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UNIVERSITY OF ALBERTA

CHEMICAL CHARACTERIZATION OF ODORS FROM LASER CUTTING OF WOOL

BY

SEET LIN TAN ©

A THESIS
SUBMITTED TO THE FACULTY OF GRADUATE STUDIES AND RESEARCH
IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR
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ABSTRACT

Odors generated from the laser cutting of wool are offensive and potentially harmful by-products. The odors are given off during the laser cutting operations and also afterward from the cut material. The chemical composition of these odors were unknown and therefore their potential health hazards and methods of avoiding such hazards were impossible to determine. This project was initiated to evaluate the chemical composition of these odors.

In order to analyze the odors, it was necessary to develop appropriate methods of sampling and analysis. Such methods were developed for two types of samples which are defined as source samples and out-gas samples. A source sample was described as a sample obtained from the laser effluent during the laser cutting operations. An out-gas sample was one that was obtained from the odors emitted from the cloth cut by the laser. Pre-concentration with Tenax and Molecular Sieve 5A followed by gas chromatography mass spectrometry (GC/MS) and gas chromatography flame photometric detection (GC/FPD) analysis. Also, whole gas sampling followed by Fourier transform infrared spectrometry (FTIR) was used to analyze the source sample.

The qualitative analysis of the source sample with FTIR and GC/MS indicated the presence of 46 known compounds. Specific malodorous compounds determined were hydrogen sulfide, carbonyl sulfide, methyl mercaptan, carbon disulfide, N-metylmethamine, and ammonia. Other compounds found can be grouped under alkyl-benzenes, aliphatic hydrocarbons and nitriles.

The qualitative results of out-gas sample indicated the presence of 9 known compounds. The specific malodorous compounds found were carbonyl sulfide and butyraldehyde. Quantitative measurements were attempted but the results were deemed to be insufficient to be conclusive.

The individual odor characteristics were determined by an odorgram technique that gave a descriptive quality to the peaks analyzed by a gas chromatograph with an flame ionization detector (GC/FID). The odors have a combined characteristics of burnt hair. This odor after being split into its individual components with the odorgram method was described as sweet, hydrogen sulfide, sulfurous, sweet and nauseous, burnt, petroleum, burnt rubber, drug and cyclohexane. Specific chemical identification of all these odorous compounds was not obtained.

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LIST OF ABBREVIATIONS

CW - continuous wave
ECD - electron capture detector
FID - flame ionization detector
FPD - flame photometric detector
FSOT - fused silica open tubular column
FTIR - Fourier transform infrared spectrometry
GAC - granulated activated carbon
GC - gas chromatography
GC/MS - gas chromatograph with a mass spectrometer detector
GC/FID - gas chromatograph with a flame ionization detector
GC/FPD - gas chromatograph with a flame photometric detector
GLC - gas liquid chromatography
GSC - gas solid chromatograph
kPa - kilopascal
Kw - kilowatt
L - litre
LC - liquid chromatograph
HPLC - high performance liquid chromatography
ICP - inductive coupled plasma
I.D. - inner diameter
IR - infrared
J - joules
ppbv - parts per billion by volume
ppm - parts per million
ppt - parts per trillion
pg - picogram
ug - microgram
um - micrometer
mg - milligram
min - minutes(s)
mm - millimeter
MS - mass spectrometer
N - Newton
O.D. - outer diameter
TEM_{00} - Gaussian transverse electromagnetic field
TLV - threshold limit values.

1. INTRODUCTION

1.1 BACKGROUND

A laser is a device that creates a situation in which light waves amplifies itself by drawing directly upon energy stored in atoms. In 1954, C.H. Towns, J.P. Gordan and H.J. Zeiger laid the foundation for laser technology by creating the first maser (microwave amplification by simulated emission of radiation). The first ruby laser was developed by H. Maimon of Hughes Corporation in 1960 (Brotherton 1964).

Since C.H. Towns, many types of lasers and laser applications have been developed. The two major classifications of laser are gas and solid state laser. Table 1.1-1 lists a number of common industrial lasers (Coherent 1980). Laser applications can be broadly categorised as laser instrumentations and measurements, material processing, holography, chemical applications and communications. In 1988, it was estimated that 53% of all laser installed were carbon dioxide lasers and that a majority of these lasers were used in material processing (Belforte and Levitt 1989). In material processing, carbon dioxide lasers have been used for cutting, welding, drilling, scribing, marking and many thermal surface

TABLE 1.1-1 TYPES OF COMMON INDUSTRIAL LASERS*

GAS	SOLID-STATE
ARGON	SYNTHETIC RUBY
CARBON-DIOXIDE	GALLIUM-ALUMINUM-ARSENIDE
HELIUM-CADMIUM	GALLIUM-ARSENIDE
HELIUM-NEON	NEODYMIUM:GLASS

* Adapted after Coherent 1980

modifications of many metallic and non-metallic materials. The laser processing of these materials have generated many unwanted products. Although considerable research has been expended on the development of laser technology and it's applications yet little research have been carried out on the laser induced decomposition products some of which are odorous. These odorous compounds are at the very least unpleasant and at their worst may represent an occupational hazard.

This project was initiated due to the lack of information available on the possible decomposition products generated from the laser cutting of most natural materials such as wool, leather and cotton. These obnoxious odors were a problem even after the fabric was cut in an evacuated chamber, as residual odors were slowly given off from the cut fabric. This project was initiated to investigate the chemical nature of the odors given off during the laser cutting process and from the cut wool.

1.2 OBJECTIVES

The objectives of this thesis were concerned with the odorous by-products generated during and after cutting of fabric material using a continuous wave carbon dioxide laser. While the procedures developed apply to all such operations, the results of this work were focused specifically on the cutting of wool material. Hence, the specific objectives were:

a) To attempt a quantitative gas sampling procedure for trace contaminants;

b) To develop the chemical analysis procedures to identify the gases formed during the laser cutting process and from the cut fabric;

c) To characterize the chemical composition of the odors generated by the laser cutting of wool;

d) To identify gases which contribute to odors during the cutting process and from the cut fabric; and

e) To estimate the concentration of the odors and gases.

2. LITERATURE REVIEW

2.1 BACKGROUND

Lasers are routinely employed by the manufacturing sector for material-processing. New laser applications are continually being developed to process a wide range of materials each year. There are several hazards associated with the use of lasers. The ocular, electrical and radiation hazards have been exhaustively investigated and these have been documented in many publications such as Henderson (1983) and Rockwell (1986). The potential of chemical hazards have been recognized by Mackeen et al. as early as 1968. However only four groups have reported investigations into chemical composition of gaseous effluents generated in laser cutting operations. There has been no research into the chemical composition of odors generated from the laser cutting of wool material. Original work on sampling and analysis of these odorous emissions had to be developed.

A broad literature survey was undertaken to document all work related to investigations into the chemical nature of laser effluent, odors, air sampling and analysis methods, laser pyrolysis studies, composition of wool, combustion studies and methods of sulfurous gas analysis.

2.2 PREVIOUS WORK DONE ON LASER CUTTING EFFLUENTS

An extensive investigation into laser-induced decomposition of polyvinyl chloride polymer (PVC) was first reported by Lum (1976). He used a continuous wave (cw) argon-ion laser to vaporize samples of unplasticized PVC directly into the source cell of a mass spectrometer system. He found the decomposition products generated from laser cutting of unplasticized PVC were hydrogen chloride, benzene and toluene in the ratios of 100:10:1. Lum also discovered that irradiation of PVC with either the plasticizer, 2-ethylhexyl phthalate or antimony oxide, a flame retardant, would change the amount of toluene and hydrogen chloride evolved respectively. Van Cleave in 1979 reported that organic fumes produced by laser cutting of Kevlar-epoxy laminate were analyzed using a mass spectrometer. The laminate was cut with a carbon dioxide laser and the compounds found in the effluent were hydrocarbons, carbon dioxide, toluene, xylene, benzene, water and phenol.

In 1985, Doyle and Kokosa investigated the formation of hazardous by-products produced from the laser cutting of PVC and polymethyl methacrylate (PMMA). Irradiation of the samples was performed in a partially evacuated chamber by a Sylvania 973 carbon dioxide (CO_2) laser running at 1.6 kW power for a duration of 0.2 seconds. The gaseous effluents were withdrawn through a septum in the chamber and were analyzed by gas-chromatograph with a mass spectrometer detector (GC/MS). The condensed products were analyzed by GC/MS and high pressure liquid chromatography (HPLC). The major gaseous products found for PMMA were methyl methacrylate, benzene and toluene. Hydrogen chloride, carbon dioxide, toluene, xylene, benzene, vinyl chloride, propene, toluene and styrene were major products produced from the laser cutting of PVC. Doyle and Kokosa found that PAHs (polycyclic aromatic hydrocarbons) in the flue from laser cutting of PVC and PMMA. They also simulate sampling of fumes generated by plastic in a work environment by pumping air into an enclosed cutting chamber and sampling with first a Teflon (polytetrafluoroethene) prefilter followed by styrene-divinyl copolymer adsorbent and a charcoal adsorbent. Doyle and Kokosa discovered that this result correlated well with their earlier experiments.

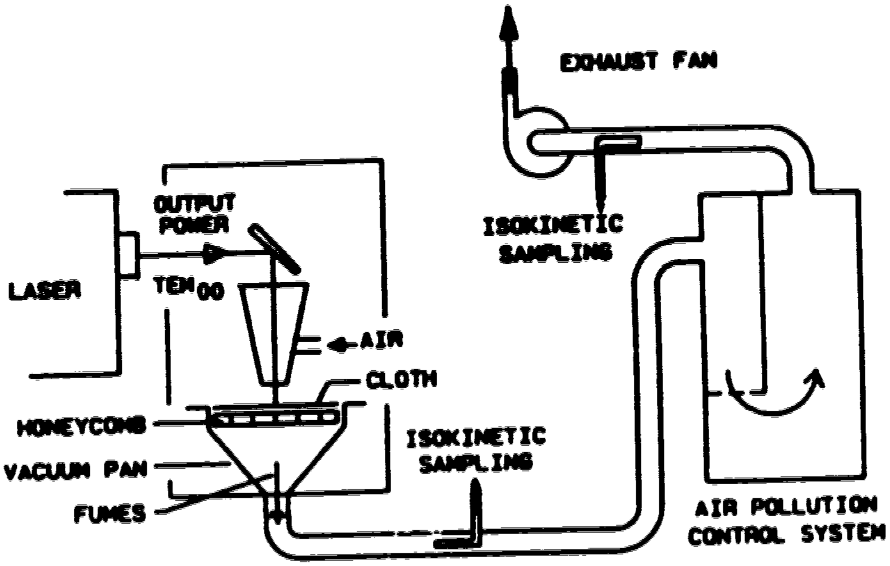
Research concentrated on collecting data on the physical and chemical nature of gaseous effluent generated from laser cutting was carried out by Ball et al. from 1984 to 1990. Specific references to their work were reported in Ball et al. (1986), Kulik and Ball (1989) and

Ball et al. (1989). In these studies, a laboratory effluent testing station was designed and built by Kulik and Stoncel as shown in Figure 2.2-1. The material tested were cut by either a fast axial flow continuous wave (cw) carbon dioxide laser or a slow flow continuous wave CO_2 laser. A TEM_{00} (Gaussian shaped transverse electromagnetic field) mode of operation at 200 to 500 watts was used for either laser. The fumes were sampled isokinetically with Tedlar bags and charcoal adsorbent tubes. The gas mixtures were analyzed by GC/MS and Fourier transform infrared spectrometer (FTIR). The particulates were trapped by electroprecipitation of the dust particulates onto aluminum foil or trapped with glass fiber filters. Inorganic analyses of the dust were performed using ICP (Inductively Coupled Plasma). They studied the effluents generated from the laser cutting of polyester, leather, PVC, Kevlar, Kevlar Epoxy composite and a straight chain polyethylene material (Spectra). Their results are reported in Table 2.2-1.

To discuss the relevance of the above work to this project, a brief description of this project is provided below.

The purpose of this investigation was to determine the chemical composition of odors generated by laser

FIGURE 2.2-1 LABORATORY EFFLUENT TESTING STATION *



*After Ball et al. 1986

TABLE 2.2-1* MAIN DEGRADATION PRODUCTS IDENTIFIED FROM THE LASER CUTTING OF NON-METALLIC MATERIALS

Decomposition Products	Materials, Wt(%)				
	Polyesters	Leather	PVC'S	Kevlar	Kevlar Epoxy Composite
(a) FTIR ANALYSIS					
Acetylene	0.3-0.9	4.0	0.1-0.2	0.5	1.0
Carbon Monoxide	1.5-4.8	6.7	0.5-0.6	3.7	5.0
Ethylene	1.6-5.4	4.3	0.7	-	0.3
Methane	0.2-0.4	0.8	0.0-0.1	-	0.3
Hydrogen Chloride	-	-	9.7-10.9	-	-
Hydrogen Cyanide	-	-	-	1.0	1.3
C6-C8 alkenes	-	-	0.7-0.8	-	-
(b) GC analysis					
Benzene	3.0-7.2	2.2	1.0-1.5	6.8	1.8
Benzonitrile	-	-	-	0.5	0.7
Biphenyl	-	-	0.01-0.09	0.0	-
Chlorobenzene	-	-	0.01-0.04	-	-
Ethyl-benzene	0.1-0.4	0.1	0.01-0.06	0.1	-
Naphthalene	-	-	0.00-0.01	-	-
Nitric Oxide	-	-	-	-	0.2
Nitric Dioxide	-	-	-	0.6	0.5
Phenyl-acetylene	0.2-0.4	trace	-	0.1	-
Styrene	0.1-1.1	0.3	0.01-0.05	0.3	-
Toluene	0.3-0.9	0.1	0.06-0.1	0.2	0.2
Vinyl chloride	-	-	0.02	-	-
1-Decene	-	-	-	-	-
1-Heptene	-	-	-	-	-
1-Hexene	-	-	-	-	-
1-Octene	-	-	-	-	-

* Adapted after Ball et al. (1989)

cutting of wool in a laser cutting operation. It is also important to determine the chemical composition of the odors emitted from the laser cut fabric. To stimulate a real work environment, the laser used for this experiment must be a continuous wave (cw) carbon dioxide laser generating a power in the range of 200 w to 1 Kw irradiating in the infrared region of 10.6 um. The laser beam should be focused onto the work piece with a nozzle assembly. The focussing lens should be cooled with an inert gas. The laser beam should be in a TEM_{00} mode. In addition, it is desirable to identify as many of the degradation products as possible and not only the major products. This is because the intensity of the odors is not proportional to the relative proportion of the chemical that causes it. A compound present in minute quantities can contribute in a major way to the characteristic odor of the sample.

The study conducted by Lum (1976) is not applicable to this work because he used an argon laser irradiating in the near UV (0.35 um) spectrum. The carbon dioxide laser irradiates in the infrared region of 10.6 um. He also conducted the experiment under controlled laboratory conditions and not under typical laser cutting operations.

Van Cleave (1979) used a carbon dioxide laser but experimental details of the study on determination of the laser induced decomposition of Kevlar were not reported. Doyle and Kokosa (1986) conducted his experiment under laboratory conditions and stimulated typical laser cutting operations. His results however indicated a incomplete analysis of the very volatile compounds. He reported only 6 major gaseous decomposition products from PVC while Ball et al.(1989) reported a total of 14 compounds from laser cutting of PVC. Sampling with charcoal adsorbents with solvent desorption were used both by Ball et al. (1986, 1989) and Doyle and Kokosa (1985). There are two limitations in this technique. The desorption efficiencies of many polar compounds are very low from charcoal adsorbent and the desorbed species are diluted by the solvent.

The purpose of all of the above studies were not directed to identification of the chemical composition of odors of the laser effluent. Thus the method of sampling were not designed to measure ppbv(parts per billion by volume) concentrations of organic compounds. These studies also did not address the problems of the out-gassing of fumes from materials cut by laser. Finally, none of these studies were performed with wool.

The testing station employed by Ball's group was used in this study. The sampling method had to be modified. Adsorbents such as Tenax (2,6 diphenyl-p-phenylene oxide), chromosorb 102 (hydrophobic cross-linked polystyrene resin) and molecular sieve 5A will be used for sampling the laser effluent. Thermal desorption of the Tenax and molecular sieve 5A was used to obtain a sample 1000 times more concentrated than those obtained from solvent desorption. A method suitable for sampling the out-gas effluent was also developed.

2.3 SAMPLING OF ODORS

The human nose is the organ for the detection of chemical substances in the human environment. The first indication of the presence of a chemical compound in the air is detected by the nose as odors. Odorous emissions are generally a mixture of many compounds. At ambient temperature and pressure, these compounds are in the gaseous state and are usually mixed with particulates and moisture. The species responsible for the odors are the vaporized organic compounds and not the particulates, (NRC 1979). Thus in the sampling of odors, the particulates are removed with filters. Katz (1977) describes a variety of filter media available in air sampling. Moisture is often removed during sampling. Once the particulates and moisture are separated from the gas mixture, the odors may be sampled by a variety of analytical techniques. The simplest method of sampling is to collect a grab sample in a container. This method is unsuitable for odorants that are in very low concentration. It has been reported that as little as 10^9 molecules (a mole of gas contains $6.02*10^{23}$ molecules) can be detected by the olfactory system (NRC 1979). In order to sample sufficient quantities of these odorants, pre-concentration techniques for gas sampling must normally be used. The types of enrichment sampling that have been used in odors are cryogenic trapping, solid adsorbent and absorption collection with impingers.

2.3.1 COLLECTION OF GRAB SAMPLES

Collection of grab samples may be achieved by using either rigid or flexible samplers. Flexible samplers include plastic bags made of either Tedlar (polyvinyl fluoride), Teflon (polytetrafluoroethene), Mylar (polyethylene terephthalate foil) or polyethylene. Schuetzle et al (1975) found that polyethylene, Saran (vinyl-vinylidene chloride co-polymer) and Mylar bags were not suitable for storing odorous stack emissions of paint spray and bake oven. They also found 7.3 to 38.2% loss of hydrocarbons over several days and as much as 82% loss of some odors. The amount of loss of odors was found to be highly dependent upon the original sample concentrations. These losses may be minimized by pre-dilution. Leonardos et al. (1980) concluded that sampling with Tedlar bags can be a valid method for the evaluation of source sampling, if it was known that the volatile species were the primary odorants. He also stated that sufficient pre-dilution must be used for the above method.

Rigid devices such as glass bulbs, gas-tight syringes and stainless steel canisters may be used to store samples for periods from several days to months. The sampling may be accomplished by first evacuating the sampler in advance and allowing the sample to enter the container. Alternately, the sampling device may also be equipped with inlet and outlet valves. The sampling is accomplished by flushing the sample into the canister until an equilibrium was achieved prior to sealing the vessel. Glass bulbs are frequently used for sampling odorous emissions (Benforado et al.1969). The disadvantage of this type of sampling is that the compounds may condense and or adsorb onto the walls of the container. To overcome these losses, preconditioned container surfaces with SUMMA^{R} polishing. SUMMA^{R} polishing is a proprietary electrochemical process used to make stainless steel so smooth that no adsorption would occur. Molectrics Corporation is licenced to sell the equipment and chemical solution for this process. This method is suitable for sampling relatively stable, volatile compounds such as low molecular weight hydrocarbons and chlorinated hydrocarbons with boiling points less than 150 °C.

2.3.2 CRYOGENIC TRAPPING

Cryogenic trapping of air borne vapors can be accomplished by condensing the analyte onto a suitable trap such as stainless steel, nickel or glass tubing. The length of the trap should allow enough residence time for the organic vapors to cool and condense. The cooling liquids that have been used include dry ice and acetone (-78 °C), liquid oxygen (-183 °C), liquid argon (-186 °C) and liquid nitrogen (-196 °C) (Weast et al. 1986).

Dry ice and acetone should be used with caution because the temperature (-78 °C) may not be cold enough to trap volatile organics. Also the probability of contamination with the large quantity of solvent is high. Liquid nitrogen is not acceptable because it also condenses oxygen from the air. Liquid oxygen will react with many condensibles and the resultant reactions may be explosive. For the same reasons, liquid oxygen, as a coolant, should be used with caution because of the safety hazards involved. Liquid Argon is a preferred coolant. The samples collected may be recovered by flash heating into the analytical equipment.

Cryogenic trapping is an attractive alternative to other enrichment methods because of the following advantages summarised by Riggin (1983) :

1) Many types of organic material can be collected including low molecular weight contaminant.
2) No sample workup is required prior to analysis.
3) No contamination should result from adsorbents or solvents.
4) Recoveries should be consistent.

The major difficulties encountered with this technique have been the trapping of water and formation of fog. Trapped water causes problems in GC and GC/MS analysis. Aerosol formation will reduce trapping efficiency. (Bertsh et al. 1974a). Drying agents such as sodium hydroxide pellets, phosphorus pentoxide and calcium carbonates were reported to be non-adsorptive of organics (Schlitt et al. 1979). The type of drying agents should be chosen with care. Some researchers have found that drying agents such as magnesium perchlorate will adsorb carbonyls, ethers, nitriles and nitro compounds. Concentrated sulphuric acid will adsorb unsaturated hydrocarbons, sulfides and some carbonyls (Williams 1965 ; Farrington et al. 1959.).

2.3.3 SOLID ADSORBENT TECHNIQUES

Trapping of air-borne organics using solid adsorbent is a commonly used air sampling technique. This method is very effective for sampling large volumes of air containing ppbv levels of volatiles. The type of adsorption of the organics are either physical adsorption or chemisorption or both. It is preferable to have physical adsorption for trace sampling. Physical adsorption is characterised by fast adsorption without electron transfer and good recoveries by thermal or solvent desorption. Chemisorption involves specific chemical interactions with electron transfer. Desorption may or may not be possible with thermal or solvent desorption. The Polanyi-Dubinin potential plot can be used for predicting the adsorption of trace organics over a wide range of pressures and temperatures if the molar volume of the adsorbate V and the saturation vapor pressure, P0 is known. This is a plot of log volume adsorbed vs. T/V logP0/P, where T is the experimental temperature and P is the partial pressure of the adsorbate in the experiment. (Ballou,1976).

In this technique sampling is achieved by drawing the volatiles into a cartridge containing solid sorbents. The adsorbed volatiles can then be recovered by solvent extraction or by thermal desorption. Thermal desorption is normally used if the compounds have a boiling point range of 80 °C to 200 °C. Solvent extraction is used for boiling points above 150 °C. Thermal desorption is preferable in cases where the entire sample is to be introduced into the analytical instrument and automation is necessary. Solvent extraction is attractive when thermally unstable species are analyzed, concentration adjustments are necessary and replicate analysis of the sample is required.

Adsorbents are packed in cartridges which are usually made of tubular pyrex glass with I.D. ranging from 8 mm to 15 mm and length that varies between 40 mm to 100 mm. (Bertsch et al. 1974a).

Solid sorbents are either organic polymers, inorganic or carbon adsorbents. Adsorbents such as Tenax GC, XAD-2, Chromosorb 102, Porapak Q and Porapak P are organic polymers. These material are hydrophobic and generally have good recoveries, making them the preferred sorbents for air sampling (Pellizzari et al.1975).

Adsorbents such as silica gel, alumina, florisil and molecular sieves are inorganic adsorbents. These are polar adsorbents which will effectively retain polar compounds. The main disadvantage is that large amounts of water are also retained. Activated carbon adsorbents such as activated charcoal and Carbopaks are much less polar than inorganic adsorbents and exhibit much stronger adsorption than the polymeric sorbents. Thus activated carbons can be used to trap very volatile species such as vinyl chloride. The recoveries of polar species are usually poor because of this strong adsorption property (Riggin. 1983).

Adsorbents commonly used in odor sampling have been the organic polymeric type. Chromosorb 102, hydrophobic cross-linked polystyrene resin was used to sample diesel exhaust odor. The Diesel exhaust odors that were sampled with chromosorb 102 and desorbed with cyclohexane were described as kerosene, oily, smoky burnt and irritating (Levins et al. 1974, Hames et al. 1980 and Partridge et al. 1987).

Tenax GC (2,6 diphenyl-p-phenylene oxide) have also been used to sample for diesel odors (Daudel et al. 1979). Tenax GC is an excellent general adsorbent, stable to 400 °C (Parsons and Mitzner 1975). Tenax GC shows selectivity towards certain classes of compounds. Alkanes, alcohols and amines are more efficiently trapped than aldehydes, ketones and phenols. Tenax GC is very hydrophobic and the presence of an aromatic moiety greatly increases the affinity of Tenax for organic vapors (Bertch et al. 1974b).

The cleaning and conditioning of virgin Tenax was explained in detail by Krost et al. (1982). The Tenax resin should be extracted in a Soxhlet apparatus for a minimum of 18 hours with acetone and hexane, dried in a vacuum oven at 100 °C for 3 to 5 hours at 7 kPa. For cartridges of Tenax GC to be recycled, the sorbent is extracted in soxhlet as described above and further extracted with hexane.

Odorous emissions comprising of sulfur compounds may be sampled with adsorbents such as XAD-2 and molecular sieve 5A. XAD-2 resin was used for sampling malodorous sulfur compounds emitted from the sulphate liquor recovery process and semi-alkaline pulping process (Himberg et al. 1986). Black et al. (1978) evaluated the possibility of using Tenax GC (60/80), Carbopak B, Porapak Q, Porapak P, Chromosorb 102, molecular sieve 13X and molecular sieve 5A for sampling sulfur compounds. They found that molecular sieve 5A was the best adsorbent for sulfur dioxide and hydrogen sulfide in terms of capacity of adsorption and recoveries in desorption. A comparison of break through volumes for sulfur dioxide and hydrogen sulfide evaluated on different adsorbent is as shown in Table 2.3.3-1. The recoveries using molecular sieve 13X and molecular sieve 5A are listed in Table 2.3.3-2.

2.3.4 ABSORPTION COLLECTION

Absorption collection can defined as trapping the gases in a medium in which they are soluble . This collection involves passing the gas stream through an aqueous solution or organic solvent. The solvent is generally cooled at temperatures above it's freezing point to decrease the amount of solvent lost through evaporation. This technique is not suitable for sampling trace organics as large volume of air cannot be sampled because of solvent evaporation during sampling. Inorganic gases are quite successfully sampled by this procedure (Axelrod and Lodge 1976).

2.4 ODOR IDENTIFICATION

There are two common approaches for measuring odors. One is generally referred to as the sensory method and the other is the analytical method. The sensory method involve measuring the principal sensory properties of odors such as odor intensity, change in intensity with dilution,

TABLE 2.3.3-1 BREAK-THROUGH VOLUMES FOR SULFUR DIOXIDE AND HYDROGEN SULFIDE EVALUATED ON DIFFERENT ADSORBENTS*

Adsorbent	Breakthrough volume L/g[a]	
	SO_2	H_2S
Carbopack B	0.1	0.1
Chromosorb 102 (60/80)	3.6	0.1
Molecular Sieve 5A (60/70)	>25	22.5
Molecular Sieve 13X (60/70)	>25	>25
Porapak Q (80/100)	1.3	0.1
Porapak P (80/100)	0.1	0.1
Tenax (60/80)	0.1	0.1

[a] Volume required to elute 50% of adsorbed compound at 25°C.

* Adapted after Black et al. 1978

TABLE 2.3.3-2 COLLECTION EFFICIENCY OF SULFUR GASES EXAMINED FOR MOLECULAR SIEVE 13X AND MOLECULAR SIEVE 5A*

Sulfur gas	Amount adsorbed ng	Recovered (%)	
		13X	5A
Sulfur dioxide	50	22 ± 6	87 ± 3
Sulfur dioxide	22	10 ± 5	83 ± 5
Hydrogen Sulfide	55	45 ± 6	82 ± 4
Hydrogen Sulfide	20	32 ± 6	75 ± 5

[a] Average and standard deviation of 5 separate determinations.

* Adapted after Black et al. 1978

threshold, quality or character and hedonic tone. Analytical methods involve the determination of the principal chemicals and their concentrations that causes the odors. The latter is a more precise method that will provide information on the origin and composition of the odors. The analytical method will be discussed because it is the method that is most suited to achieve the objectives of this investigation.

The selection of sampling and analytical method is dependent on the physical and chemical properties of the species to be measured. An odor is usually a result of a mixture of odorants. Two approaches are available to handle mixtures. One approach uses instruments that will identify a specific compound or group of compounds. The other alternative is to separate the mixture into a single component that can be identified. The type and concentrations of chemical component for odors are numerous and often unknown. Therefore, it is unlikely that any single sampling technique and analysis will be useful for all odor assessment problems. Often a combinations of sampling and analytical methods are used. The sampling procedures should complement the analytical techniques (NRC, 1979).

A method that combines a cryogenic procedure for concentrating trace gases such as fluorocarbons, halogenated carbons and carbonyl sulfide and FTIR with cell path length of 120 m was described by Hanst et al. (1975). Their analytical method involved cryogenic condensation of the ambient air sample and then distillation of it's individual components into long path infrared cells. This combination of sampling and analysis was capable of measuring carbonyl sulfide, carbon tetrachloride, fluorocarbon-11 (trichlorofluoromethane), fluorocarbon-12 (dichlorodifluoro methane) with partial pressures down to 10^{-16} atm.

Morimoto et al.(1976) reported quantitative measurements of the composition of gaseous combustion products of polymers by IR measurement. The gaseous component consisting of hydrogen chloride, carbon dioxide, nitrous oxide, carbon monoxide, carbonyl sulfide, sulfur dioxide, ammonia, hydrogen cyanide, methane, ethylene and acetylene were collected in a cylindrical gas cell with a path length of 100 mm. Grassie and Jenkins (1973) also use IR (Infra red spectrometry) to study the photothermal degradation of copolymer of methyl methacrylate and n-butyl acrylate. Chatfield et al.(1979) also used a combination of IR and GC/MS to analyse for the thermal decomposition products of polyamide fabric under conditions of pyrolysis, oxidative degradations and flaming combustions at temperatures of 450 °C and 550 °C. A total of 28 compounds were identified in the pyrolysis experiments with the major products being water, carbon dioxide, carbon monoxide, benzonitrile, benzene and methane. Oxidative degadations yield 19 volatile compounds with the major products being water, carbon dioxide and carbon monoxide.

FTIR spectroscopy can be used to identify and quantify gas mixtures. Almost all organic compounds and some inorganic compound show characteristic absorption bands in the infrared region. A mixture of these compounds will have overlapping spectras. Fortunately, many compounds have characteristic bands in different parts of the spectrum. The part of the spectum of one compound that is not masked by another compound can then be used to identify and quantify the compound. Thus, two major issues in this techniques are the choice of the proper wavelength region for quantification and the spectral resolution. The resolution of the FTIR is defined by Strang et al. (1989) as "the inverse of the length of mirror travel beyond the zero path difference, which is expressed in reciprocal centimeters (cm^{-1}) or wavenumber." Strang et al. (1989) performed preliminary research to show that FTIR is appropriate for quantitative air monitoring at a semiconductor manufacturing facility. They determined the optimal wavelength region for quantitative measurements. It was also reported that decreasing the resolution from 0.5 to 8 cm^{-1} did not significantly affect the separation and quantitative analysis of the overlapping organic compounds. Lishi et al. (1989a) concluded that FTIR can be used to detect and quantitate individual gases and vapors in air at concentrations at or below their TLVs (threshold limit values). They also determine the limit of detection (LOD) and optimal spectral region for quantitating 38 organic compounds. With these optimal operating conditions, the LOD for 32 of the compounds tested were below 50 ppbv. The highest LOD was for acetonitrile with a LOD of 1500 ppbv and the lowest LOD was for ethyl ether with a LOD of 6 ppbv. They also demonstrated that the FTIR can be used for quantitative measurements of individual components in a simulated 12 component paint solvent mixture (Li-shi and Levine 1989b). Table 2.4-1 gives a summary of some of their results.

The other approach to handling mixtures uses either GLC (gas-liquid chromatography), GSC (gas-solid chromatography), LC (liquid chromatography) or HPLC (high pressure liquid chromatography) to separate the myriad of compounds into a series of discrete compounds. After the separation, a multitude of detectors such as the FID (flame ionization detector), ECD (electron capture

TABLE 2.4-1 LIMITS OF DETECTION (LOD) AND ABSORPTIVITY FOR PAINT SOLVENT MIXTURE TAKEN INDIVIDUALLY AND IN A MIXTURE AT RESOLUTION OF 2 CM^{-1}*

Solvent	TLV* (ppm-v/v)	LOD (ppm-v/v) Individual	 In Mixture	Absorptivity (x10-4)
Toluene	100	0.067[A]	0.2	6.2
o-Xylene	100	0.067	0.1	8.5
m-Xylene	100	0.06	0.1	5.2
p-Xylene	100	0.08	0.1	4.8
Ethylbenzene	100	0.029	0.5	4.1
n-Butylacetate	150	0.005	0.2	20
2-Ethoxyethylacetate	2	0.004	0.2	14
Methylisobutylketone	50	0.026	0.2	6.9
Methylamylketone	50	0.06	0.2	2.5
n-Propanol	200	0.07	0.05	2.6
n-Butanol	50	0.01	0.2	4.8

[A] Linear to the LOD. All compounds not marked with A are linear only to 0.5 ppm. Below that point, questions of wall adsorption must be addressed.

* Adapted after Li-shi and Levine (1989 b)

detector), FPD (flame photometric detector), IR (infra-red detector) and MS (mass spectrometer detector) can be used. The type of detector used will depend on the chemical characteristic of the odors. The FID is used to measure the hydrocarbons while the ECD is sensitive to halogenated compounds. The FPD is good for analysis of sulfur compounds. The MS and IR can identify the chemical compounds by their inonized molecular fragmentation patterns and adsorption spectra. Riggin (1983) gives an excellent review of all the methods and their sensitivities for the measurement of organic compounds in ambient air.

A major weakness of the analytical methods is that they do not indicate which of the sample components cause the odor of the complete sample. To overcome this disadvantage, the analytical method can be coupled with a partial sensory method known as chromatographic sniffing or the odorgram method. This approach uses a GC to separate the odorous mixture. The flow of the separated component coming out of the gas chromatograph is then split into two flows, one going to the FID detector of the GC and the other going to the nose. In this way, the analyst can evaluate the odor simultaneously as a peak is detected by the FID detector. A description of the odorgram method was reported by Dravnieks (1975).

2.5 SAMPLING AND ANALYSIS OF SULFUR COMPOUNDS

A large number of instrumental and wet chemistry techniques have been used to sample and analyze sulfur compounds. The wet chemistry methods includes sampling with impingers or impregnated filters and analysis with spectrophotometry (Jacobs et al. 1957), ion chromatography (Hansen et al. 1979, Margeson et al. 1985a) or titrimetry (Margeson et al. 1985b). These wet techniques are only suited to measure single inorganic sulfur compound or total sulfur compounds such as the measure of all the organosulfur as TRS (Total Reduced Sulfur). The method developed by Jacobs et al. (1957) can only be used to analyze hydrogen sulfide while the techniques used by Margeson et al. (1985b) can only be used to measure TRS. Another limitation of these wet chemistry techniques is that it cannot identify the unknown sulfur compound present.

In cases where mixtures of sulfur compounds are to be identified, it is necessary to separate the mixture into individual components using GC and HPLC or use specific detectors such as FTIR or triple quadrupole mass spectrometer. The most popular and practical technique for analysis of a mixture of sulfur compounds is GC with an

FPD detector. The FPD detector is specific for either phosphorus or sulfur detection. Sulfur or phosphorus compounds in a hydrogen-air flame of the FPD will emit light of a certain frequency. The FPD consists of a photomultiplier. A filter is positioned in front of the photomultiplier to allow only light emitted from one of the elements (either sulfur or phosphorus) to be detected. The limit of detection have been reported to be from 2 ppb to 50 ppb for sulfur (Adams 1976).

There are two major difficulties in measuring sulfur compounds at ultra trace levels. The GC/FPD equipment have to be adjusted to achieve optimal sensitivity. The other problem arises from the nature of these sulfur compounds. Sulfur compounds have high affinity for the walls of stainless steel or glass columns as well as many packing material used to separate these compounds. The GC/FPD system is at optimum sensitivity when the "dead volume" in FPD is reduced and when the flows of hydrogen and oxygen to the FPD are in the ratio of 1:1.5. The high affinity of sulfur can be greatly reduced by deactivating column walls and packing material with any of the materials reported by Farwell et al. (1979). A variety of packed columns have been used for the separation of ppm (parts per million) levels of carbon dioxide, carbonyl sulfide, hydrogen sulfide, carbon disulfide and sulfur dioxide. The most successful columns have been developed by De Souza et al. (1975). De Souza used a GC with a FPD detector. The column used was an acetone-washed Teflon tube 3.175 mm O.D. and 0.46 m long, packed with 80/100 mesh acetone-washed Porapak QS. It was necessary to condition the column with several injections of concentrated sulfur gases.

Farwell et al. (1979) proposed the use of a deactivated glass capillary column. The cryogenic sampling traps were also deactivated with polysiloxane and 5% methyl silicon, dimethyldichlorosilane, triethanolamine, benzyltriphenyl-phosphonium chloride and 1-aziridineethanol. Two sampling traps were used in the process. The sample was first trapped in a large trap and re-cryofocus (re-condensed) into a capillary trap before being flushed into the capillary columns. The capillary column tested were 30m x 0.25 mm i.d. coated with SE 30, Carbowax 20M, OV-17 and deactivated 30 to 38 meter columns coated with OV-101 and SE-54. The temperature program was from -10 °C to 100 °C at the rate of 16 °C/min. It was found with this system, the quantitative repeatability for hydrogen sulfide, carbonyl sulfide, methyl sulfide, dimethyl sulfide, carbon disulfide and dimethyldisufide was within the limits of ± 25 % when working in the ppb/ppt (part per trillion) range.

Barinaga et al. (1987) reported that it was possible to separate low molecular weight reactive sulfur gases without any cryogenics in the GC oven. In their investigation, they used a combination of:

1) a cryogenic sampler, attached to the injector port of the GC with flows which were compatible with a wide-bore FSOT (fused silica open tubular) column.
2) a thick film DB-1/DB-wax, megabore FSOT combination column.
3) a reduced dead volume FPD.

The mixed phase column consisted of a 30 m x 0.53 mm DB-1 with d*f*(film thickness)=5 um coupled to 3m x 0.53 mm DB-Wax, d*f*=1 um. The temperature program used was 30 °C for 1.2 min, then 30 °C/min to 140 °C. They manage to separate hydrogen sulfide, carbonyl sulfide, methyl sulfide, dimethyl sulfide, carbon disulfide and dimethyldisulfide in 5 min without the use of any cryogenics. In this study they were successful in eliminating the disadvantage inherent in both the packed column system and thin film capillary column. Packed column gas-solid chromatographic techniques are usually limited by inadequate resolution and detection limits due to band broadening, by column conditioning and memory effects. The disadvantages of thin-film capillary columns was that the volume and flow rate of the pre-concentration device were not compatible with those in the capillary column.

