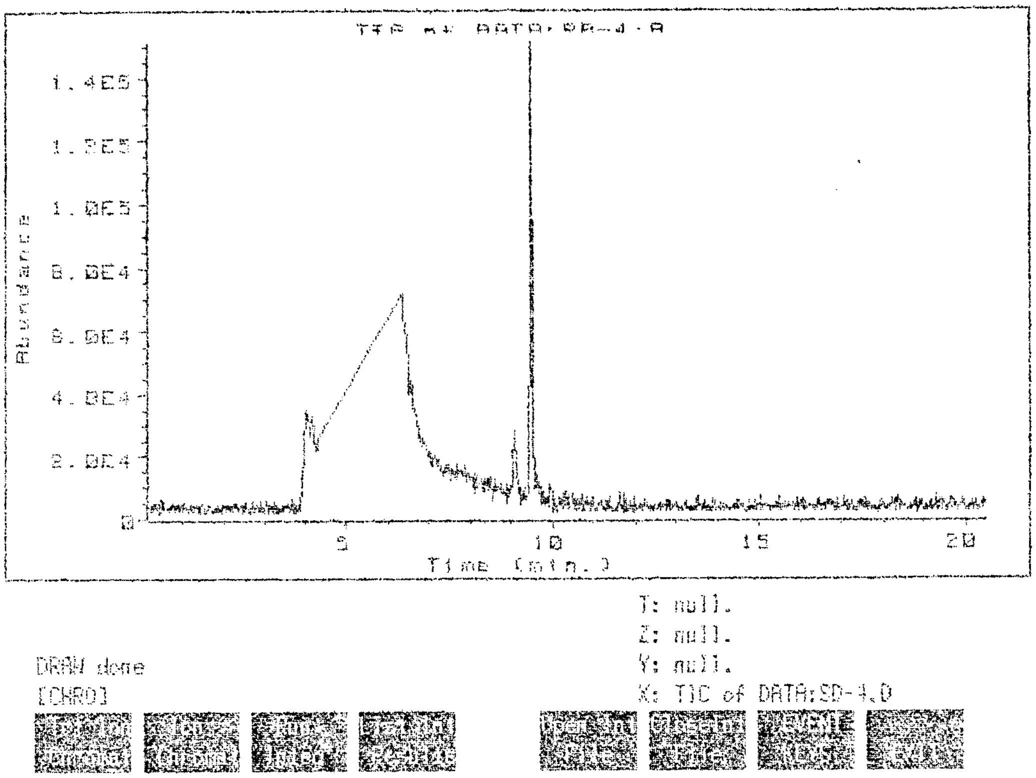
no peaks detected



SD-3

```
                                              T: TIC of DATA:SD-4.D
                                              Z: null.
DRAW done                                     Y: null.
[DE]                                          X: TIC of DATA:SD-3.D
```

SD-4



T: null.
Z: null.
Y: null.
X: TIC of DATA:SD-4.D

DRAW done
[CHRO]

TIC of DATA:SD-4.D
JOU'S EXTR.,4X10ML, 4X3MIN MW, BP-AQ,JAN-15-88

No peaks detected

E-2

Studies with hydrocarbon loaded GAC in a fluidized bed

Experiments described in chapter E-3

GC graphs (for Blanks - HP-1, HP-2 - see Appendix D-3):

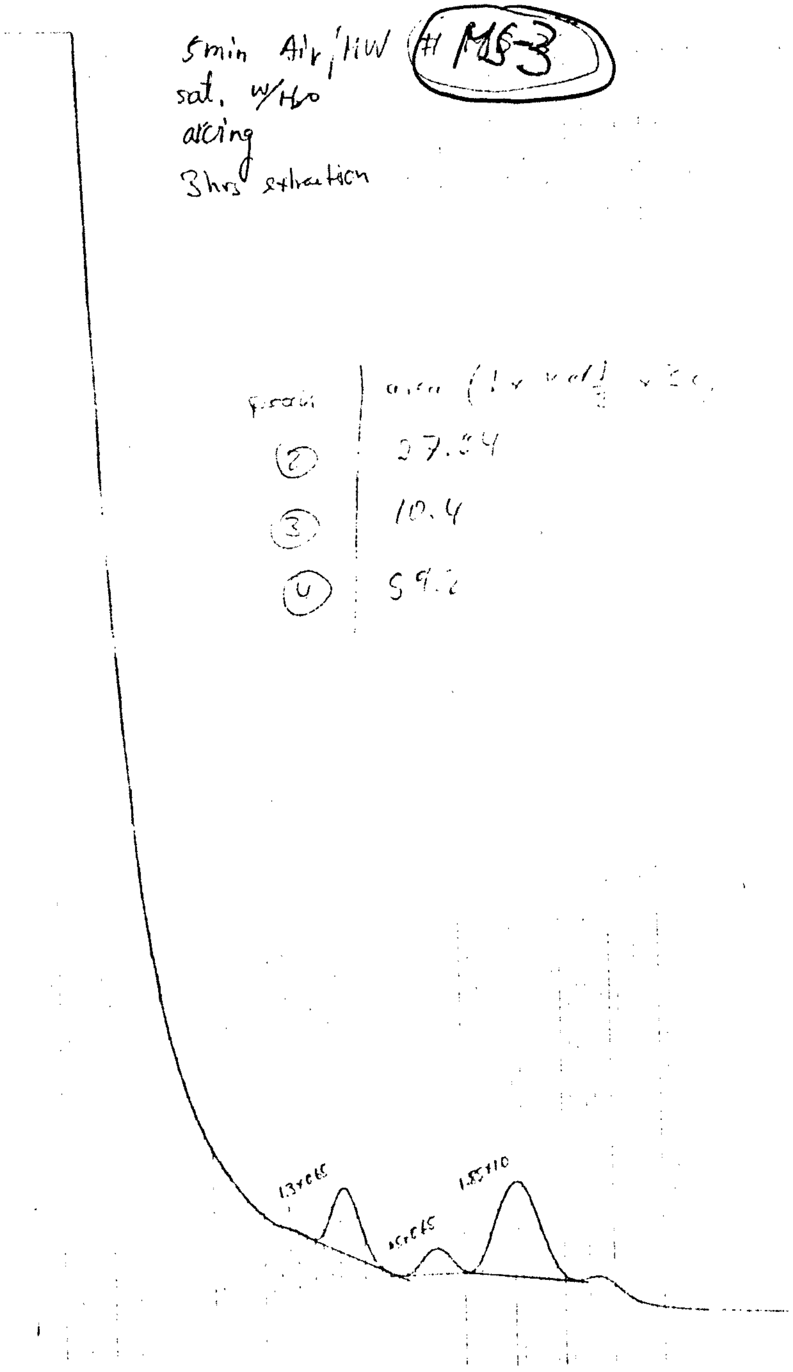
MS-3   MS-4

GC-MS graphs and areas (for parameters see Appendix D-3):