2.6 COMPOSITION OF WOOL

Wool keratin is composed of amino acids. The number of moles of each of these amino acids in 10^5 g of protein is shown in Table 2.6-1 (Bolker 1974). The elemental composition of wool is carbon, 49.3 %, hydrogen 7.6 %, nitrogen 15.9 %, oxygen 24 % and sulfur 3.6 %.(Napperley and Sewell 1973). The amino acid, cystine with its disulfide groups, makes wool very reactive. The wool fiber has both helical alpha-keratin and sheet-like ß-keratin conformations. Its adjacent molecular chains are cross-linked through the S-S bonds of cystine units. (Bolker 1974).

2.7 THERMAL DECOMPOSITION PRODUCTS OF WOOL

Thermal decomposition of wool begins with dehydration followed by a sort of melting at 240 °C (Menefee and Yee 1965). At about 247 °C the disulfide bond breaks releasing mainly carbon disulfide and carbon dioxide (Carrol-

TABLE 2.6-1 AMINO ACID COMPOSITION OF WOOL KERATIN*

AMINO ACID	COMPOSITION EXPRESSED AS MOLES PER 105 GRAMS OF PROTEIN
Alanine	46
Arginine	60
Aspartic acid + asparagine	54
Cystine	49
Glutamic acid + glutamine	96
Glycine	87
Histidine	7
Leucine	86
Lysine	19
Methionine	5
phenylalanine	22
Proline	83
Serine	95
Threonine	54
Tryptophane	9
Tyrosine	26
Valine	40

* Adapted after Bolker 1974

Porcznski 1971). Pyrolysis-gas chromatography of wool at temperatures of 600 °C to 925 °C yields hydrogen cyanide, benzene, toluene and carbon oxides (Cullis and Hirschler 1981). Several researchers have reported the presence of carbon monoxide, hydrogen cyanide and nitrogen oxides. The amount of hydrogen cyanide, carbon monoxide and nitrogen oxides released during thermal decompositions is temperature dependent. The amount of carbon monoxide will increase with temperature and the amount of hydrogen cyanide will increase steadily until a maximum at 727 °C and decrease slowly to about 927 °C (Mapperley et al. 1973). The amount of nitrogen oxides will decrease to a minimum at about 527 °C and increase slowly to about 727 °C. (Skidmore and Sewell. 1974).

A more complete analysis of the thermal decomposition products was done by Chaigneau and Le Moan (1976). They analysed the gaseous, liquid and solid products of pyrolysis by mass spectrometry. They found that the quantity and composition of the pyrolysis products were dependent on the temperature at which it was pyrolysed. Major decomposition products of wool pyrolysed at 500 °C were carbon dioxide, hydrogen sulfide, carbon monoxide, hydrogen cyanide and hydrocarbons. Pyrolysis of wool at 1000 °C produced the following major decomposition products: hydrogen, hydrogen cyanide, carbon monoxide and hydrocarbons. Hydrogen sulfide, carbon disulfide, carbonyl sulfide and methyl mercaptan were found for pyrolysis at 500 °C and 1000° C. Traces of sulfur dioxide was also evolved at 500 °C but not at 1000 °C. Signficantly larger quantities of hydrogen sulfide and carbon dioxide and smaller quantities of hydrogen cyanide were found at 500 °C than at 1000°C. Table 2.7-2 shows the thermal decomposition products from the pyrolysis of wool at 500 °C and 1000 °C under vacuum.

In the same study by Chaigneau and Le Moan, they also studied the amount of hydrogen cyanide and hydrogen sulfide released from the combustion of wool. They found that the quantities of both gases were highly dependent on the temperature, rate of introducing the sample in the furnace, and rate of delivery of air to the sample. The maximum amount, 92.8 L of HCN per kilogram of wool and 101 L of H_2S per kilogram wool, was obtained at a temperature of 1200 °C, rate of delivery of air of 6 L/hr and rapid introduction of wool into the furnace. The minimum amount, 0 L of HCN per kilogram of wool and 0.8 L of H_2S per kilogram of wool were obtained at 1200 °C, an air flow rate of 8L/hr and slow sample introduction.

TABLE 2.7-2 **THERMAL DECOMPOSITION PRODUCTS FROM THE PYROLYSIS OF WOOL AT 500°C and 1000 °C UNDER VACUUM***

PRODUCT	YIELD AT 500°C (MOL PER CENT)	YIELD AT 1000°C (MOL PER CENT)
HCN	7.7	20.0
H_2	1.1	36.0
CH_4	7.2	13.8
C_2H_6	-	0.1
C_3H_8	6.0	0.2
C_4H_{10}	0.5	TRACE
C_2H_4	0.8	0.6
C_3H_6	2.9	0.1
C_4H_8	1.9	1.0
C_5H_{10}	0.8	-
C_2H_2	0.6	1.0
C_3H_4	0.4	-
C_6H_6	TRACES	0.5
$CH_3C_6H_6$	0.1	TRACES
C_5H_8	2.3	-
N_2	1.9	1.3
CO_2	30.9	7.7
CO	11.3	16.4
H_2S	17.7	1.7
SO_2	TRACES	-
COS	4.8	0.1
CS_2	0.3	0.5
CH_3SH	0.8	-

* Adapted after Chaigneau and Le Moan, 1976.

2.8 TECHNIQUES USED TO STUDY THE THERMAL DEGRADATION OF POLYMERS

There are two areas of concern in researching the thermal degradation of polymers. One concern is the toxicity of fumes evolved from polymers in a fire and the other, is to use the degradation products as a "fingerprint" to identify the original polymer. In the first, the techniques used involve heating the sample from about 200°C to about 800°C. These temperatures are usually achieved with electrically heated filament or an electrically heated tube furnace. Gases such as air, helium or nitrogen can be introduced into the furnace. The gases produced are collected with a cooled trap, an evacuated bulb or a trap containing an inorganic solution. The identification of inorganic components is usually achieved with colorimetric methods and organics using either IR or a combination of IR, GC/MS and HPLC (Chatfield et al. 1979).

Those that are interested in "fingerprinting" polymers use pyrolysis to break down the polymers. Pyrolysis is defined generally as the subjection of organic materials to elevated temperatures in the absence of oxygen. Mild pyrolysis occurs in the temperature range of 300 °C to 500 °C, normal pyrolysis at 500 °C to 800 °C and vigorous pyrolysis occurs at temperatures above 800 °C . A pulse ruby laser is the most commonly used source of pyrolyzing polymers over 800 °C. The first reported study of laser degradation of aromatic compound was done by Wiley and Veeraga in 1968. He reported that laser beam interaction with a solid and liquid substance is a more complex affair than merely thermal degradation. The first pulse ruby laser pyrolyzer on-line with a GC was demonstrated by Folmer and Azarraga in 1969. They also showed that the chromatograms achieved by a ruby laser exhibited simple patterns and allowed greater distinction between similar types of substances than achievable through conventional pyrolyzers.

Lasers produce a beam of focus monochromatic light beam and it is difficult to determine the temperature at which the material is vaporised. The exact temperatures at which the material is pyrolysed cannot be measured directly. Estimates of this temperature can be obtained by measurement of the surface of metals where the laser had interacted. Using this technique, the temperature range at which a laser beam interacted with matter was reported to be in the range of 927 °C to 7727 °C (Ristau and Vanderborgh 1971). Another method of estimating the temperature of pyrolysis by pulse ruby laser is to analyse the composition of the vapor ejected by a focused laser beam. Berkowitz and Chupka (1964) used the above method and estimated that a pulse ruby laser emitting 3J/pulse would interact with matter at about 3727 °C .

3. METHODS

3.1 SAMPLING METHODS

Two kinds of sampling system were required. The first involved sampling for the fumes during the laser cutting processes and the second involved sampling for the vapors emitted from the laser-cut fabric. The first type of sampling would be referred to as source sampling and the second as out-gas sampling.

Factors to be considered in the selection of sampling and analysis methods are outlined in Table 3.1-1. The first four items were unknown at that stage. Therefore some intuitive assumptions based on literature reviews were required for the selection process. The chemical and physical nature of the compounds targeted for analysis may be surmised from the literature reviews of section 2.6, 2.7, and 2.8. From the composition of wool studies it was apparent that the degradation products contained products with nitrogen, sulfur and oxygen. Pyrolysis studies reported that the laser beam interactions with polymers occurred at temperatures of 927 °C and 7727 °C. Table 2.7-2 lists the degradation products from the combustion of wool at 500 °C and 1000 °C. It was therefore logical to assume that the degradation products will be

TABLE 3.1-1 FACTORS TO BE CONSIDERED IN THE SELECTION OF SAMPLING AND ANALYSIS METHODS*

1) Physical and chemical properties of compounds
2) Concentrations of compounds
3) Relative importance of various chemicals to program objectives
4) Method performance characteristics
5) Time resolution requirements
6) Budget restraints

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* Adapted after Riggin (1983)

similar to some of the compounds outlined in Table 2.7-2. These included sulfur compounds, hydrocarbons and nitrogenated inorganic gases.

The concentrations of the source samples should be in the ppm range. This information was obtained from the author's own unpublished results carried out for the papers by Ball et al. (1986, 1989). The concentrations of the out-gas sample will be much lower than ppm range. They were assumed to be in the ppb range.

The above assumptions led to the following conclusions:

a) Pre-concentration techniques may not be necessary for the source sample but would be vital for the out-gas sample.
b) Cryogenic pre-concentration techniques were not feasible because of water condensation and polar compounds expected. Also coolants such as liquid oxygen and argon are too expensive and were not available.
c) Pre-concentration using adsorbents was deemed the most suitable sampling methods. Several adsorbents were required to sample for hydrocarbons, carbonyls, nitrogenous and sulfur compounds.

3.1.1 SOURCE SAMPLING

Three source sampling methods were developed. The first, (S1), was developed to obtain a whole sample in a Tedlar bag. The second, (S2), was designed to obtain a more concentrated sample with an adsorption tube. The last type of sampling,(S3), was devised to obtain a quantitative sample with an adsorption tube.

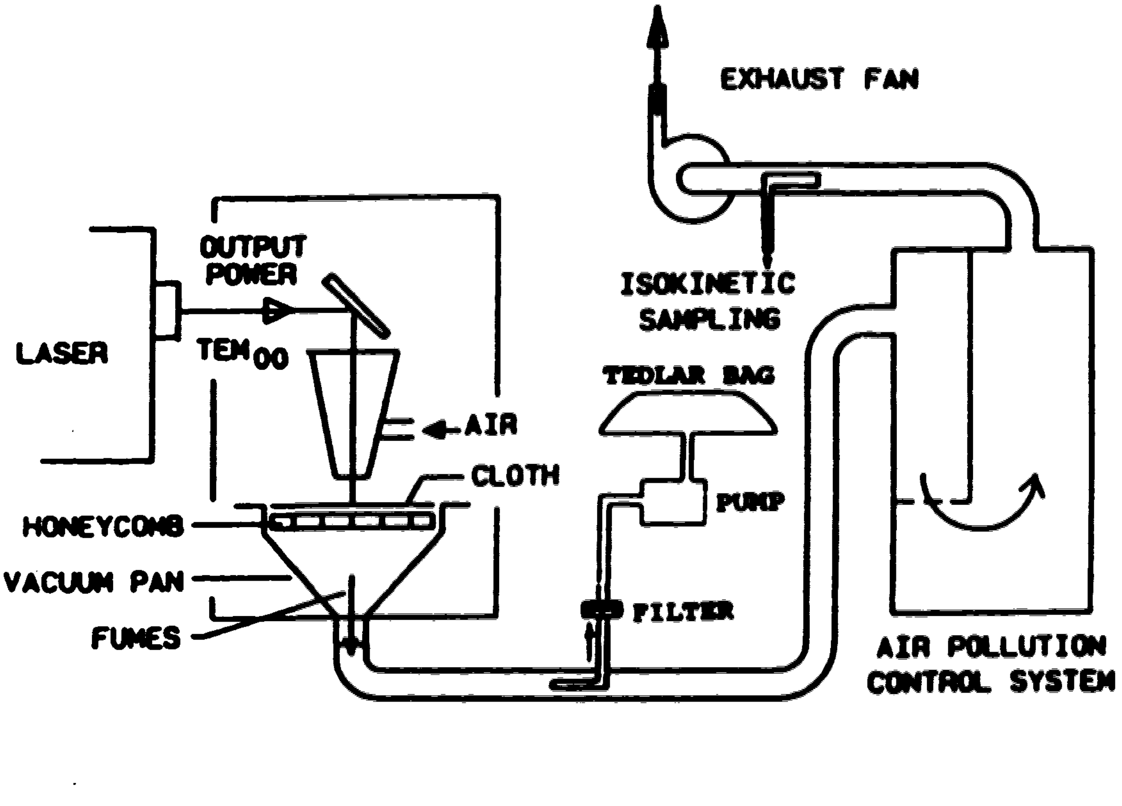
All three sampling methods used the laboratory effluent testing station built by Kulik and Stoncel shown in Figure 2.2-1 and described in Appendix A.

Prior to sampling, the acrylic box and metal vacuum pan were vacuumed to remove pieces of cut fabric. The honeycomb cutting bed was also cleaned by using the laser to burn over the entire surface while the system was continuously evacuated.

The first source sampling method, System S1 is shown in Figure 3.1.1-1 and is defined in Appendix A. This was used for obtaining a gas sample in a Tedlar bag which could be subjected to direct FTIR analysis.

The second sampling system (System S2) was similar to

FIGURE 3.1.1-1 SOURCE SAMPLING METHOD S1



System S1 as shown in Figure 3.1.1-2. This was used to obtain a concentrated sample by adsorption for qualitative analysis.

System S3 is shown in Figure 3.1.1-3. System S1 was modified to allow sampling to be obtained through an adsorption tube instead of a Tedlar bag.

3.1.2 OUT-GAS SAMPLING

Three sampling systems were developed and experimented with. The first two systems (described in Appendix A) were not able to perform the task they were designed for. Their respective problems will be discussed in Section 4.1. The third system, OG-3 (shown in Figure 3.1.2-1), performed successfully and was used to sample out-gas vapors. The operation of System OG-3 is described n Appendix A.

3.1.3 PREPARATION OF ADSORPTION TUBES

Sampling methods S2, S3 and OG-3 required the use of adsorbent tubes. These tubes had to be carefully prepared to avoid artifacts in sampling. The preparative procedures are described in Appendix A.

FIGURE 3.1.1-2 SOURCE SAMPLING METHOD S2

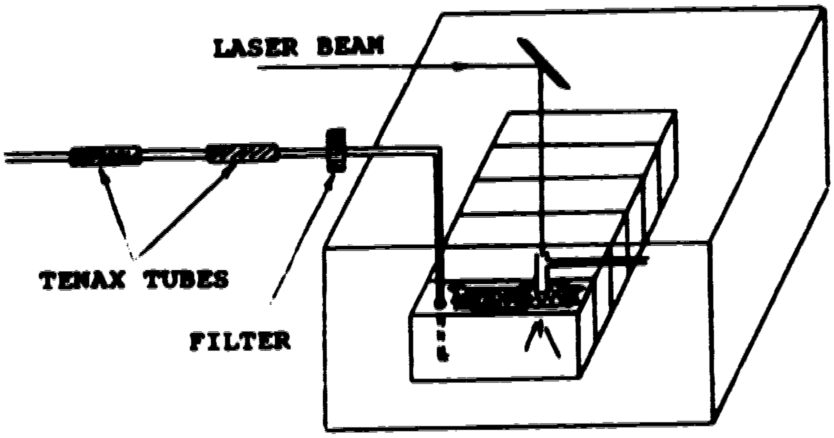


FIGURE 3.1.1-3 SOURCE SAMPLING METHOD S3

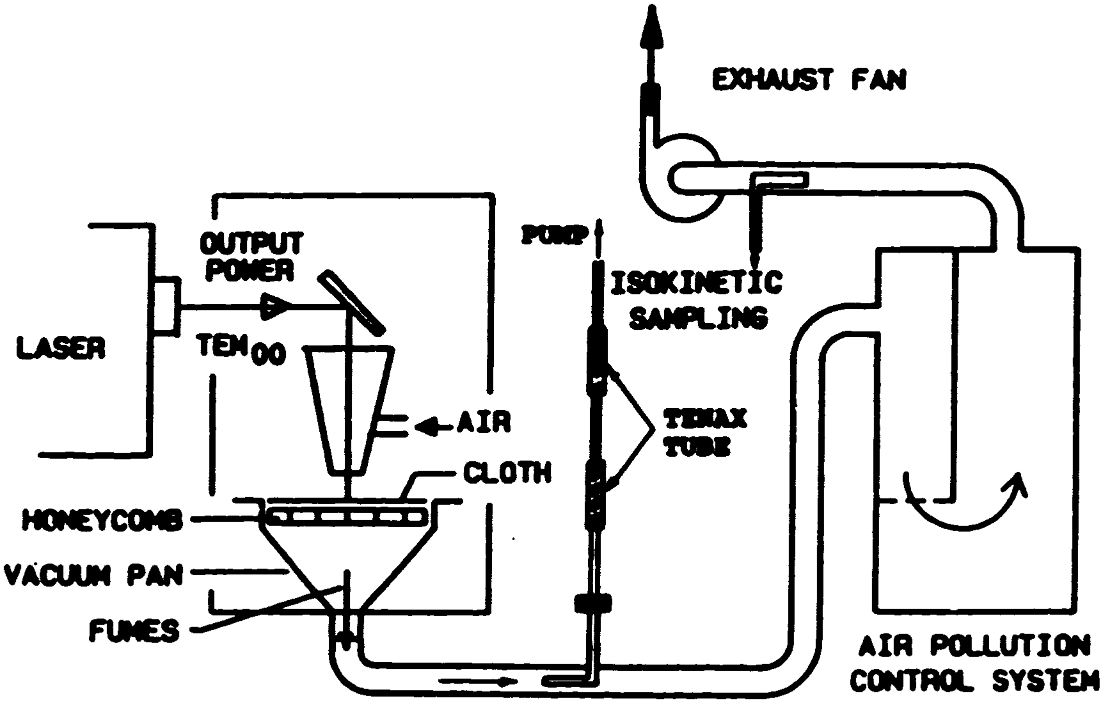
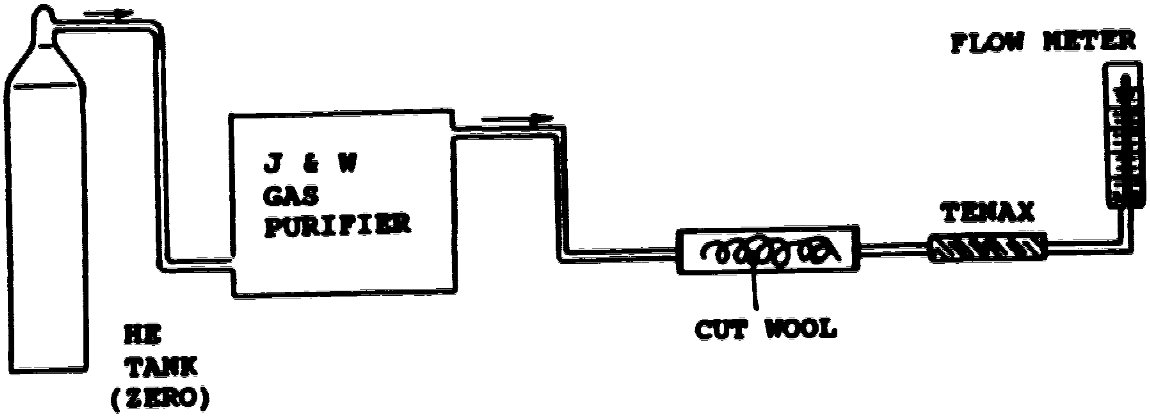


FIGURE 3.1.2-1 SYSTEM OG-3 OUT-GAS SAMPLING SYSTEM



3.2 THERMAL-DESORPTION GC/FID ANALYSIS

Preliminary tests for sampling methods S2, S3, and OG-3 were achieved through thermal desorption of the samples adsorbed into Tenax and desorbed into the GC with an FID. The purpose of these tests were to examine whether:

a) the blank adsorbent tubes were cleaned;
b) the controls were relatively free of interferences; and
c) the sample was concentrated enough to be detected by the GC/FID detector.

Two gas chromatographs, each with a flame ionisation detector and two thermal desorber were used for the GC analysis. The first thermal desorber was an Envirochem 850 hooked up to a HP5890 GC. A flow rate of 7 mL/min of helium flowing through the thermal desorber. This flow was split in half to 3.5 mL/min prior to entering the injector port of the GC. The samples were desorbed at 200 °C for 2 min. The column used was a 30 m SPB-5 capillary column. A temperature program of -50 °C for 2 minutes increasing at 20 °C/min and a final temperature of 250 °C for 35 minutes was used. Detector temperature used was 250 °C.

A second portable thermal desorber had to be developed (described in Appendix B). It was attached to a Varian 3300 GC. The samples were desorbed at 200 °C for 4 minutes, cryofocused for about 8 minutes and flash heated to 200 °C for a minute. The column used in this GC was a 60 m DB1 column. Temperature was programed at 40 °C for 2 minutes, increasing at 5 °C/min to a final temperature of 250 °C for 30 minutes.

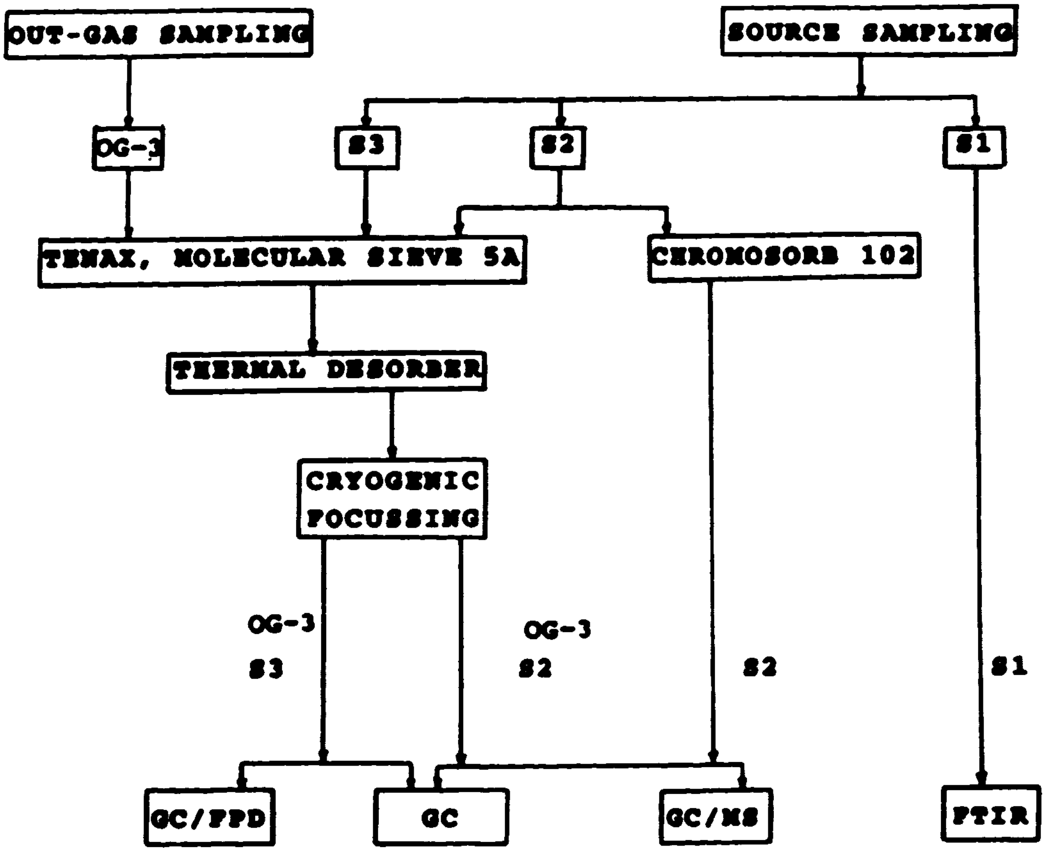
3.3 QUALITATIVE ANALYSIS OF THE ODORS FROM SOURCE SAMPLES

The overall strategy for the analysis of the odors is summarized by the flowchart in Figure 3.3-1.

The source samples were concentrated enough to be collected in a Tedlar bag and analysed on an FTIR (Fourier transform infra-red spectrophotometer). The purpose of this method was to determine some of the inorganic gases such as ammonia, carbon monoxide and organic compounds such as carbonyl sulfides and methane. FTIR also provided an excellent qualitative overview of the chemical species in the whole air sample which have had no sample manipulation.

Sampling with chromosorb 102 and solvent desorption

FIGURE 3.3-1 FLOW CHART ILLUSTRATING THE STRATEGY FOR SAMPLING AND ANALYSIS OF ODORS



followed by GC/MS was also a successful method of analyzing source samples. Chromosorb 102 was chosen because it was used in many investigations into odors generated from diesel exhausts. Laser exhausts exhibited similar burnt-like odors as in diesel exhaust. This method gave an insight into the chemical composition of the heavier hydrocarbons.

The more volatile vapors can be sampled and analyzed using thermal desorption and GC/MS analysis. The adsorbents chosen for this procedure was Tenax and molecular sieve 5A. Tenax is reported in many papers as an excellent general sorbent and the molecular sieve 5A is shown to be the best adsorbent for sulfur compounds.

3.3.1 ANALYSIS BY FTIR

Source samples from the laser cutting of 100% wool was obtained with the S1 sampling procedures. The gaseous vapors were collected using a 10L Tedlar bag purchased from Alltech Ltd. A Gilian Hi flow sampler pump with a model number HFS 113A was used for sampling. The gas sample was obtained at a pressure of 100.8 kPa. The sample flow rate was 3 L/min and sampled for 3.78 min. A total of 10.0 g or 94 lines (each line being 440 mm long) of 100 % wool material were cut. A cw Photon Source laser with a cutting speed of 90 mm/s was used to cut the fabric. The Tedlar bag containing the odors was immediately transported to the Spectral Services Department at the University of Alberta for FTIR analysis. The procedure and the raw data are summarized in Appendix C

3.3.2 SOLVENT DESORPTION GC/MS ANALYSIS

Source sampling of the laser cutting of wool was obtained with method S2. The fumes were adsorbed on chromosorb 102 and desorbed with cyclohexane. Solvent desorption was used instead of thermal desorption because of the following reasons:

a) compounds with boiling points above 150 °C can be easily desorbed; and
b) the solvent desorption of chromosorb 102 with cyclohexane had been used successfully in the study of diesel odors.

Details of this analysis are provided in Appendix D.

3.3.3 THERMAL DESORPTION AND GC/MS ANALYSIS

A source sample, using the S2 sampling method was obtained. The adsorbent used for these samples were molecular sieve 5A and Tenax. A drying agent, sodium sulfate, was used to dry the gaseous vapors prior to adsorption onto the molecular sieves. Two types of samples were obtained for each type of sorbent. A controlled sample was obtained for each sorbent. The flow rate used was 1 L/min. All samples were obtained at a temperature between 22 °C and 22.5 °C. About 90 mg of wool was cut. The sampling time was 3 minutes.

A cw Photon Source laser operating at 450 watts and a cutting speed of 70 mm/s was used to cut the fabric. A control experiment was carried out for both the source and out-gas sample. The control experiments for source samples included normal sampling while the laser was cutting over the surface without cloth samples. Details of the analysis are provided in Appendix D.

3.4 QUALITATIVE ANALYSIS OF OUT-GAS SAMPLE

A type OG-3 method of out-gas sampling was employed. The adsorbents used for these samples were molecular sieve

5A and Tenax. A drying agent, sodium sulfate was used to dry the gaseous vapors prior to adsorption onto the molecular sieves. A controlled experiment was obtained for each sorbent. The flow rate used was 200 mL/min. The pressure required to maintain a flow rate of 200 mL/min for out-gas sample was 14 to 28 kPa. All samples were obtained at a temperatures between 22 °C and 22.5°C. The amount of cut material used were between 6.2 g to 6.3 g. The sampling time for out-gas samples were from 45 minutes to 48 minutes. All laser operating parameters, equipment interface between desorber, GC and GC/MS and GC operating conditions were as discussed in Appendix D. Controlled experiments for out-gas samples were sampled in a similar manner with the exception of having a piece of un-cut fabric (not cut by laser) in place of the usual laser cut fabric in the sampling cannister.

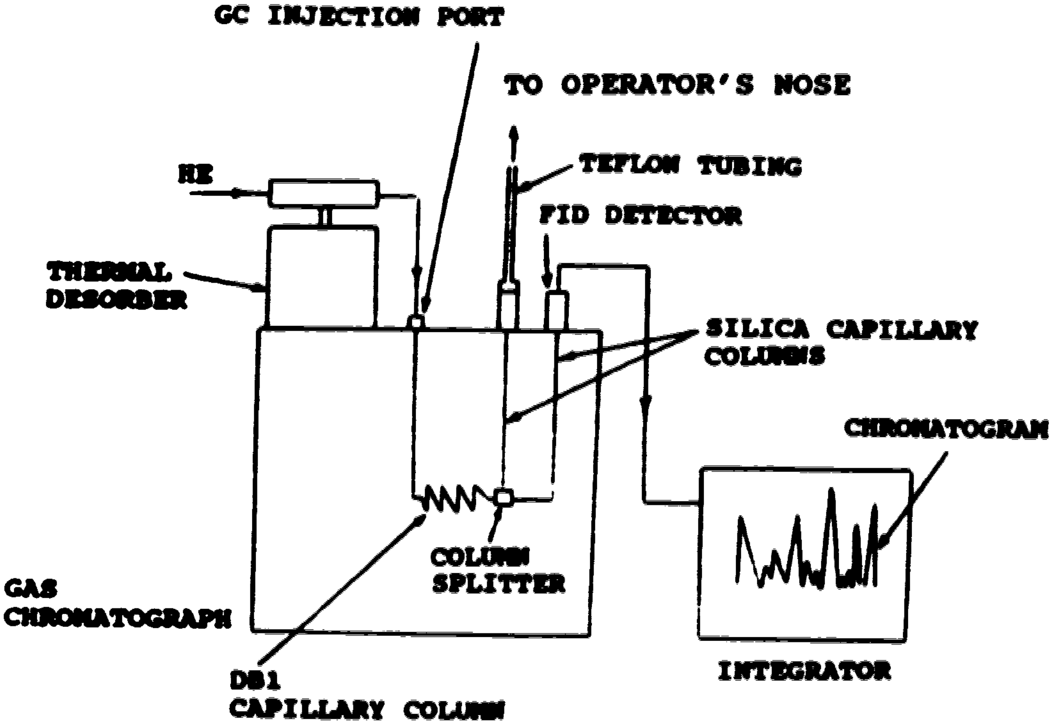
3.5 ODORGRAM METHOD

An experiment was conducted where a source sample was obtained from the laser cutting of pure wool. An S2 sample was obtained on Tenax. The sample was desorbed into a GC and split into two flows, one flow was directed to the nose and the other was directed into an FID detector. This was carried out to correlate the odors perceived by the human nose with the peaks detected at the FID. A diagram of this experimental set-up is shown in Figure 3.5-1.

This experiment was carried out on a Varian 3300 GC with an FID detector, and a 60 m DB1 capillary column. A splitter purchased from Mandel Scientific Ltd. was used. This GC had two outlets to two FID detector ports. An additional flow of zero air was supplied as make-up gas to the port monitored by the operator's nose. The column in the gas chromatograph was split into two transfer lines, one leading to a FID detector port and the other to the operator's nose.

The experiment was performed by desorbing the adsorbed vapors into the GC. The perception of the odors were followed by assignment of their characteristics to the corresponding peaks eluting on the integrator. It was difficult to write the characteristics of the odors on the peaks as they eluted. Instead, the retention time of the eluting peaks were recorded beside the perceived odor. After the entire chromotogram was printed, the characteristic odors were then labeled above the peaks with the corresponding retention times. The results from the first test run were discarded because of the difficulty in recording the retention times on the graph. A second successful run was carried out and the results are shown in Figure 4.5-1 in section 4.5.

FIGURE 3.5-1 EXPERIMENTAL SET-UP FOR THE ODORGRAM EXPERIMENT



The instrumental set-up was tested using two known compounds. Duplicate runs were carried out for each compound. The objective of this test was to ensure that the time of elution of the peak coincided with the detection of the odor. Each sample of ethanol vapor was injected into the GC. The odor (ethanol) perceived by the operator corresponded to the peak eluted from the GC. A similar experiment was conducted using carbon disulfide vapor. The results confirmed the findings of the ethanol experiment.

3.6 QUANTITATIVE ANALYSIS OF SOURCE AND OUT-GAS SAMPLE

Quantitative analyses for source samples were carried out using both FTIR and GC/FPD detectors (gas chromatograph with a flame photometric detector). The out-gas samples, however, were quantified using only GC/FPD system because the FTIR was not sensitive enough to detect the lower concentration in the out-gas sample.

3.6.1 QUANTITATIVE ANALYSIS OF SOURCE SAMPLE BY FTIR

The quantitative measurement of the chemical compounds in a source sample was obtained in exactly the same fashion as described in Appendix C. All experimental conditions and equipment characteristics are identical to the one in Appendix C. The quantitative analysis was achieved by analyzing a calibration mixture under the same experimental conditions. Gas standards were prepared using a syringe technique. This involved cleaning a gas-tight syringe with the pure gas. A known quantity of gas was then drawn into the syringe and injected into the FTIR gas cell. Quantitative analysis was obtained by using a least squares fit program. A set of digitized quantitative reference spectra was created on the Nicolet 7199 FTIR instrument. The least squares method was used to generate a standard curve of concentration versus absorbance.

3.6.2 QUANTITATIVE ANALYSIS OF OUT-GAS AND SOURCE SAMPLES BY GC/FPD

Quantitative analysis of the sulfur gases from out-gas and source sample were performed on a thermal desorber GC/FPD system. This method was chosen because the FPD detector is very sensitive towards the sulfur species, A total of four out-gas samples and three source samples were analyzed. Details of sampling and analysis are provided in Appendix E.

3.7 VERIFICATION EXPERIMENTS

These experiments were conducted to test the accuracy and precision of the sampling and analysis procedures used. The methods tested are the quantitative measurement of sulfur gases using GC/FPD and the source sampling using the experimental laser testing station. In both of these experiments, a known quantity of an authentic compound was sampled and analyzed by the respective methods. Recovery of the compound was then measured. A comparison of the amount introduced and the amount recovered would give an indication of the performance of the particular method.

3.7.1 EVALUATION OF THE GC/FPD METHOD

In order to test the feasibility of this method, the following experiments were conducted:

1) Authentic compounds of known concentrations were prepared in a glass calibration bulb. This involved injecting known volumes of the authentic compounds in a 1 L glass calibration bulb. All calibrations were carried out at atmospheric pressure and room temperature. The type and concentrations of the calibration mixtures prepared are listed below:

a) 10 ppm carbon disulfide

b) 10 ppm methyl mercaptan and 10 ppm hydrogen sulfide

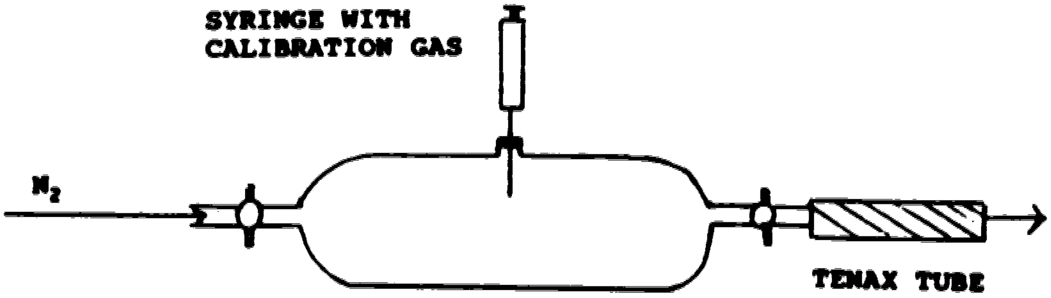
c) 10,000 ppm of hydrogen sulfide.

d) 20,000 ppm of hydrogen sulfide and 10,000 ppm methyl mercaptan.

2) Quantities of 1 mL of hydrogen sulfide were introduced into adsorbent tubes filled with molecular sieve 5A. These were desorbed to check for reproducible retention times and quantities. To introduce the calibration mixtures into the adsorbent bed, two methods were evaluated. These methods are described below:

2(a) The experimental set-up involved connection of the adsorption tube to one end of a calibration bulb while the other end was attached to a tank of pre-purified nitrogen. A stream of nitrogen was allowed to flow through the sorbent tube. A known volume of calibration mixture was introduced into the flow of nitrogen (see Figure 3.7.1-1). Two types of samples were obtained. One type dried the calibration gases prior to adsorption onto the molecular sieve 5A. The other employed direct sampling without the sodium sulfate drying stage. These experiments were designed to check if the

FIGURE 3.7.1-1 METHOD OF INTRODUCING A CALIBRATION SAMPLE ONTO AN ADSORBENT



drying agent would adsorb any of the sulfur gases and to test the desorption efficiencies of the molecular sieve 5A.

2(b) The calibration mixtures was spiked onto the adsorbent via the valve system of a commercial thermal desorber known as Dynatherm 850. The calibration mixture consisted of 10,000 ppm hydrogen sulfide, 10,000 ppm methyl mercaptan and 8 ppm carbon disulfide. The gas valves and transfer lines of the thermal desorber were heated to about 100 °C.

3.7.2 EVALUATION OF SOURCE SAMPLING FROM THE LASER TESTING STATION

The purpose of these experiments was to determine the recovery of a known substance spiked into the laser testing station. These experiments were conducted by introducing a known quantity of a known low boiling point compound into the sampling system. Low boiling point compounds were used to generate a vapor with less chance of losses due to condensation.

Four methods were experimented with. The first two methods, L1, L2, failed to produce a vapor concentrated enough to be detected by the sampling and analysis protocol developed. The sampling method S2 for Method L3 was non-quantitative and therefore was not suitable for verification experiments. Methods L1, L2 and L3 are described in Appendix F. Method, L4, was successful in carrying out the verification experiments and the method is as follows.

This method was similar to method L3 except the sampling procedure was changed. A S3 sampling method was used in this case. The experimental conditions for this experiment and results of recovery of acetone are recorded in Table 3.7.2-1.

Acetone was found to be too reactive for these experiments. Cyclohexane was used in place of acetone. To ensure that all the cyclohexane vapors were completely removed, the sampling procedure had to be modified. This required that the vapors were generated for 12 minutes while sampling continued for another 12 minutes. Thus the sampling time is 24 minutes. The generation of the organic vapors were stopped by shutting off the flow of air to the cyclohexane trap.

Two types of controlled experiments were performed. In one, the samples were collected and analyzed in an

TABLE 3.7.2-1 EXPERIMENTAL CONDITIONS FOR RECOVERY TEST USING METHOD L4 AND TWO TENAX TUBE

Acetone Used (g)	Qt (L/min)	Qs (L/min)	Ts (mins)	Recovery (%)
0.4806	2	0.50	5.0	0.03
1.4152	2	0.50	5.0	0.01

Qt	Purge rate through gas trap containing solvent
Qs	Sampling flow rate
Ts	Total sampling time

identical manner except no cyclohexane was added during the sampling period. The second controlled experiment allowed the cyclohexane to stay in the sampling chamber for 12 minutes with all conditions equivalent to the above experiments. The significant difference was that no air was allowed to purge through the cyclohexane trap. The weight of the cyclohexane was then determined before and after the 12 minutes. The experimental conditions for these experiments are tabulated in Table 3.7.2-2 and the results are reported and discussed in Section 4.7.2.

TABLE 3.7.2-2 EXPERIMENTAL CONDITIONS FOR RECOVERY TEST USING METHOD L4

Sample Tubes No	Cyclohexane (g)	Qt (L/min)	Qs (L/min)	Ts (mins)	Tenax used
1	0.37	1.0	0.5	12 + 12	2
2	0.38	1.0	0.5	12 + 12	2
3	0.52	1.0	0.5	12 + 12	2
4	0.05	1.0	0.5	11 + 10	3
5	0.02	1.0	0.5	10 + 10	3
6	0.02	1.0	0.5	10 + 10	3
7	0.02	2.0	0.3	10 + 10	3
8	0.02	2.0	0.4	10 + 10	3

Qt	Purge rate through gas trap containing solvent
Qs	Sampling flow rate
Ts	Total sampling time

4. RESULTS AND DISCUSSIONS

4.1 SAMPLING METHODS

The three source sampling procedures developed were designated S1, S2 and S3. Method S1 was designed to obtain whole gas samples (a sample containing all the components of the gas without any sample manipulation) for FTIR analysis. Method S2 was designed to obtain a very concentrated but non-quantitative sample to be analyzed by GC/MS. Method S3 was developed to obtain a quantitative sample to be analyzed by GC/FPD. The concentrations of the organic vapors obtained by these sampling methods were all significantly above the limit of detection of all the analytical instruments for a substantial number of components. Thus all the three sampling methods provided results which supplied useful information towards the project objectives.

Three out-gas sampling methods were developed but only system OG-3 was able to achieve the requirements for out-gas sampling (i.e. to obtain a sample of the trace quantities of odorous emissions of the materials cut by laser). The sample obtained had to be concentrated enough to be within the detection limits of the analytical equipment used. To accomplish this, the maximum amount of the minute traces of odors must be captured, concentrated and stored until it can be analyzed.

The first approach to the above problem was to create a vacuum around the cut fabric and draw the vapors onto an adsorbent. The sampling system OG-1 utilized this strategy but did not work. The seal in the desiccator was achieved with an with an o-ring which required a fast rate of evacuation. The sampling flow rate used in system OG-1 was only 2 L/min which was too slow to create a pressure differential in order to achieve an airtight seal. Instead air was leaking through the O-ring seal. This flaw was identified because only laboratory air and not the vapors out-gassing from the fabric were apparently adsorbed onto the Tenax. The chromatogram obtained from the sampling method OG-1 was similar to that obtained from laboratory air.

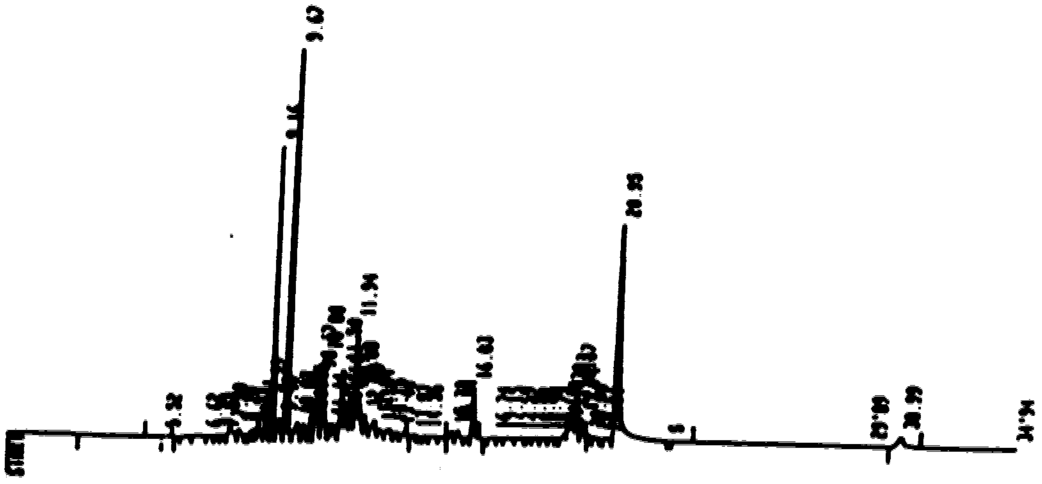
The second out-gas sampling method, OG-2 sought to transfer the odors onto the adsorbent by drawing a flow of air through the cut fabric to purge out the odors. This system was unsatisfactory because the sampling period was too long and many of the impurities in laboratory air were also concentrated. These impurities could not be removed even though it was pre-purified with calcium sulfate, granular activated carbon and molecular sieve. Calcium sulfate and molecular sieve were used to remove moisture while activated carbon was used to remove hydrocarbons.

The chromatogram of the controlled experiment where pre-purified laboratory air was drawn into the cut fabric in the canister and out of the adsorbent tubes via a pump attached through the sorbent tubes is illustrated in Figure 4.1-1. This chromatogram showed 10 large impurities. One possible solution to the above dilemma was to purge the cut fabric using a zero grade inert gas such as nitrogen or helium. This modification did not succeed because the diameter of the adsorbent tube was only 4 mm and a fairly high pressure was required to gain an appreciable flow of helium through these tubes. The lid securing the acrylic canister had a surface area of 194 cm^2 when a 70 kPa pressure was applied, the resultant 1358 N force blew the lid off the top.

The last sampling system tested was system OG-3. Three controlled experiments were carried out to test this method. The first, was to check that the blank Tenax tube was clean. This experiment is illustrated in Figure 4.1-2.

The second was designed to check the background interferences when no sample was in the canister. Figure 4.1-3 shows the chromatogram of helium being purged

FIGURE 4.1-1 CHROMATOGRAM OF PRE-PURIFIED LABORATORY AIR PURGED THROUGH THE SAMPLING APPARATUS OF SYSTEM OG-2



Column = SPB 5, 30 m long capillary column.

Temperature Program: Initial Temperature = -50 °C,

Initial Time = 4 mins

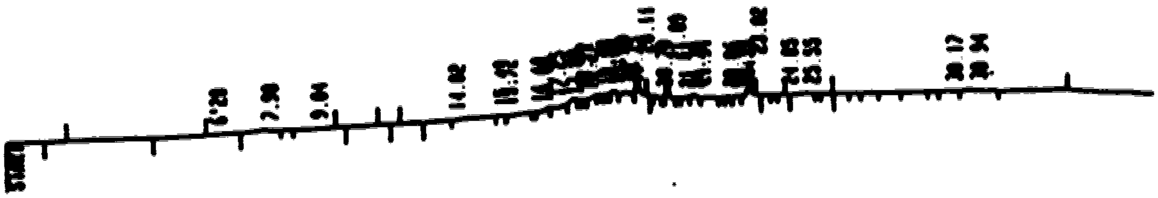
Rate = 20 °C/min

Final Temperature = 250 °C

Final Time = 35 mins

Attenuation = 2^8

FIGURE 4.1-2 CHROMATOGRAM OF BLANK TENAX TUBE FOR SYSTEM OG-3



Column = SPB 5, 30 m long capillary column.

Temperature Program: Initial Temperature = -50 °C,

Initial Time = 2 mins

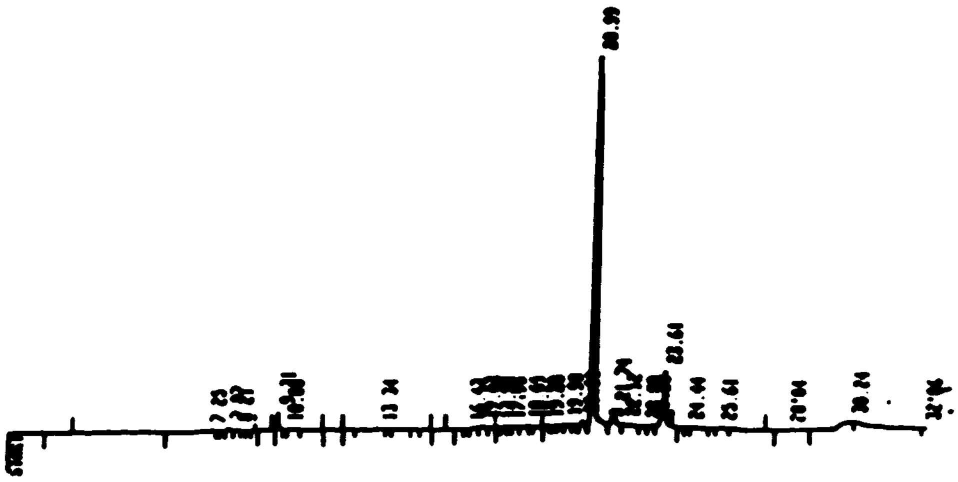
Rate = 20 °C/min

Final Temperature = 250 °C

Final Time = 35 mins

Attenuation = 2^8

FIGURE 4.1-3 CHROMATOGRAM OF HELIUM PURGED THROUGH THE SAMPLING APPARATUS OF SYSTEM OG-3



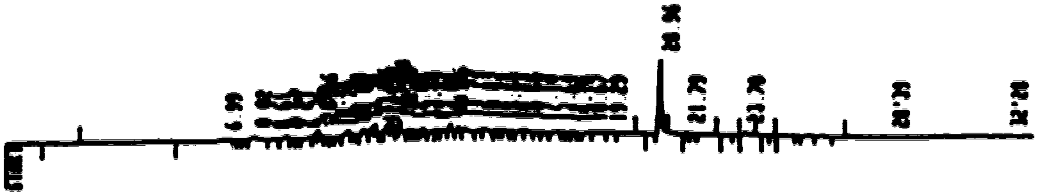
Sampling Canister = acrylic canister obtained from Pierce Chemical Co.
Column = SPB 5, 30 m long capillary column.
Temperature Program: Initial Temperature = -50 °C,
Initial Time = 2 mins
Rate = 20 °C/min
Final Temperature = 250 °C
Final Time = 35 mins
Attenuation = 2^8

through the apparatus set-up of system OG-3. Figure 4.1-4 shows the chromatogram of the Tenax tube prior to the sampling of the control experiment. This test was similar to the second experiment except a piece of wool, un-cut by laser was placed in the canister. The canister used was the canister obtained from Pierce Chemical Company. The chromatogram of this experiment is shown in Figure 4.1-5. The chromatogram of a sample of compounds that have out-gassed from laser-cut fabric is illustrated in Figure 4.1-6.

The chromatograms from the control experiments are very clean with just two contaminant peaks. The out-gas sample of compound have retention times that fall in between these two blank impurities allowing them to be detected by the FID or the Mass Spectrometer detectors.

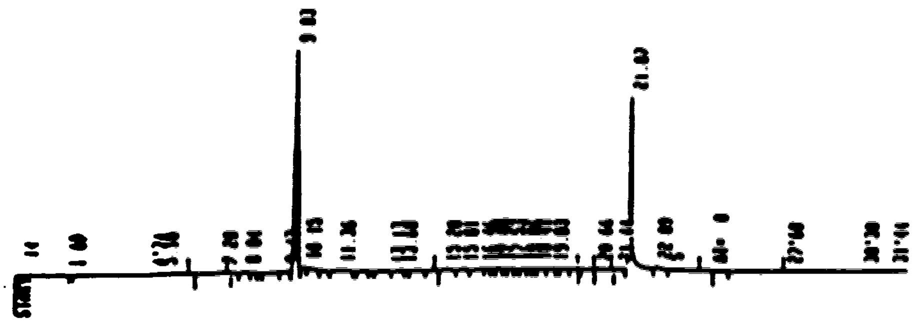
The impurity peaks were not identified at this stage. A control experiment carried out later with the stainless steel canister and GCMS under different chromatographic conditions indicated the presence of many siloxane peaks as impurities which likely arose from the septum and capillary column of the gas chromatograph.

FIGURE 4.1-4 CHROMATOGRAM OF BLANK TENAX TUBE BEFORE SAMPLING OF THE CONTROL EXPERIMENT



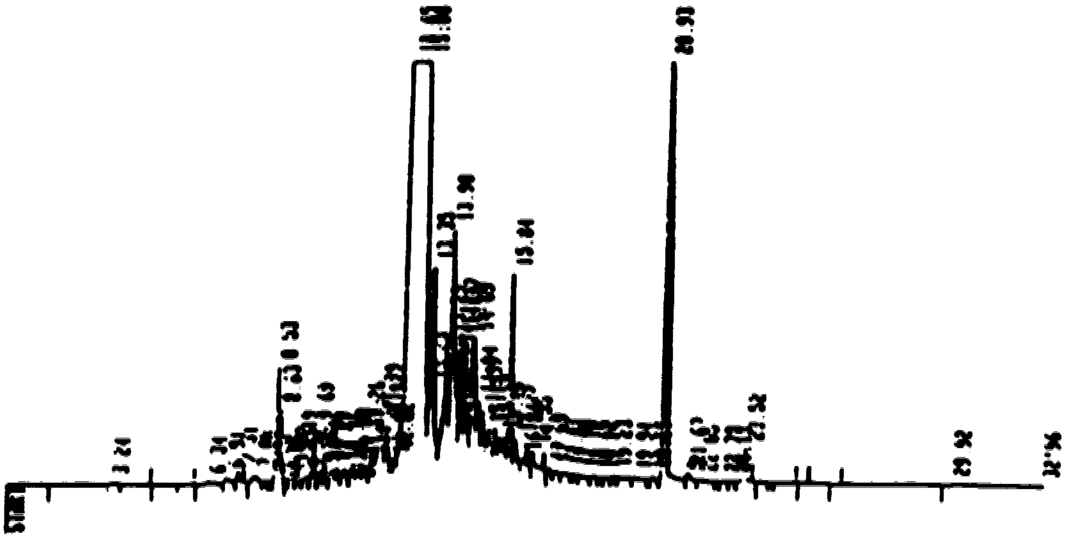
Column = SPB 5, 30 m long capillary column.
Temperature Program: Initial Temperature = -50 °C,
Initial Time = 2 mins
Rate = 20 °C/min
Final Temperature = 250 °C
Final Time = 35 mins
Attenuation = 2^8

FIGURE 4.1-5 CHROMATOGRAM OF CONTROL EXPERIMENT WITH WOOL UN-CUT BY LASER IN SAMPLE CANISTER OF SYSTEM OG-3



Column = SPB 5, 30 m long capillary column.
Temperature Program: Initial Temperature = -50 °C,
Initial Time = 2 mins
Rate = 20 °C/min
Final Temperature = 250 °C
Final Time = 35 mins
Attenuation = 2^8

FIGURE 4.1-6 CHROMATOGRAM OF AN OUT-GAS SAMPLE OF ODORS OBTAINED SYSTEM OG-3



Column = SPB 5 30 m long capillary column.

Temperature Program: Initial Temperature = -50 °C,

Initial Time = 2 minutes

Rate = 20 °C/min

Final Temperature = 250 °C

Attenuation = 2^8

4.2 THERMAL DESORPTION AND GC/FID ANALYSIS

Preliminary tests to check the cleanliness of the Tenax adsorbent and limit of detection of thermal desorption combined with GC/FID analysis indicated that this method was satisfactory. The peaks obtained from these preliminary experiments (not shown) were sharp and large.

4.3 PROBLEMS ENCOUNTERED IN THE USE OF THE PORTABLE THERMAL DESORBER

Although developing the portable thermal desorber involved a substantial amount of experimental effort, subsequent evaluation showed that major problems occurred with it's use. These led to an initial erroneous conclusion that the sampling methods used were not sufficiently sensitive to measure the odors. The problem was later found to be attributable to the back pressure from the GC preventing the transfer of the sample desorbed from the thermal desorber onto the GC. Details of the extensive trouble shooting of these methods are discussed in Appendix G.

Once the trouble shooting of the portable thermal desorber identified the source of the problems the equipment was retested on the GC/FID system. The pressure of the GC injector port was lowered to 14 kPa prior to desorption. After desorption the needle connecting the desorber to the GC was removed from the GC and the pressure was increased to 70 kPa. The chromatograms of these tests all showed many large peaks.

In the final analysis, it was the losses arising from the improper use of the portable thermal desorber that was the reason for not being able to identify the odors on the first GC/MS experiment.

4.4 GC/MS RESULTS

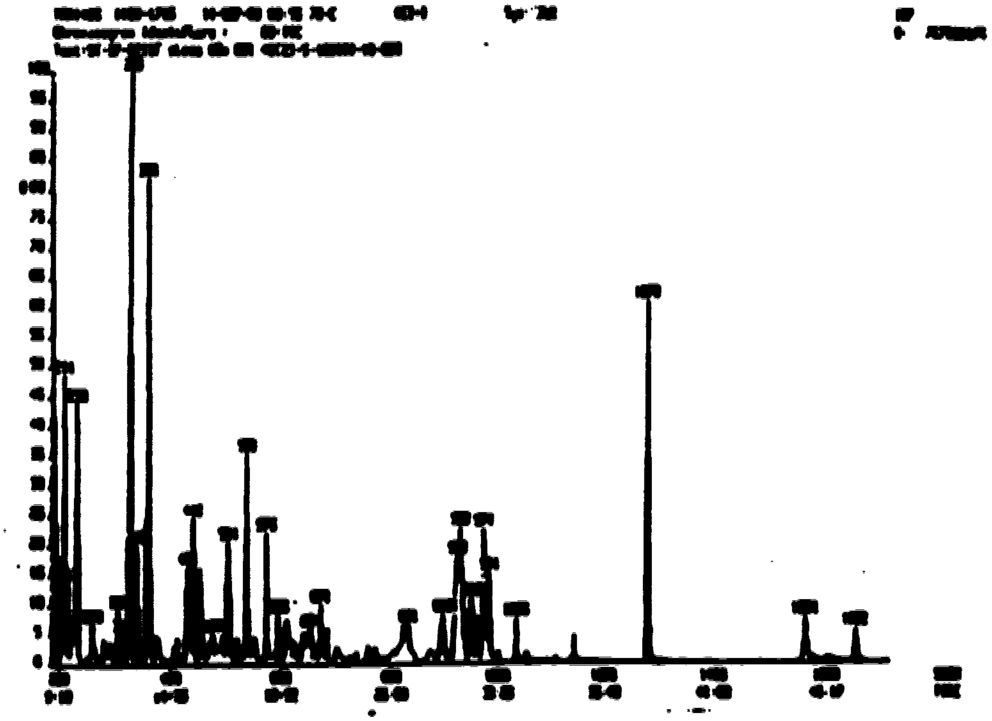
Three types of GC/MS results were obtained. The first type was from solvent desorption of a S2 sample on Chromosorb 102. The second set of results were obtained from thermal desorption of a S2 sample on Tenax and molecular sieve 5A. The third set was from thermal desorption of OG-3 sample on Tenax and molecular sieve 5A.

4.4.1 GC/MS RESULTS OF SOLVENT DESORPTION OF CHROMOSORB 102

Solvent desorption was conducted on the front and back portions of the chromosorb 102 resin. These two extracts were sniffed to assess the characteristics of the odors. The front extract had a combination of strong burnt and sulfurous odor. The back portion had a very faint burnt and sulfur odor. The GC/MS analysis for the odor sample is illustrated by the chromatogram in Figure 4.4.1-1. The control experiment conducted under the identical conditions is shown in Figure 4.4.1-2. The compounds, identified with the assistance of library match, are reported in Table 4.4.1-1. The compounds reported in this table were not found in the control experiment except for toluene. Toluene was reported because the apparent quantity was more than 10 times greater in the wool cutting experiment than in the control.

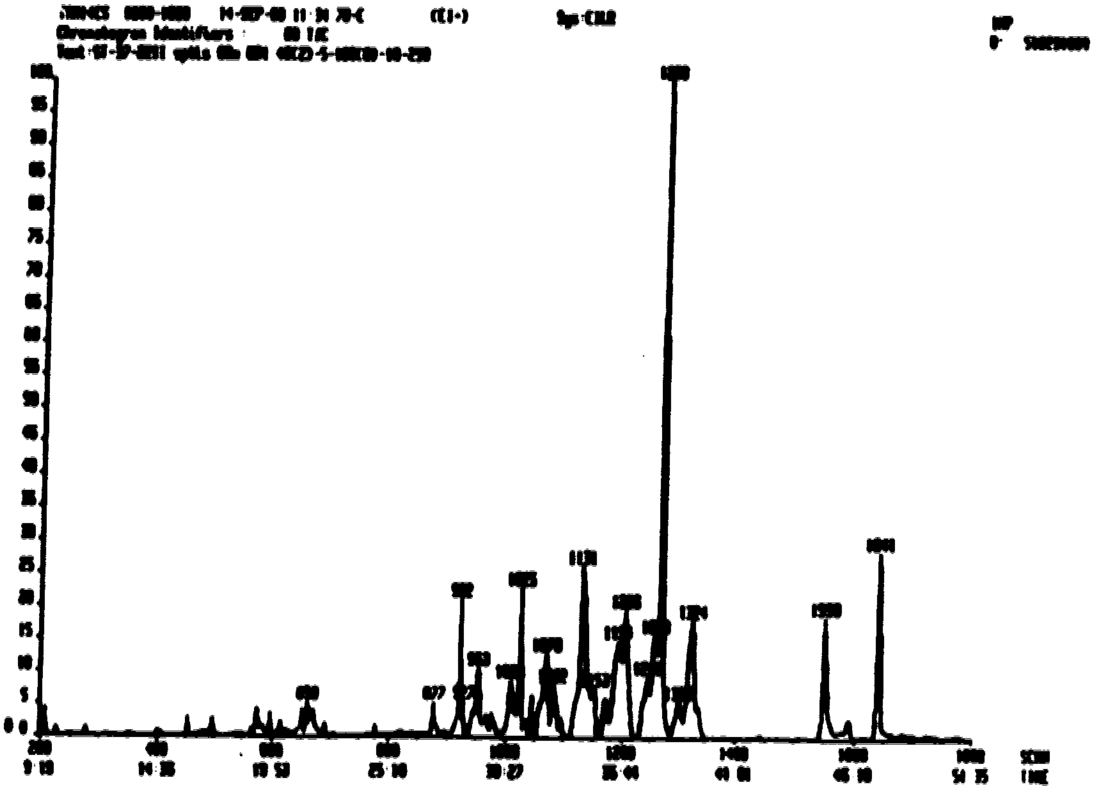
The results shows the presence of many aromatic and unsaturated hydrocarbons, chlorobenzene and dibromopropane. The presence of chlorobenzene and dibromopropane was not expected. Chlorinated and brominated compounds are not found in natural material such as wool. The control did not show the presence of these chlorinated and brominated compounds so they are not from the contamination of the system. The results of the control experiment are recorded in Table 4.4.1-2. The only explanation lies in the introduction of these compounds in processing of the raw wool into wool fabric.

FIGURE 4.4.1-1 CHROMATOGRAM FROM GCMS ANALYSIS OF CHROMOSORB 102 SOLVENT EXTRACT



Column: 60m long DB1 capillary column
Temperature Program: Initial Temperature = 40 °C,
Initial Time = 2 min
Rate = 5 °C/min
Temperature 2 = 100 °C
Rate 2 = 10 °C
Final Temperature =250 °C
Final Time = 30 mins

FIGURE 4.4.1-2 CHROMATOGRAM OF CONTROL FOR THE CHROMOSORB 102 SOLVENT EXTRACT



Column: 60m long DB1 capillary column
Temperature Program: Initial Temperature = 40 °C,
Initial Time = 2 mins
Rate = 5 °C/min
Temperature 2 = 100 °C
Rate 2 = 10 °C
Final Temperature =250 °C
Final Time = 30 mins

TABLE 4.4.1-1 DECOMPOSITION PRODUCTS FROM THE LASER CUTTING OF WOOL TENTATIVELY IDENTIFIED BY SOLVENT DESORPTION GC/MS ANALYSIS

DECOMPOSITION PRODUCTS*
HYDROCARBON (C_7H_{16})
TOLUENE
HYDROCARBON (C_8H_{18})
UNKNOWNS
DIMETHYLBENZENE
ETHYL BENZENE
ETHYNYL BENZENE
ETHENYL BENZENE
DECENAL
METHYL ETHYL BENZENE
DIBROMOPROPANE
PROPENYL BENZENE
BENZALDEHYDE
PROPYL BENZENE
PROPYLNYL-BENZENE
DICHLORO-BENZENE
PHENYL -PROPENOL
BUTENYL BENZENE
BENZONITRILE
AROMATIC ALCOHOL ($C_9H_{10}O$)
HYDROCARBON ($C_{11}H_{22}$)
BENZENE ACETONITRILE
AROMATIC HYDROCARBON ($C_{10}H_{10}$)

* Results from a single experiment

All except toluene were not present in the control experiment. Toluene was included because the amount of toluene in the experiment was much larger than the control.

TABLE 4.4.1-2 COMPOUNDS TENTATIVELY IDENTIFIED FROM THE EFFLUENT OF CONTROL EXPERIMENT OF THE LASER CUTTING OF WOOL IDENTIFIED BY SOLVENT DESORPTION GC/MS ANALYSIS*

COUMPOUNDS PRESENT IN CONTROL EXPERIMENT
TOLUENE
UNKNOWN
HEXAMETHYL CYCLOTRISILOXANE
2,2,6-TRIMETHYL-OCTANE
OCTAMETHYL-CYCLOTETRASILOXANE
HEXACHLOROETHANE
1-ETHENYL-3-ETHYL-BENZENE
2,4,6,-TRIMETHYL-OCTANE
1-BROMO-4,3,1,13,8-TRICYCLO-UNDECANE
DECAMETHYL-CYCLOPENTASILOXANE
DEHYDRO-2,6-DIMETHYL-NAPHTHALENE
1-METHYLENE-1H-INDENE
UNKNOWN
1,2,4-TRIETHYL-BENZENE
2,6-BIS(1,1-DIMETHYLETHYL)-4-METHYL PHENOL
2-METHYL-1-(1,1-DIMETHYLETHYL)-PROPANOIC ACID
2,6,11-TRIMETHYLDODECANE
UNKNOWN SILICON-TYPE COMPOUNDS
DOCOSANE
UNKNOWN SILICON TYPE COMPOUNDS
TRIDECANOL
UNKNOWN PHTHALATE-TYPE COMPOUNDS

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* Results from a single experiment

4.4.2 GC/MS RESULTS FROM THERMAL DESORPTION OF TENAX AND MOLECULAR SIEVE 5A

Two types of samples were obtained on two types of adsorbents. Table 4.4.2-1 lists the types of chemical compounds found in the laser effluent from source sampling. The data obtained were tentatively identified with library matches. Extra information were also obtained from EPA/NIH Mass Spectral Data Base book (Heller and Milner.1980; Heller et al.1983.).

The mass spectrum, #239 from the molecular sieve 5A sample likely consists of three compounds coeluting together. These were identified as hydrogen sulfide, carbonyl sulfide and some unknown compound. Hydrogen sulfide and carbonyl sulfide were identified because the very characteristic parent peak of 34 for hydrogen sulfide and 60 for carbonyl sulfide was observed in this spectrum. Number 249 from the molecular sieve 5A sample likely consisted of 2 coeluting peaks of methyl mercaptan and 1-butene. This spectrum was identified as such because superimposing spectrums of 1-butene and methyl mercaptan gave an almost identical match to that of peak #249. Table 4.4.2-2 shows the chemical compounds identified in the control compound. These inferences must remain as tentative because they have not been verified by

TABLE 4.4.2-1 VOLATILE CHEMICALS TENTATIVELY IDENTIFIED AS GENERATED FROM THE LASER CUTTING OF WOOL MATERIAL[*]

CHEMICALS FROM TENAX SOURCE SAMPLE	CHEMICALS FROM MOLECULAR SIEVE 5A SOURCE SAMPLE
CARBON DIOXIDE	CARBON DIOXIDE
CARBONYL SULFIDE	HYDROGEN SULFIDE
N-METHYLMETHANAMINE	PROPENE
METHYL-PROPENE	CARBONYL SULFIDE
DIMETHYL CYCLOPROPANE	METHYL MERCAPTAN
PROPANONE	CARBON DISULFIDE
PENTADIENE	BUTENE
PROPENENITRILE	CYCLOPROPANE CARBONITRILE
METHYL-PROPENOL ACETATE	METHYL PROPENOL ACETATE
TETRAHYDRO-DIMETHYL 2H PYRANONE	BUTENOIC ACID
UNKNOWNS	BENZENE
BENZENE	SULFUR DIOXIDE
DIMETHYLBUTANENITRILE	TOLUENE
ISOTHIAZOLE	ETHYL BENZENE
PENTADIENENITRILE	ETHENYL BENZENE
TOLUENE	UNKNOWNS

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[*] Results from a single experiment

Compounds sampled on molecular sieve 5A and Tenax were tentatively identified by thermal desorption and GC/MS analysis

TABLE 4.4.2-2 THE VOLATILE CHEMICALS TENTATIVELY IDENTIFIED FROM THE CONTROL EXPERIMENT FROM SOURCE SAMPLING*

CHEMICALS FROM TENAX	CHEMICALS FROM MOLECULAR SIEVE 5A
SILOXANE COMPOUNDS	CARBON DIOXIDE
METHYL-OXO-TRIMETHYLSILYL	METHANETHIOL HOMOPOLYMER
BUTANOIC ACID	BUTENE
$C_{12}H_{24}O_3$	TRIMETHYL SILANOL
OCTAMETHYL TRISILOXANE	PROPOXY-PROPENE
UNKNOWN	BENZENE
	METHYL HEXANAMINE
	TOLUENE
	C_4H_9
	SILOXANE COMPOUNDS
	TRISILOXANE OCTAMETHYL
	METHYL PENTADECANE
	SILOXANE COMPOUNDS
	OCTAMETHYL TRISILOXANE
	TRIDECATRIENENITRILE
	UNKNOWNS

---

* Results from a single experiment
Compounds sampled on molecular sieve 5A and Tenax were tentatively identified by thermal desorption and GC/MS analysis

determining the retention times of appropriate standards.

A list of the chemicals tentatively identified in the vapors emitted from cut-wool are reported in Table 4.4.2-3. The control experiment are reported in Table 4.4.2-4.

There were many significant differences in the types of compounds sampled onto Tenax and molecular sieve 5A. In general more nitriles were found from Tenax samples and more sulfur compounds were acquire from molecular sieve 5A. These results are consistent with expectations from the literature survey. For example, Black et al. (1978) found empirically that molecular sieve 5A can retain hydrogen sulfide and sulfur dioxide about 200 times more efficiently than Tenax. These compounds could also be recovered to 80 % within 2 days of storage time. Consequently, each of these adsorbents should be selected for the specific class of compounds known to be suited to the adsorbents capabilities.

4.5 RESULTS FROM ODORGRAM EXPERIMENT

Using authentic ethanol and carbon disulfide, tests correlating odors sensed by the human nose with the peaks sensed by the FID detector confirmed that the odor sensed by the nose corresponded with the retention time of the

TABLE 4.4.2-3 VOLATILE CHEMICALS TENTATIVELY IDENTIFIED AS EMITTED FROM WOOL MATERIAL AFTER IT HAD BEEN CUT BY LASER*

CHEMICALS FROM TENAX OUT-GAS SAMPLE	CHEMICALS FROM MOLECULAR SIEVE 5A OUT-GAS SAMPLE
CARBON DIOXIDE	CARBON DIOXIDE[3]
N-METHYLMETHAMINE	N-METHYLMETHAMINE[1]
	CARBONYL SULFIDE[1]
	SULFUR DIOXIDE[1]
	PROPANE[1]
	BUTYRALDEHYDE[1]
	BUTENOIC ACID[3]
	DIMETHYL PROPANAL[1]
	METHYL BUTANOL[2]
	UKNOWNS[3]

[*] Compounds sampled on molecular sieve 5A and Tenax were tentatively identified by thermal desorption and GC/MS analysis. The Tenax sample was from a single experiment and the molecular sieve 5A samples were from two experiments.

[1] indicates compound presence on first spectrum

[2] indicates compound presence on second spectrum

[3] indicates compound presence on both spectrum

TABLE 4.4.2-4 VOLATILE CHEMICALS TENTATIVELY IDENTIFIED AS EMITTED FROM OUT-GAS CONTROL EXPERIMENT*

CHEMICALS FROM TENAX	CHEMICALS FROM MOLECULAR SIEVE 5A
CARBON DIOXIDE	ARGON[1]
ARGON	CARBON DIOXIDE[2]
SILOXANE TYPE COMPOUNDS	SILOXANE TYPE COMPOUNDS[1]
DECAMETHYL CYCLOPENTASILOXANE	DECAMETHYL CYCLOPENTASILOXANE[1]
DODECAMETHYL CYCLOHEXASILOXANE	DODECAMETHYL CYCLOHEXASILOXANE[2]
	METHYL-(DIMETHYLETHYL)-PROPANOIC ACID[2]
	BUTYL-METHYL-PROPYL-1,2-BENZENE-DICARBOXYLIC ACID[1]
	BIS(2-ETHYL HEXYL) PHTHALATE[2]
	SQUALENE[1]

* Compounds sampled on molecular sieve 5A and Tenax were tentatively identified by thermal desorption and GC/MS analysis. The Tenax sample was from a single experiment and the molecular sieve 5A samples were from two experiments.

[1] indicates compound presence on first spectrum

[2] indicates compound presence on both spectrum

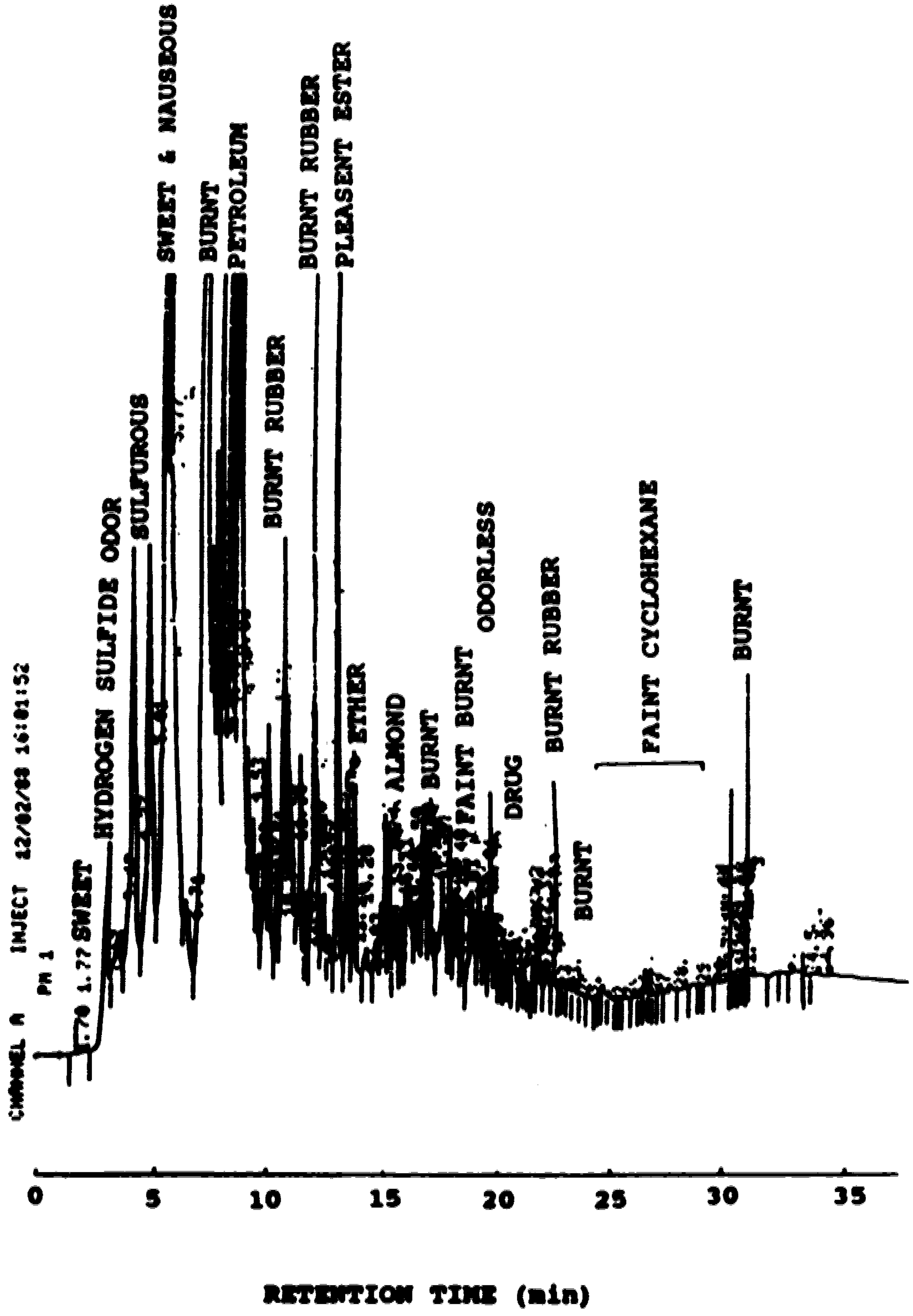
peak on the chromatogram.

The results from the single experiment with odors from source sampling indicated the presence of 11 basic types of odors. These are identified by the author's nose test as being hydrogen sulfide, sulfurous ,sweet but nauseous, burnt rubber, pleasant ester, almond, ether, burnt, drug, petroleum and cyclohexane. Figure 4.5-1 shows a chromatogram of odors obtained from source sampling. Table 4.5-1 shows the retention time and corresponding odors.

The odorgram results were compared with results of chemical compounds identified from thermal desorption in Table 4.4.2-1. The results were recorded in order of compounds elution from the column. It can be seen from Table 4.4.2-1 that sulfurous compounds were eluted first followed by n-methylamine, a series of hydrocarbons and then nitiles. The literature review of diesel exhaust indicated that aromatic hydrocarbons had the following characteristic odors described as:

a) oily (petroleum -like odor)
b) burnt
c) pungent
d) unpleasant and burnt.

FIGURE 4.5-1 TYPICAL ODORGRAM OF THE EXHAUST GENERATED FROM LASER CUTTING OF WOOL*



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*Observations from a single experiment

TABLE 4.5-1 RETENTION TIME AND CORRESPONDING ODOR CHARACTERISTICS OF THE ODORGRAM FROM FIGURE 4.5-1

RETENTION TIME (MIN)	ODOR CHARACTERISTICS
1	SWEET
1 TO 2	STRONG HYDROGEN SULFIDE
3 TO 5	STRONG SULFUR
5 TO 6.7	SWEET AND NAUSEOUS
7	STRONG BURNT
8.5	BURNT
8.5 TO 9.5	PETROLEUM
9.5 TO 12.2	BURNT RUBBER
12.5	PLEASANT ESTER
13.5 TO 14	ALMOND
15 TO 16	BURNT
18 TO 20	NO SMELL
20 TO 21	DRUG
21 TO 22	BURNT RUBBER
22 TO 23	BURNT
22 TO 28	FAINT CYCLOHEXANE

It is also reported that nitriles and hydrogen cyanide have an almond smell. The odorgram corresponded well with the type of compounds found from GC/MS analysis.

The results in this experiment were obtained by one observer. It is known that different observers may give different descriptions to the same odors. There are great variations in sensitivity of odor perception ability from one individual to another. The odorgram experiment was conducted only as a check on the results of the analytical experiment. Only an in depth study with a trained odor panel, many duplicated experiments and varying conditions can produce results with a high level of confidence.