BP-M1 (Blank)   BP-MS4

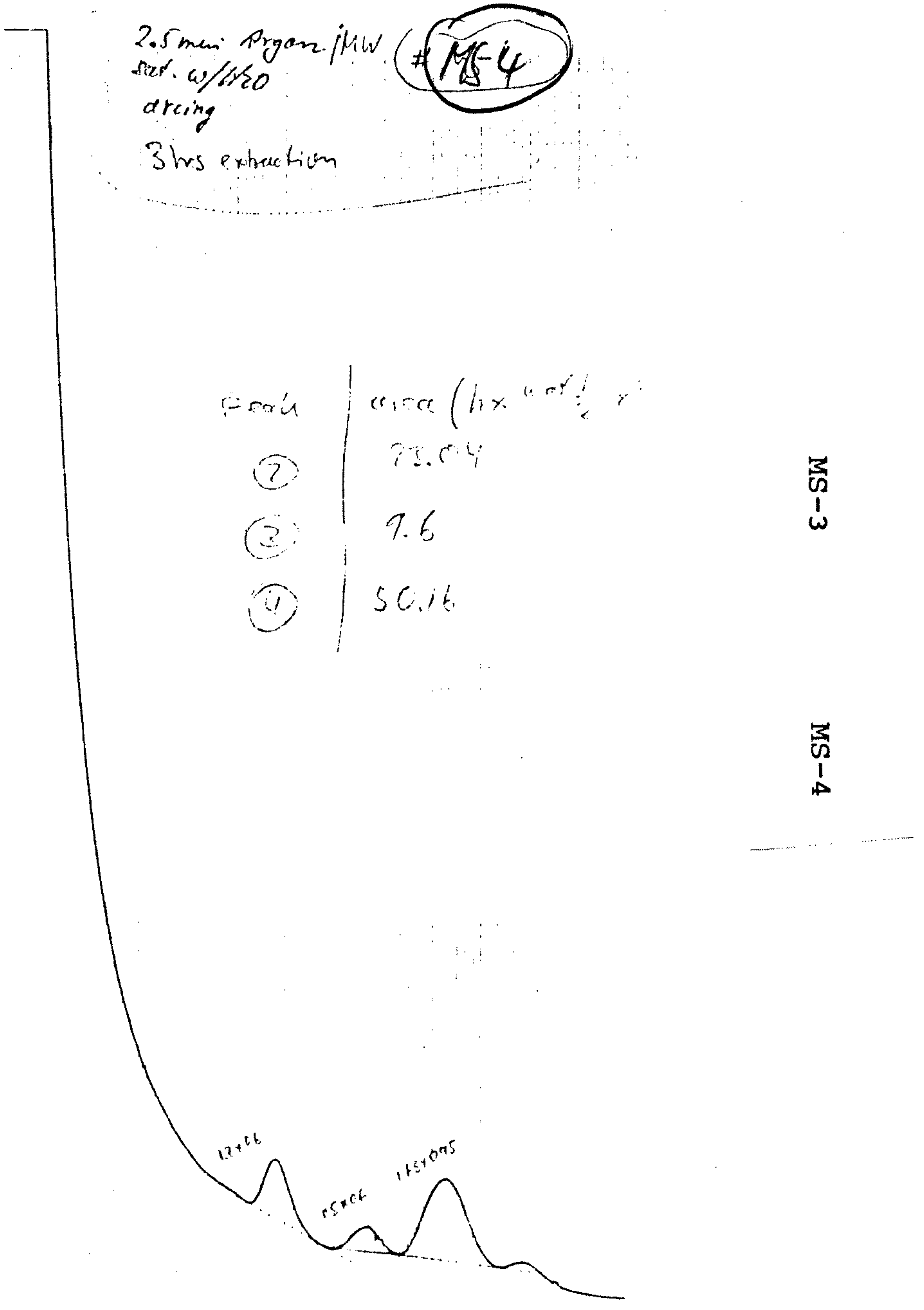
MS-3

MS-4



5min Air, MW #MS-3
sat. w/H2O
arcing
3hrs extraction

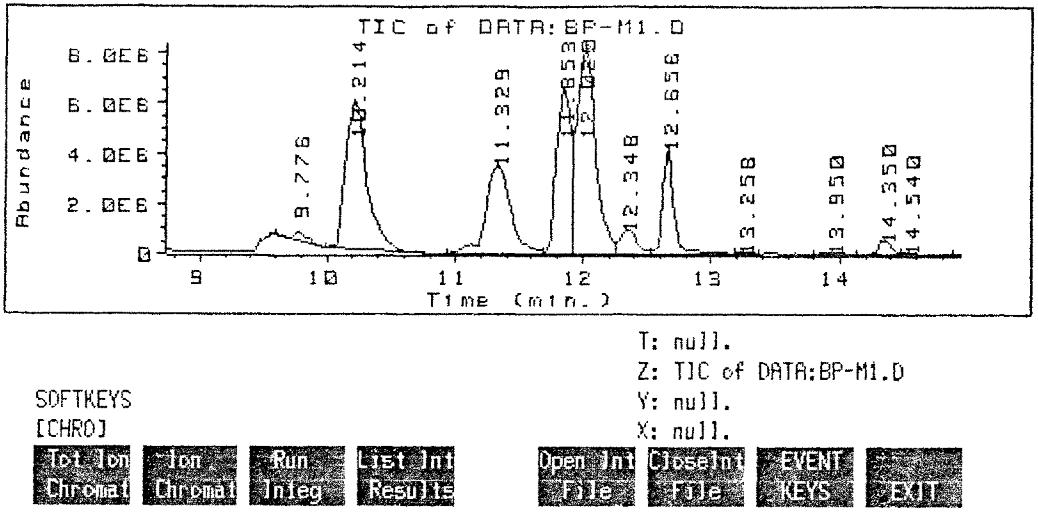
peak	area (h x w½ x 32
②	27.04
③	10.4
④	59.2



2.5min Argon MW #MS-4
sat. w/H2O
arcing
3hrs extraction

peak	area (h x w½ x
②	23.04
③	9.6
④	50.16

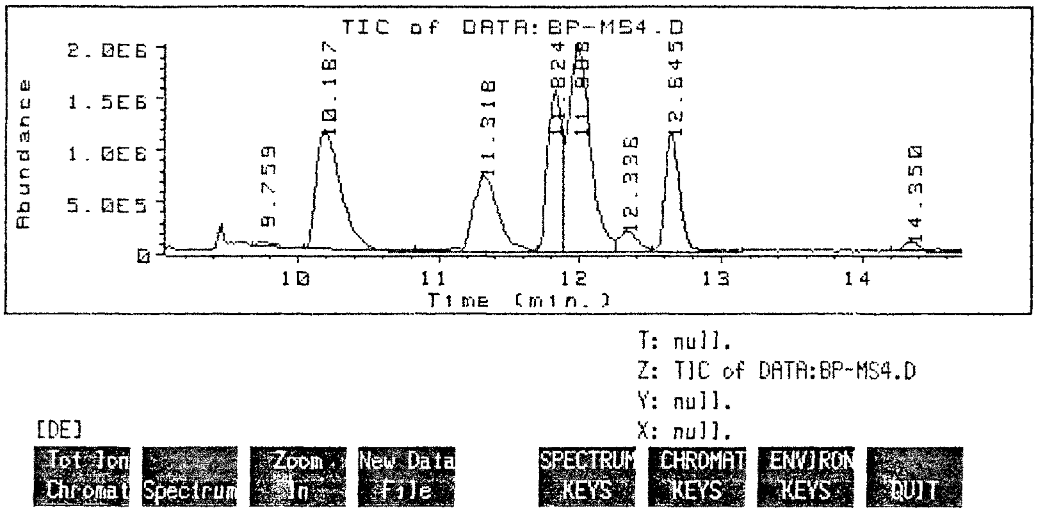
BP-M1 (Blank)



```
                                    T: null.
                                    Z: TIC of DATA:BP-M1.D
SOFTKEYS                            Y: null.
[CHRO]                              X: null.
```

```
TIC of DATA:BP-M1.D
GEORGE'S SOX-EXTRACTION, BP:SITE#9757, NO TREATMENT

Peak#  Ret Time  Type  Width        Area    Start Time    End Time
  1      9.776   BV    0.105    20283457         9.602       9.984
  2     10.214   PV    0.187   687241718         9.984      10.926
  3     11.329   PV    0.212   473772226        10.926      11.693
  4     11.853   VV    0.134   529932535        11.693      11.925
  5     12.020   VV    0.148   813670269        11.925      12.254
  6     12.348   VV    0.136    84282969        12.254      12.515
  7     12.656   VV    0.098   260467732        12.515      13.179
  8     13.258   VV    0.101     2719789        13.179      13.372
  9     13.950   PV    0.179     3629333        13.788      14.132
 10     14.350   VV    0.109    35373561        14.132      14.476
 11     14.540   VV    0.124     4541488        14.476      14.875
```

Σ1,343,602,8



```
T: null.
Z: TIC of DATA:BP-MS4.D
Y: null.
X: null.
```

```
TIC of DATA:BP-MS4.D
SOXHLET-EXTRACTION, 2.5MIN ARGON ARCING W/GAC 10g,

Peak#  Ret Time   Type   Width        Area      Start Time    End Time
   1      9.759   BV     0.127     2862851          9.669      10.037
   2     10.187   PV     0.189   137024905         10.037      10.831
   3     11.318   PV     0.204    91523579         10.831      11.693
   4     11.824   VV     0.107   105064538         11.693      11.889
   5     11.988   VV     0.165   211750720         11.889      12.257
   6     12.336   VV     0.136    17215162         12.257      12.507
   7     12.645   VV     0.110    79354709         12.507      13.148
   8     14.350   BV     0.144     8775413         14.200      14.775
```

} 316.82 ×10⁶
316815258

E-4

Studies with a fluidized GAC bed and TCE vapors

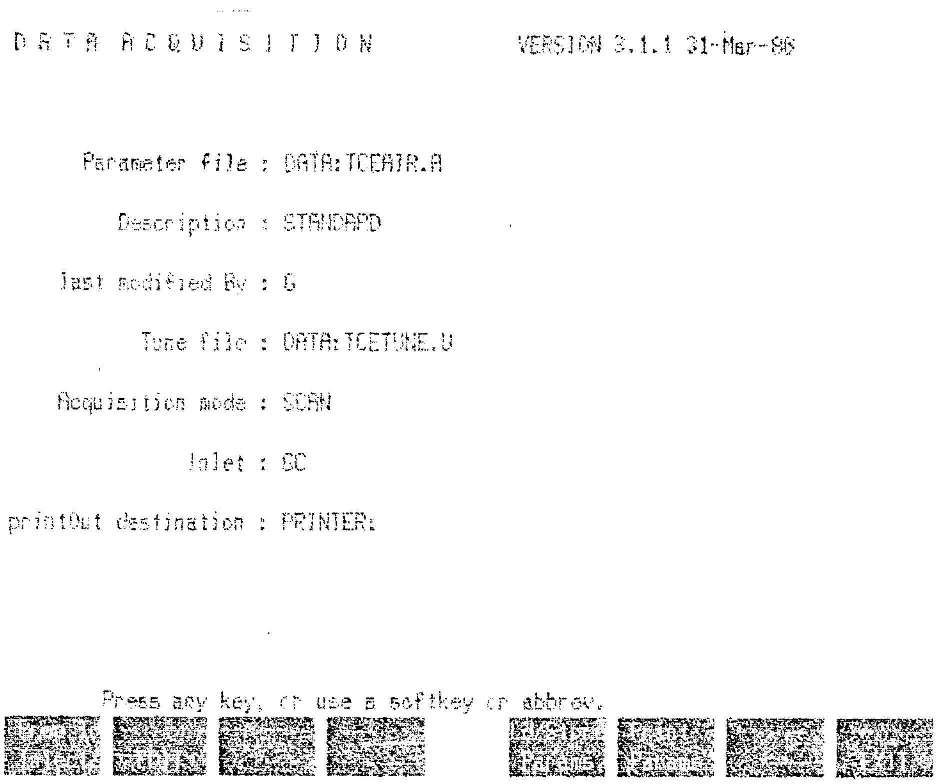
GC-MS parameters for experiments described in chapter E-4

Data aquisition

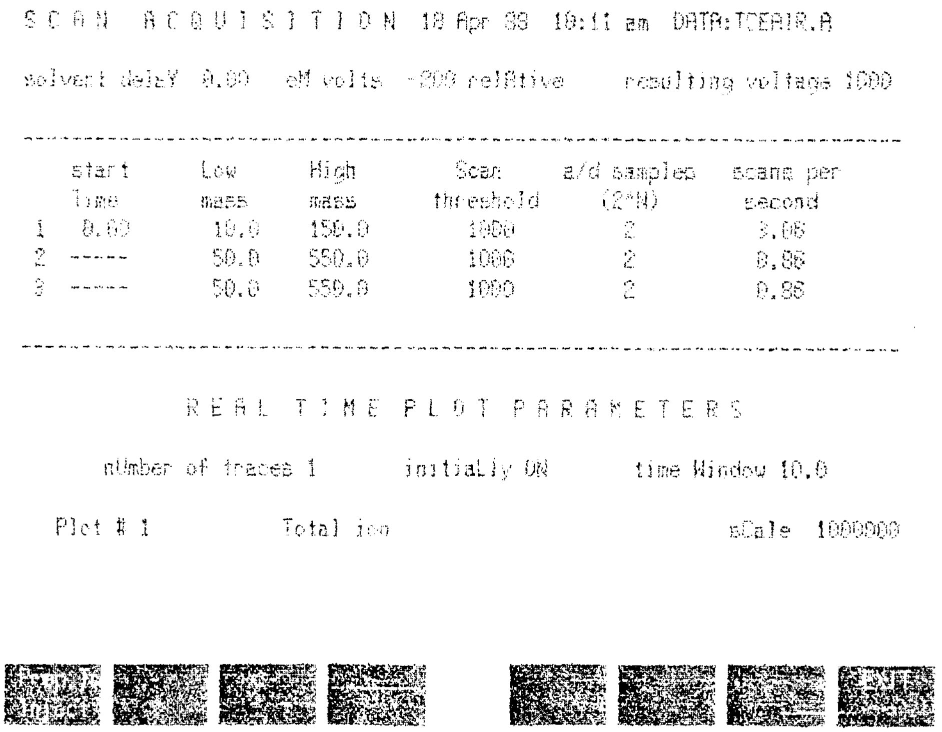
Integrator events for TCE, Argon, Nitrogen