4.6 QUANTITATIVE RESULTS FOR SOURCE AND OUT-GAS SAMPLE

The quantitative results acquired by FTIR analysis were reported in Table 4.6-1. There was no sample work-up for the sample used in FTIR analysis. Therefore, all artifacts from sample manipulations were eliminated. The draw backs of this method was in the possible loss of the more permeable gases during storage, and through condensation of compounds on the wall of the bag. The first disadvantage was minimized by having the analysis

TABLE 4.6-1 RESULTS FROM FTIR ANALYSIS OF SOURCE SAMPLE COLLECTED IN A TEDLAR BAG[*]

COMPOUNDS IDENTIFIED	QUANTITY (PPM)	WAVENUMBER (CM^{-1})
ACETYLENE	TRACE	730
AMMONIA	50	930/965
CARBON DIOXIDE	1340[a]	2349
CARBON MONOXIDE	61	2142
CARBONYL SULFIDE	5	2060
ETHYLENE	0	957
HYDROGEN CHLORIDE	0	714
HYDROGEN CYANIDE	43	714
METHANE	11	3032
NITROUS OXIDE	0	2220
NITRIC OXIDE	0	1876
NITROGEN DIOXIDE	0	1618

[*] Results of a single experiment

[a] Included ppm of CO_2 in air (450 ppm) and sample (890 ppm)

performed within an hour of sampling. Since the FTIR was carried out at room temperature and pressure, any vapor that will condense out at room temperature cannot be determined by this technique.

Syringe injections of the source samples obtained as whole samples in Tedlar bags did not show any peaks. Ordinarily, these concentrations were high enough that quantitative measurements could be acquired without pre-concentrations if the GC/FPD was in a good working order. Pre-concentration was necessary in this case. The results obtained from source sampling and analyzed by GC/FPD are detailed in Table 4.6-2. The results of samples obtained from out-gas sampling System OG-3 and analyses by GC/FPD are presented in Table 4.6-3.

The results obtained from the GC/FPD analysis were deemed not accurate and should be viewed as only very rough approximations of real concentration of these sulfur compounds. There is one major reason and a minor reason for this. The major problem was that the FPD was not working at it's optimum sensitivity and authentic carbonyl sulfide was not available for calibration. The calibration factor for calculation of the carbonyl sulfide was assumed to be similar to methyl mercaptan. An in depth discussion of this problem is provided in Appendix H

TABLE 4.6-2 TYPES AND QUANTITIES OF SULFUR GASES FROM SOURCE SAMPLES ANALYZED BY THERMAL DESORPTION GC/FPD

SAMPLE NO.	H2S (PPM)	COS* (PPM)	CH3SH (PPM)	TOTAL SULFUR (PPM)
1	6.0	1.0	0.1	7.1
2	2.0	5.4	1.0	8.4
3	3.0	5.0	1.0	9.0
AVE	3.7±1.7	3.8±2.0	0.7±0.4	8.2±0.8

± denotes the standard deviation for three samples.

* concentration of COS was estimated using the calibration factor for methyl mercaptan.

TABLE 4.6-3 QUANTITY OF CARBONYL SULFIDE FROM OUT-GAS SAMPLES ANALYZED BY THERMAL DESORPTION GC/FPD

SAMPLE NO.	COS* (PPB)
1	42
2	46
3	20
4	35
AVE	36±10

± denotes the standard deviation for 4 samples.

* concentration of COS was estimated using the calibration factor for methyl mercaptan.

4.7 RESULTS FROM QUANTITATIVE ANALYSES

A series of evaluations were conducted to determine the ability of the procedures being used to provide quantitative results. These results are described in Appendix H. Overall quantitative results were inconsistent and the recovery of a spiked known compound, cyclohexane was extremely low, (average of 12.4 %). Consequently the results from this study must be considered strictly qualitative with the exception of the single set of FTIR results.

4.8 FINAL DISCUSSION

The sampling and analysis methods developed were able to identify some of the chemical compounds generated in the laser cutting of wool. These methods were also successful in identifying some of the out-gas chemicals emitted from laser cut wool. The odorgram method corresponded extremely well with the compounds identified by GC/MS. This method also confirmed that many of the chemical species separated were odorous. Thus, the first four objectives defined for this project were achieved. The last objective however, was not attained. The method used to quantify the sulfur compound was capable of measuring the chemicals accurately.

The poor results from the quantitative measurements were attributed mainly to FPD detector. The portable thermal desorber, although invaluable to this project, contributed to poor quantitative measurement. Two major shortcomings of this equipment in quantitative measurements arose from back pressure and dead spaces in the instrument it interfaced with. Back pressure may be resolved by lowering the pressure in the injector port. This process may allow some of the vapors to be trapped in dead spaces. If the portable desorber were to interface with a capillary column, the back pressure problem could also be resolved by using a shorter megabore column. The portable thermal desorber was designed to be small, transportable and easy to interface with any GC system. These features were particularly useful for qualitative analysis. However, for quantitative analysis a commercial thermal desorber permanently hooked up to a GC, with the problems of dead spaces and back pressure solved, should give better quantitative results. The early stages of this project would have been accomplished much more effectively if there had been a permanent thermal desorber, GC/MS system set up for air analysis. Each machine the thermal desorber was interfaced with had its own dead spaces and back pressure problems that had to be recognised and minimised before the effective work could commence.

A total of 46 different compounds were tentatively identified as present in the source sample. Table 4.8-1 presents a combined list of all different compounds. Approximate concentrations of gas detected by FTIR are reported on the basis of the one sample subjected to this analysis. Approximate concentrations of the gas detected by GC/FPD were also reported.

The control experiment obtained for the source sample on a Tenax adsorbent was relatively clean, containing mainly siloxane type of compounds. These compounds come mainly from the GC column and septum. These type of compounds were often detected as background in most GC/MS runs. A similar control experiment obtained on a molecular sieve 5A adsorbent showed many siloxane compounds and traces of methanethiol polymer and some hydrocarbons. These traces are probably out-gassed from the walls of the laser effluent station.

A total of nine compounds were identified to be present in the out-gas cut fabric sample. The types and some concentrations are reported in Table 4.8-2. The control experiments for these samples on molecular sieves 5A and Tenax were mainly carbon dioxide, argon, siloxane

TABLE 4.8-1 COMBINED LIST OF CHEMICALS TENTATIVELY IDENTIFIED FROM THE LASER CUTTING OF PURE WOOL MATERIAL

COMPOUNDS TENTATIVELY IDENTIFIED	CONCENTRATION (PPM)	ODOR CHARACTERISTICS (THRESHOLD,PPM)
ACETYLENE		
AMMONIA	50[a]	PUNGENT
AROMATIC ALCOHOL ($C_9H_{10}O$)		
ALKYL BENZENE ($C_{10}H_{10}$)		
BENZALDEHYDE		BURNT AND SMOKY[b]
BENZENE		SWEET SOLVENT
BENZENE ACETONITRILE		
BUTENE		
BUTENOIC ACID		
BUTENYL BENZENE		RUBBERY, MUSTY, OILY[b]
CARBON DIOXIDE	1,340[a,c]	ODORLESS
CARBON DISULFIDE		
CARBON MONOXIDE	61[a]	ODORLESS
CARBONYL SULFIDE	5[a], (3.0±2.0)	
CYCLOPROPANE CARBONITRILE		
DECENAL		
DIBROMOPROPANE		
DICHLORO BENZENE		
DIMETHYL CYCLOPROPANE		
DIMETHYLBENZENE		PUNGENT[b]
DIMETHYLBUTANENITRILE		
ETHENYL BENZENE		UNPLEASANT[b]
ETHYL BENZENE		PUNGENT[b]
ETHYNYL BENZENE		
HYDROCARBON ($C_{11}H_{22}$)		
HYDROCARBON (C_8H_{18})		
HYDROCARBON (C_7H_{16})		

(CONTINUED...)

TABLE 4.8-1 (CONTINUED)

COMPOUNDS TENTATIVELY IDENTIFIED	CONCENTRATION (PPM)	ODOR CHARACTERISTICS (THRESHOLD,PPM)
HYDROGEN CYANIDE	43[g]	ALMOND
HYDROGEN SULFIDE	(3.7±1.7)	ROTTEN EGG(0.0005 to 0.032)[a]
ISOTHIAZOLE		
METHANE	11[g]	
METHYL ETHYL BENZENE		
METHYL MERCAPTAN	(0.7±0.4)	DECAY CABBAGE(0.0021)[a]
METHYL-1,2PROPEN-1-OL ACETATE		
METHYL-PROPENE		
N-METHYLMETHANAMINE		FISHY
PENTADIENE		
PENTADIENENITRILE		
PHENYL-PROPENAL		
PROPANONE		
PROPYL BENZENE		
PROPYLNYL-BENZENE		
SULFUR DIOXIDE		PUNGENT & IRRITATING[c]
TETRAHYDRO-DIMETHYL 2H PYRANONE		
TOLUENE		ODORLESS[b]
UNKNOWNS		

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a) from NRC, 1979.
b) Springer et al., 1973
c) Dague, 1972
d) combination of CO_2 in air and sample
e) estimated concentrations in brackets were from GC/FPD results
(±) denotes standard deviation of three GC/FPD experiments
f) results from FTIR are from a single experiment
g) estimated concentrations from FTIR analysis

TABLE 4.8-2 COMBINED LIST OF CHEMICALS REPORTED IN THE OUT-GAS ODORS EMITTED FROM CUT WOOL MATERIAL

COMPOUND IDENTIFIED	ESTIMATED CONCENTRATION (PPB)	ODOR CHARACTERISTICS
BUTENOIC ACID		
BUTYRALDEHYDE		BURNT, SMOKY, METALLIC[a]
CARBON DIOXIDE		ODORLESS
CARBONYL SULFIDE	36±10[c]	
DIMETHYL PROPANAL		
METHYL BUTANOL		
N-METHYLMETHAMINE		
PROPANE		
SULFUR DIOXIDE		PUNGENT & IRRITATING[b]
UNKNOWNS		

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[a] Springer et al., 1973

[b] Bague, 1972

[c] quantitative analysis was by GC/FPD

± denotes the standard deviation of four samples compounds and phthalates. The carbon dioxide and argon comes from air and siloxanes comes from the septums and capillary columns. It is uncertain where the phthalates come from, however, phthalates are plasticizers commonly present in fabrics and plastics.

The chemicals identified from source sampling can be compared with Chaigneau and Le Moan (1976) pyrolysis studies of wool in a vacuum and combustion of wool, discussed in section 2.7. Only their results at 1000 °C (rather than those at 500 °C) will be used in this comparison because the temperature at which lasers cut the wool is expected to be higher than 1000 °C. Their results were reported in Table 2.7.2. Most of the products found in their studies were also found in this study. Hydrogen, nitrogen, ethylene, ethane and propane which were not found in this study. Neither hydrogen nor nitrogen would have been detectable by the methods used in this study.

In this investigation many compounds were tentatively identified which were not reported by Chaigneau and Le Moan. A whole series of unsaturated hydrocarbons, nitriles, aromatic hydrocarbons, a few alcohols and acids were also found. The concentrations of these compounds are probably several orders of magnitude less than those found in Chaigneau and Le Moan (1976) studies and in FTIR analysis conducted in this investigation. Thus the Chaigneau and Le Moan (1976) studies are best compared to the FTIR results. In their study, the amount of compounds which were identified by mass spectrometry in descending order were hydrogen cyanide, carbon monoxide, methane and carbon dioxide. In this investigation, however, the compounds found with concentrations in descending order were carbon dioxide, carbon monoxide, ammonia, hydrogen cyanide, methane and carbonyl sulfide. The major sulfur compound found in this study was carbonyl sulfide while the major sulfur species found in Chaigneau and Le Moan was hydrogen sulfide in the pyrolysis study. They also found that the amounts of hydrogen sulfide and hydrogen cyanide found in their combustion study were dependent on temperature, air supply and rate of pyrolysis.

A considerable amount of ammonia was found in this study but was not determine in Chaigneau and Le Moan (1976). The laser cutting operation is neither a simple combustion nor a simple pyrolysis process. Because of the complexity of degradation processes occurring and the wide range of temperatures involved, it was expected that there may be some notable differences in the degradation products compared with combustion and pyrolysis studies. However, the major degradation products of pyrolysis and combustion were also obtained in the laser operation.

5. SUMMARY AND CONCLUSION

1. A combination of air sampling and analytical methods were devised and used in the characterization of a complex mixture of odorous compounds generated during the laser cutting of wool and cut fabric. The sampling methods used were whole gas sampling with a Tedlar bag and pre-concentration with Molecular Sieve 5A, Tenax and Chromosorb 102. The samples were analyzed on GC/MS, FTIR and GC/FPD systems.

2. A portable thermal desorber was designed to provide an easy interface with a gas chromatograph. It can be used successfully only if the back pressure problem is minimized. The thermal desorber was designed to be used only for qualitative analysis and may not be suitable for quantitative trace analysis in the ppb range.

3. The odors from source and out-gas sampling were described as having the "smell of burning hair". The odorgram method separated the complex odor mixtures and identified eleven basic odors in laser effluent. These odors were described as sweet, hydrogen sulfide, sweet and nauseous, sulfur, burnt, petroleum, burnt rubber, pleasant ester, almond, burnt, drug, faint

cyclohexane. The order of elution of the smells corresponded to the compounds identified by the analytical method.

4. The concentrations of the species identified by FTIR are reasonably accurate but those obtained on the GC/FPD are unreliable.

5. Only 12 % of a surrogate chemical (cyclohexane) introduced into the laser testing station could be recovered by the sampling and analysis method used.

6. A total of 46 compounds were tentatively identified to be present in the source sample.

7. A total of nine compounds were identified to be present in the out-gas cut fabric sample.

8. The results of this work are qualitative in nature and they provide an insight into the likely by-products of laser cutting of wool. This insight could form the basis for pursuing a quantitative evaluation of emission by-products which could be necessary to develop a reliable understanding of occupational health risks.

6. RECOMMENDATIONS

This investigation produced a useful insight into the chemical composition of decomposition products and odors generated and emitted from laser cutting of wool. However, it was not possible to provide a good quantitative measure of the odorous compounds due to instrument failure and financial constraints. More consistent quantitative measurements of these odors are required to determine their chemical health hazards and to design engineering controls required. Suggested analytical procedures for further research are:

1. The quantitative measurements of the sulfur compounds can be conducted on a GC/FPD analytical system but this system would have to be modified to obtain a reduced dead volume FPD detector. A megabore mixed phase (DB-1/DB-WAX) capillary column will probably give a better separation and better quantitative results. This system was described in detail by Barinaga (1987). No pre-concentration of sample will be required for this instrument because it's detection limits are only 40 to 60 pg.

2. Quantitative measurement of hydrocarbons, aldehydes and nitriles should be performed on a thermal desorber

attached to a GC/FID or GC/MS system.

3. The odorgram experiment should be conducted with a trained odor panel.

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APPENDIX A

A1. DESCRIPTION OF LABORATORY EFFLUENT TESTING STATION

The laser cutting chamber consisted of an acrylic sampling enclosure. This enclosure had a metal vacuum pan, a cutting bed, a nozzle assembly and a positioning system. The nozzle assembly consisted of a nozzle, a 127 mm focal length lens and an air supply. The cutting bed was made from a sheet of aluminum with numerous holes in the shape of a honeycomb. In this system, the laser beam was directed by a series of mirrors which channeled the beam through a nozzle. The nozzle and lens assembly focused the beam onto the surface of the material to be cut by the laser. The nozzle was hooked up to a flow of air. As the laser beam cut the fabric, the continuous stream of air passing through the nozzle prevented a fire from starting and directed the dusts and decomposition products away from the lens in the nozzle right into the cutting bed and vacuum pan below. The honeycomb surface of the cutting bed was designed to dissipate excess laser energy and allowed gaseous vapors and particulate formed during the cutting process to be blown into the vacuum pan below. During the laser cutting operation, the vacuum pan would move in the X direction as the nozzle moves in the Y direction. This movement was controlled by a positioning system known commercially as the ANORAD positioner. The vacuum pan and nozzle-air supply assembly were completely enclosed in the acrylic sampling chamber. The sampling enclosure was kept under negative pressure by operating the exhaust fan. The velocity pressure of the flue gas was measured with a differential pressure gauge. The flow rate, Q, could then be calculated from the velocity pressure (Table A1-1)

TABLE A1-1 CALCULATION OF FLOW RATE (Q) OF EXHAUST FROM ACRYLIC SAMPLING BOX

$$Vp = Tp - Sp$$

$$Vp = (v^2 d)/2$$

$$v = (2Vp/d)^{1/2}$$

$$Q = v * A$$

Tp = total pressure (Pa)
Sp = static pressure (Pa)
Vp = velocity pressure (Pa)
v = velocity of flow (m/s)
Q = flow rate (m^3/s)
A = cross section area of pipe (m^2)
d = density of air = 1.2 Kg/m^3

A2. SOURCE SAMPLING SYSTEM S1

A small sampling probe was inserted into the exhaust pipe (Figure 3.1.1-1). A sample of the vapors was then collected into a Tedlar bag by drawing the sample through a membrane filter with a diaphragm pump while the exhaust kept the entire sampling enclosure under negative pressure. The pump could be adjusted to draw an air sample at a certain flow rate. Short length of flexible Tygon tubing was used to connect the sampling probe to the pump.

A3. SOURCE SAMPLING SYSTEM S2

The vacuum pan and the corresponding acrylic chamber were identical to System S1 (Figure 3.1.1-2). The difference between S1 and S2 was in the method of sampling. The vacuum pan was partitioned into 1/6 of it's original volume and the sampling enclosure was not kept under negative pressure when the sampling was in progress. Instead, sampling commenced immediately as 2 to 10 cuts were made. Each cut was 70 mm long. This was continued for another 5 minutes after the laser and air assist have been turn off. In this way, a concentrated non-quantitative sample was obtained.

A4. SOURCE SAMPLING SYSTEM S3

In this system, a sample of the source effluent was obtained by drawing the effluent through a membrane filter into adsorbent tubes with a diaphragm pump (Figure 3.1.1-3). The entire sampling chamber was kept under negative pressure during this process while a well mixed source effluent with a uniform concentration was obtained. Therefore, quantitative analysis could be conducted using the measured flow quantities.

A5. SYSTEM OG-1

In System OG-1 (Figure A5-1), the laser-cut material was stored in a desiccator. One end of the adsorbent tube was connected to the outlet of the desiccator and the other end was attached to a diaphragm pump. Air was pumped out of the desiccator through the Tenax tube.

A6. SYSTEM OG-2

In System OG-2 (Figure A6-1), the cut material was placed into a special canister. This canister was made of an acrylic pipe sealed with an O-ring and a lid at the ends. Two Swagelok fittings were secured about 2 mm from the top and bottom of the cannister. These fittings

FIGURE A5-1 SYSTEM OG-1 OUT-GAS SAMPLING

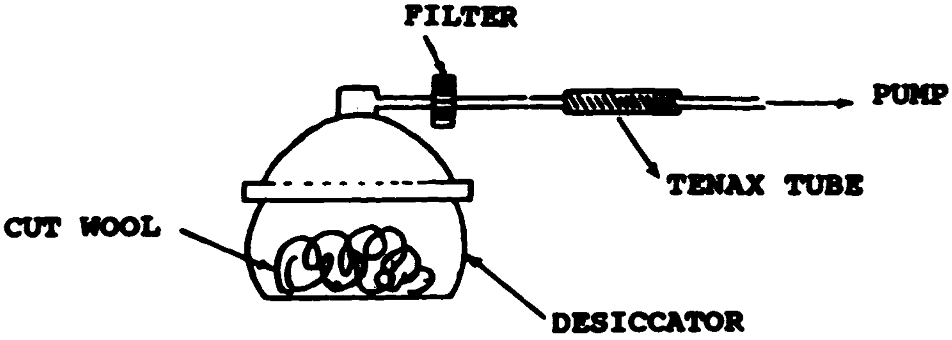
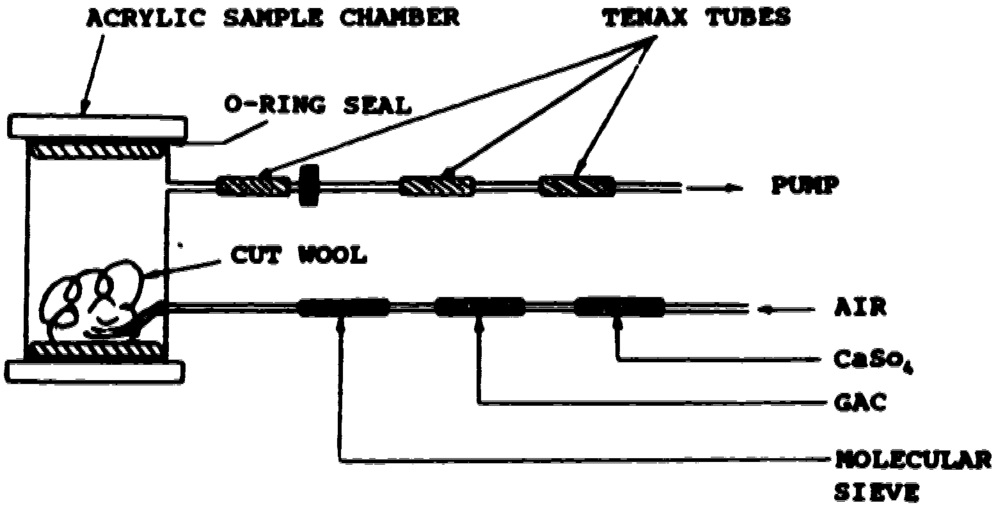


FIGURE A6-1 SYSTEM OG-2 OUT-GAS SAMPLING SYSTEM



permitted the attachment of tygon connections. Air was drawn from the bottom of the canister into the cut material and then through a filter into two Tenax tubes. The air drawn in, was purified by passing it through calcium sulfate, granular activated carbon (GAC) and molecular sieves. Control experiments with System OG-2 without any cut fabric were conducted at room temperature and pressure. The sampling time was between 20 and 30 minutes. A modification of this experiment was carried out by passing prepurified nitrogen rather than air.

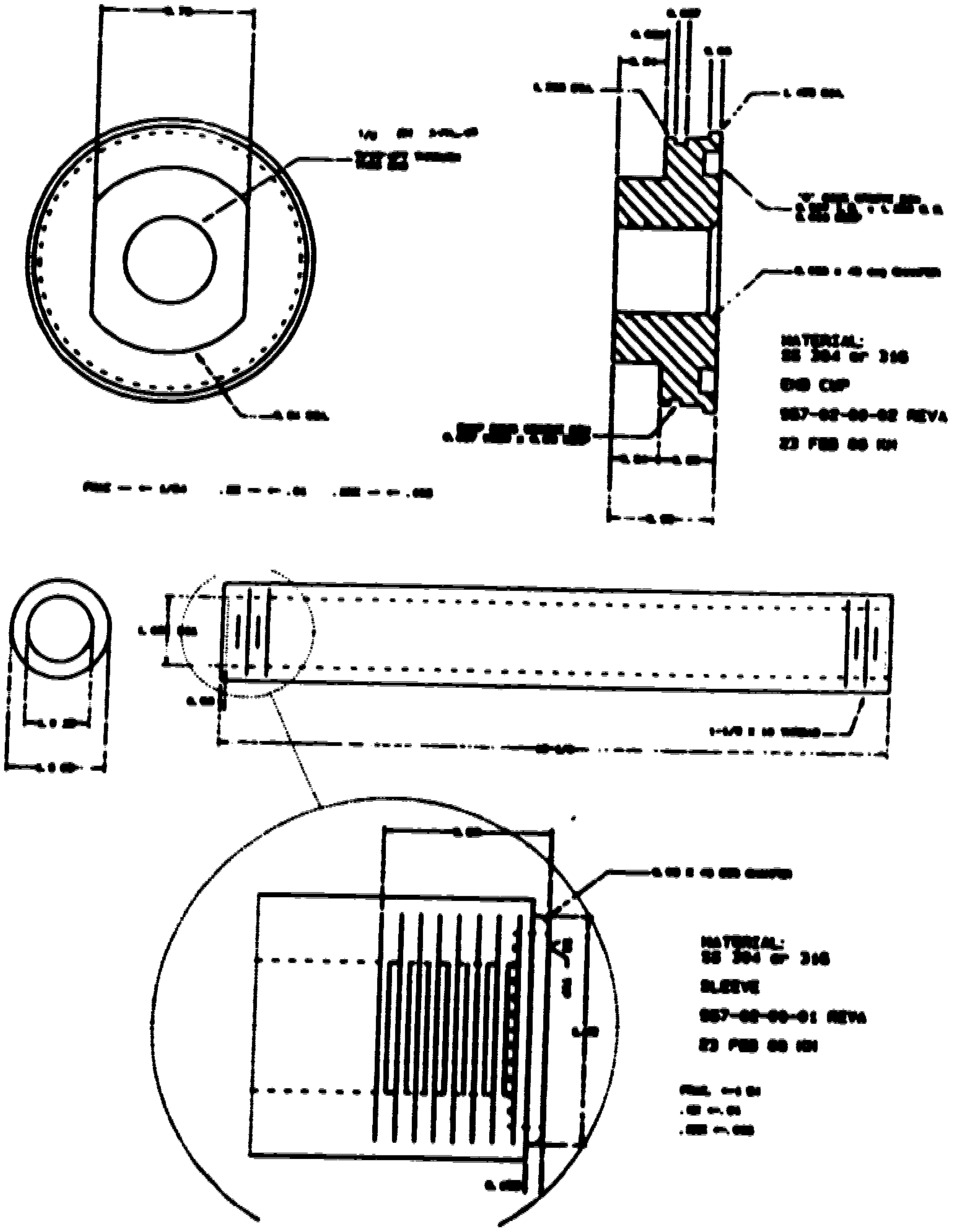
A7. SYSTEM OG-3

In System OG-3 (Figure 3.1.2-1), helium gas was connected to a J&W gas purifier that would remove hydrocarbons, oxygen and moisture. The gas purifier was attached to a custom made stainless steel canister and this in turn was connected to two Tenax tubes. The design of the stainless steel canister was adapted from a commercial canister purchased from Pierce Chemical Company. The commercial canister was constructed from an acrylic tube with aluminum fittings. These materials were not sufficiently inert for sampling odors. A stainless steel canister was therefore constructed. The production drawings of the canister used to construct it are illustrated in Figure A7-1. Preliminary tests on the suitability for this type of sampling were performed with the commercial version. Subsequent sampling for GC/MS and GC/FPD were performed on the stainless steel canister. Stainless steel was used because it is very inert and an inert surface was necessary to prevent adsorption of odors onto the surface. All fittings used were Swagelok fittings. The Swagelok fittings from the gas tank to the canister were made of brass and tubing was made of copper. All fittings used after the stainless steel canister were made of stainless steel and all tubing was Teflon.

A8. PREPARATION OF ADSORPTION TUBE

Pyrex glass tubing of O.D. 6 mm and I.D. 4 mm were cut into lengths of 12 mm with a diamond saw. The tubes were cleaned in succession with soap, water and acetone to remove the cutting oil from the saw. The ends of the tubes were flamed to smooth out the rough edges. The tube were then soaked in chromic acid overnight, rinsed with tap water and distilled water and baked at 200 °C. The tubes were packed with either Tenax, Chromosorb 102 or molecular sieve 5A. A plug of glass wool was inserted into both ends of the glass tubing. The glass wool were inserted such that there was about 15 mm of glass wool on one end and 25 mm of glass wool on the opposite end. Chromosorb 102 was

FIGURE A7-1 DRAWING USED TO BUILD THE STAINLESS STEEL CANISTER USED FOR OUT-GAS SAMPLING



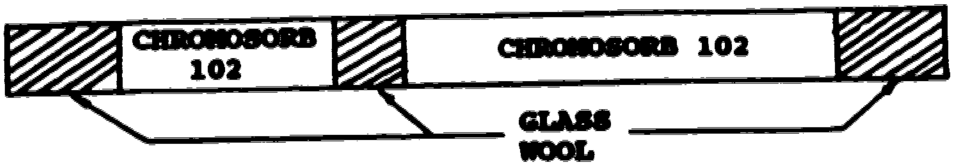
packed as shown Figure A8-1.

The virgin Tenax was cleaned after the tubes were packed by baking them in an oven at 200 °C overnight and then at 200 °C for 15 minutes to 1 hour in a flow of zero grade helium. The Tenax used was Tenax TA, 60/80 mesh purchased from Applied Science Labs. The used Tenax tubes were baked overnight at 200 °C, soaked in methanol for an hour, baked again overnight at 200 °C and then baked in a flow of Helium for 20 minutes to an hour. After this process a blank desorption was carried out to check if the tubes were completely cleaned. If the tubes were not completely cleaned, it was heated in a flow of helium again.

Chromosorb 102 was cleaned by soaking in cyclohexane for 3 days. It was then washed with purified methanol and vacuum filtered and dried in the oven at about 100 °C for an hour. After drying, about 0.5 g of Chromosorb 102 was desorbed with 1 mL of cyclohexane to check the cleanliness of adsorbent. After this test, the rest of the adsorbent was then packed as described in section 3.2.

Both new and used molecular sieve 5A were cleaned by baking overnight at 200 °C from 20 minutes to one hour. As with the Tenax tubes, a blank desorption was carried out.

FIGURE A8-1 GLASS TUBING PACKED WITH CHROMOSORB 102



APPENDIX B

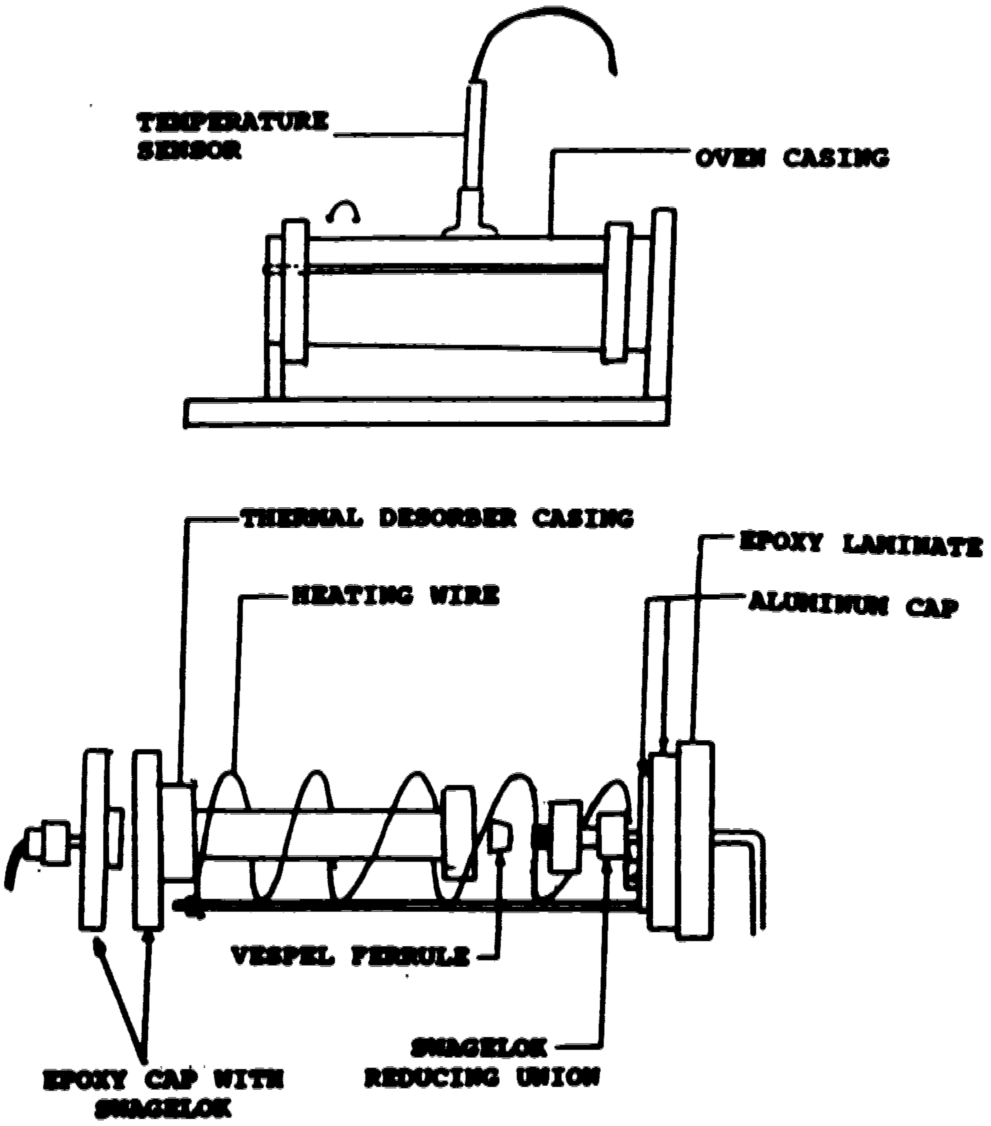
B1. DEVELOPMENT OF THERMAL DESORBER

The University of Alberta does not have a facility where a thermal desorber was permanently connected to a GC/MS. It was necessary to develop a portable thermal desorber which could be easily hooked-up with either a GC or a GC/MS. The thermal desorber was developed specifically for this project. The thermal desorber allowed a flow of helium to sweep through the adsorption tube while it was being heated to a certain temperature. When the adsorbent was heated, the compounds were released. The flow of helium carried the compounds into the cryogenic/heating coil. When a coolant such as liquid nitrogen was applied to this coil it acted as a cryogenic coil. This coil could also be heated by applying a current to it. The trapping of the compounds, released by the sorbent through cooling, and the subsequent flash heating back into the GC is known as cryo-focussing. The cryo-focussing process was used because compounds are normally released very slowly from the adsorbents over a period of minutes creating broad peaks which are not desirable for GC detection. Cryo-focussing was necessary to obtain sharp peaks on the GC.

B2. OVEN FOR THE THERMAL DESORBER

The oven was a cylinder with O.D. of 5 cm and length of 13 cm. This was constructed from a thin sheet of aluminum obtained from a pop can. The ends of the can were cut and a torch was used to burn the paint off the aluminum sheet. The sheet was then enclosed in a sheet of brass screen and held together with two aluminum caps each shaped like a cylindrical ring. The two rings were held together with two aluminum rods. Each end of the cylindrical ring rested on another circular support which in turn was attached to a phenolic resin laminate base. The oven casing was constructed in this fashion to allow it to rotate freely. This feature permitted the oven casing to be easily disassembled from the phenolic laminate support. The oven was heated by a heating element inside the oven casing as shown in Figure B2-1. There was a Swagelok reducing union from 6.4 mm (1/4") to 3.2 mm (1/8") inside the oven. A special aluminum casing for the thermal desorber tube was machined. This tubing was anodised from silver to black to improve it's heat absorption and radiation characteristics. The tube casing can be screwed onto the Swagelok fitting inside the oven. The outside end of this casing was machined into a circular cap with an O.D. of 6mm. The cap main function was to close the opening in the oven. The second function was to provide a larger surface for a better grip on the

FIGURE B2-1 OVEN OF THE THERMAL DESORBER



tube casing so that a good seal may be achieved. A similar disk was fitted to another Swagelok reducing union. The 6.4 mm (1/4") end of the union was embedded in the resin disk and the 3.2 mm (1/8") connection was attached to a Teflon tubing. The teflon tubing was in turn joined to the gas regulator on the helium tank. This construction permitted a flow of helium through the desorber tube into the cryogenic coil and GC column whenever the ferrules in the Swagelok fitting were tightened.

B3. SENSOR PROBE

A small hole was drilled through the middle of the oven casing. A brass tubing holder, O.D. 8 mm and 25 mm long was machined to cover this hole. A sensor probe was inserted into the holder. The probe rested on the surface of tube casing. This probe senses the temperature and regulates it at the same time. The sensor probe consisted of a tiny electronic chip, a brass cap and a glass tubing. The chip, a F3105 platinum RTD element was purchased from Omega Engineering Inc. It had two platinum leads which were about 3 cm long. These leads were cut to approximately 1 cm in length and silver solder to two leads by using a small acetylene flame.The chip was glued to the brass cap. This, in turn was glued to the glass tubing. The entire assembly was filled with epoxy resin. This assembly was constructed in such a way that prevented the two platinum leads from coming into contact with each other. A similar probe was constructed and fitted into section of the cryogenic coil immediately next to the needle injector unit to ensure that no cold spots occurs. A diagram of this probe is as shown in Figure B3-1.

B4. CRYOGENIC-HEATING COIL

The cryogenic coil was made with a chromatographic stainless steel tubing 3.2 mm (1/8") O.D. and about 85 cm long. The coil was obtained from Terochem. One end of the coil was attached to a Swagelok reducing union and a thread was machined on the opposite side. In order to reduce the final length of this coil it was wound into 5 circles with a radius of 17.5 mm. A brass cap was machined to screw onto the threaded section of the cryogenic coil. This assembly is as detailed in Figure B4-1.

The GC septum provided a good seal around the needle. The septum was obtained by cutting a GC septum with a small piece of tubing with an O.D of 4.2 mm and I.D. of 3.3 mm and a sharpened edge. The stainless steel needle was a Hamilton make with a part No. 80437 and 26S gauge. The cryogenic-heating coil was cooled by plunging

FIGURE B3-1 DIAGRAM OF THE SENSOR PROBE

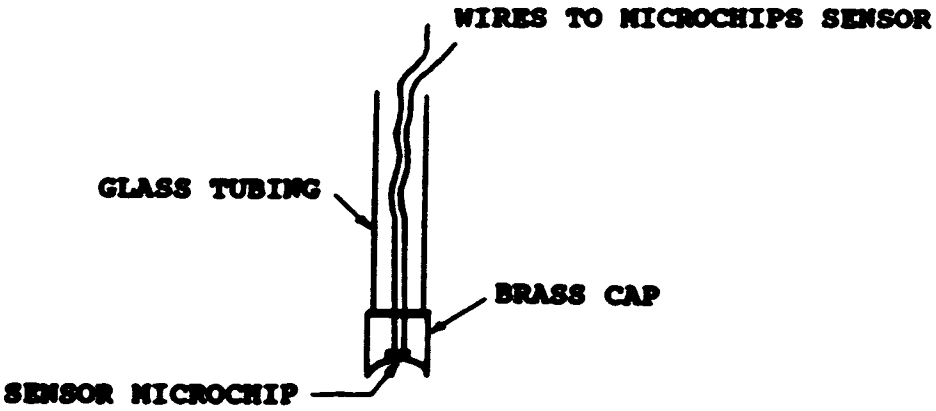
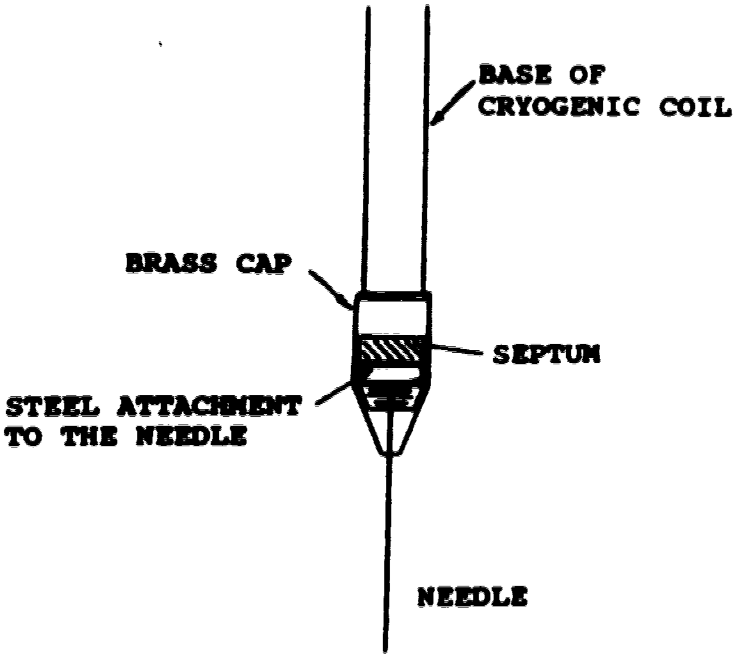


FIGURE B4-1 DIAGRAM OF THE BRASS CAP-NEEDLE ASSEMBLY



the coil into either an isopropanol dry-ice mixture or liquid nitrogen. It was then converted to a heating coil by removing the cryogen and then electrically heating the coil using it's resistivity.

B5. OPERATION OF THE THERMAL DESORBER

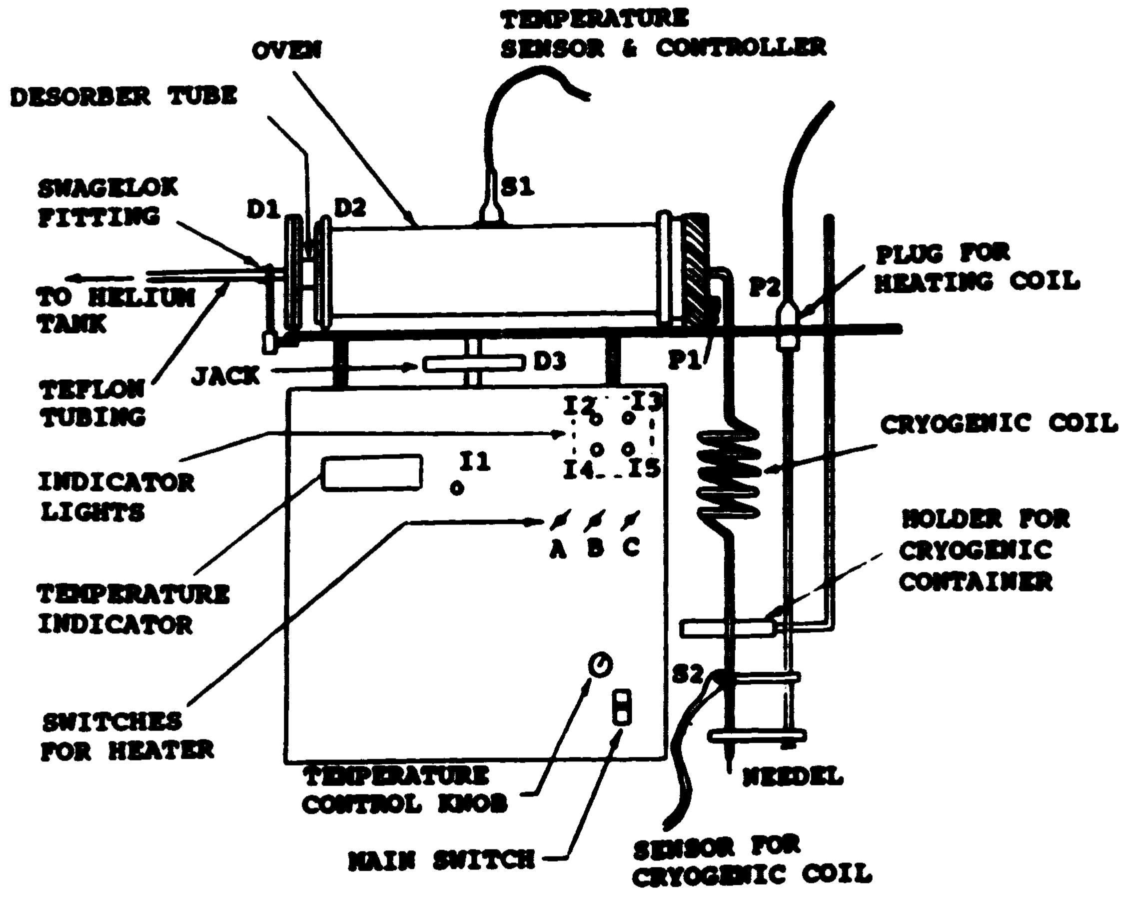
A diagram of the thermal desorber with all lights and switches labeled is shown in Figure B5-1. The thermal desorber was turned on by switching on the main switch. The oven temperature is set by switches A, B and C. The indicator light I, turns green, I2 and I3 lights when A, B and C are turned on. The green light, I1, indicates that the temperature read-out was representing the temperature set. The desired temperature was set by rotating the temperature control knob. Lights I2 and I3 indicated that S1 was activated and the heater was turned on. Conversely when A,B,C are flipped downward, I1 turned red,lights I4 and I5 turned on. When I1 is red, the indicator is showing the actual temperature of either S1 or S2. I5 indicates that the heater is shut off. To supply a current to the oven or cryogenic-heating coil the physical connection to the heater must be plugged into either plugs P1 or P2 respectively.

B6. DESORPTION PROCESS

Desorption can be achieved by following the procedures:

1. Insert adsorbent tube into the oven barrel.
2. Finger tighten the tube by turning D1 counter clockwise and D2 clockwise.
3. Open Helium gas valve.
4. Check for leaks around needle insertion of the brass cap-needle assembly into clean methanol and check for bubbles. If a leak is detected, finger tighten the brass cap or change the septum.
5. Check for flow rate by insertion of the needle through a septum attached to a bubble flow meter. The flow rate should be about 20 to 30 ml/min when the pressure in the injector port of the GC is about 2 PSI.
6. Pour coolant into an insulated container and immerse the cryogenic coil into the coolant. Secure the coolant container with the holder. The holder is held in position by a small spring clip C.
7. Flip switch A upward, green light comes on and rotate temperature control knob until the desired temperature shows on the digital display.

FIGURE B5-1 DIAGRAM OF THE THERMAL DESORBER



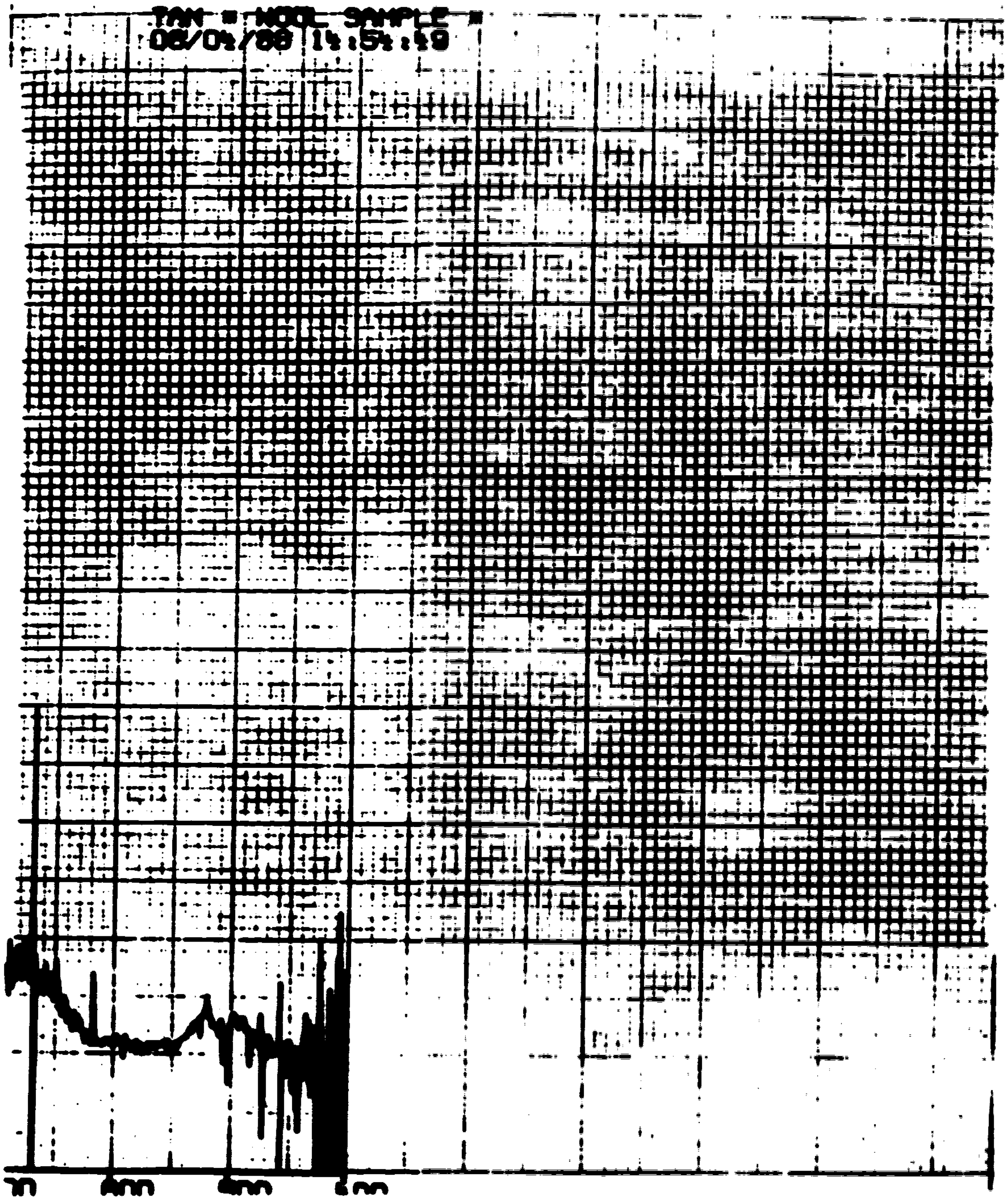
8. Flip switch A downward, red light comes on indicating the actual temperature is now being read.
9. Plug into P1
10. Flip switches B and C upward, I2 and I3 should turn on.
11. An alarm timer should now be set and turned on.
12. After desorption is completed. Flip svtich C down to turn heater off. The needle is lowered into the injection port of a GC by rotating the disc D3. This adjusts the jack to the desired height.
13. Plug into P2.
14. Flip switch A up, adjust the temperature control knob to the desired temperature, Flip switch A down to read the actual temperature.
15. Remove coolant from the coil.
16. Flip switch C upward to heat cryogenic coil.
17. Set timer for 0.5 to 1 minute then flip C downward to shut heater off.
18. Lift the needle out of injection port by rotating D3 again.

APPENDIX C

C1. ANALYSIS BY FTIR

James Hoyle in the Spectral Services Department at the University of Alberta would transfer the sample from the gas bag to a 20 m gas cell obtained from Wilks Scientific Ltd. A Nicolet 7199 FTIR spectrophotometer equipped with a mercury cadmium telluride detector was used to collect the data. The FTIR spectrum was obtained at room temperature and 1 atmosphere. The spectrum was run from 4000 wavenumber to 400 wavenumber. A total of 100 interferograms were co-added for each sample and reference. One-sided interferograms has 16,000 data points and 32,000 transform points with a resultant spectral resolution of 1 cm^{-1} before apodization. All the Fourier transformations were Happ-Genzel apodization. The Happ-Genzel apodization is a mathematical manipulation of spectral artifact of FTIR. The FTIR process effectively adds many sine waves known as interferograms together. When only 16,000 data points were taken, spectral artifacts in the form of many side bands with amplitude as large as 20 % of the main peak amplitude would be observed. These do not correspond to the information previously acquired but they influence the instrument line shape function. Apodization is therefore a mathematical technique to truncate these side bands. Detailed description for Happ-Genzel apodization may be obtained from Herres (1987).

RAW FTIR DATA FOR TABLE 4.4-1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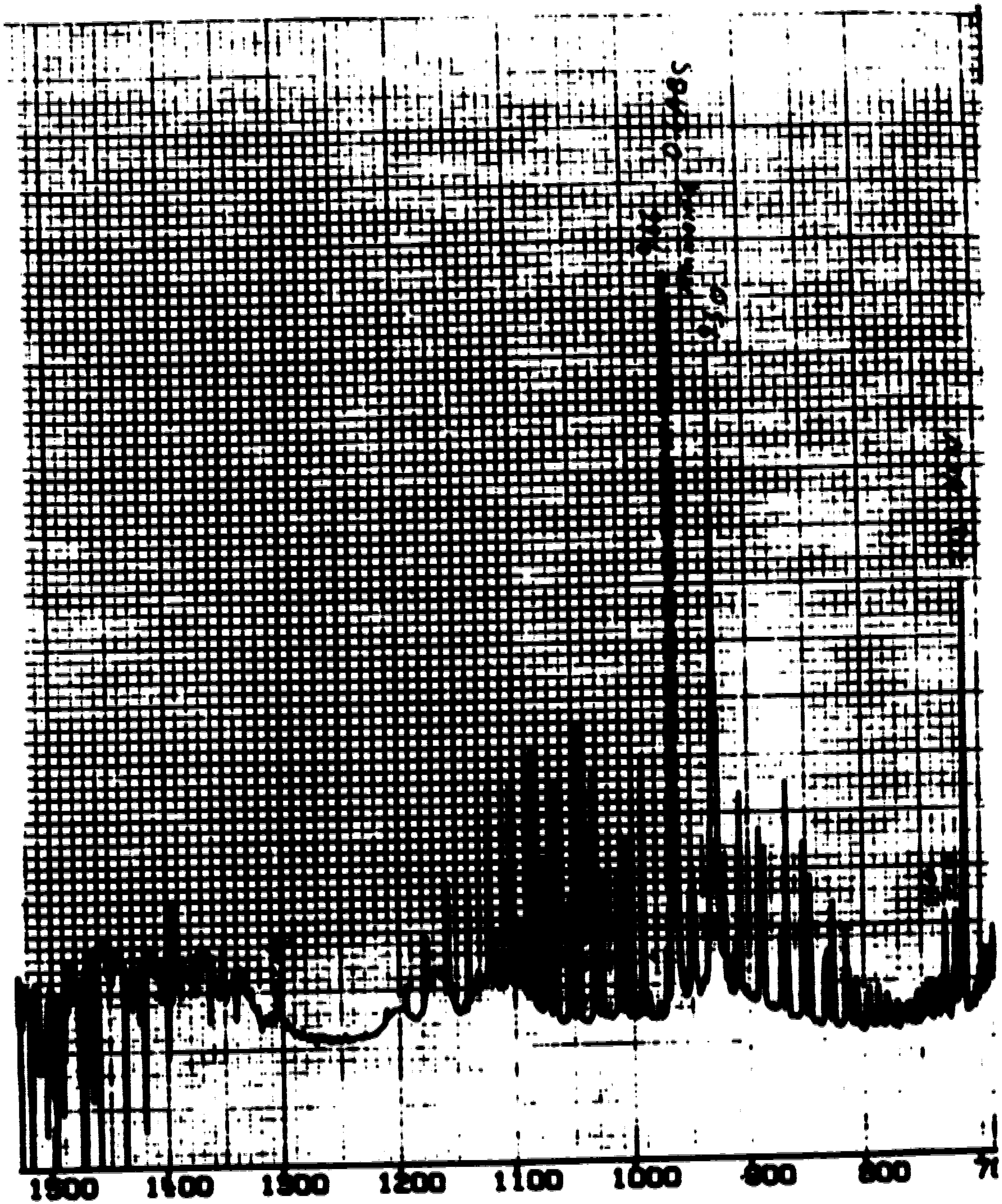
08/04/88 14:54:59
00
200
400
600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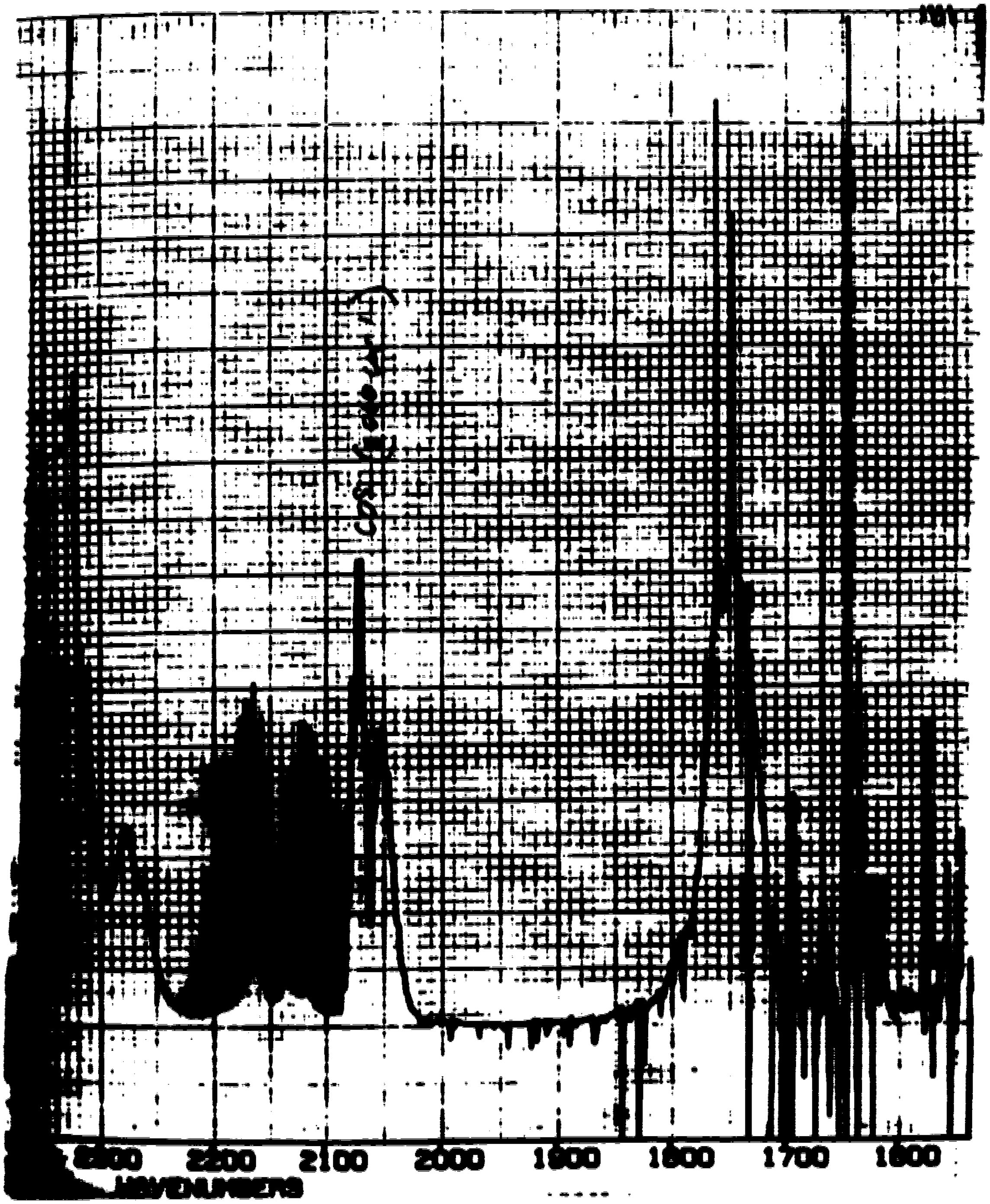
1400
1300
1200
1100
1000
900
800
70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2200
2100
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1900
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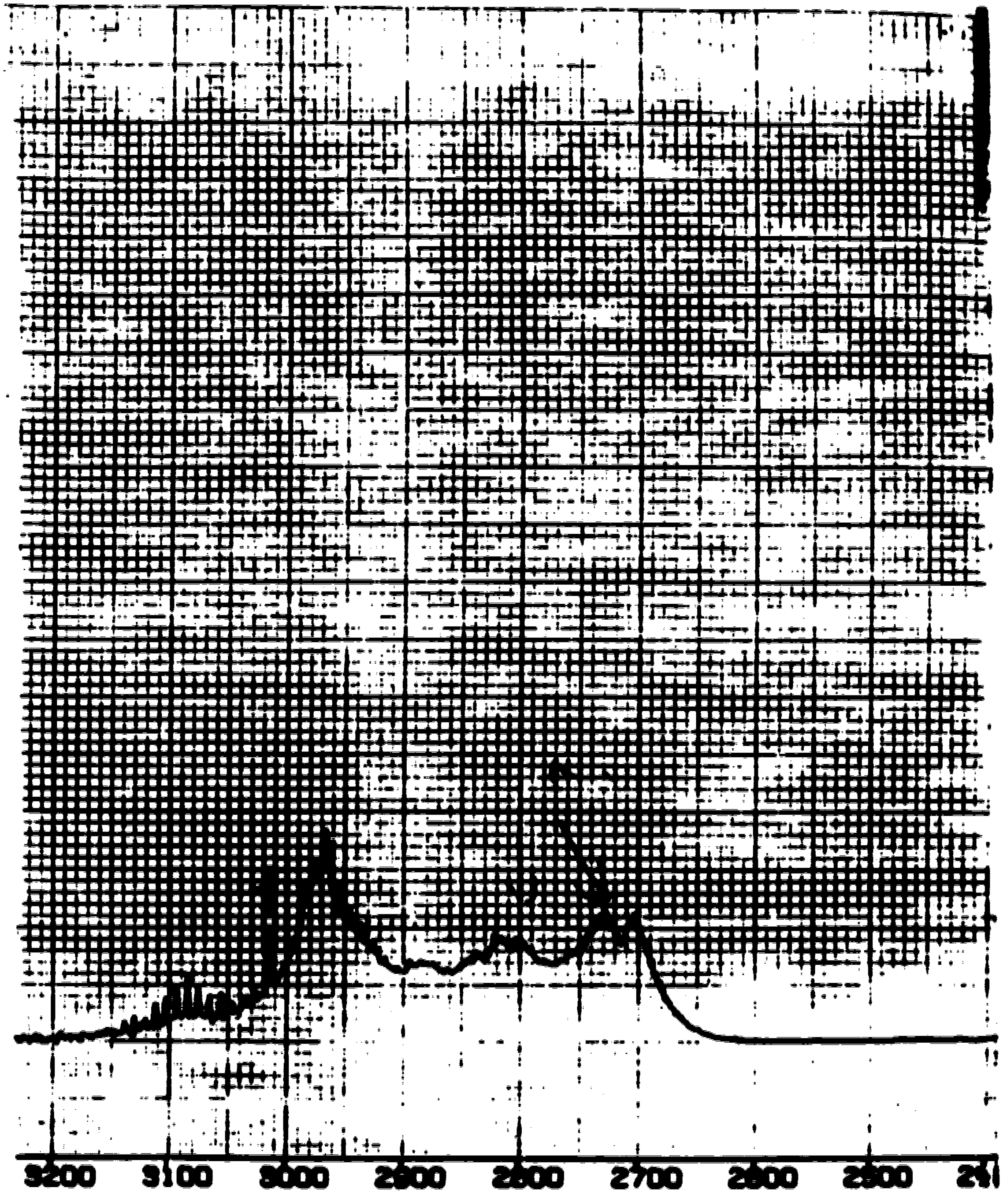
1700
1600
WAVENUMBERS


3200
3100
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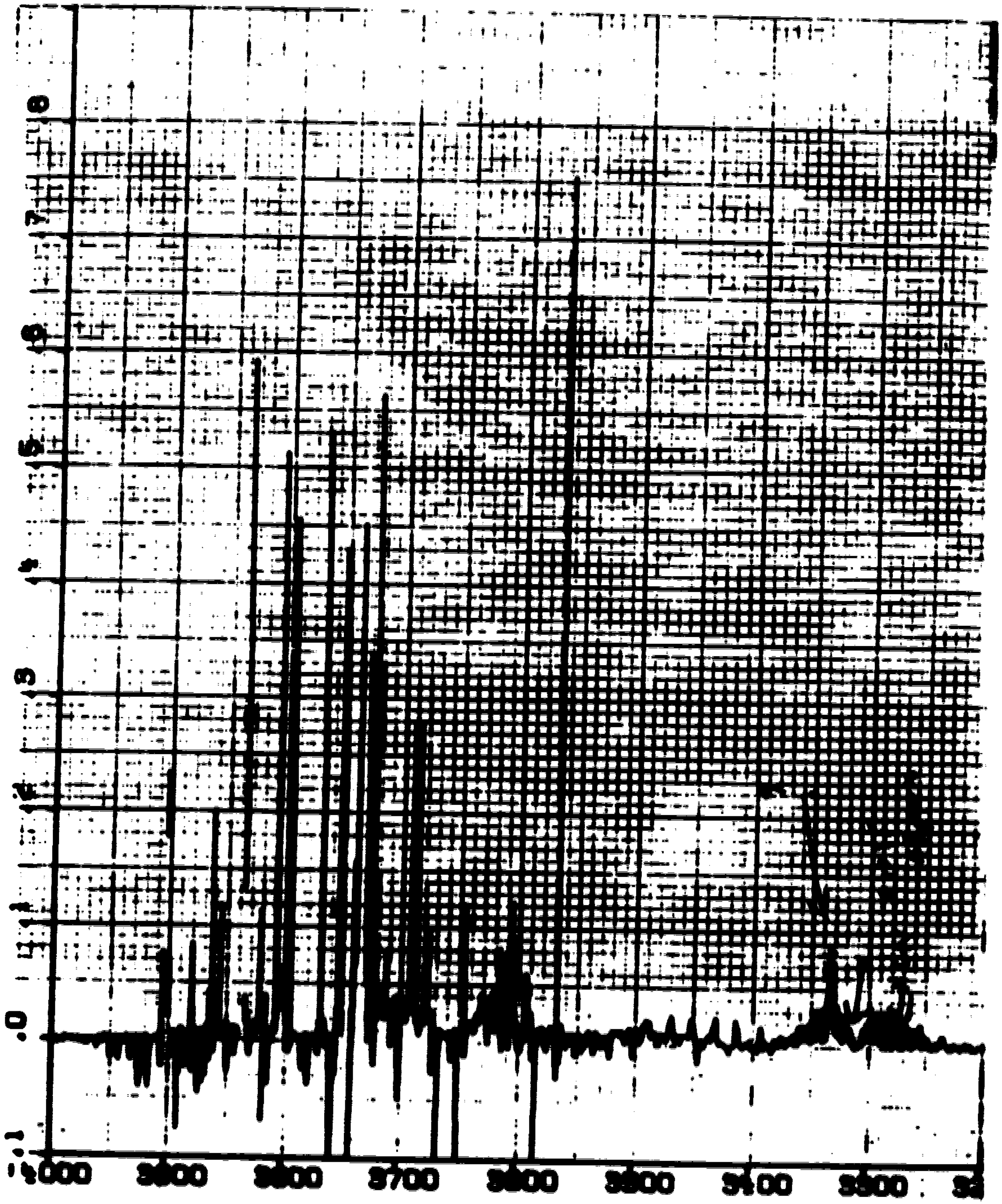
2500
2


.8
.7
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-.1
4000
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3400
3300

APPENDIX D

D1. SOLVENT DESORPTION GC/MS ANALYSIS

For this analysis S2 sampling method was used. All Teflon connections were pre-washed in soap solution, rinsed thoroughly with water, distilled water and dried at 80 °C. The honeycomb cutting surface was completely cleaned prior to sampling by using the laser beam to completely burn off the fine particulates stuck on the cutting bed.

A Photon Source laser operating at 400 watts was used. The cutting speed was 50 mm/s and the length of cut was 70 mm. The temperature at which the sample was obtained was 23.5 °C. The sampling rate was 1.2 L/min. The amount of fabric cut was 2.0 grams. A similar sample was obtained with all conditions identical, except no wool fabric was cut. In other words, the laser was allowed to cut over the entire length of the cutting surface without a fabric while sampling was in progress. The sampling time for the control experiment and actual source sample were 49.25 minutes and 59.23 minutes respectively. The fumes were sampled onto Chromosorb 102. After the collection of the organic vapors, the sorbents was divide into 2 samples. The front portion consisted of 240 mg of chromosorb which was extracted with 2 mL of Aldrich gold label cyclohexane. Half a milliliter of cyclohexane was used to desorb the rest of the resins which was about 80 mg. The desorption was achieved by transferring the front portion of the adsorbent into a clean culture tube. Two millilitres of cyclohexane was pipetted into the tube. The mixture was then shaken vigorously by hand for about 3 minutes and the Chromosorb 102 was left to soak in the cyclohexane overnight. The cyclohexane was then pipetted out and sent for GC/MS analysis. The GC/MS analysis were performed by Susan Daignault from Environmental Engineering and Science in the Department of Civil Engineering at the University of Alberta. The GC/MS comprised of a Varian 6000 GC coupled to a VG 7070E mass spectrometer with a 11250 data system. The GC/MS was temperature programed at 40 °C for 2 minutes, and temperature was increased at a rate of 5 °C/min to 100 °C and then at a rate of 12 °C/min to 250 °C and maintained at 250 °C for 30 mins.

D2. THERMAL DESORPTION AND GC/MS ANALYSIS.

To carry out the thermal desorption of the samples into the GC/MS, the thermal desorber was mounted on top of the Varian 6000 GC which was coupled to a VG 7070E mass spectrometer with a 11250 data system. The mass spectrometer was operated in the electron impact mode of

40 eV. The samples were desorbed at 200 °C for 4 min and flash heated to 200 °C in about a minute. The GC in the GC/MS system did not have a cryogenic unit and thus, to improve separation, the oven's temperature was lowered by adding dry ice. In this way, the oven temperature was maintained between -1 °C to 10 °C. The temperature program was set at an initial temperature of 1 °C for 4 minutes with a rate of increase of 5 °C/min to 100°C and a second rate of increase of 10 °C/min to 250 °C.

To improve the separation of the peaks, approximately 100 mm of the capillary column was immersed in liquid nitrogen for a duration of 2 to 4 min while the thermal desorption was in progress. After the desorption, the column was removed from the cryogen and the oven was heated by the temperature program.

RAW GC/MS DATA FOR SOURCE AND OUT-GAS SAMPLE

NOTES:

1. GC/MS spectrum labeled TAM14DS contains the raw data from solvent desorption of Chromasorb 102 for Table 4.4.1-2

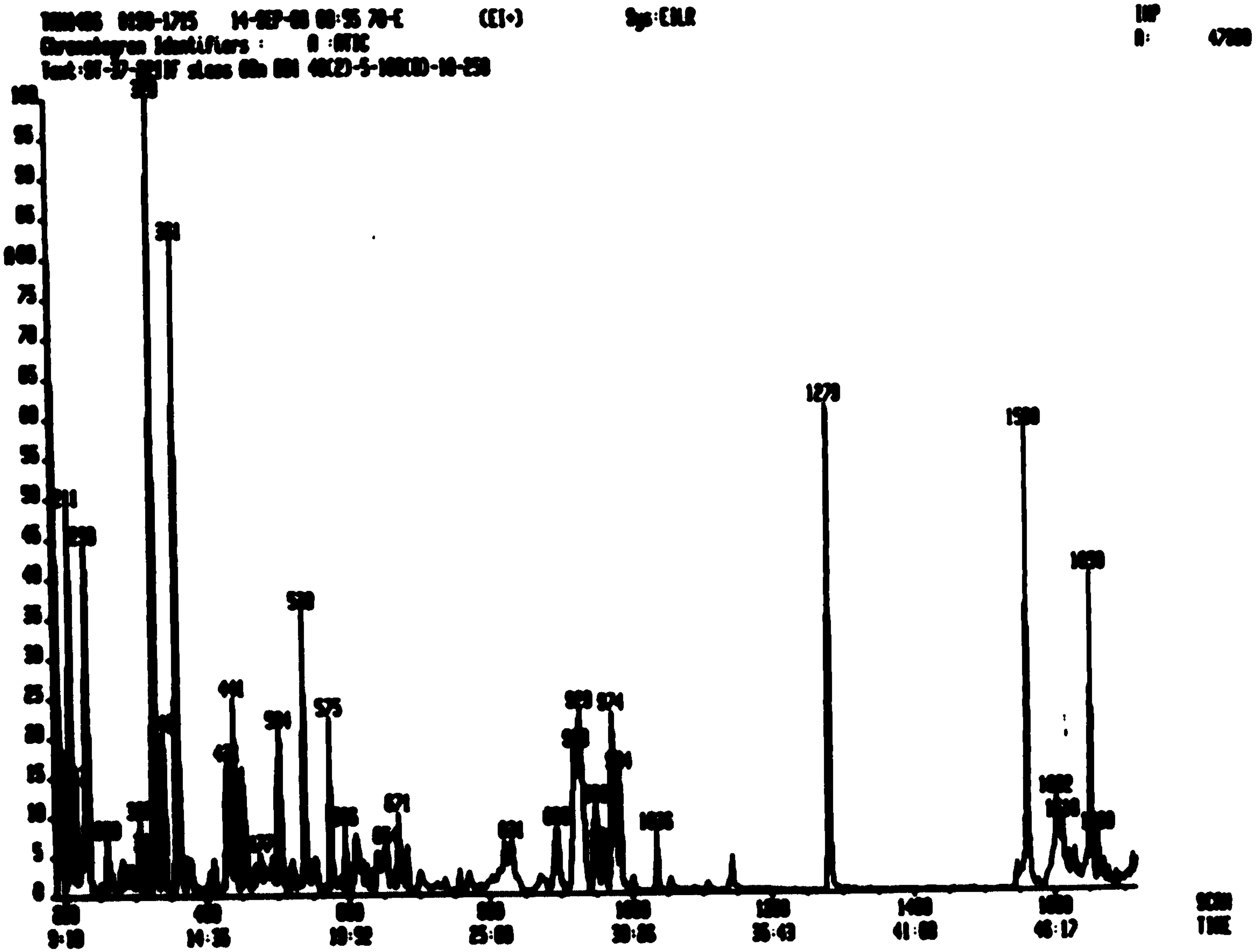
2. GC/MS spectrum labeled TAM2C contains the raw data from thermal desorption of molecular sieve 5A from source sample for Table 4.4.2-1

3. GC/MS spectrum labeled TA[illegible]D contains the raw data from thermal desorption of Tenax from source sample for Table 4.4.2-1

4. GC/MS spectrum labeled TA[illegible]C contains the raw data from thermal desorption of Tenax from out-gase sample for Table 4.4.2-3

5. GC/MS spectrum labeled TA[illegible]D contains the raw data from thermal desorption of molecular sieve 5A from out-gase sample for Table 4.4.2-4

6. GC/MS spectrum labeled TA[illegible]B contains the raw data from thermal desorption of molecular sieve 5A from out-gase sample for Table 4.4.2-4


(EI+)
Chromatogram Identifiers :
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20
25
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40
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60
65
70
75
80
85
90
95
100
400
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1600
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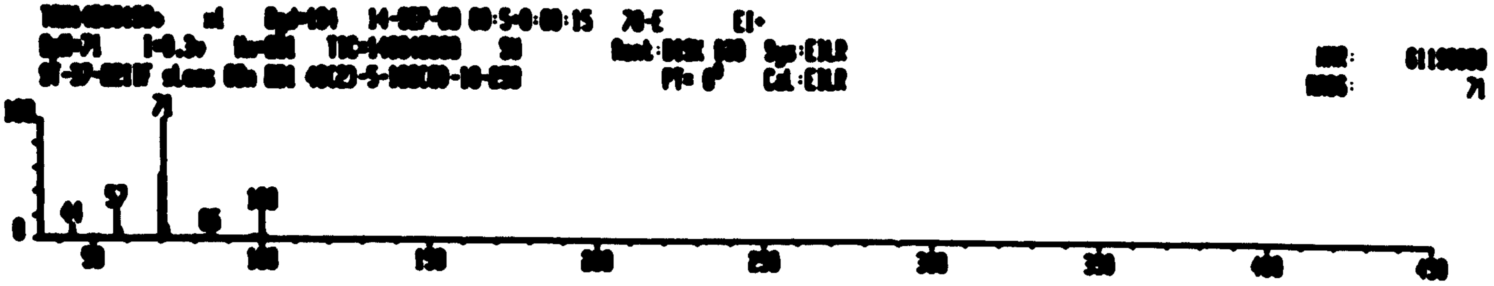
35:43
41:00
46:17
SCAN
TIME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Cal:EILR
Sys:EILR
PT= 0°
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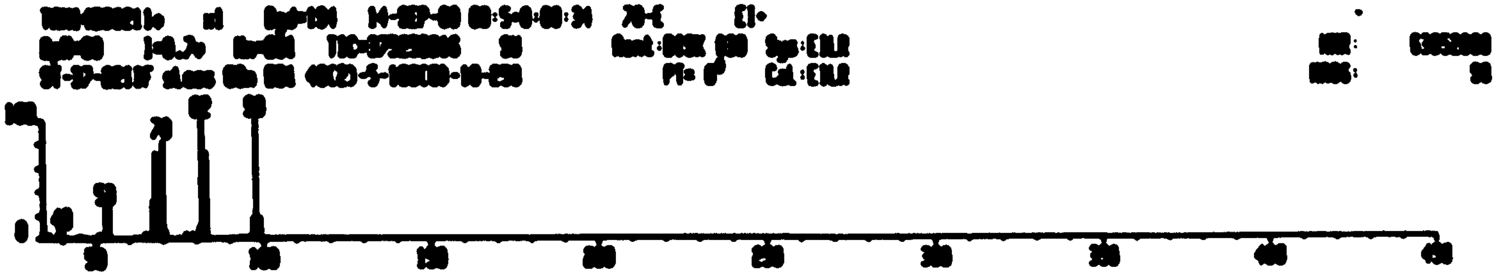
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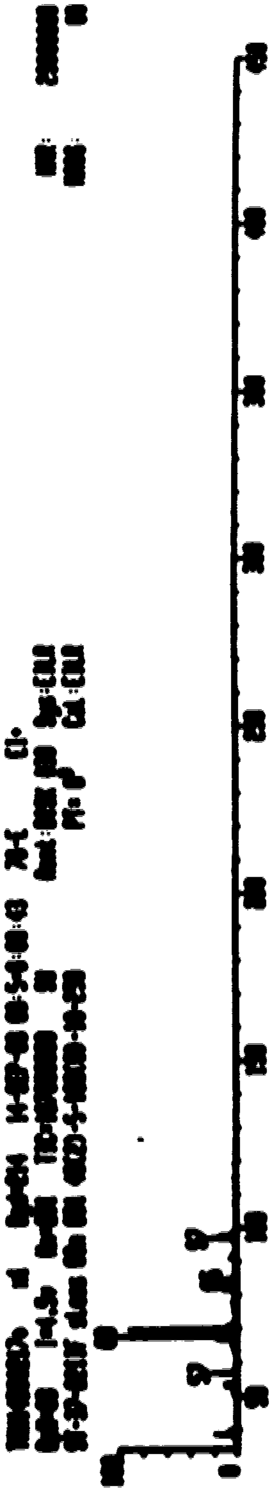