TIC and area calculation for:

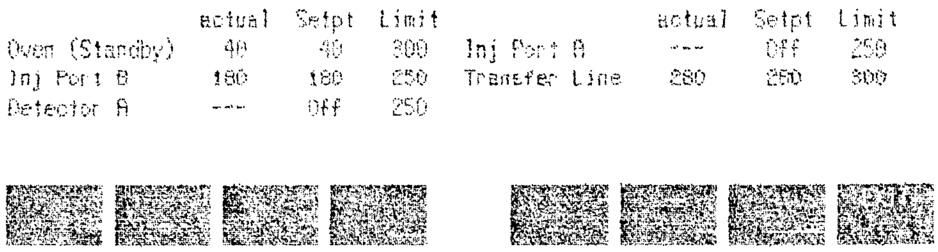
#40 #41 #42 #44 #45 #46 #48 #54



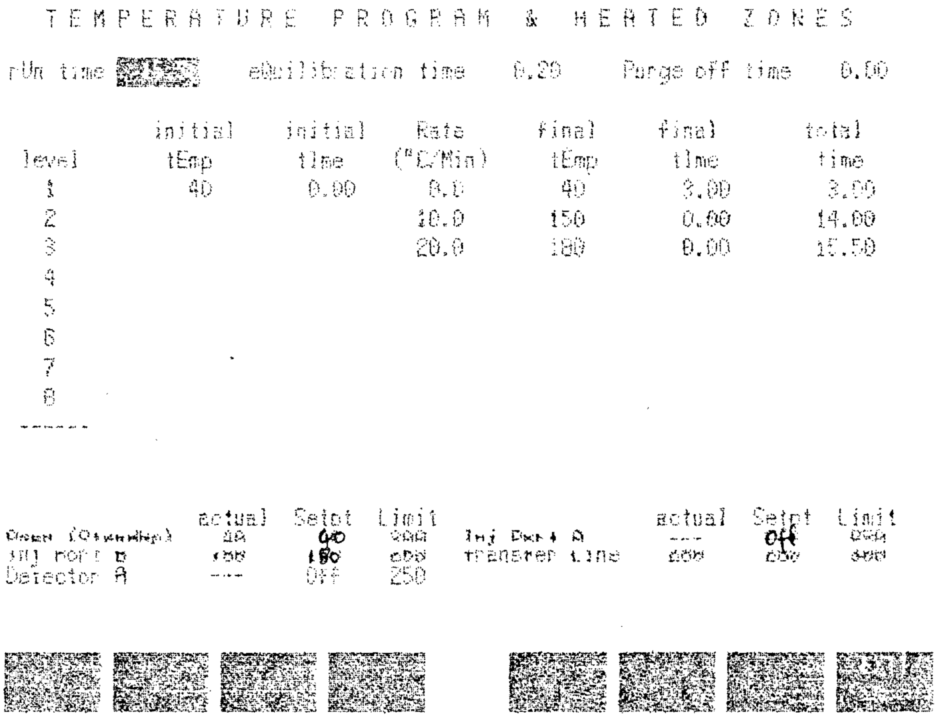
```
D A T A   A C Q U I S I T I O N          VERSION 3.1.1 31-Mar-86


      Parameter file : DATA:TCEAIR.A

         Description : STANDARD

    last modified By : G

           Tune file : DATA:TCETUNE.U

    Acquisition mode : SCAN

               Inlet : GC

printOut destination : PRINTER:



       Press any key, or use a softkey or abbrev.
```



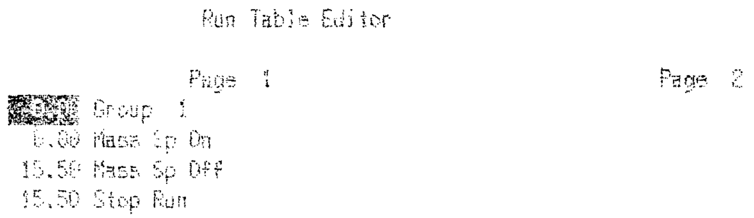
```
S C A N   A C Q U I S I T I O N  18 Apr 89  10:11 am  DATA:TCEAIR.A

solvent delaY  0.00   eM volts  -200 relAtive     resulting voltage 1000

-------------------------------------------------------------------------
    start        Low      High        Scan      a/d samples   scans per
    Time         mass     mass      threshold      (2^N)        second
 1   0.60        10.0     150.0       1000           2           3.06
 2  -----        50.0     550.0       1000           2           0.86
 3  -----        50.0     550.0       1000           2           0.86

-------------------------------------------------------------------------

             R E A L   T I M E   P L O T   P A R A M E T E R S

      nUmber of traces 1       initiaLly ON       time Window 10.0

   Plot # 1            Total ion                         sCale   1000000
```



```
                  actual  Setpt  Limit                     actual  Setpt  Limit
Oven (Standby)      40      40    300   Inj Port A          ---     Off    250
Inj Port B         180     180    250   Transfer Line       280     250    300
Detector A         ---     Off    250
```



```
  T E M P E R A T U R E   P R O G R A M   &   H E A T E D   Z O N E S

rUn time [illegible]    eQuilibration time    0.20     Purge off time    0.00

            initial    initial    Rate       final     final      total
 level       tEmp       tIme     (°C/Min)    tEmp      tIme       time
   1          40        0.00       0.0        40        3.00       3.00
   2                              10.0       150        0.00      14.00
   3                              20.0       180        0.00      15.50
   4
   5
   6
   7
   8
 ------

                  actual  Setpt  Limit                     actual  Setpt  Limit
Oven (Standby)      40      40    300   Inj Port A          ---     Off    250
Inj Port B         180     180    250   Transfer Line       280     250    300
Detector A         ---     Off    250
```



```
                Run Table Editor

              Page  1                                   Page  2
[illegible] Group  1
   0.00 Mass Sp On
  15.50 Mass Sp Off
  15.50 Stop Run
```

```
          *** Integrator Events ***

Initial    Peak Width          0.020
Initial    Threshold          13
Initial    Area Reject         1
             Shoulders  OFF

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

Integrator events: TCE

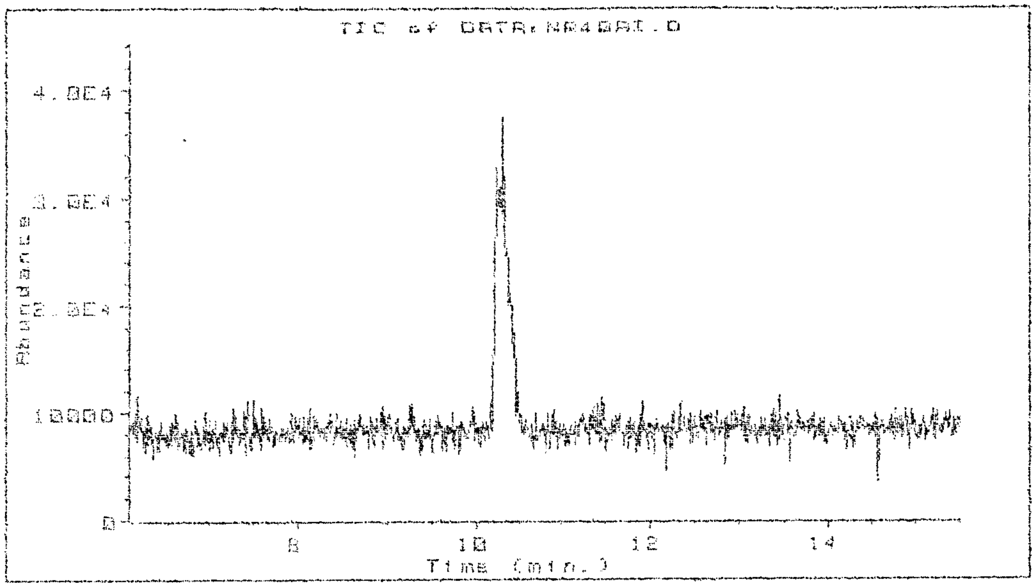
```
          *** Integrator Events ***

Initial    Peak Width          0.020
Initial    Threshold          13
Initial    Area Reject         1
             Shoulders  OFF

   0.000   Integ OFF
   4.000   Integ ON
   4.000   Area Sum ON
   6.000   Integ OFF
   6.600   Area Sum OFF
```

Integrator events: Argon

```
          *** Integrator Events ***

Initial    Peak Width          0.020
Initial    Threshold          13
Initial    Area Reject         1
             Shoulders  OFF

   0.000   Integ OFF
   3.500   Integ ON
   3.500   Area Sum ON
   6.000   Integ OFF
   6.600   Area Sum OFF
```

Integrator events: Nitrogen

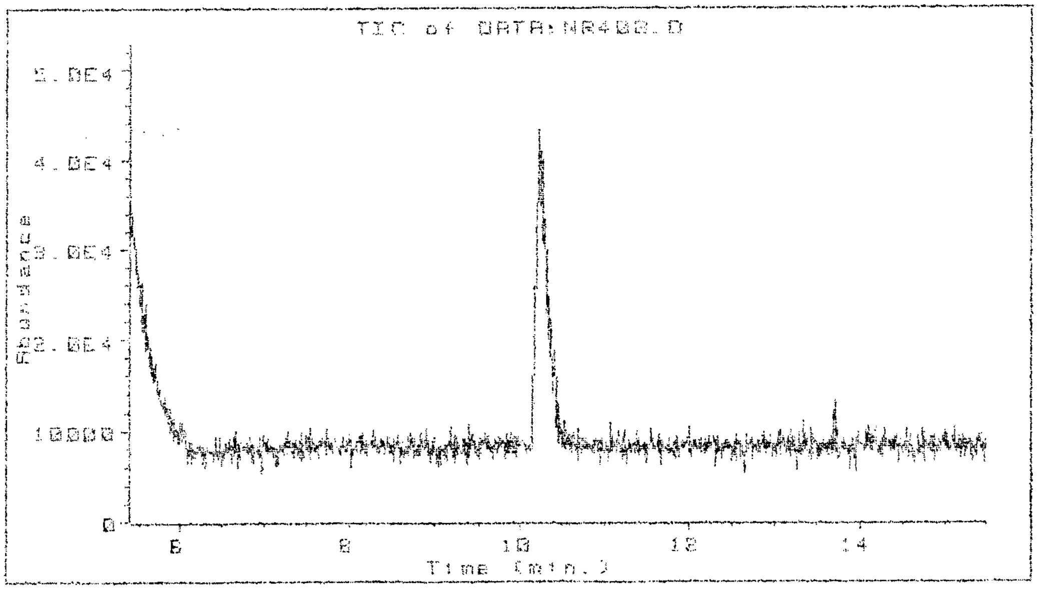
40



40A
before reaction

T: null.
Z: null.
Y: null.
X: TIC of DATA:NR40A1.D

[DE]



40B =
after reaction

T: TIC of DATA:NR40A1.D
Z: null.
Y: null.
X: TIC of DATA:NR40B.D

[DE]

40