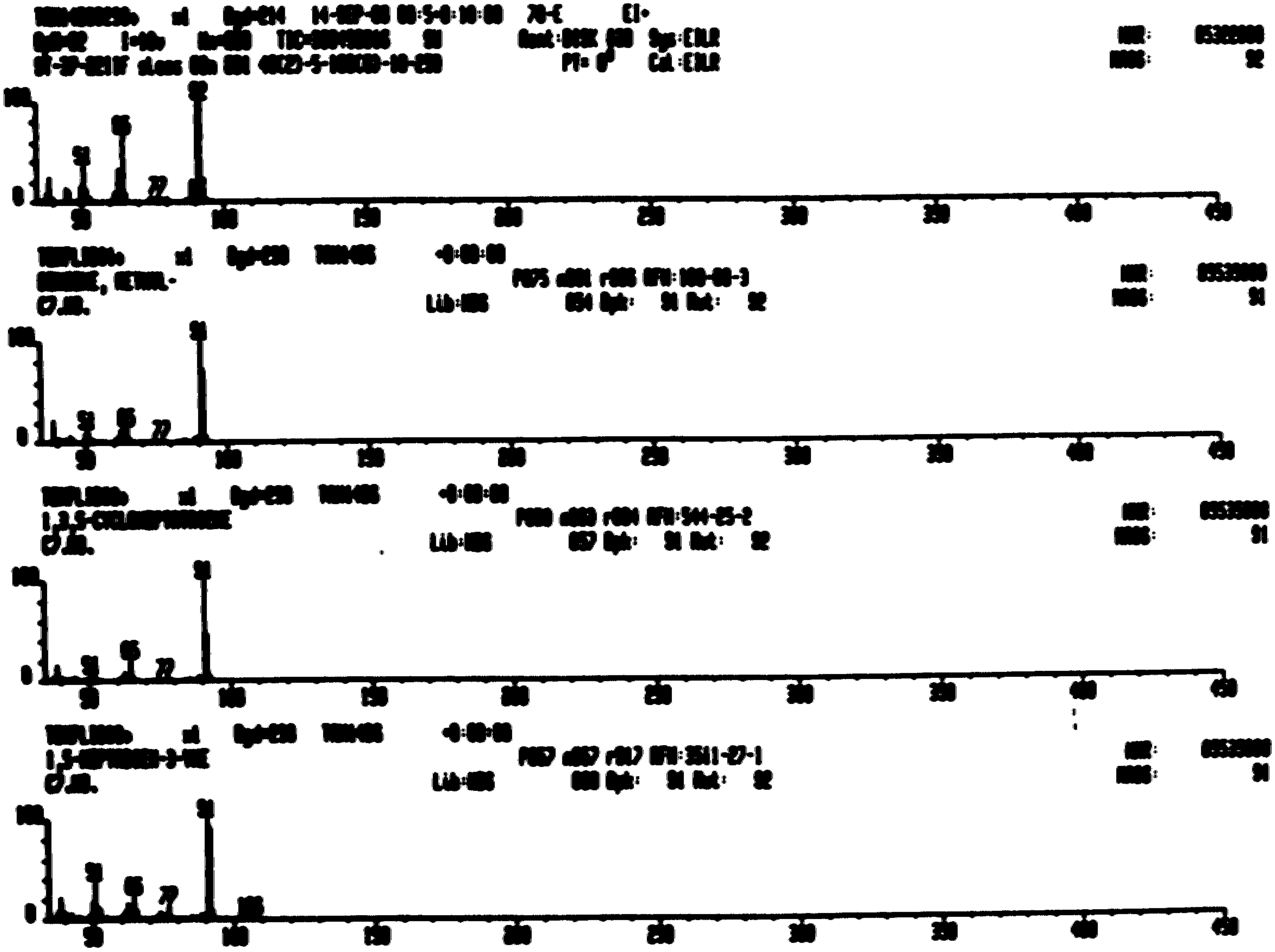
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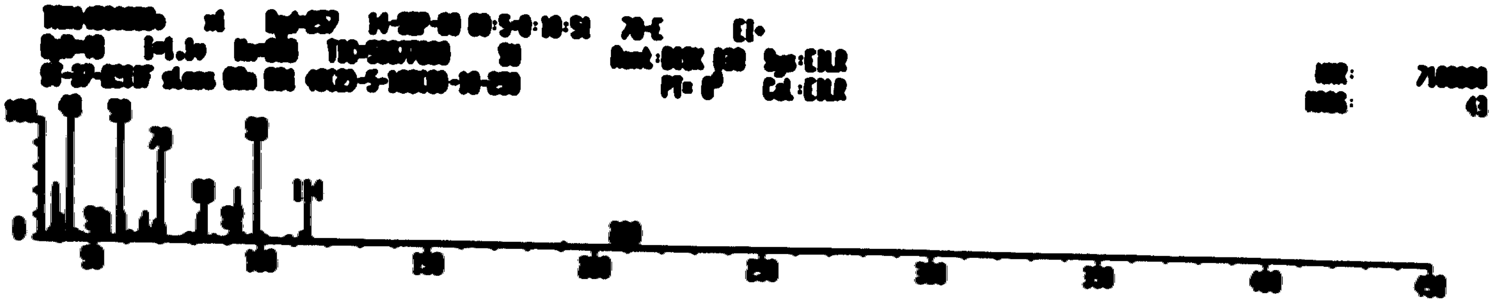
EI+


70-E
EI+
Sys:EILR
Cal:EILR
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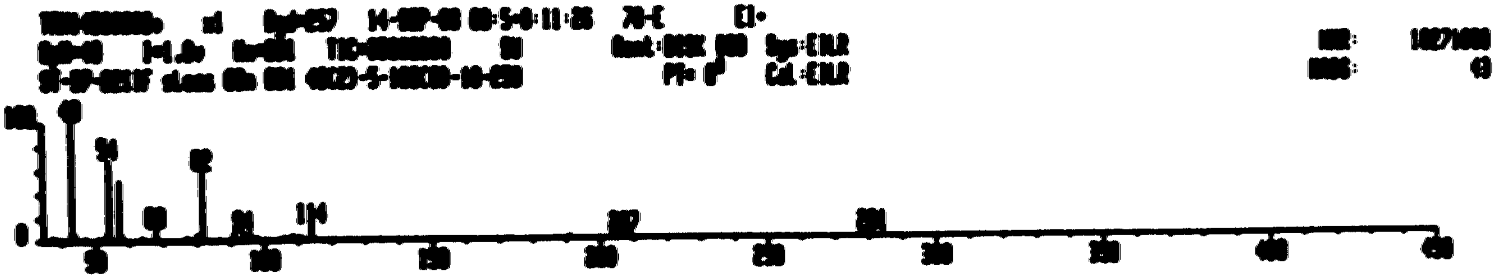
350
400
450
43


EI+
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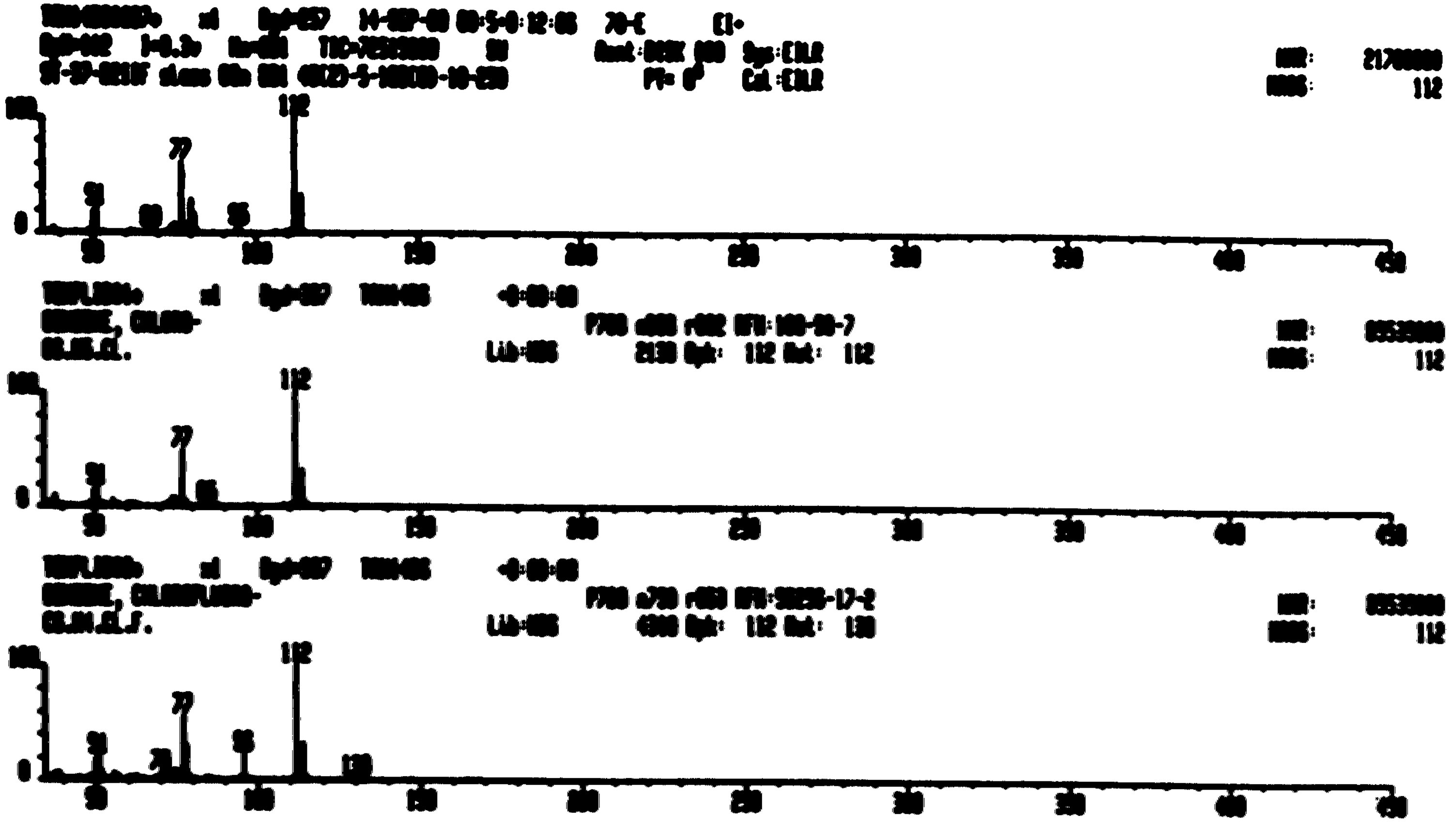
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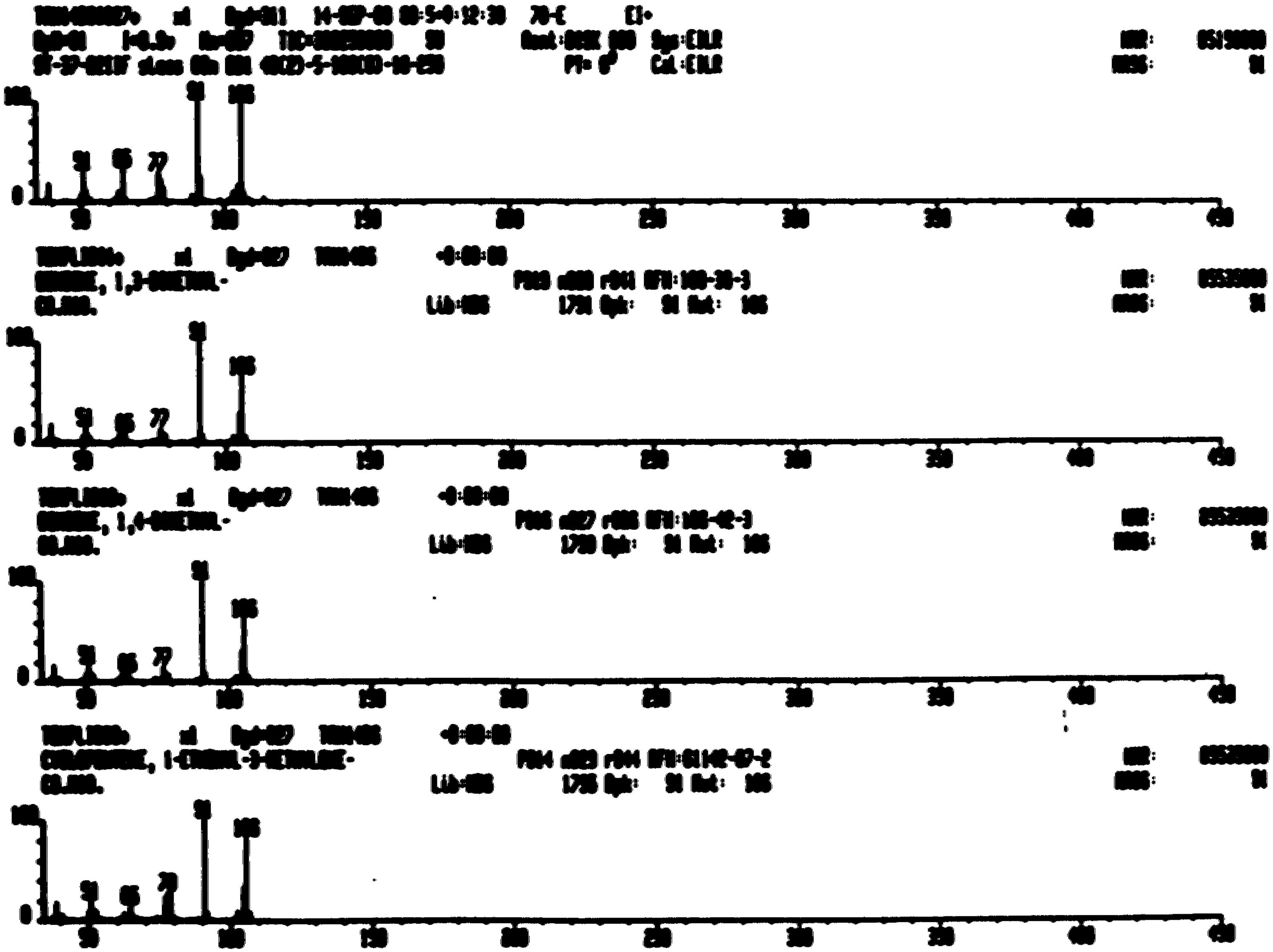
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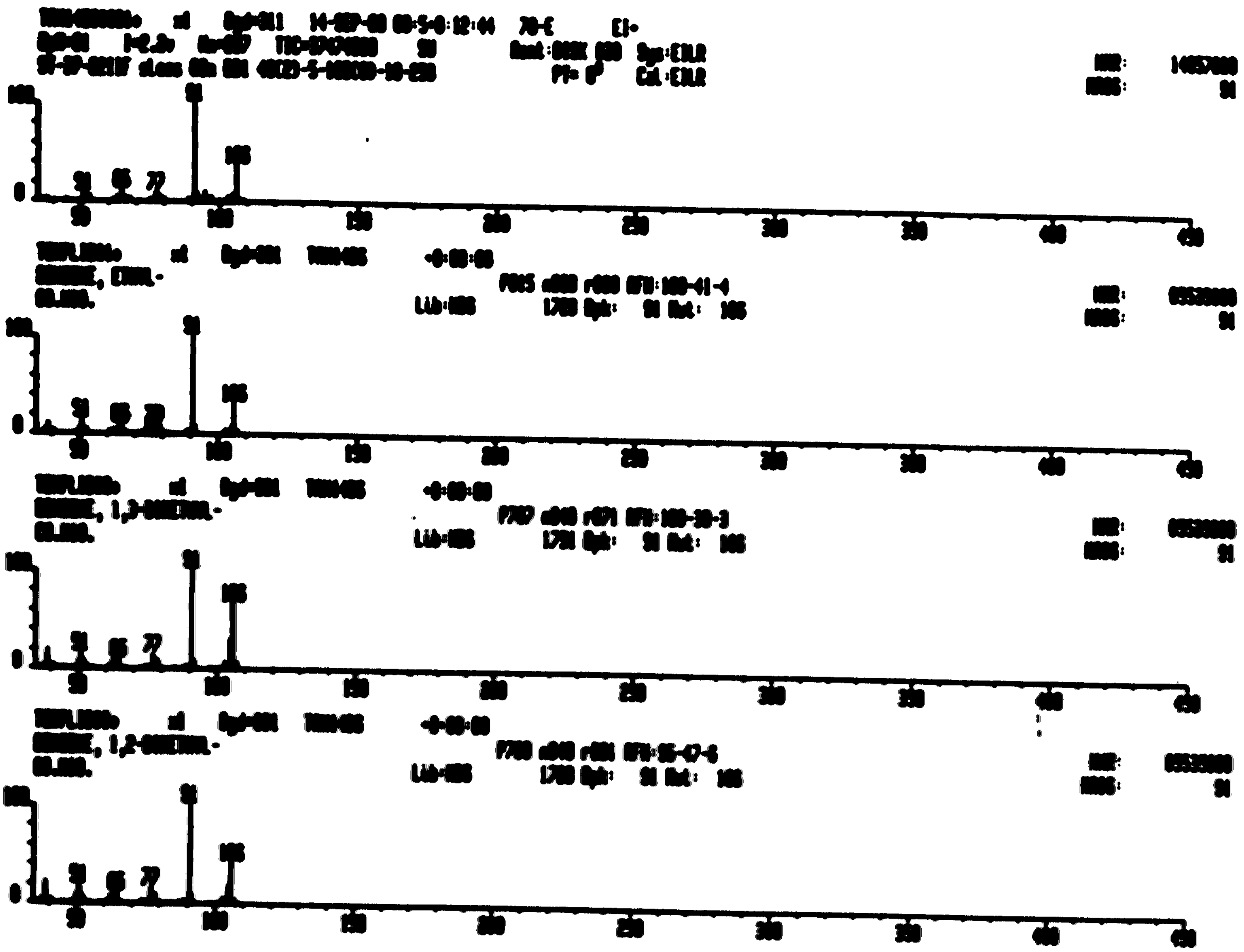
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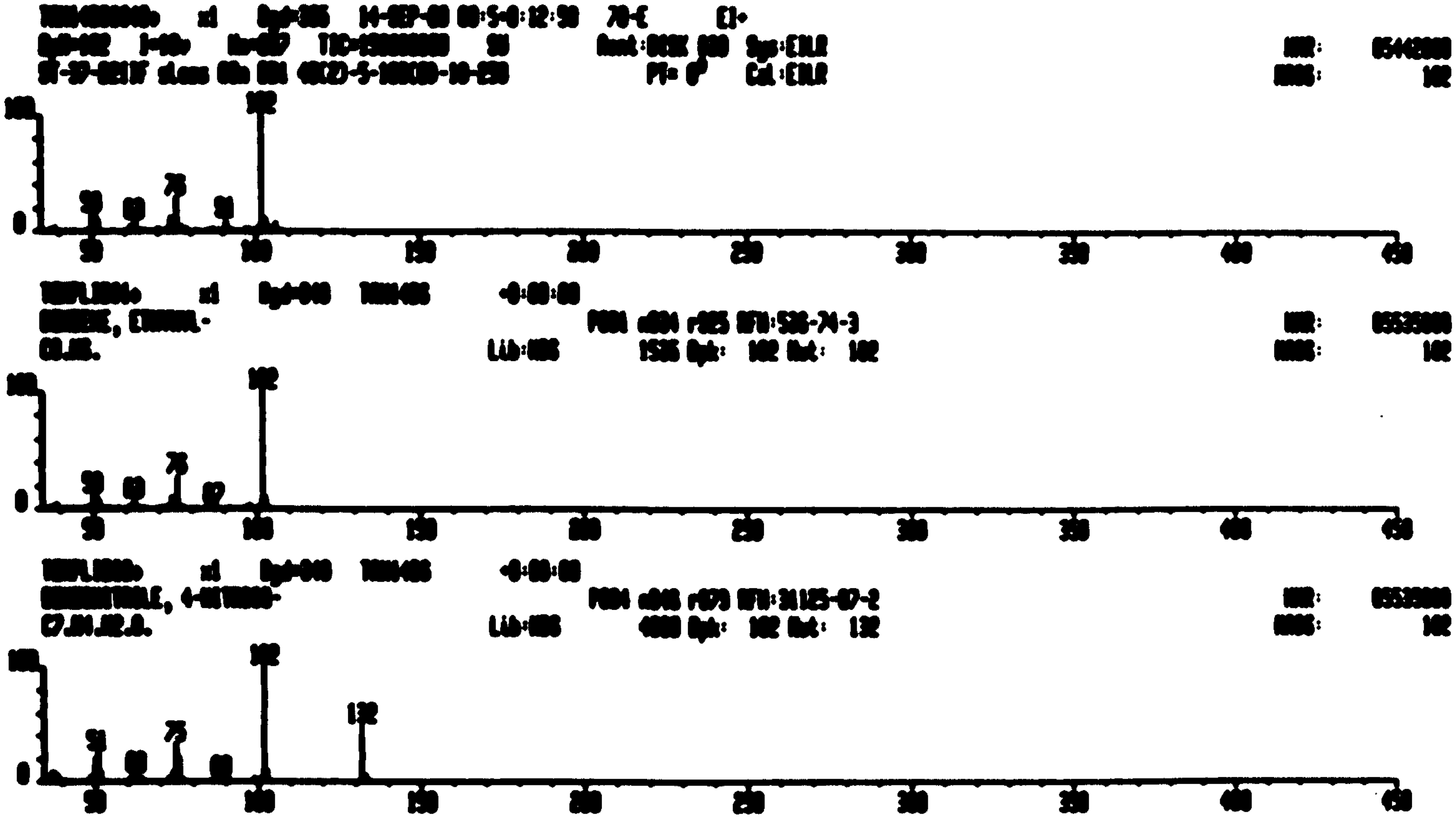
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14-SEP-88
70-E
EI+
TIC
Sys:EILR
Cal:EILR
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50
63
75
91
150
200
250
300
350
400
450
x1
+0:00:00
BENZENE, ETHYNYL-
536-74-3
Lib:
1536
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87
x1
+0:00:00
Lib:
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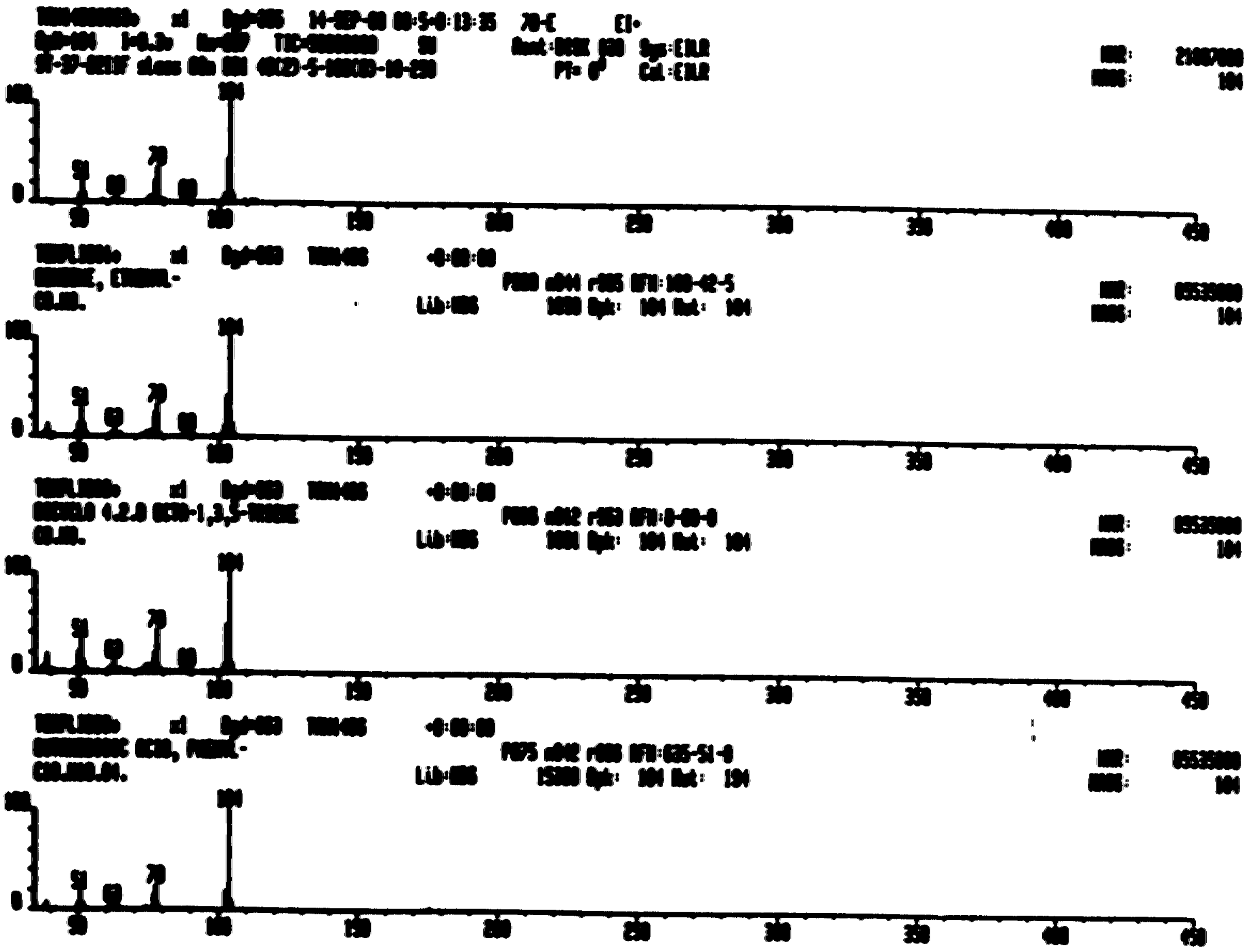
63
75
89
132



EI+
Lib:
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400
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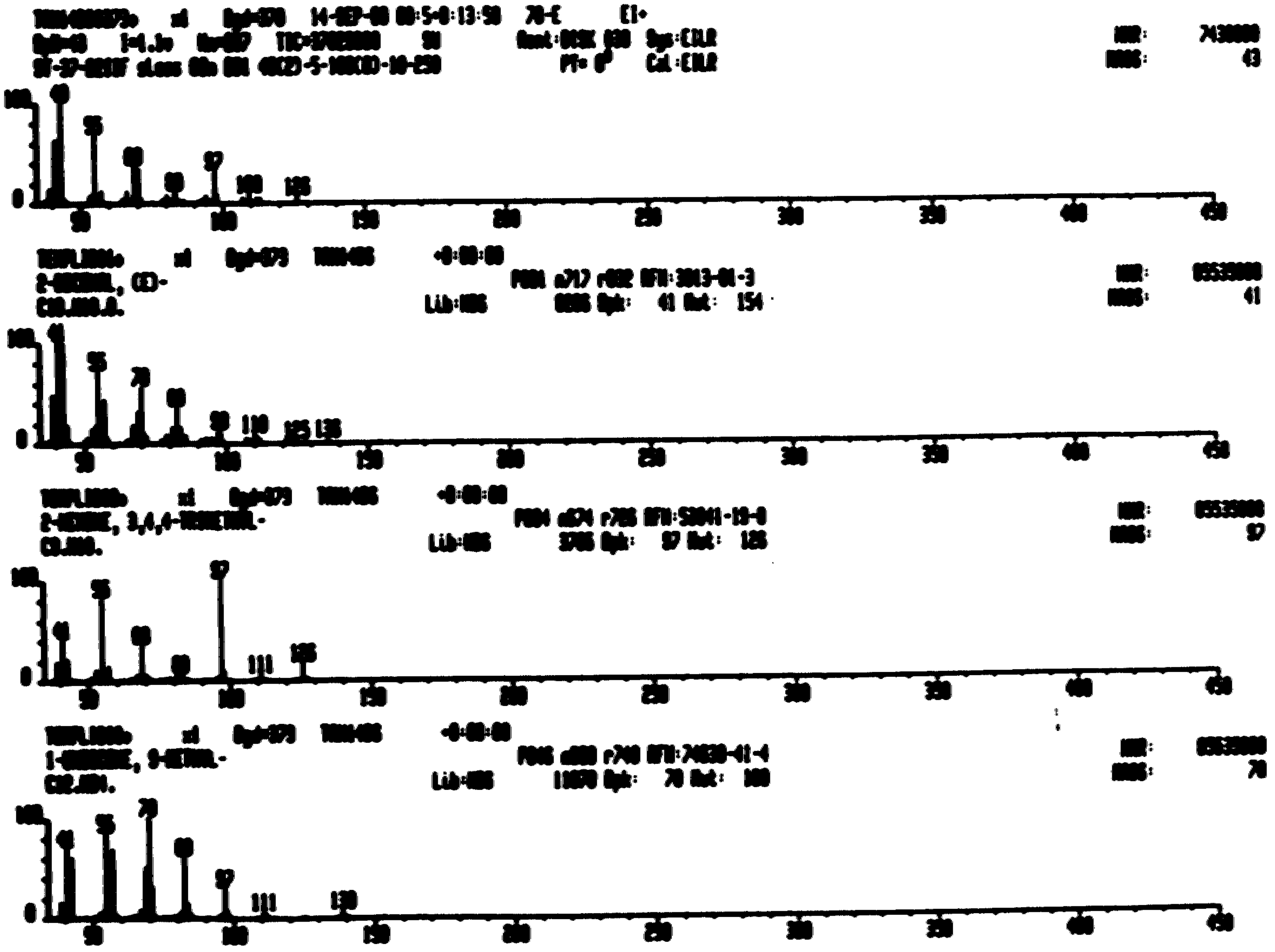
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EI+
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55
69
83
97
50
100
150
200
250
300
350
400
450
Lib:
41 Ret: 154
41
55
70
83
110
138
2-HEXENE, 3,4,4-
97 Ret: 126
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41
55
69
111
126
1-
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83
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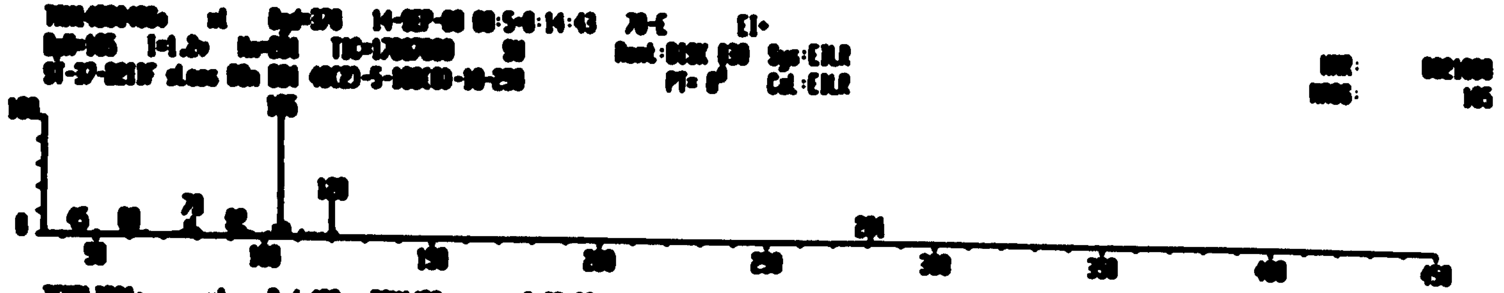
111
139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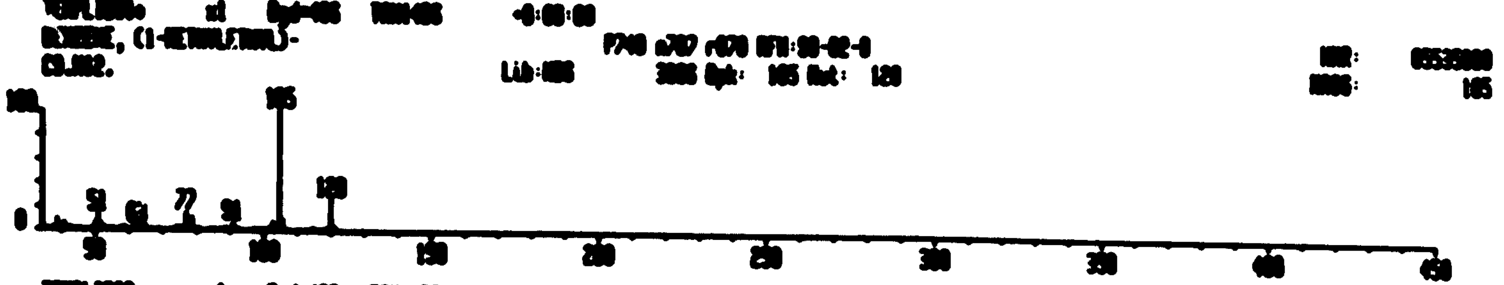
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F740 a707 r670 [illegible]:98-82-8
Lib:[illegible] 3086 Bpk: 105 [illegible]: 120
[illegible]: [illegible]
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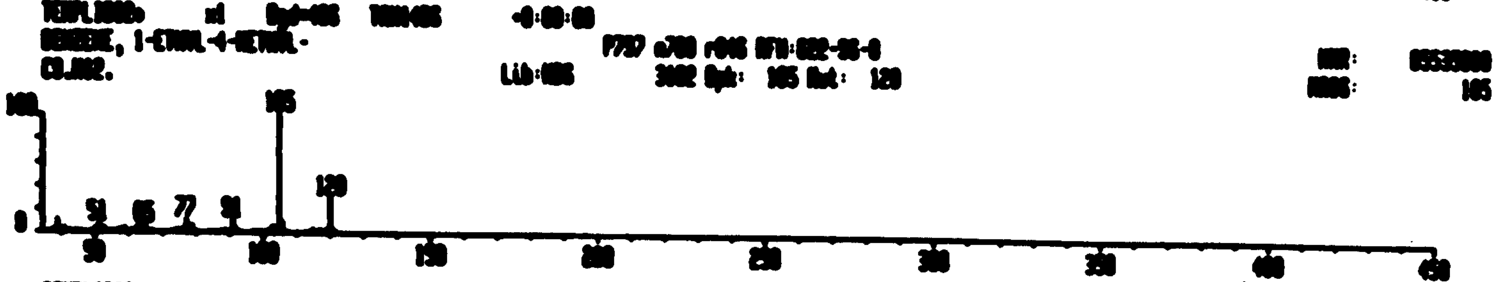
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F737 a700 r046 [illegible]:622-96-8
Lib:[illegible] 3082 Bpk: 105 [illegible]: 120
[illegible]: [illegible]
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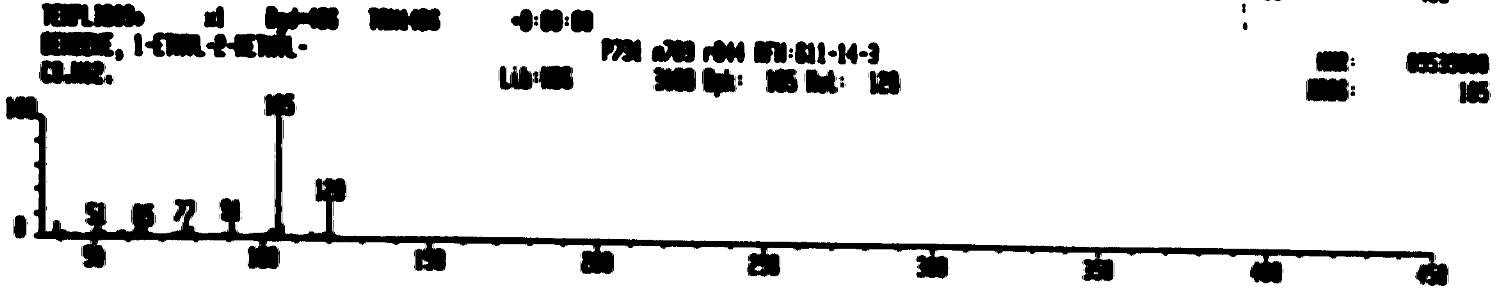
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C9.H12.
F731 a703 r044 [illegible]:611-14-3
Lib:[illegible] 3080 Bpk: 105 [illegible]: 120
[illegible]: [illegible]
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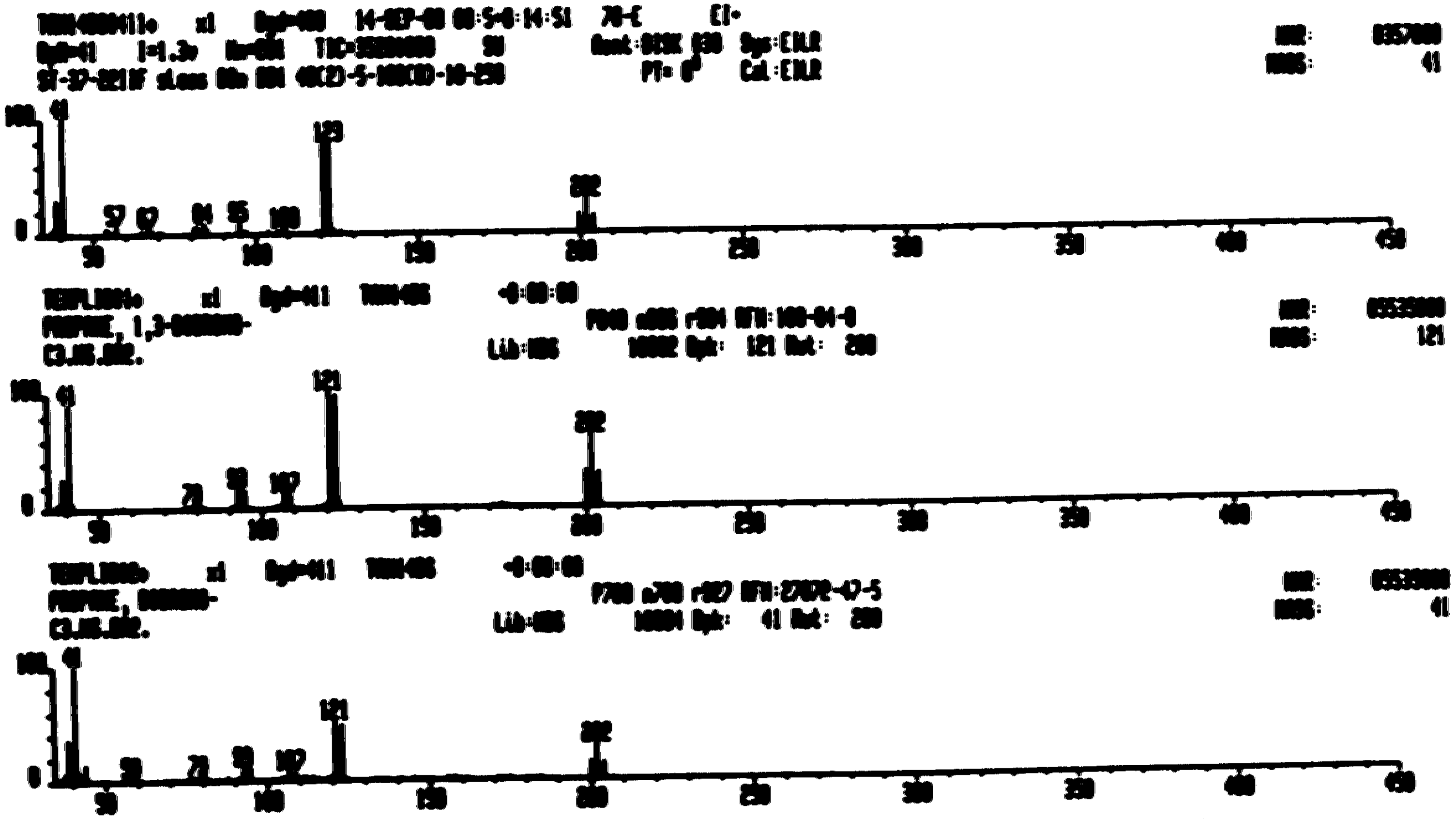
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EI+
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57
62
84
95
108
202
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0
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150
200
250
300
350
400
450
41
x1
-0:00:00
Lib:
121
41
71
93
107
121
202
100
0
50
100
150
200
250
300
350
400
450
x1
-0:00:00
Lib:
41
41
55
71
93
107
121
202
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100
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200
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300
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400
450

[illegible] x1 [illegible] 14-SEP-88 [illegible]:15:19 70-E EI+
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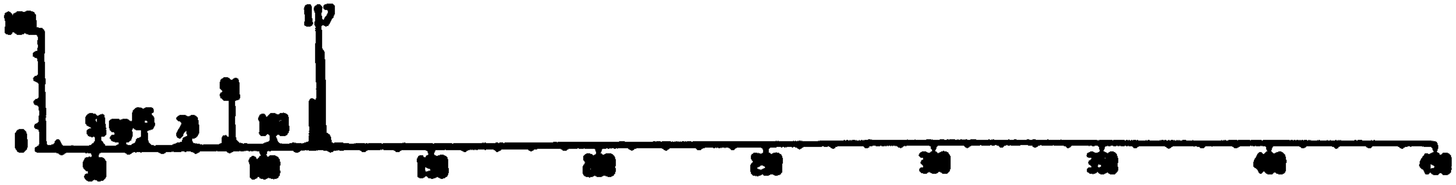

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C17.H18. Lib:NBS [illegible] Bpk: 117 [illegible]: [illegible]: 117

TEMPL.1003 x1 [illegible] +0:00:00
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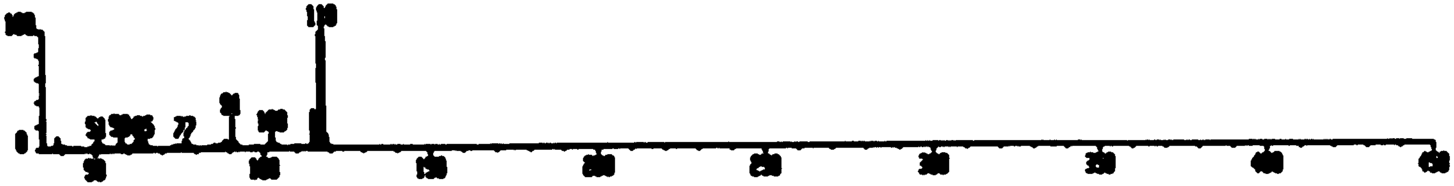
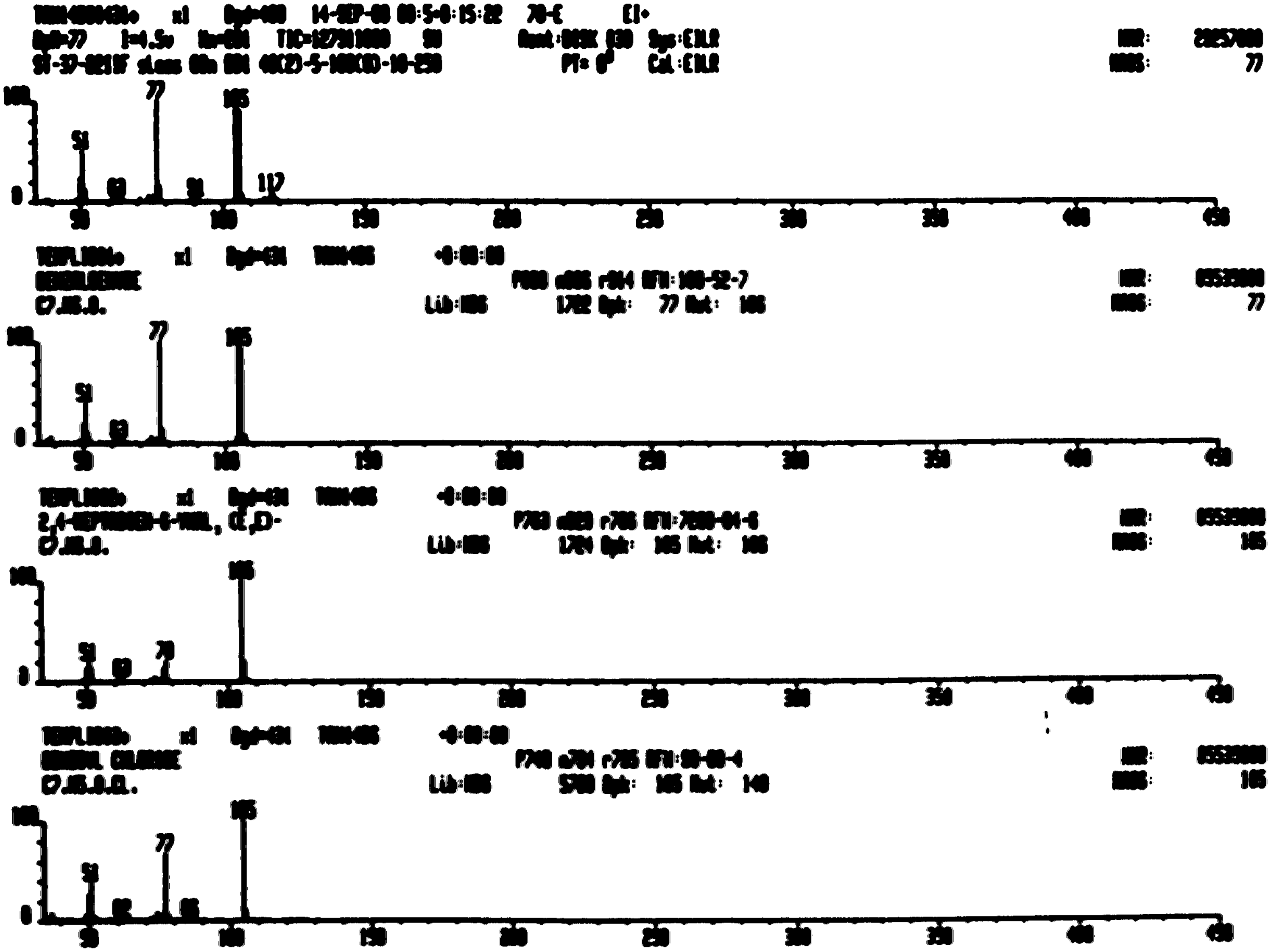
C9.H10. Lib:NBS [illegible] Bpk: 117 [illegible]: 118 [illegible]: 117

TEMPL.1003 x1 [illegible] +0:00:00
BENZENE, ETHENYLETHYL- [illegible]:28013-15-4 [illegible]: [illegible]
C10.H12. Lib:NBS 2879 Bpk: 118 [illegible]: 118 [illegible]: 118

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0
51
79
105
100
0
51
77
105


EI+
Lib:
104-63-2
7700
151
BENZENE, PROPYL-
103-65-1
3087
120
BENZENEACETALDEHYDE
122-78-1
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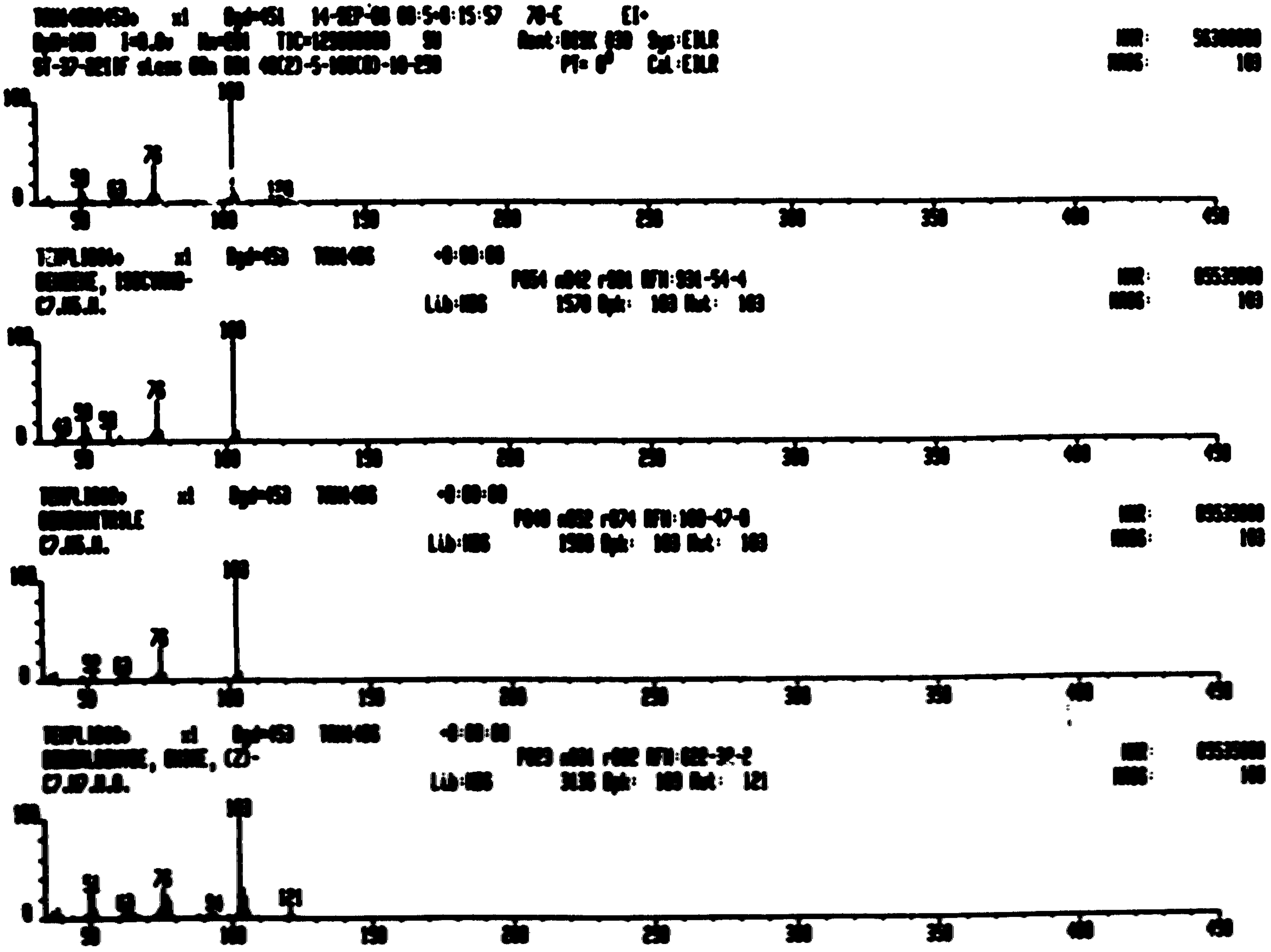
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250
300
350
400
450
x1
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931-54-4
C7.H5.N.
Lib:NBS
BENZONITRILE
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C7.H5.N.
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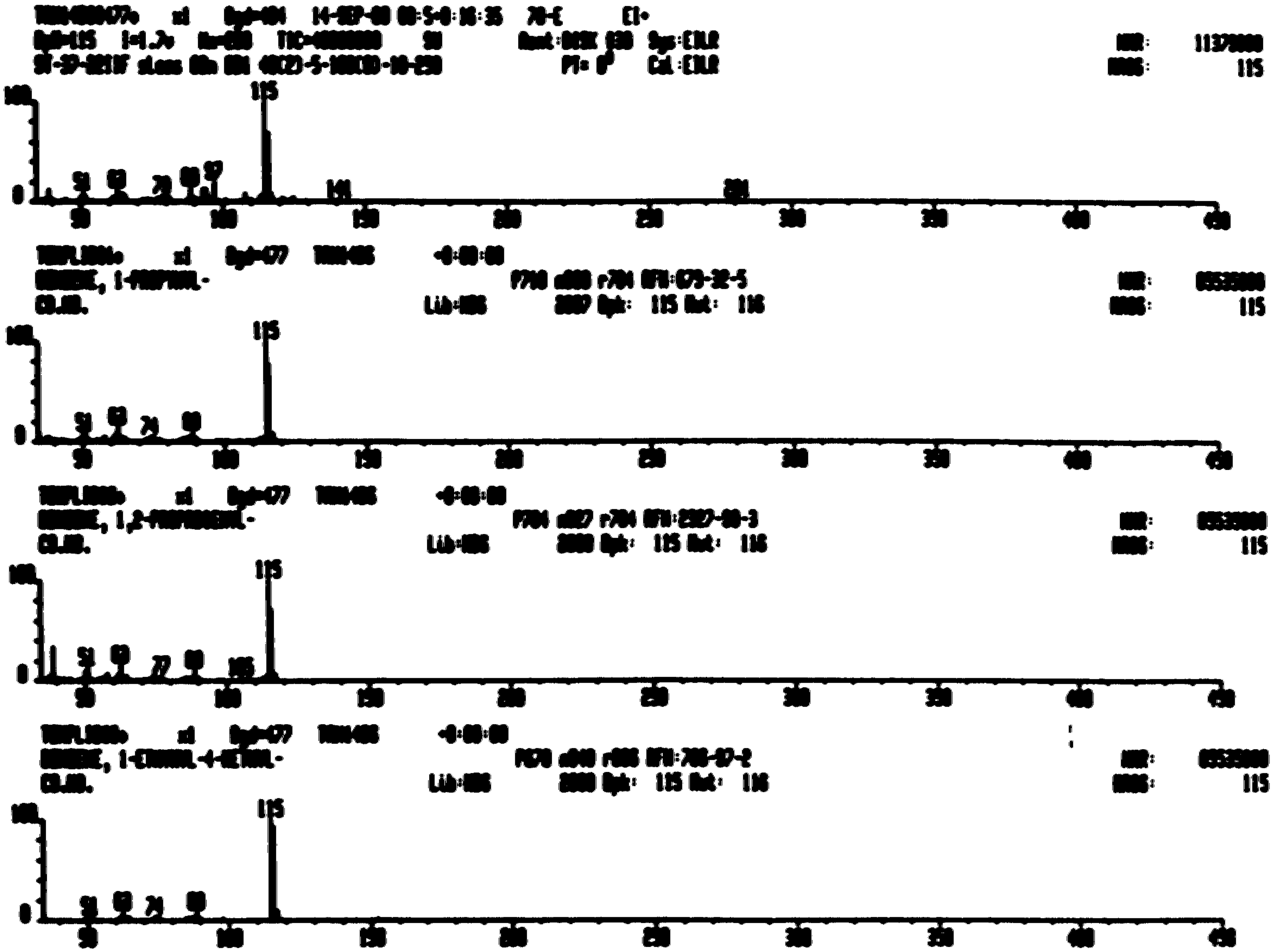
622-32-2
C7.H7.N.O.
121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141
201
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63
77
89
97
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673-32-5
BENZENE, 1,2-PROPADIENYL-
2327-99-3
BENZENE, 1-ETHYNYL-4-METHYL-
766-97-2
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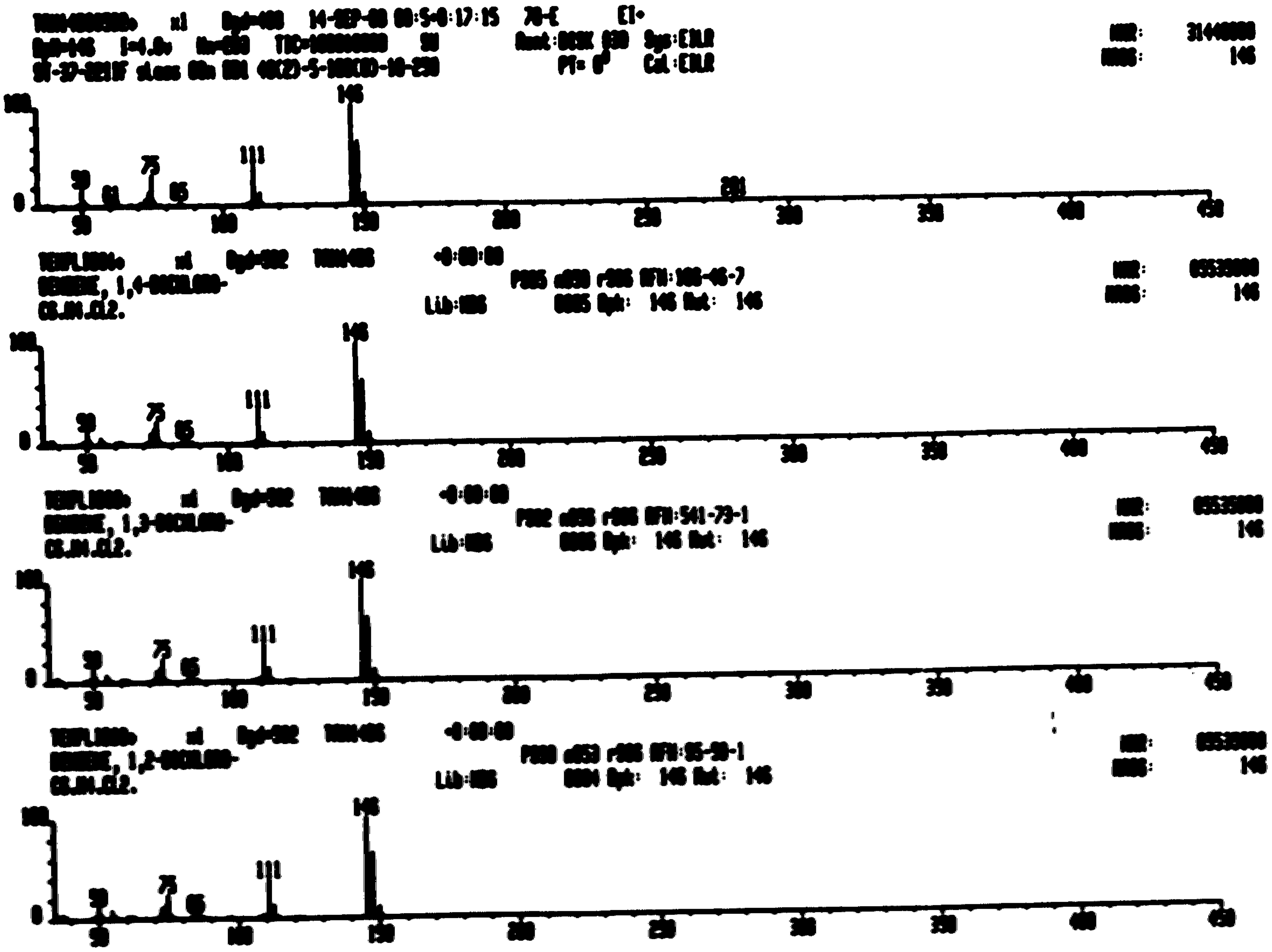
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C6.H4.CL2.
Lib:NBS
106-46-7
BENZENE, 1,3-DICHLORO-
C6.H4.CL2.
541-73-1
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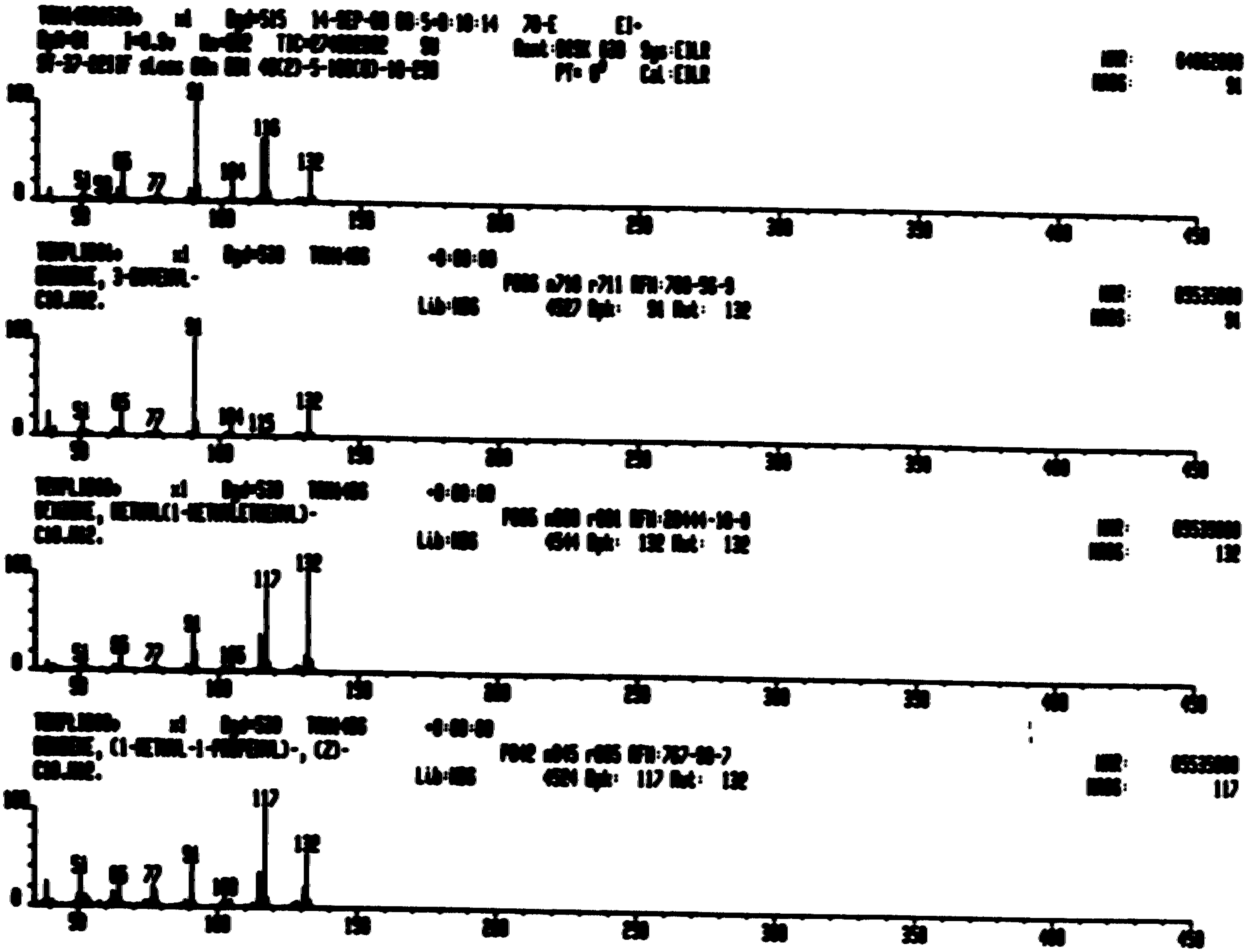
C6.H4.CL2.
95-50-1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BENZENE, 3-BUTENYL-
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768-56-9
Lib:NBS
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132
BENZENE, METHYL(1-METHYLETHENYL)-
C10.H12.
26444-18-0
Lib:NBS
132
132
BENZENE, (1-METHYL-1-PROPENYL)-, (Z)-
C10.H12.
767-99-7
Lib:NBS
117
132
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117
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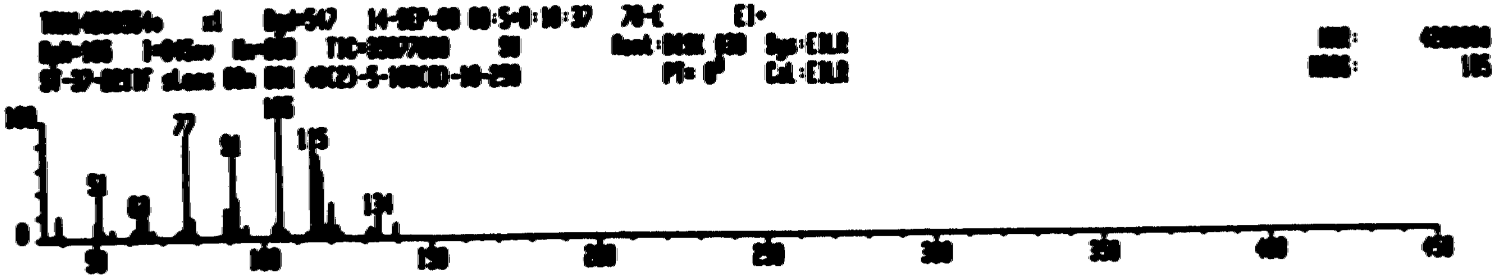
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TIC=
Cal:EILR
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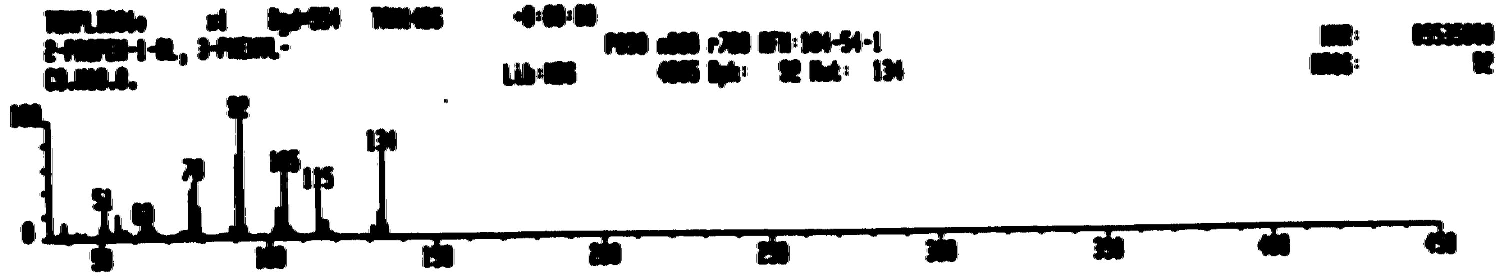
2-PROPEN-1-OL, 3-PHENYL-
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Lib:
Bpk: 92 Rmt: 134
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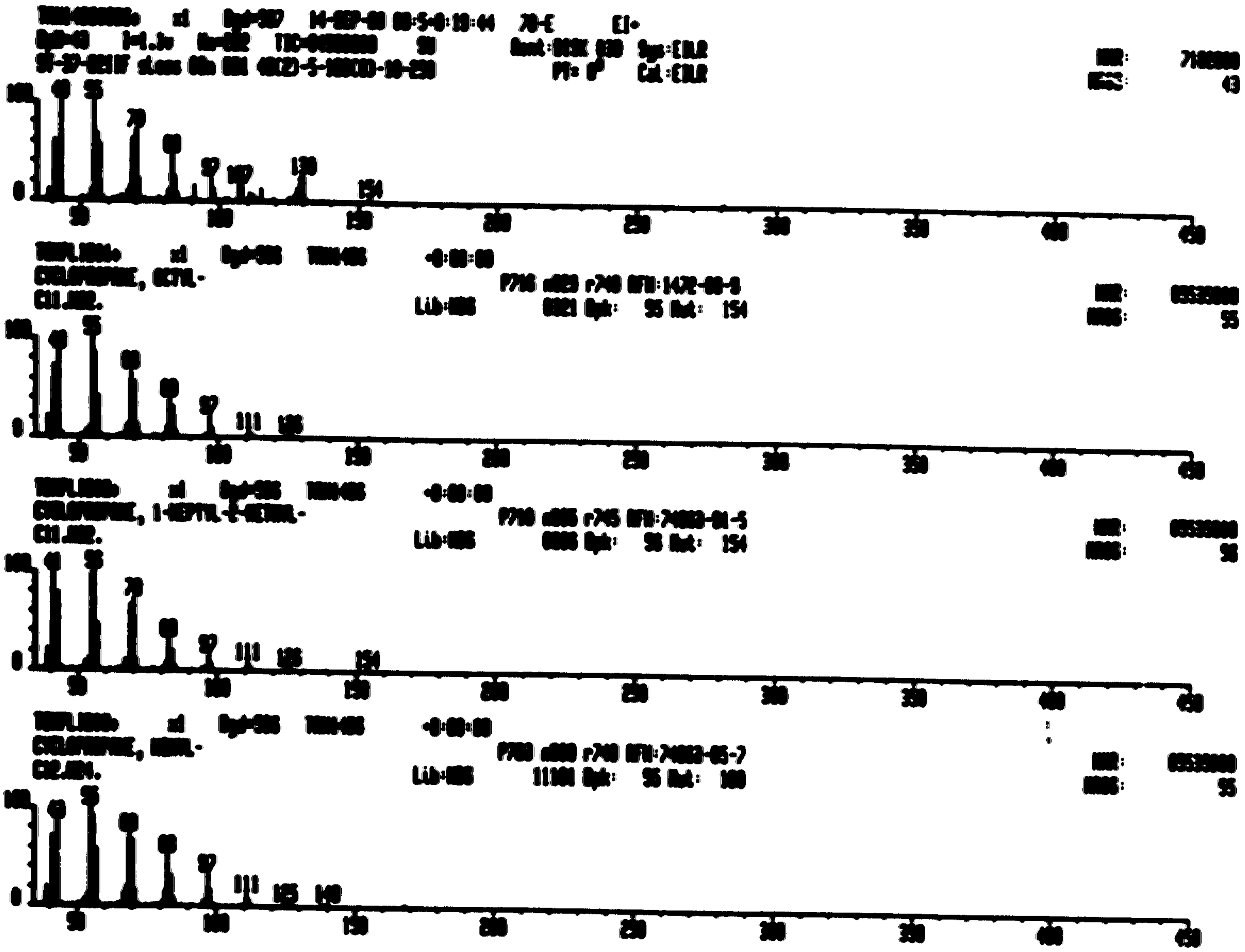
EI+
CYCLOPROPANE, OCTYL-
C11.H22.
CYCLOPROPANE, 1-HEPTYL-2-METHYL-
C11.H22.
CYCLOPROPANE, NONYL-
C12.H24.
Lib:
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97
139
154
69
111
125
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100
150
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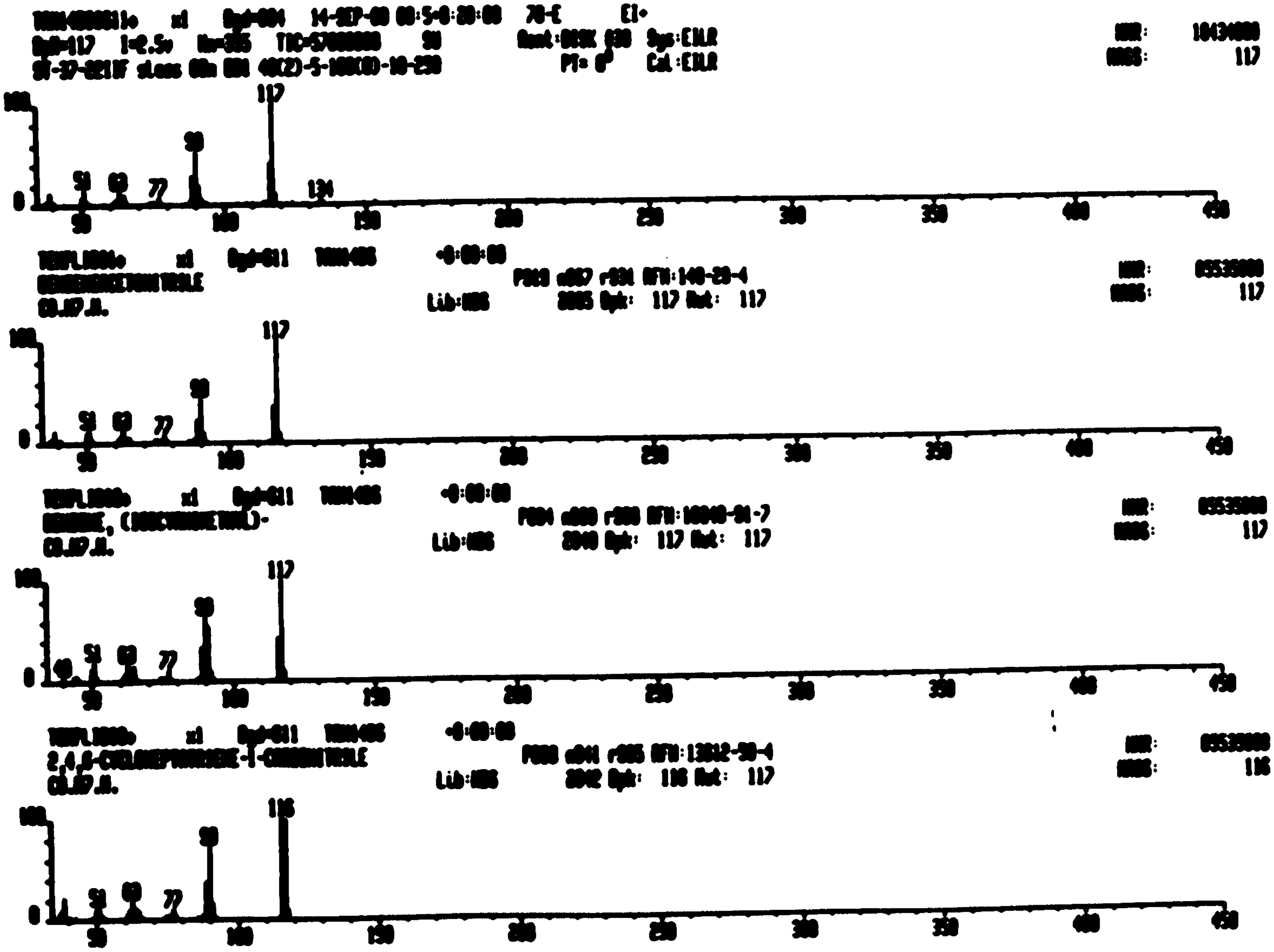
250
300
350
400
450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EI+
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Sys:EILR
PT= 0
Cal:EILR
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117
90
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63
77
134
BENZENEACETONITRILE
CFN:140-29-4
Lib:NBS
2005 Bpk: 117 Rmt: 117
C8.H7.N.
117
117
90
51
63
77
BENZENE, (ISOCYANOMETHYL)-
CFN:10340-91-7
Lib:NBS
2040 Bpk: 117 Rmt: 117
C8.H7.N.
117
117
90
40
51
63
77
2,4,6-CYCLOHEPTATRIENE-1-CARBONITRILE
CFN:13612-59-4
Lib:NBS
2042 Bpk: 116 Rmt: 117
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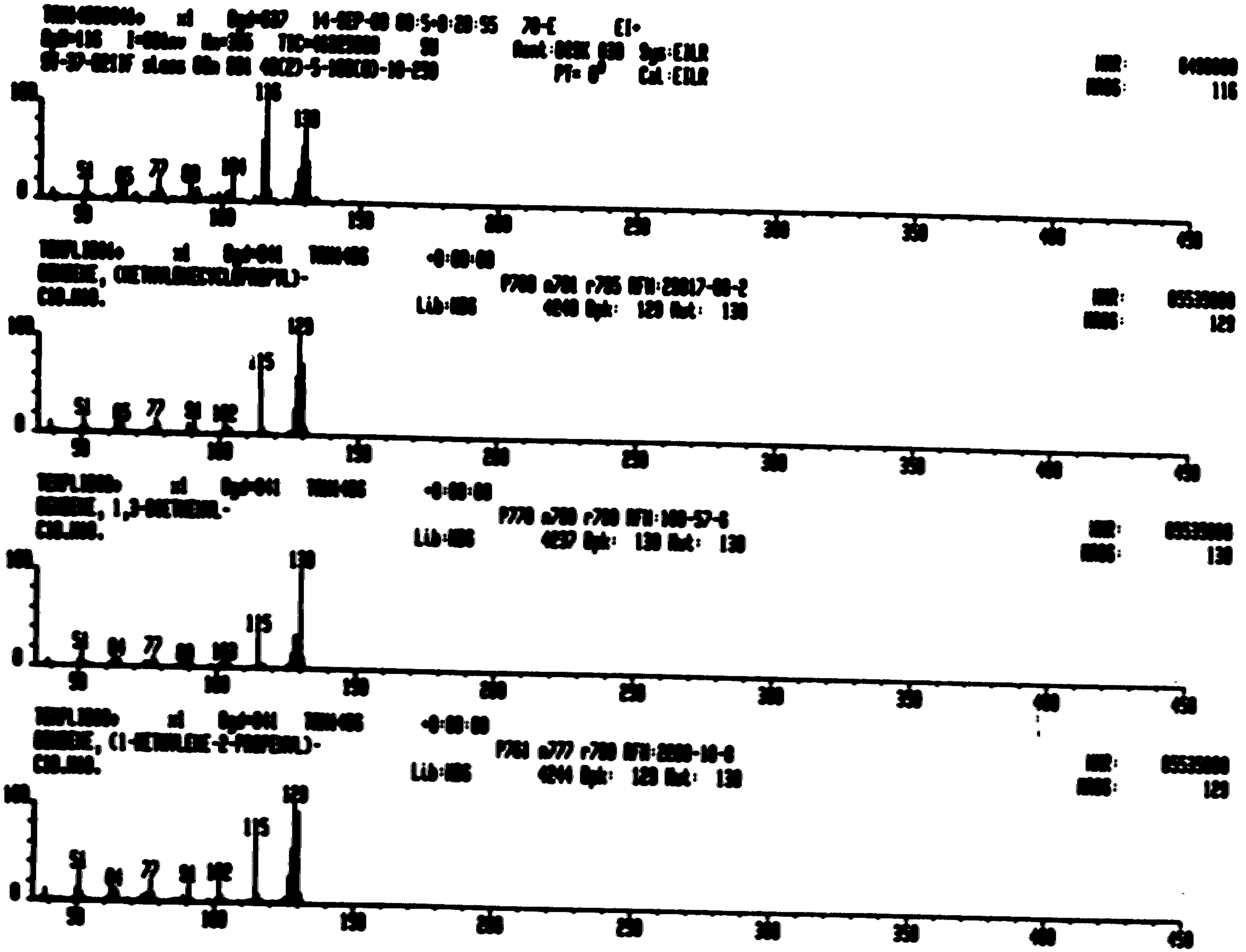
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65
77
91
102
115
129
100
0
51
64
77
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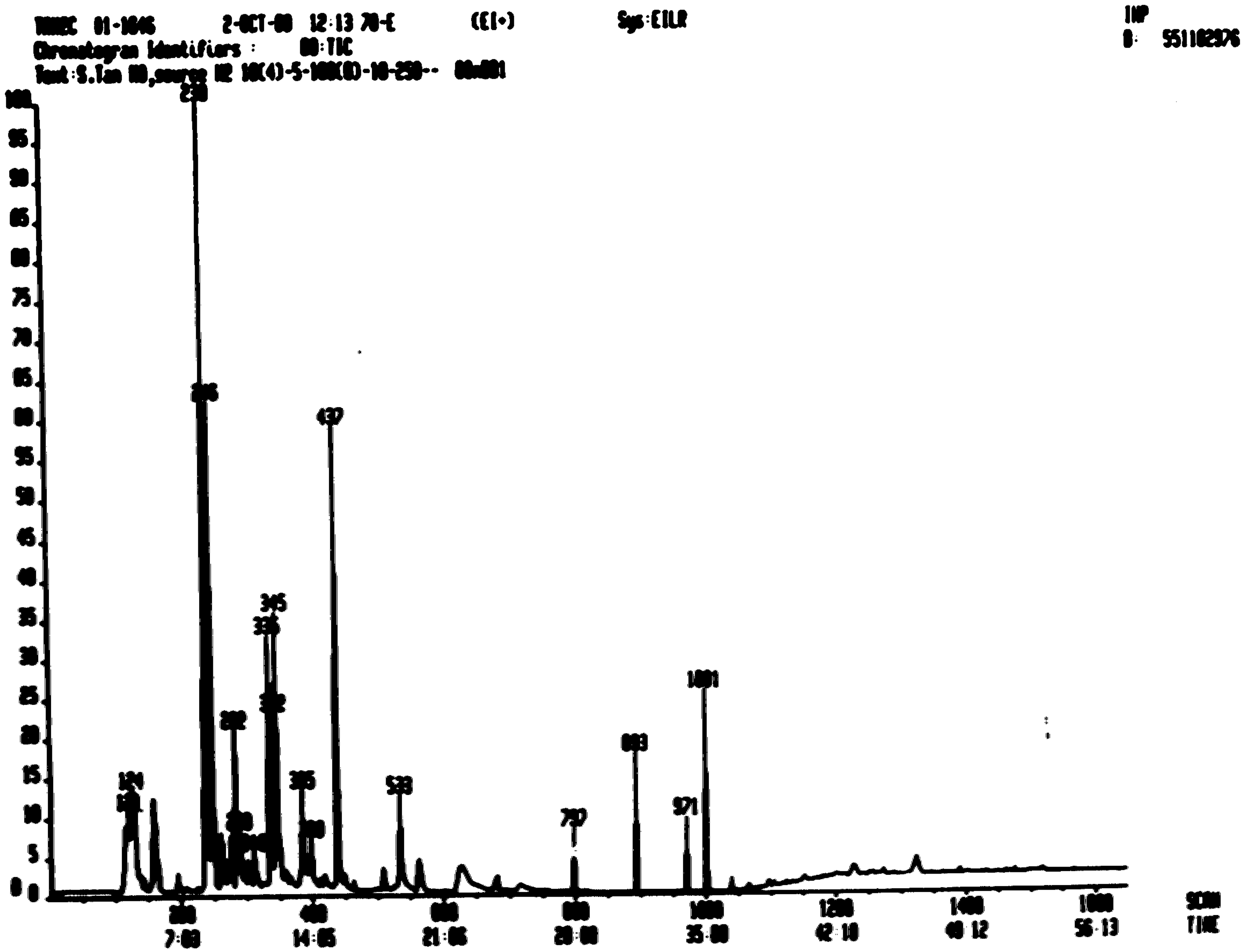
115
129
C10.H10.
C10.H10.
C10.H10.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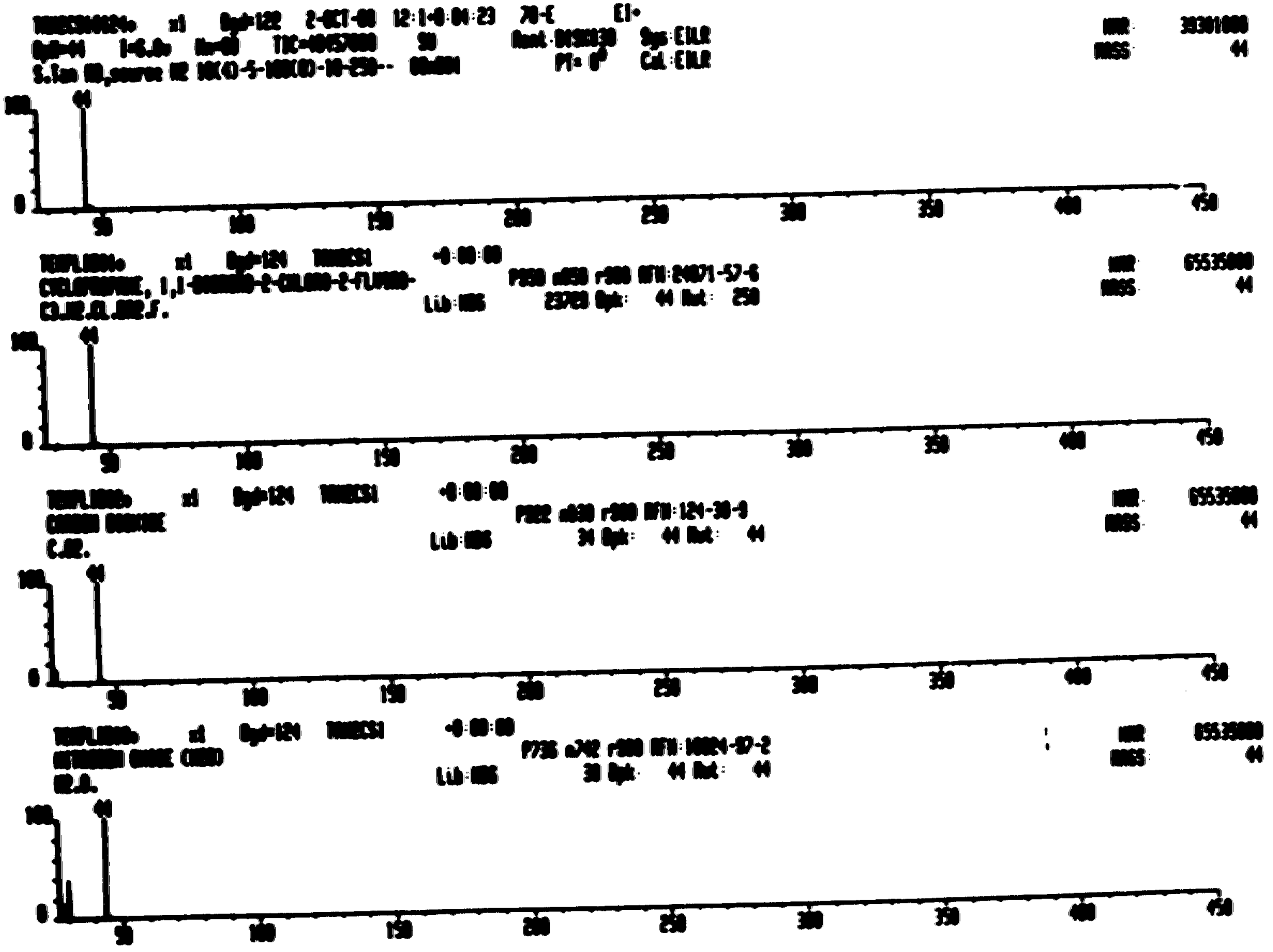
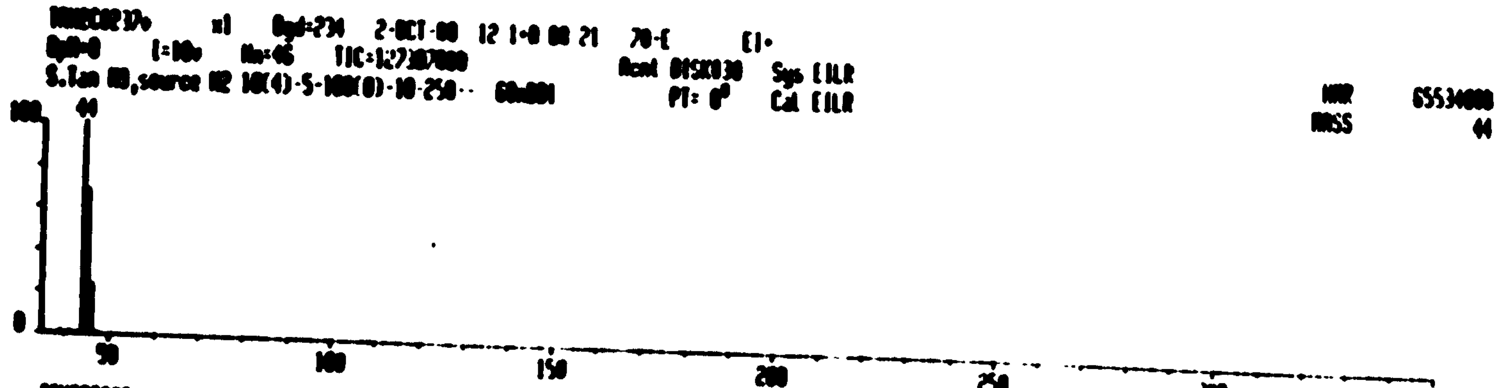
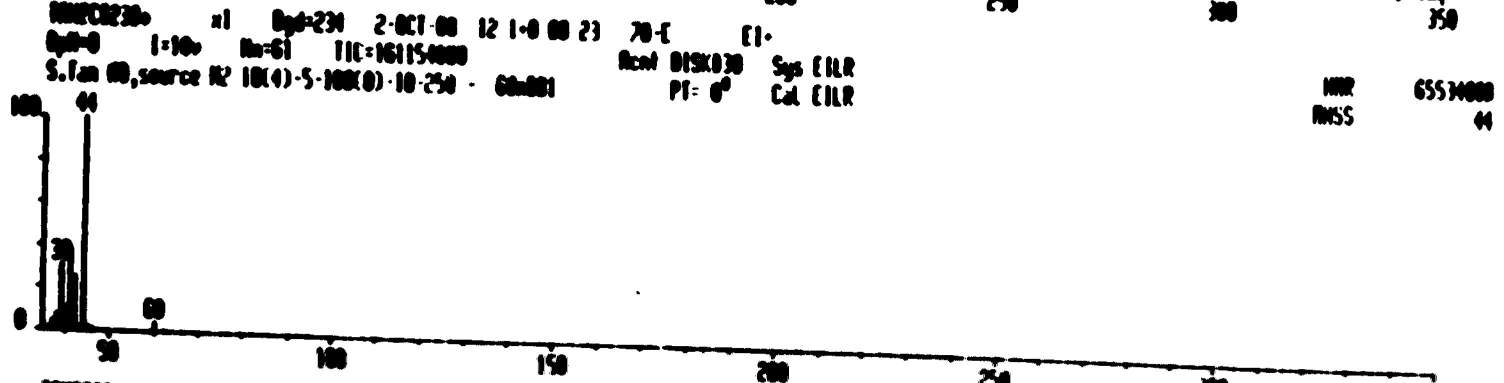
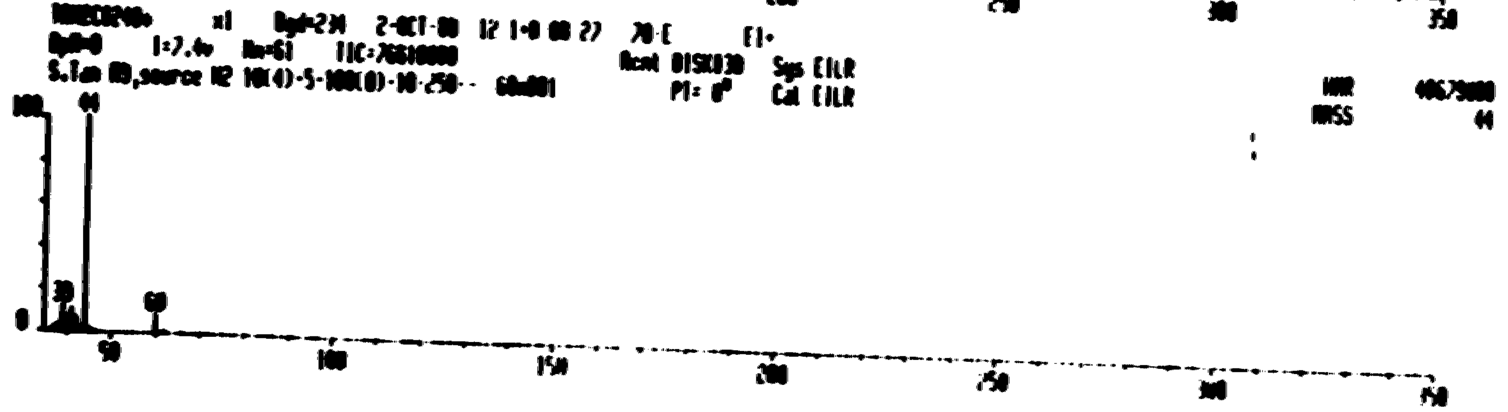
56:13
SCAN
TIME