```
                              *** Area Percent ***

                            Report by Retention Time
==================================================================================
Operator: 6                                                    8 Feb 88  12:58 pm
Sample Info : 10.0UL AIRSAMPLE, ARG BUBB THRU TCE SAT. H2O,
Misc Info:  TCEAIR.A,8-FEB-88 BEFORE MW
Integration File Name : DATA:NR40AIAR.I
                                   Bottle Number : 0
```

Argon before reactor

```
Ret Time   Signal Descr      Type      Area  Height   % Pk   % Sg  % LPk  % LSg
==================================================================================
  4.198   38.00-  41.00 amu 4.4370E+008 1.45E+006 100.00 100.00 100.00 100.00
----------------------------------------------------------------------------------
                              *** Area Percent ***

                            Report by Retention Time
==================================================================================
Operator: 6                                                    8 Feb 88  12:38 pm
Sample Info : 10.0UL AIRSAMPLE, ARG BUBB THRU TCE SAT. H2O,
Misc Info:  TCEAIR.A,8-FEB-88
Integration File Name : DATA:NR40B-AR.I
                                   Bottle Number : 0
```

Argon after Reactor

```
Ret Time   Signal Descr      Type      Area  Height   % Pk   % Sg  % LPk  % LSg
==================================================================================
  4.143   38.00-  41.00 amu 5.7812E+008 1.57E+006  48.69 100.00  94.90 100.00
  4.143      Total Ion      6.0919E+008 2.07E+006  51.31 100.00 100.00 100.00
----------------------------------------------------------------------------------
  4.532  130.00- 134.00 amu BB +  1180737    2669 100.00 100.00 100.00 100.00
----------------------------------------------------------------------------------
                              *** Area Percent ***

                            Report by Retention Time
==================================================================================
Operator: 6                                                    8 Feb 88  12:58 pm
Sample Info : 10.0UL AIRSAMPLE, ARG BUBB THRU TCE SAT. H2O,
Misc Info:  TCEAIR.A,8-FEB-88 BEFORE MW
Integration File Name : DATA:NR40AI.I
                                   Bottle Number : 0
```

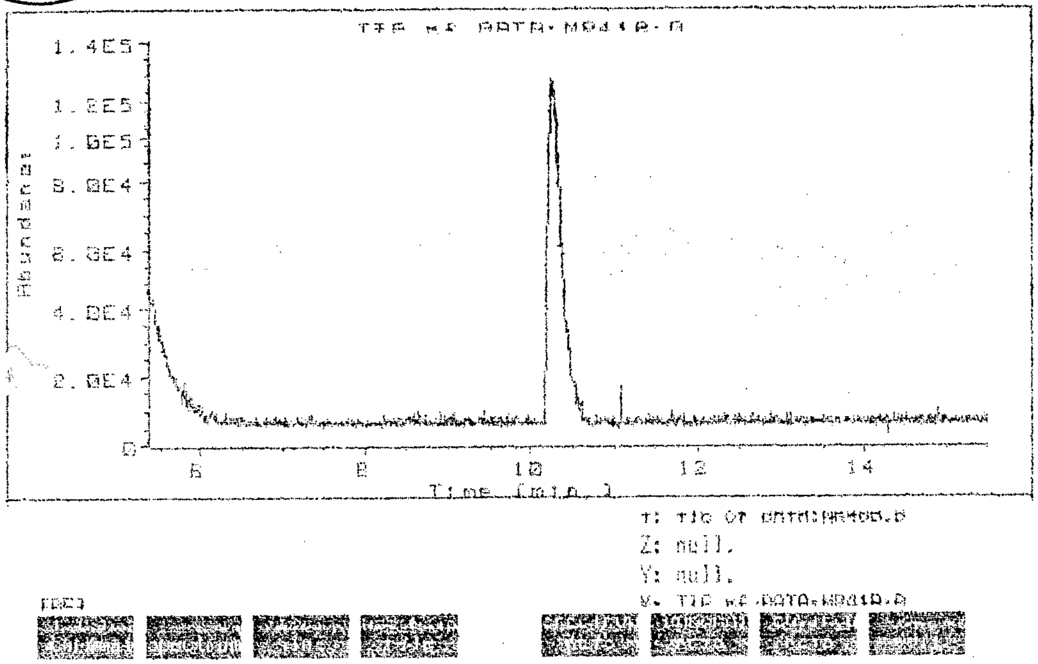
TCE before Reactor

```
Ret Time   Signal Descr      Type      Area  Height   % Pk   % Sg  % LPk  % LSg
==================================================================================
  4.216   26.00-  30.00 amu BB + 43244125  157673 100.00 100.00 100.00 100.00
----------------------------------------------------------------------------------
                              *** Area Percent ***

                            Report by Retention Time
==================================================================================
Operator: 6                                                    8 Feb 88  12:38 pm
Sample Info : 10.0UL AIRSAMPLE, ARG BUBB THRU TCE SAT. H2O,
Misc Info:  TCEAIR.A,8-FEB-88
Integration File Name : DATA:NR40B.I
                                   Bottle Number : 0
```

TCE after reactor

```
Ret Time   Signal Descr      Type      Area  Height   % Pk   % Sg  % LPk  % LSg
==================================================================================
  4.134   26.00-  30.00 amu BB +   960943    9808 100.00 100.00 100.00 100.00
----------------------------------------------------------------------------------
```

41



41B =
after reactor

41A = TIC
before reactor
accidentally
deleted.

(41)

```
                    *** Area Percent   ***

                 Report by Retention Time
================================================================================
Operator: 6                                                8 Feb 88    4:23 pm
Sample Info : ARG BUBB THRU TCE SAT H20,10.0UL AIRSAMPLE BEFORE
Misc Info:  MW, TCEAIR.A,FEB-8-88
Integration File Name : DATA:NR41A-AR.I
                               Bottle Number : 0
```

Argon before reactor

```
Ret Time  Signal Descr      Type      Area  Height    % Pk    % Sg  % LPk  % LSg
================================================================================
  4.232   38.00-  41.00 amu 7.0213E+008 2.03E+006 100.00 100.00 100.00 100.00
--------------------------------------------------------------------------------
```

```
                    *** Area Percent   ***

                 Report by Retention Time
================================================================================
Operator: 6                                                8 Feb 88    4:42 pm
Sample Info : ARG BUBB THRU TCE SAT H20,10.0UL AIRSAMPLE AFTER
Misc Info:  MW, TCEAIR.A,FEB-8-88
Integration File Name : DATA:NR41B-AR.I
                               Bottle Number : 0
```

Argon after reactor

```
Ret Time  Signal Descr      Type      Area  Height    % Pk    % Sg  % LPk  % LSg
================================================================================
  4.154   38.00-  41.00 amu 2.5669E+008 8.30E+005 100.00 100.00 100.00 100.00
--------------------------------------------------------------------------------
```

```
                    *** Area Percent   ***

                 Report by Retention Time
================================================================================
Operator: 6                                                8 Feb 88    4:23 pm
Sample Info : ARG BUBB THRU TCE SAT H20,10.0UL AIRSAMPLE BEFORE
Misc Info:  MW, TCEAIR.A,FEB-8-88
Integration File Name : DATA:NR41A.I
                               Bottle Number : 0
```

TCE before reactor

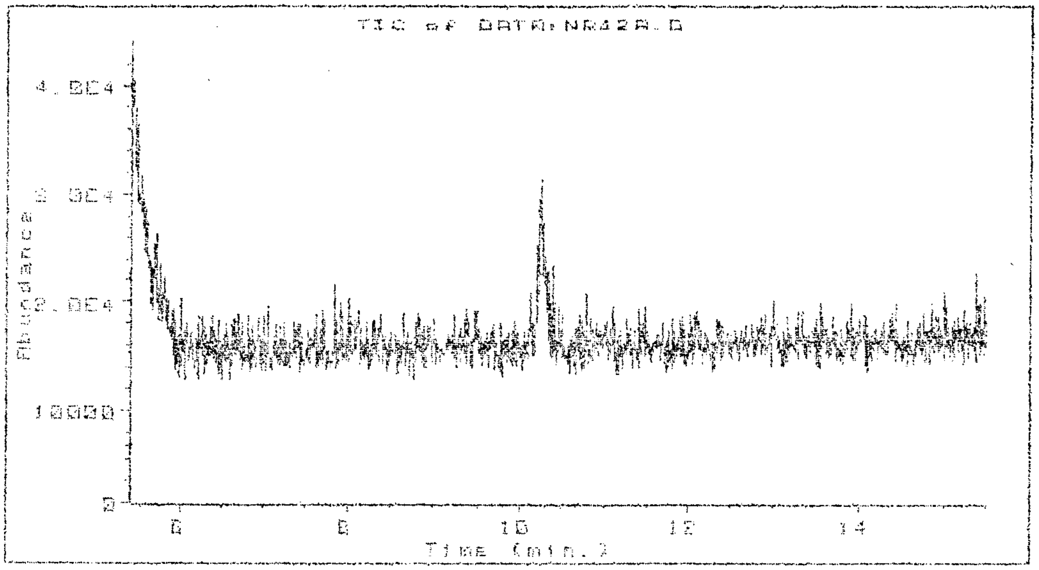
```
Ret Time  Signal Descr      Type      Area  Height    % Pk    % Sg  % LPk  % LSg
================================================================================
 10.276  130.00- 135.00 amu BB +   8885669   97384 100.00 100.00 100.00 100.00
--------------------------------------------------------------------------------
```

```
                    *** Area Percent   ***

                 Report by Retention Time
================================================================================
Operator: 6                                                8 Feb 88    4:42 pm
Sample Info : ARG BUBB THRU TCE SAT H20,10.0UL AIRSAMPLE AFTER
Misc Info:  MW, TCEAIR.A,FEB-8-88
Integration File Name : DATA:NR41B.I
                               Bottle Number : 0
```

TCE after reactor

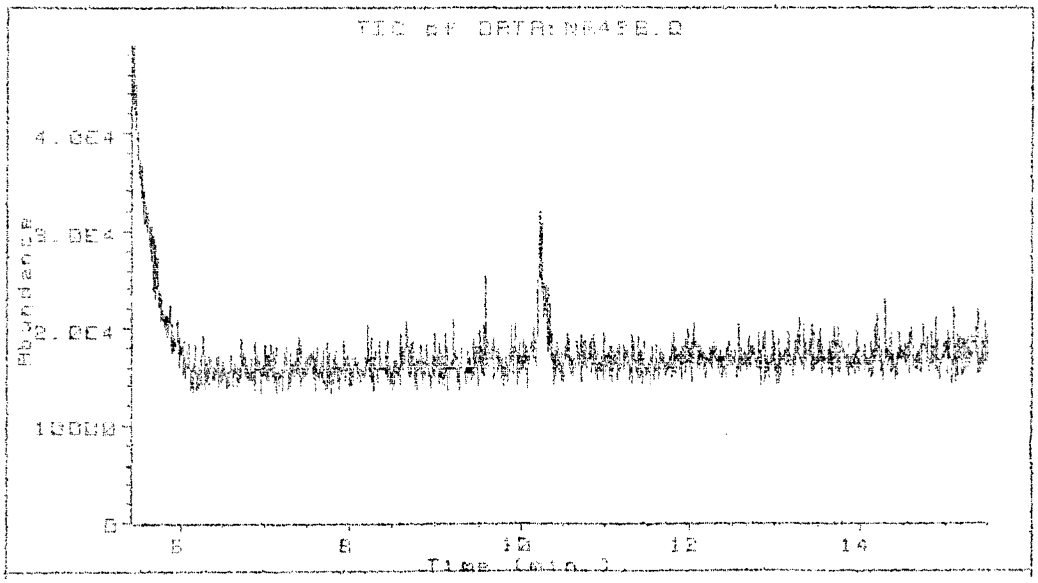
```
Ret Time  Signal Descr      Type      Area  Height    % Pk    % Sg  % LPk  % LSg
================================================================================
 10.244  130.00- 135.00 amu BB +   4334772   46248 100.00 100.00 100.00 100.00
--------------------------------------------------------------------------------
```

42



42
before
reactn

T: TIC of DATA:NR41B.D



42
aft reactn

T: TIC of DATA:NR42B.D

42

```
                        *** Area Percent  ***

                       Report by Retention Time
==========================================================================
Operator: 6                                          9 Feb 88    5:14 pm
Sample Info : ARG BUBB THRU TCE SAT H2O,TCEAIR.A, 10UL AIRSAMPLE
Misc Info:  BEFORE MW FEB 9-88
Integration File Name : DATA:NR42A-AR.I
                              Bottle Number : 0
```

Argon before reactor

```
Ret Time  Signal Descr      Type      Area   Height    % Pk   % Sg  % LPk  % LSg
==========================================================================
  4.155   38.00-  41.00 amu 3.8244E+008 1.26E+006 100.00 100.00 100.00 100.00
--------------------------------------------------------------------------
                        *** Area Percent  ***

                       Report by Retention Time
==========================================================================
Operator: 6                                          9 Feb 88    4:53 pm
Sample Info : ARG BUBB THRU TCE SAT H2O,TCEAIR.A, 10UL AIRSAMPLE
Misc Info:  AFTER  MW FEB 9-88
Integration File Name : DATA:NR42B-AR.I
                              Bottle Number : 0
```

Argon after reactor

```
Ret Time  Signal Descr      Type      Area   Height    % Pk   % Sg  % LPk  % LSg
==========================================================================
  4.153   38.00-  41.00 amu 7.2547E+008 2.81E+006 100.00 100.00 100.00 100.00
--------------------------------------------------------------------------
                        *** Area Percent  ***

                       Report by Retention Time
==========================================================================
Operator: 6                                          9 Feb 88    5:14 pm
Sample Info : ARG BUBB THRU TCE SAT H2O,TCEAIR.A, 10UL AIRSAMPLE
Misc Info:  BEFORE MW FEB 9-88
Integration File Name : DATA:NR42A.I
                              Bottle Number : 0
```

TCE before reactor

```
Ret Time  Signal Descr      Type      Area   Height    % Pk   % Sg  % LPk  % LSg
==========================================================================
  4.151   26.00-  30.00 amu BB + 52693676  352025 100.00 100.00 100.00 100.00
--------------------------------------------------------------------------
                        *** Area Percent  ***
                       Report by Retention Time
==========================================================================
Operator: 6                                          9 Feb 88    4:53 pm
Sample Info : ARG BUBB THRU TCE SAT H2O,TCEAIR.A, 10UL AIRSAMPLE
Misc Info:  AFTER  MW FEB 9-88
Integration File Name : DATA:NR42B.I
                              Bottle Number : 0
```

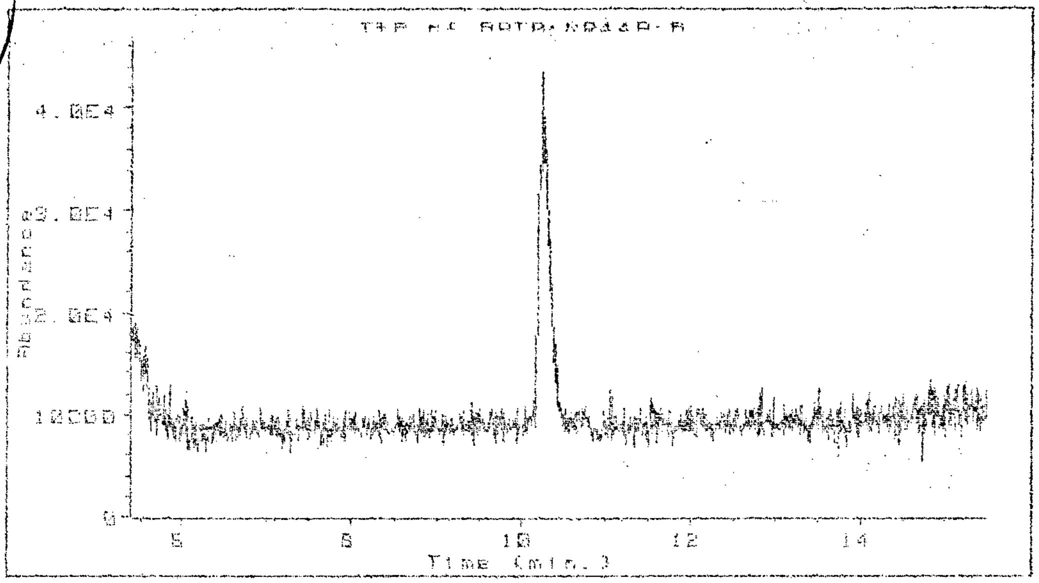
TCE after reactor

```
Ret Time  Signal Descr      Type      Area   Height    % Pk   % Sg  % LPk  % LSg
==========================================================================
  4.144   26.00-  30.00 amu BB +   7997475   81032 100.00 100.00 100.00 100.00
--------------------------------------------------------------------------
```

74

Z: null.
Y: null.
X: TIC of DATA:NR42B.D

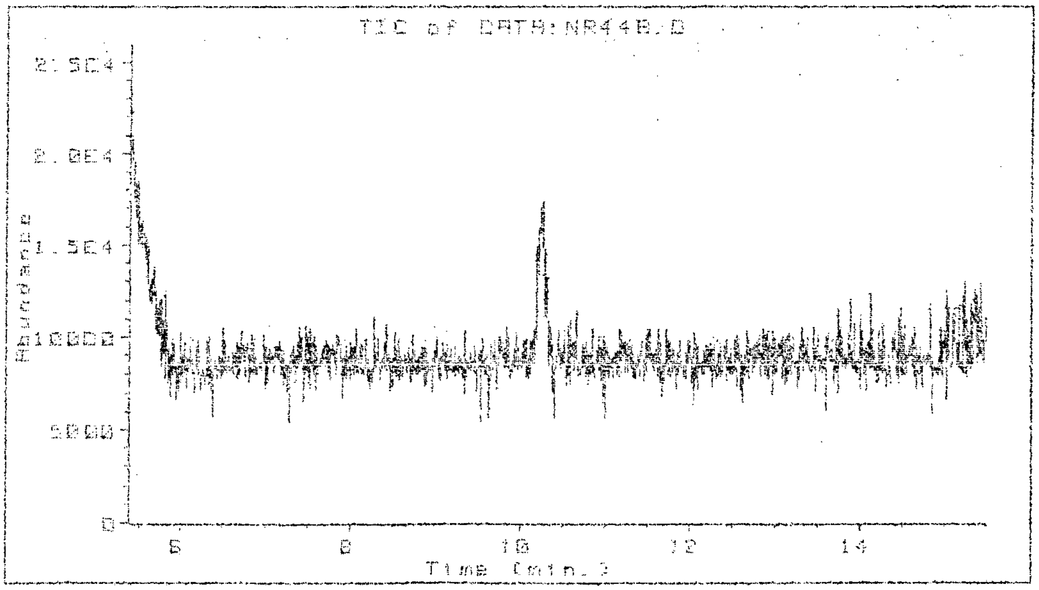
[DE]



44
before reactn

T: TIC of DATA:NR42B.D
Z: null.
Y: null.
X: TIC of DATA:NR44A.D

[DE]



44
after reactn

T: TIC of DATA:NR44A.D
Z: null.
Y: null.
X: TIC of DATA:NR44A.D

[DE]

44

```
                              *** Area Percent   ***

                             Report by Retention Time
==============================================================================
Operator: 6                                                 10 Feb 88   2:34 pm
Sample Info : ARG BUBB THRU TCE SAT H2O,AIRSAMPLE BEFORE MW 10UL
Misc Info:  TCEAIR.A            FEB-10-88
Integration File Name : DATA:NR44A-AR.I
                                 Bottle Number : 0
```

Argon before reach

```
Ret Time   Signal Descr      Type      Area  Height    % Pk    % Sg  % LPk  % LSg
==============================================================================
  4.148   38.00-  41.00 amu 1.4049E+008 5.19E+005 100.00 100.00 100.00 100.00
------------------------------------------------------------------------------
                              *** Area Percent   ***

                             Report by Retention Time
==============================================================================
Operator: 6                                                 10 Feb 88   2:15 pm
Sample Info : ARG BUBB THRU TCE SAT H2O,AIRSAMPLE AFTEP MW 10.0UL
Misc Info:  TCEAIR.A            FEB-10-88
Integration File Name : DATA:NR44B-AR.I
                                 Bottle Number : 0
```

Argon after reach

```
Ret Time   Signal Descr      Type      Area  Height    % Pk    % Sg  % LPk  % LSg
==============================================================================
  4.149   38.00-  41.00 amu 2.9895E+008 1.08E+006 100.00 100.00 100.00 100.00
------------------------------------------------------------------------------
                              *** Area Percent   ***

                             Report by Retention Time
==============================================================================
Operator: 6                                                 10 Feb 88   2:34 pm
Sample Info : ARG BUBB THRU TCE SAT H2O,AIRSAMPLE BEFORE MW 10UL
Misc Info:  TCEAIR.A            FEB-10-88
Integration File Name : DATA:NR44A.I
                                 Bottle Number : 0
```

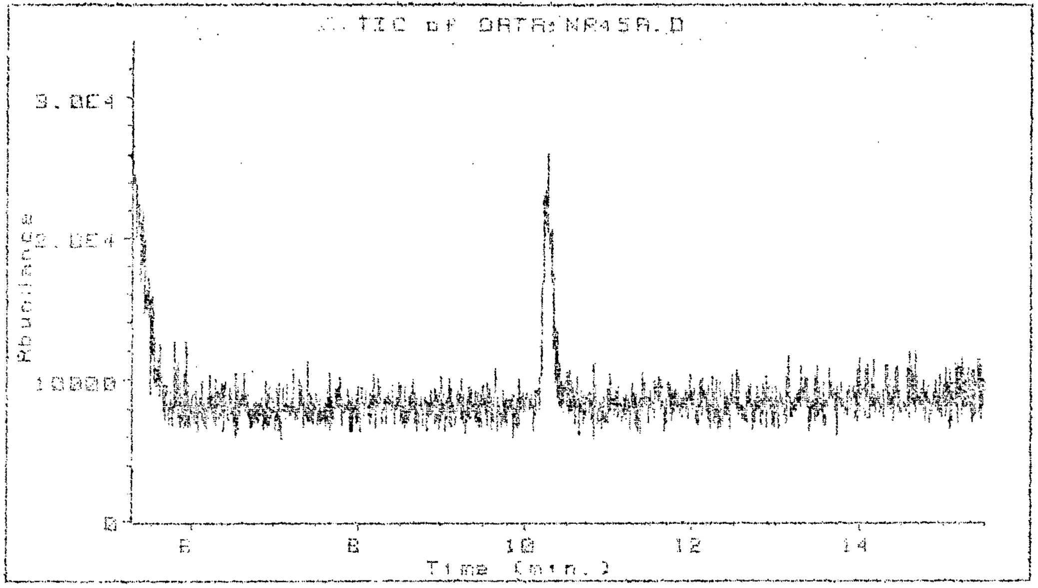
TCE before reactor

```
Ret Time   Signal Descr      Type      Area  Height    % Pk    % Sg  % LPk  % LSg
==============================================================================
  4.148   39.00-  41.00 amu 1.4049E+008 5.19E+005 100.00 100.00 100.00 100.00
------------------------------------------------------------------------------
                              *** Area Percent   ***

                             Report by Retention Time
==============================================================================
Operator: 6                                                 10 Feb 88   2:15 pm
Sample Info : ARG BUBB THRU TCE SAT H2O,AIRSAMPLE AFTER MW 10.0UL
Misc Info:  TCEAIR.A            FEB-10-88
Integration File Name : DATA:NR44B.I
                                 Bottle Number : 0
```

TCE after reactor

```
Ret Time   Signal Descr      Type      Area  Height    % Pk    % Sg  % LPk  % LSg
==============================================================================
  4.148   39.00-  41.00 amu 2.9895E+008 1.08E+006 100.00 100.00 100.00 100.00
------------------------------------------------------------------------------
```

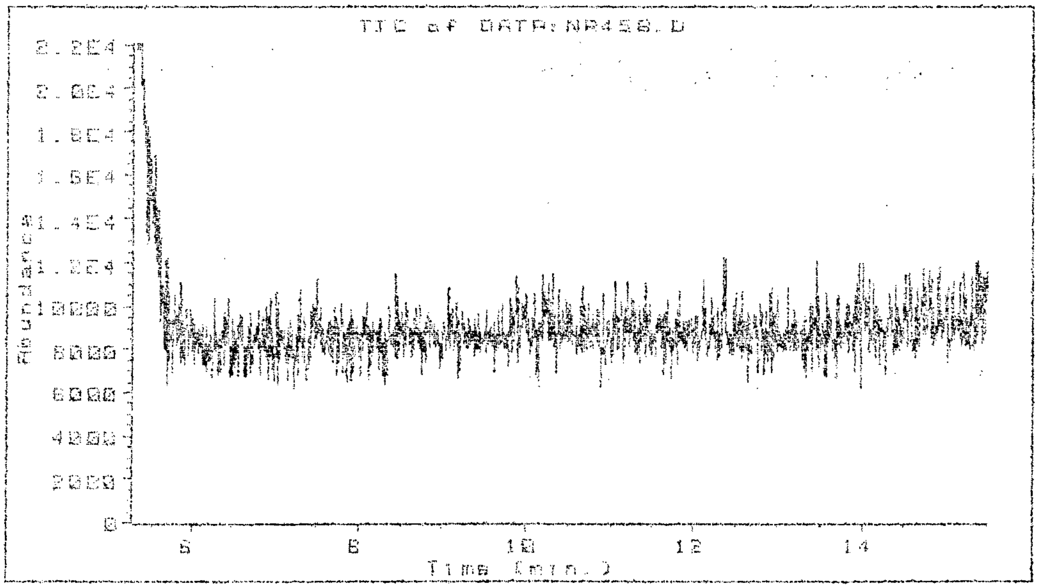
45



45
before Reactor

T: TIC of DATA:NR44B.D
Z: null.
Y: null.
X: TIC of DATA:NR45A.D

[DE]



45 aft
reactor

T: TIC of DATA:NR45A.D
Z: null.
Y: null.
X: TIC of DATA:NR45B.D

[DE]

45

```
                         *** Area Percent  ***

                       Report by Retention Time
======================================================================
Operator: 6                                       10 Feb 88   3:34 pm
Sample Info : ARG BUBB THRU TCE SAT H2O,SAMPLE BEFORE MW 10.UL
Misc Info:  TCEAIR.A     FEB-10-88
Integration File Name : DATA:NR45A-AR.I
                          Bottle Number : 0
```

Argon before react

```
Ret Time   Signal Descr      Type      Area  Height    % Pk   % Sg  % LPk  % LSg
==================================================================================
  4.134   38.00-  41.00 amu 1.5539E+008 6.07E+005 100.00 100.00 100.00 100.00
----------------------------------------------------------------------------------
                         *** Area Percent  ***

                       Report by Retention Time
======================================================================
Operator: 6                                       10 Feb 88   3:14 pm
Sample Info : ARG BUBB THRU TCE SAT H2O,SAMPLE AFTER MW,10.0UL
Misc Info:  TCEAIR.A     FEB-10-88
Integration File Name : DATA:NR45B-AR.I
                          Bottle Number : 0
```

Argon after react

```
Ret Time   Signal Descr      Type      Area  Height    % Pk   % Sg  % LPk  % LSg
==================================================================================
  4.136   38.00-  41.00 amu 2.2243E+008 8.82E+005 100.00 100.00 100.00 100.00
----------------------------------------------------------------------------------
                         *** Area Percent  ***

                       Report by Retention Time
======================================================================
Operator: 6                                       10 Feb 88   3:34 pm
Sample Info : ARG BUBB THRU TCE SAT H2O,SAMPLE BEFORE MW 10.uL
Misc Info:  TCEAIR.A     FEB-10-88
Integration File Name : DATA:NR45A.I
                          Bottle Number : 0
```

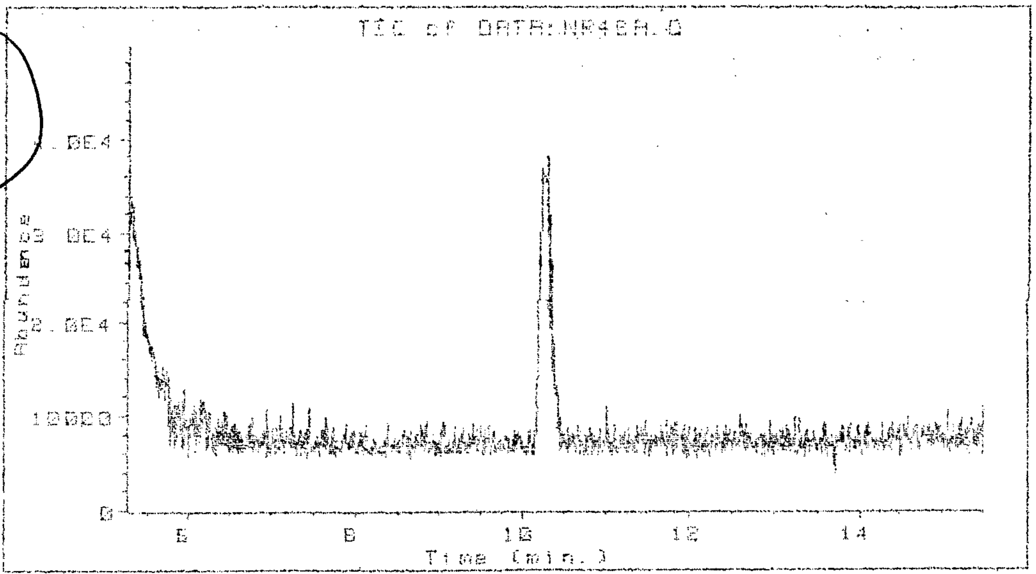
~~Argon~~ TCE before reactor

```
Ret Time   Signal Descr      Type      Area  Height    % Pk   % Sg  % LPk  % LSg
==================================================================================
  4.107   28.00-  29.00 amu 1.8794E+008 7.05E+005 100.00 100.00 100.00 100.00
----------------------------------------------------------------------------------
                         *** Area Percent  ***

                       Report by Retention Time
======================================================================
Operator: 6                                       10 Feb 88   3:14 pm
Sample Info : ARG BUBB THRU TCE SAT H2O,SAMPLE AFTER MW,10.0UL
Misc Info:  TCEAIR.A     FEB-10-88
Integration File Name : DATA:NR45B.I
                          Bottle Number : 0
```

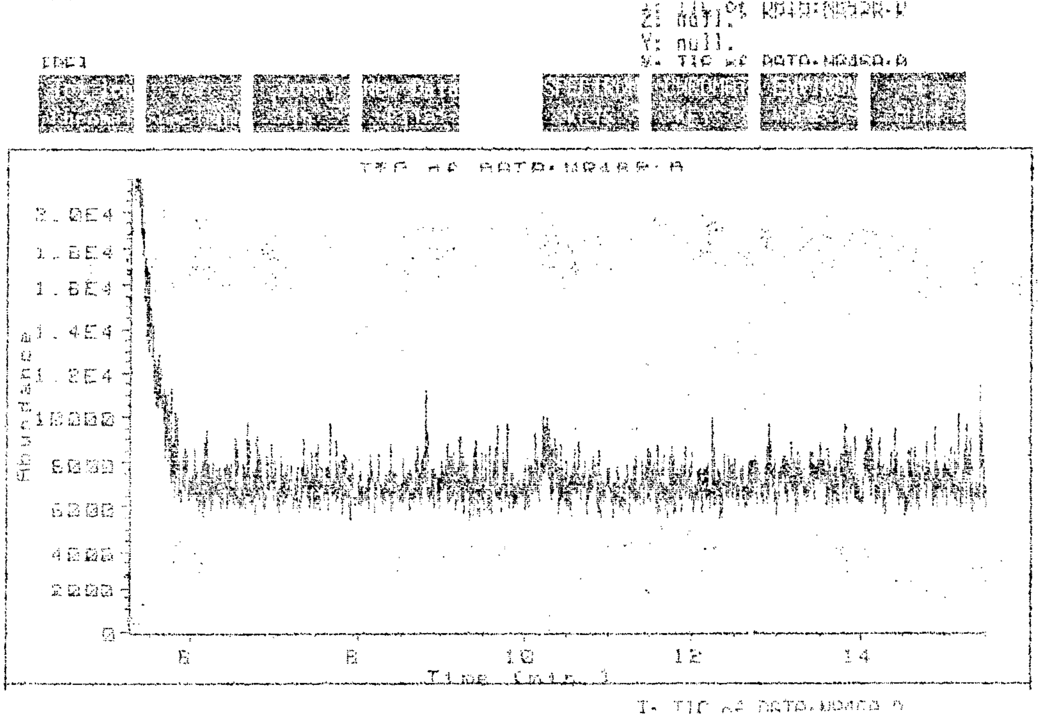
TCE after reactor

```
Ret Time   Signal Descr      Type      Area  Height    % Pk   % Sg  % LPk  % LSg
==================================================================================
  4.127   28.00-  29.00 amu 1.4891E+008 5.96E+005 100.00 100.00 100.00 100.00
----------------------------------------------------------------------------------
```

46



46 = before reactn



= 46 aft Reactn

46

```
                              *** Area Percent  ***

                             Report by Retention Time
==========================================================================
Operator: 6                                          12 Feb 88   5:21 pm
Sample Info : ARG BUBB THRU TCE SAT H2O,AIRSAMPLE BEFORE MW 10.UL
Misc Info:  TCEAIR.A        FEB-10-88
Integration File Name : DATA:NR46A-AR.I
                                Bottle Number : 0
```

Argon before reactor

```
Ret Time   Signal Descr      Type      Area   Height    % Pk   % Sg  % LPk  % LSg
==========================================================================
  4.189   38.00-  41.00 amu 3.5025E+008 1.33E+006 100.00 100.00 100.00 100.00
--------------------------------------------------------------------------
                              *** Area Percent  ***

                             Report by Retention Time
==========================================================================
Operator: 6                                          10 Feb 88   5:00 pm
Sample Info : ARG BUBB THRU TCE SAT H2O,AIRSAMPLE AFTER MW,10.UL
Misc Info:  TCEAIR.A        FEB-10-88
Integration File Name : DATA:NR46B-AR.I
                                Bottle Number : 0
```

Argon after reactor

```
Ret Time   Signal Descr      Type      Area   Height    % Pk   % Sg  % LPk  % LSg
==========================================================================
  4.194   38.00-  41.00 amu 2.7817E+008 1.04E+006 100.00 100.00 100.00 100.00
--------------------------------------------------------------------------
                              *** Area Percent  ***
                             Report by Retention Time
==========================================================================
Operator: 6                                          10 Feb 88   5:21 pm
Sample Info : ARG BUBB THRU TCE SAT H2O,AIRSAMPLE BEFORE MW 10.UL
Misc Info:  TCEAIR.A        FEB-10-88
Integration File Name : DATA:[illegible]
                                Bottle Number : 0
```

TCE before reacter

```
Ret Time   Signal Descr      Type      Area   Height    % Pk   % Sg  % LPk  % LSg
==========================================================================
  4.169   18.00-  20.00 amu PH + 12236031    47703 100.00 100.00 100.00 100.00
--------------------------------------------------------------------------
                              *** Area Percent  ***

                             Report by Retention Time
==========================================================================
Operator: 6                                          10 Feb 88   5:00 pm
Sample Info : ARG BUBB THRU TCE SAT H2O,AIRSAMPLE AFTER MW,10.UL
Misc Info:  TCEAIR.A        FEB-10-88
Integration File Name : DATA:NR46B.I
                                Bottle Number : 0
```

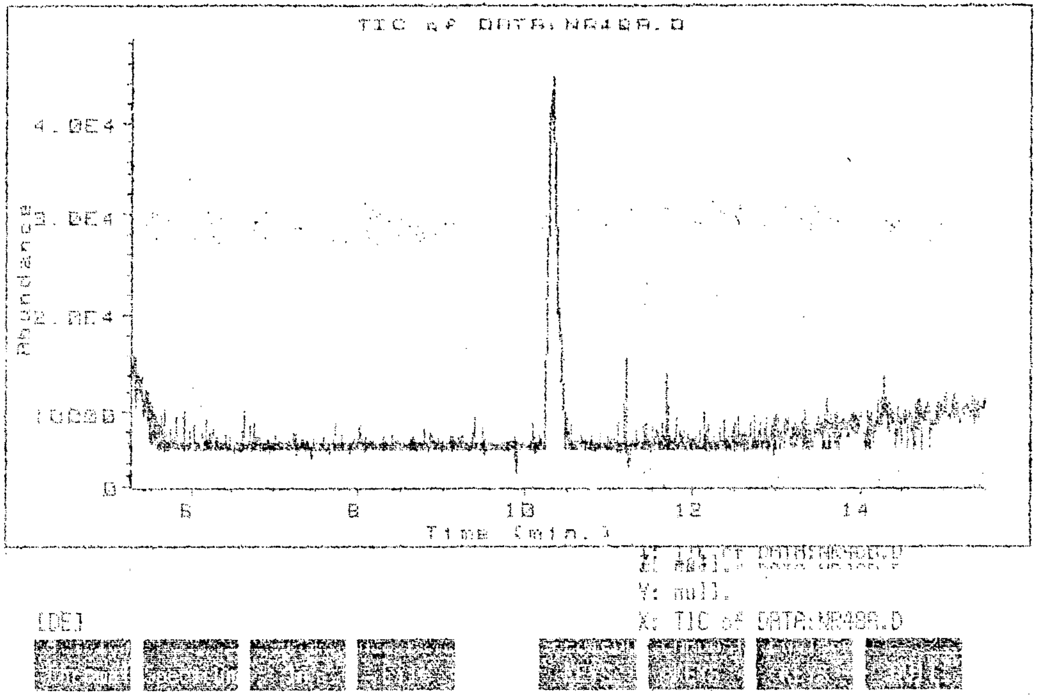
TCE after Reactor

```
Ret Time   Signal Descr      Type      Area   Height    % Pk   % Sg  % LPk  % LSg
==========================================================================
  4.189   18.00-  20.00 amu PH +  9797812    37495 100.00 100.00 100.00 100.00
--------------------------------------------------------------------------
```

48

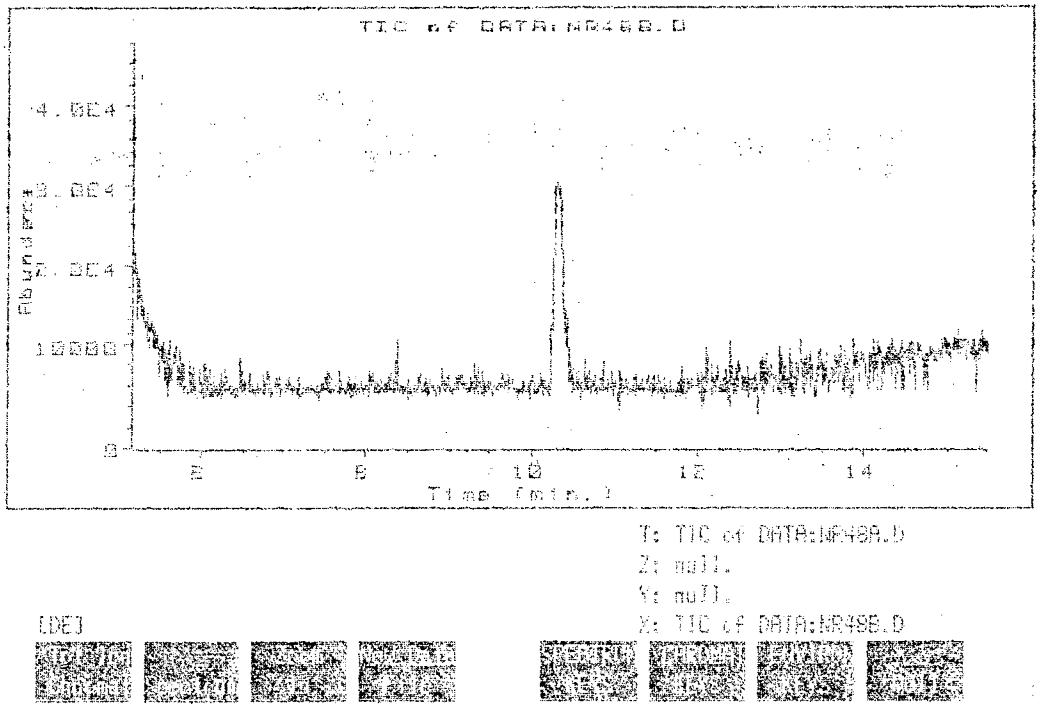
48~~B~~ =

before Reactor



48B =

after Reactor



48

```
                              *** Area Percent  ***

                             Report by Retention Time
================================================================================
Operator: 6                                                12 Feb 88    5:46 pm
Sample Info : ZEROAIR BUBB THRU TCE SAT H2O,TCEAIR.A,SAMPLE BEFOR
Misc Info:  MW 10.0UL, FEB-12-88
Integration File Name : DATA:NR48A-N2.I
                              Bottle Number : 0
```

Nitrogen before reactr

```
Ret Time   Signal Descr      Type      Area   Height    % Pk    % Sg   % LPk  % LSg
================================================================================
  4.153   28.00-  29.00 amu 1.7425E+008 8.12E+005 100.00 100.00 100.00 100.00
--------------------------------------------------------------------------------
                              *** Area Percent  ***

                             Report by Retention Time
================================================================================
Operator: 6                                                12 Feb 88    5:24 pm
Sample Info : ZEROAIR BUBB THRU TCE SAT H2O,TCEAIR.A,SAMPLE AFTER
Misc Info:  MW 10.0UL, FEB-12-88
Integration File Name : DATA:NR48B-N2.I
                              Bottle Number : 0
```

Nitrogen after reactor

```
Ret Time   Signal Descr      Type      Area   Height    % Pk    % Sg   % LPk  % LSg
================================================================================
  4.167   28.00-  29.00 amu 1.5748E+008 7.90E+005 100.00 100.00 100.00 100.00
--------------------------------------------------------------------------------
                              *** Area Percent  ***

                             Report by Retention Time
================================================================================
Operator: 6                                                12 Feb 88    5:48 pm
Sample Info : ZEROAIR BUBB THRU TCE SAT H2O,TCEAIR.A,SAMPLE BEFOR
Misc Info:  MW 10.0UL, FEB-12-88
Integration File Name : DATA:NR48A.I
                              Bottle Number : 0
```

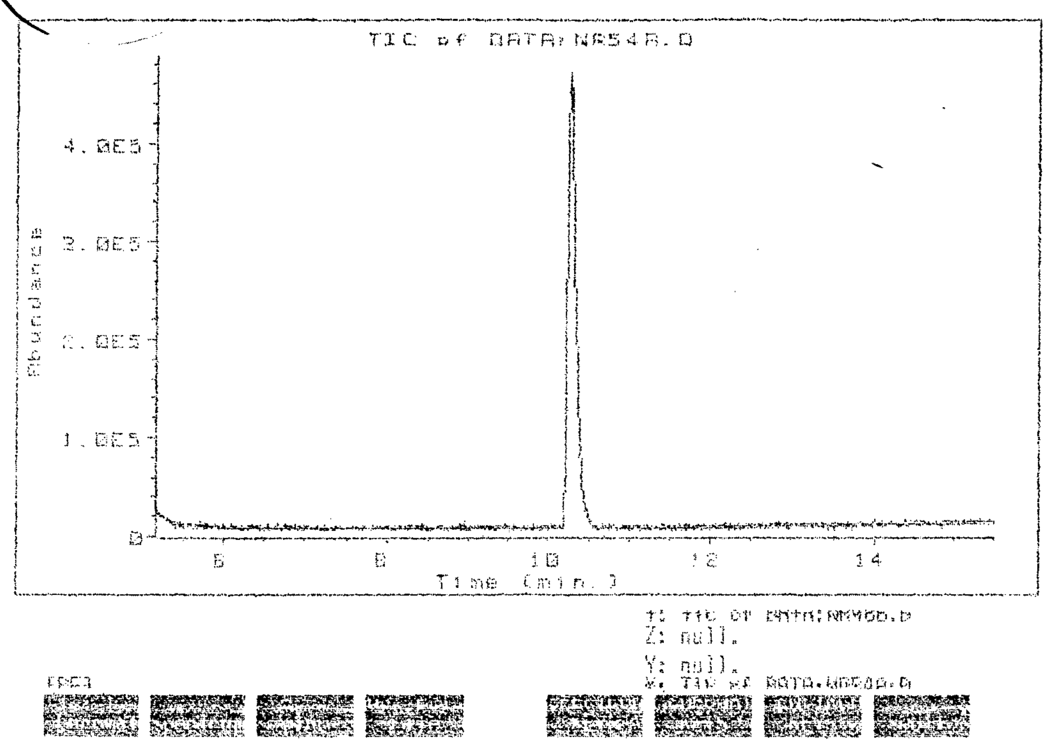
TCE before reactr

```
Ret Time   Signal Descr      Type      Area   Height    % Pk    % Sg   % LPk  % LSg
================================================================================
 10.323  130.00- 135.00 amu BB +  1393255    19594 100.00 100.00 100.00 100.00
--------------------------------------------------------------------------------
                              *** Area Percent  ***

                             Report by Retention Time
================================================================================
Operator: 6                                                12 Feb 88    5:24 pm
Sample Info : ZEROAIR BUBB THRU TCE SAT H2O,TCEAIR.A,SAMPLE AFTER
Misc Info:  MW 10.0UL, FEB-12-88
Integration File Name : DATA:NR48B.I
                              Bottle Number : 0
```

TCE after reactor

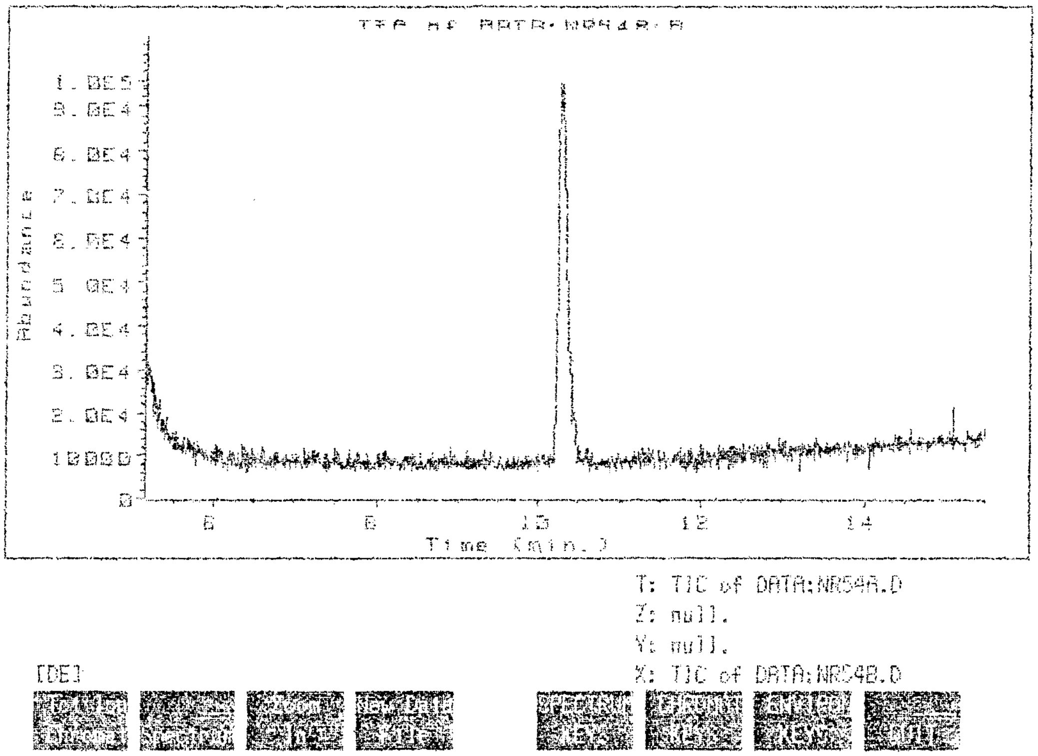
```
Ret Time   Signal Descr      Type      Area   Height    % Pk    % Sg   % LPk  % LSg
================================================================================
 10.322  130.00- 135.00 amu BB +   934279    12256 100.00 100.00 100.00 100.00
--------------------------------------------------------------------------------
```

54



T: TIC of DATA:[illegible]
Z: null.
Y: null.
X: TIC of DATA:[illegible]

54 before reactor



T: TIC of DATA:NR54A.D
Z: null.
Y: null.
X: TIC of DATA:NR54B.D

54 after reactor

54

```
                         *** Area Percent  ***

                        Report by Retention Time
========================================================================
Operator: 6                                           16 Feb 88   1:38 pm
Sample Info : AIR BUBB THRU TCE SAT H2O,TCEAIR.A,4gGAC, SAMPLE AF
Misc Info:  SAMPLE BEFOR MW, FEB-16-88
Integration File Name : DATA:NR54A-N2.I
                           Bottle Number : 0
```

Nitrogen before reactor

```
Ret Time   Signal Descr      Type      Area   Height    % Pk    % Sg  % LPk  % LSg
========================================================================
  4.079   28.00-  29.00 amu 2.8018E+008 1.32E+008 100.00 100.00 100.00 100.00
------------------------------------------------------------------------
                         *** Area Percent  ***

                        Report by Retention Time
========================================================================
Operator: 6                                           16 Feb 88   1:18 pm
Sample Info : AIR BUBB THRU TCE SAT H2O,TCEAIR.A,4gGAC, SAMPLE AF
Misc Info:  SAMPLE AFTER MW, FEB-16-88
Integration File Name : DATA:NR54B-N2.I
                           Bottle Number : 0
```

Nitrogen after reactor

```
Ret Time   Signal Descr      Type      Area   Height    % Pk    % Sg  % LPk  % LSg
========================================================================
  4.142   28.00-  29.00 amu 2.7453E+008 1.28E+008 100.00 100.00 100.00 100.00
------------------------------------------------------------------------
                         *** Area Percent  ***

                        Report by Retention Time
========================================================================
Operator: 6                                           16 Feb 88   1:38 pm
Sample Info : AIR BUBB THRU TCE SAT H2O,TCEAIR.A,4gGAC, SAMPLE AF
Misc Info:  SAMPLE BEFOR MW, FEB-16-88
Integration File Name : DATA:NR54A.I
                           Bottle Number : 0
```

TCE before reactor

```
Ret Time   Signal Descr      Type      Area   Height    % Pk    % Sg  % LPk  % LSg
========================================================================
  4.124   38.00-  42.00 amu PH +  3321459    17732 100.00 100.00 100.00 100.00
------------------------------------------------------------------------
                         *** Area Percent  ***

                        Report by Retention Time
========================================================================
Operator: 6                                           16 Feb 88   1:18 pm
Sample Info : AIR BUBB THRU TCE SAT H2O,TCEAIR.A,4gGAC, SAMPLE AF
Misc Info:  SAMPLE AFTER MW, FEB-16-88
Integration File Name : DATA:NR54B.I
                           Bottle Number : 0
```

TCE after reactor

```
Ret Time   Signal Descr      Type      Area   Height    % Pk    % Sg  % LPk  % LSg
========================================================================
  4.160   38.00-  42.00 amu PH +  2547226    12935 100.00 100.00 100.00 100.00
------------------------------------------------------------------------
```