x1
Bpk=122
12:1+0:04:23
70-E
EI+
Sys:EILR
Cal:EILR
HRR: 39301000
MASS 44
x1
Bpk=124
+0:00:00
CYCLOPROPANE, 1,1-
-2-CHLORO-2-FLUORO-
Lib:NBS
Bpk: 44 Rnk: 250
HRR 65535000
MASS 44
x1
Bpk=124
+0:00:00
CARBON DIOXIDE
C.O2.
124-38-9
Lib:NBS
Bpk: 44 Rnk: 44
HRR 65535000
MASS 44
x1
Bpk=124
+0:00:00
NITROUS OXIDE (N2O)
N2.O.
10024-97-2
Lib:NBS
Bpk: 44 Rnk: 44
HRR 65535000
MASS 44
100
0
44
50
100
150
200
250
300
350
400
450


MMECO237o x1 Bpd=234 2-OCT-00 12 1+0 00 21 70·E EI+
BpM=0 I=10v Hm=46 TIC=127307000 Acnt DISK030 Sys EILR
S.Tan 00,source N2 10(4)-5-100(0)-10-250·· 60m001 PT: 0° Cal EILR
HMR 65534000
MASS 44
100
0
44
50
100
150
200
250
300
350


MMECO238o x1 Bpd=234 2-OCT-00 12 1+0 00 23 70·E EI+
BpM=0 I=10v Hm=61 TIC=161154000 Acnt DISK030 Sys EILR
S.Tan 00,source N2 10(4)-5-100(0)-10-250 · 60m001 PT: 0° Cal EILR
HMR 65534000
MASS 44
100
0
44
30
60
50
100
150
200
250
300
350

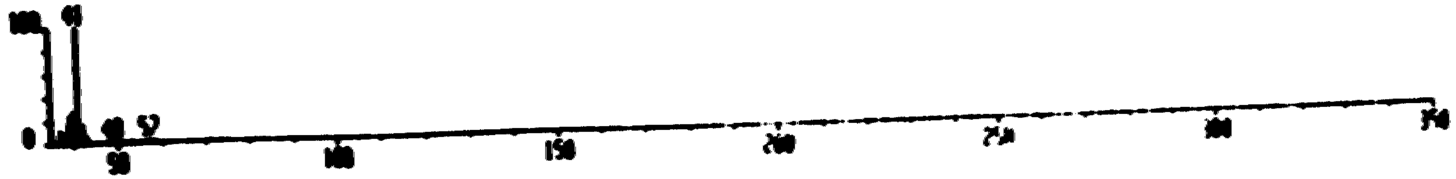

MMECO240o x1 Bpd=234 2-OCT-00 12 1+0 00 27 70·E EI+
BpM=0 I=7.4v Hm=61 TIC=76610000 Acnt DISK030 Sys EILR
S.Tan 00,source N2 10(4)-5-100(0)-10-250·· 60m001 PT: 0° Cal EILR
HMR 40679000
MASS 44
100
0
44
30
60
50
100
150
200
250
300
350

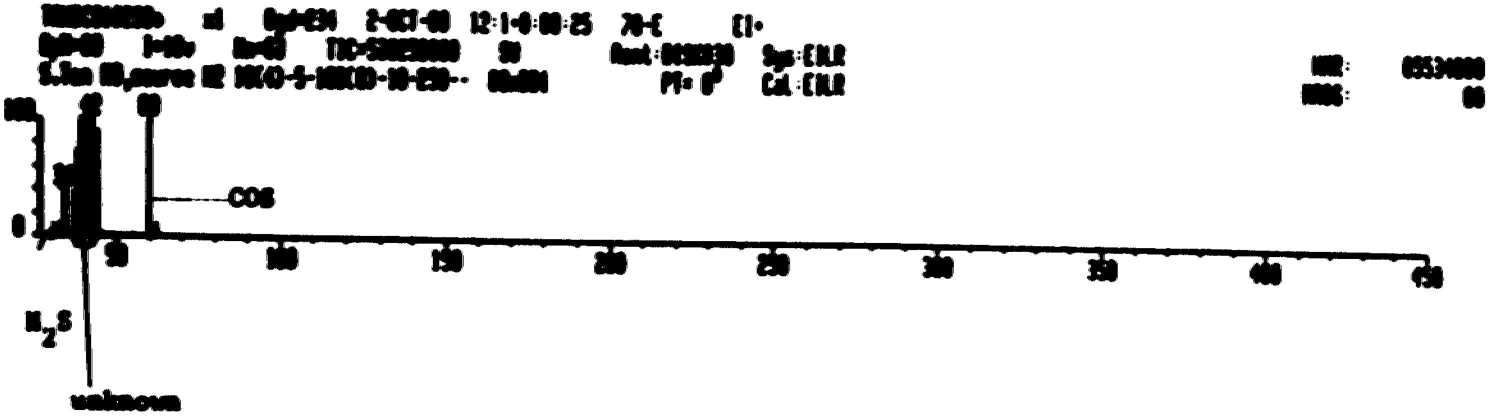
```
[illegible]     x1   Bpk=234   2-OCT-80   12 1+0 00 23   70-E        EI+                              NOR      24274000
BpM=41    I=3.7v   Hm=62   TIC=94770000   50          Acnt DISK030   Sys EILR                   MASS           41
S.Tan 00,source 02 10(4)-5-100(0)-10-250--  00n001           PI= 0     Cal EILR
```

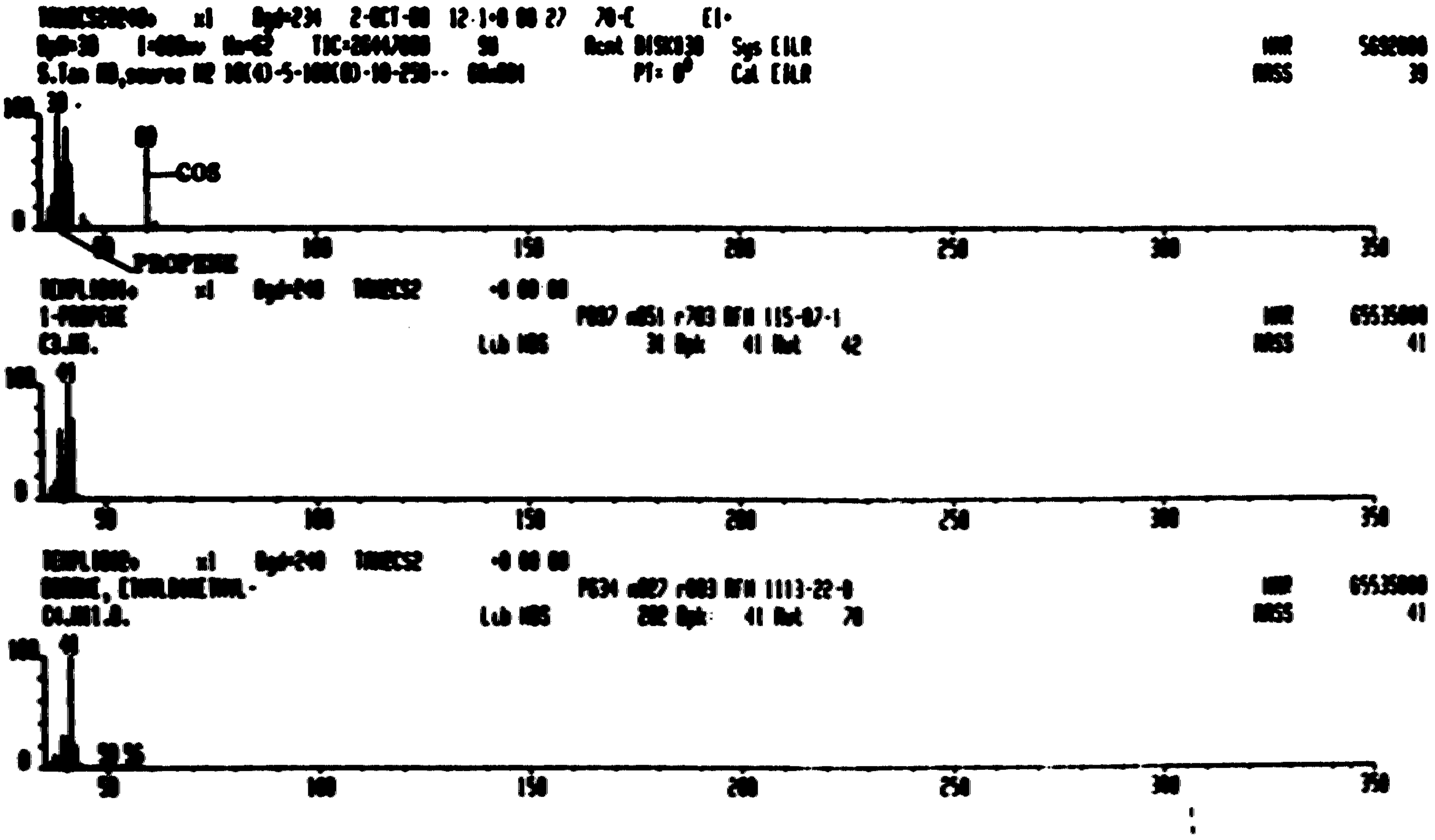
```
TEMPL[illegible]     x1    Bpk=230   TRNECS2        +0 00:00                                      NOR      65535000
1-PROPENE                                            P910 n005 r926 RFN 115-07-1               MASS           41
C3.H6.                                     Lib NBS           31 Bpk    41 Mwt    42
```

```
TEMPL[illegible]     x1    Bpk=230   TRNECS2        +0 00 00                                      NOR      65535000
BORANE, ETHYLDIMETHYL-                               P011 n056 r074 RFN 1113-22-0              MASS           41
C4.H11.B.                                  Lib NBS          202 Bpk    41 Mwt    70
```

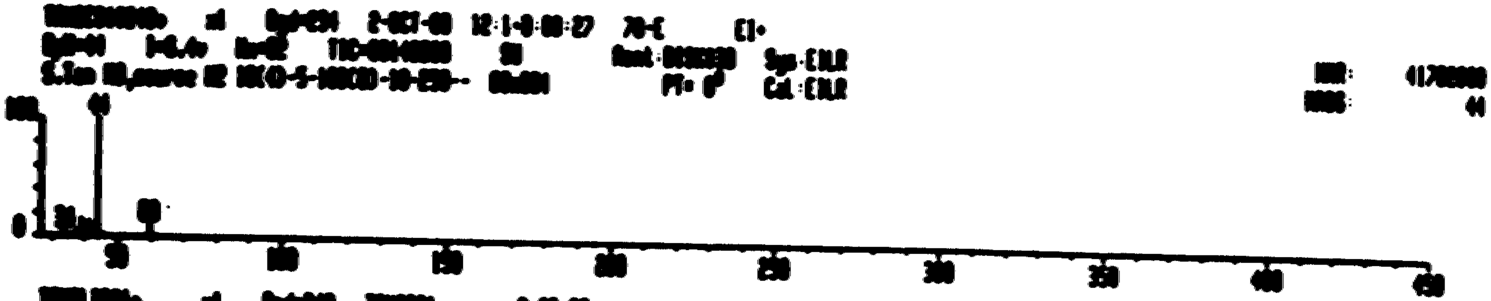
```
TEMPL[illegible]     x1    Bpk=230   TRNECS2        +0 00 00                                      NOR      65535000
BORANE, DIETHYLMETHYL-                               P764 n007 r052 RFN 1115-07-?              MASS           41
C5.H13.B.                                  Lib NBS          504 Bpk    41 Mwt    84
```

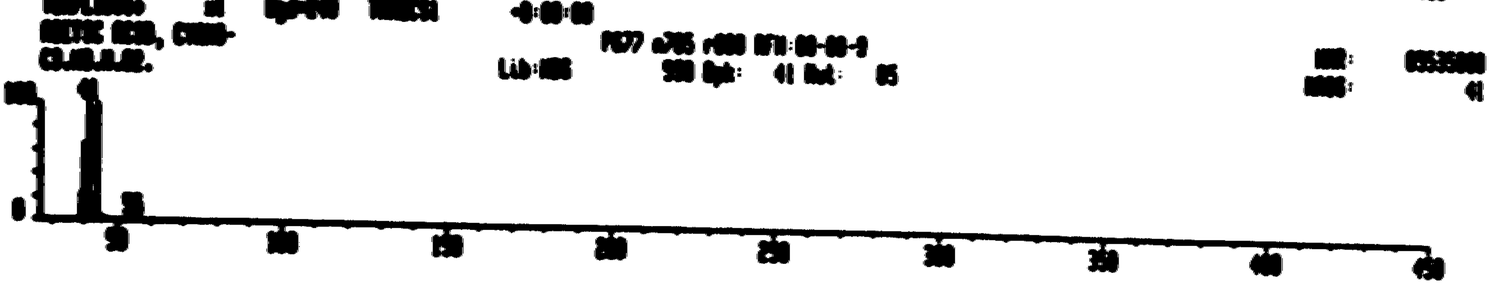


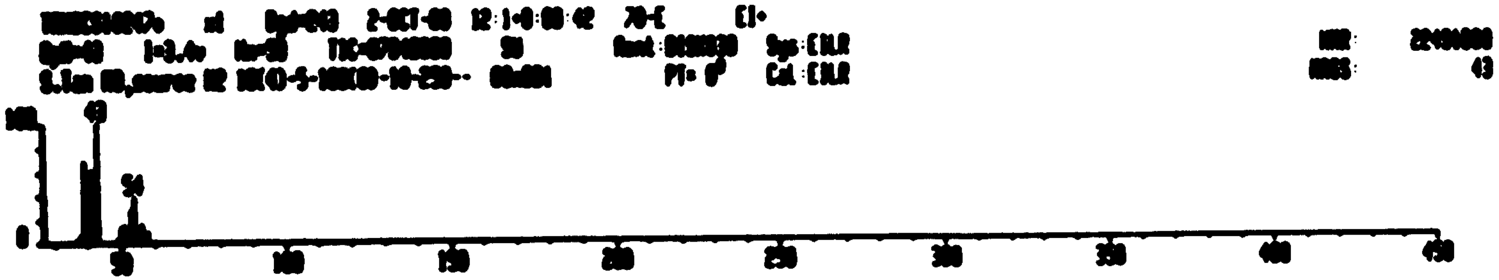

COS
H_2S
unknown
0
50
100
150
200
250
300
350
400
450

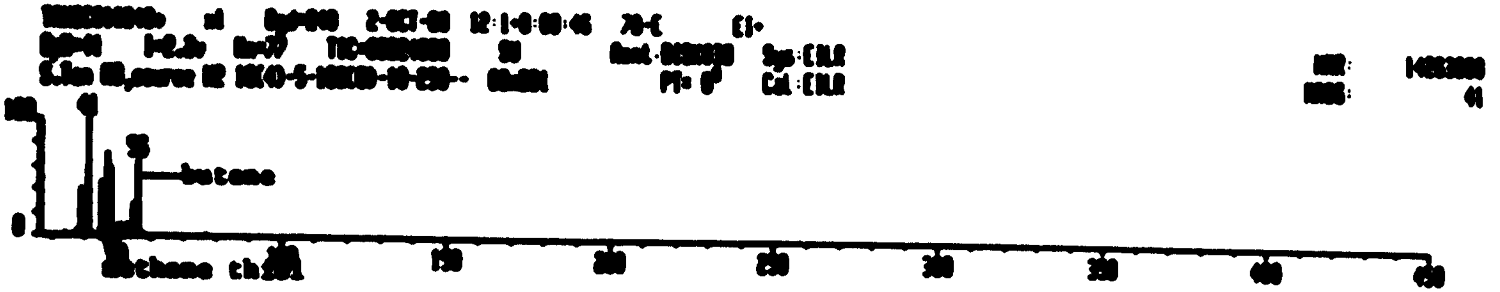


```
[illegible]    x1    Bpk=234   2-OCT-88   12:1+0 00 27   70-C       EI+
Bpk=30    I=000    Hr=62    TIC=26447000    50        Acnt DISK030   Sys EILR           HUR        5692000
S.Tan [illegible],source [illegible] 10(4)-5-100(0)-10-250--  [illegible]        PI: 0    Cal EILR           MASS           30

TEMPL000+     x1    Bpk=240    TANECS2      +0 00 00
1-PROPENE                                   P007 m051 r703 RFN 115-07-1                       HUR      65535000
C3.H6.                           Lib NBS          38 Bpk    41 Rnk    42                       MASS           41

TEMPL000+     x1    Bpk=240    TANECS2      +0 00 00
BORANE, CHLORODIETHYL-                      P634 m027 r083 RFN 1113-22-0                      HUR      65535000
C4.H10.B.                        Lib NBS         202 Bpk:   41 Rnk    70                       MASS           41
```

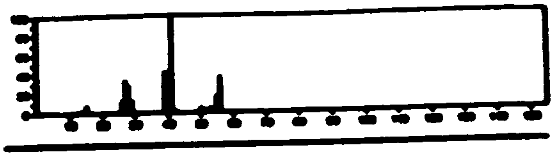

EI+
100
0
44
50
100
150
200
250
300
350
400
450


100
0
41
50
100
150
200
250
300
350
400
450

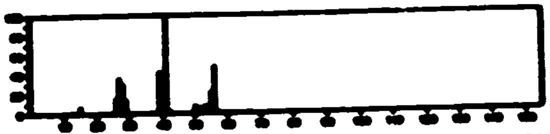

100
43
54
0
50
100
150
200
250
300
350
400
450


100
0
41
58
butane
ethane thiol
50
150
200
250
300
350
400
450
41

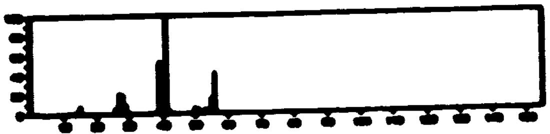
56
1-Butene
C_4H_8
106-98-9
$CH_2{=}CHCH_2CH_3$



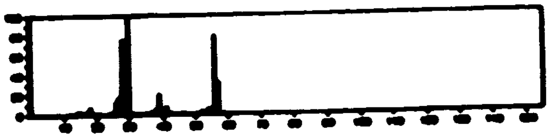
56
2-Butene
C_4H_8
107-01-7
$CH_3CH{=}CHCH_3$



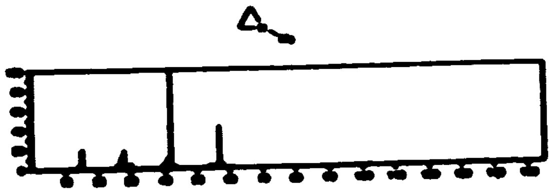
56
1-Propene, 2-methyl-
C_4H_8
115-11-7
$(CH_3)_2C{=}CH_2$



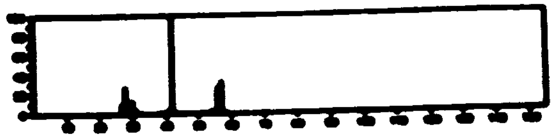
57
2-Propen-1-amine
C_3H_7N
107-11-9
$H_2NCH_2CH{=}CH_2$



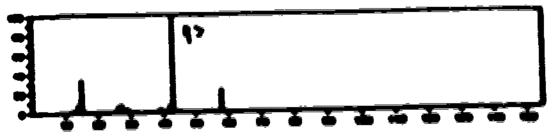
57
Aziridine, 1-methyl-
C_3H_7N
1072-44-2



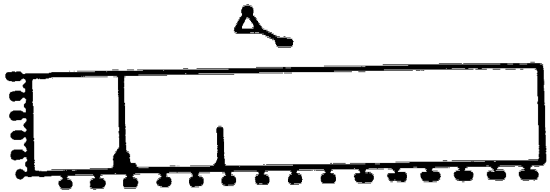
57
Ethanamine, N-methylene-
C_3H_7N
43729-97-1
$CH_2{=}NCH_2CH_3$



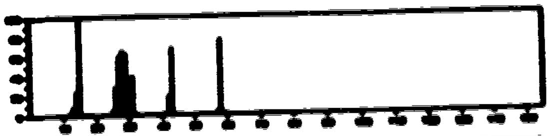
58
2-Propanone
C_3H_6O
67-64-1
CH_3COCH_3



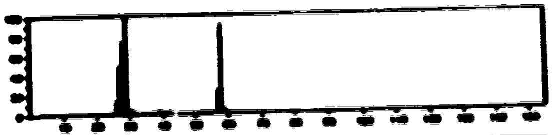
58
Oxirane, methyl-
C_3H_6O
75-56-9



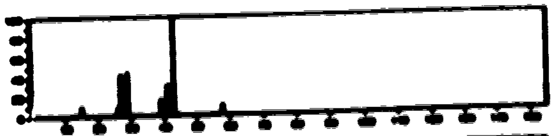
58
Ethene, methoxy-
C_3H_6O
107-25-5
$CH_3OCH{=}CH_2$



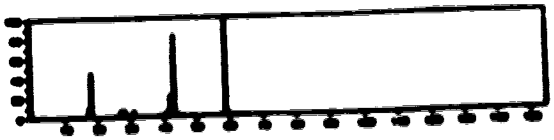
58
Propanal
C_3H_6O
123-38-6
C_2H_5CHO



58
Butane
C_4H_{10}
106-97-8
C_4H_{10}

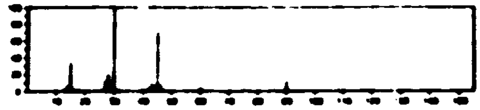


59
Guanidine
CH_5N_3
113-00-8
$(H_2N)_2C{=}NH$



45 CH_3NO 865-40-7
Methane, nitroso-

CH_3NO



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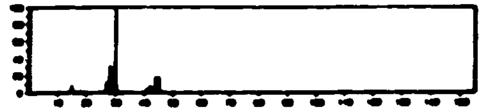
45 C_2H_7N 75-04-7
Ethanamine

$C_2H_5NH_2$



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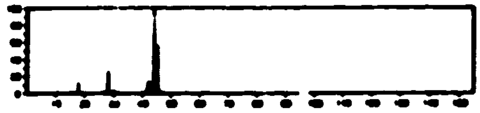
45 C_2H_7N 124-40-3
Methanamine, *N*-methyl-

$(CH_3)_2NH$



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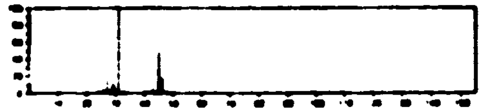
46 C_2H_6O 64-17-5
Ethanol

C_2H_5OH



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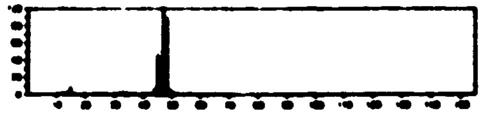
48 CH_4S 74-93-1
Methanethiol

CH_3SH



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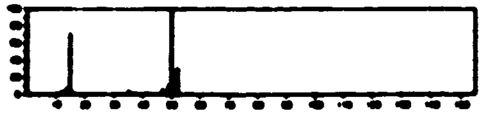
50 CH_3Cl 74-87-3
Methane, chloro-

CH_3Cl



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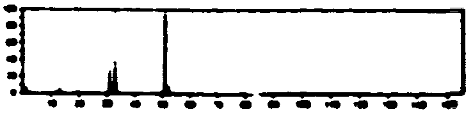
52 CH_2F_2 75-10-5
Methane, difluoro-

CH_2F_2



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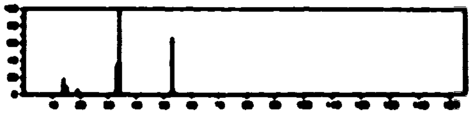
52 C_2N_2 460-19-5
Ethanedinitrile

NCCN

---

53 F_2HN 10405-27-3
Fluorimide

HNF_2



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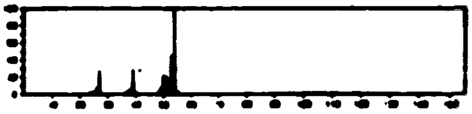
54 C_4H_6 590-19-2
1,2-Butadiene

$H_2C{=}C{=}CHCH_3$



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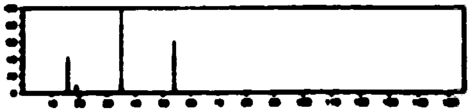
54 F_2O 7783-41-7
Oxygen fluoride (OF_2)

OF_2



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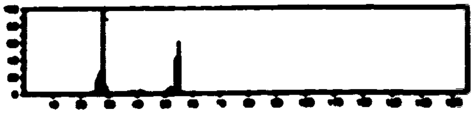
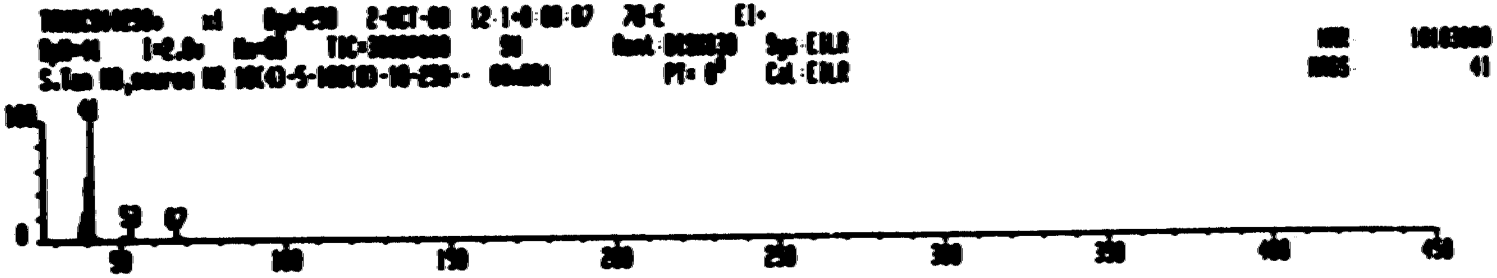
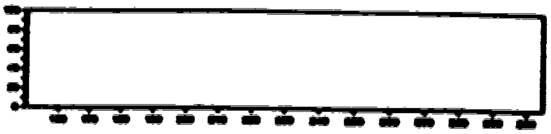
57 C_3H_7N [illegible]-27-9
Ethanamine, *N*-methylene-

$H_2C{=}NC_2H_5$



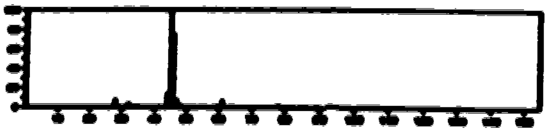


cyclopropane carbonitrile



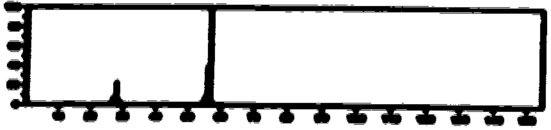
46
Methanethial, homopolymer $(CH_2S)_x$ [illegible]

$CH_2=S=CH_2$



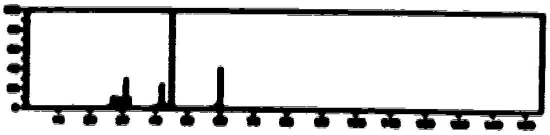
57
Methane, isocyanato- C_2H_3NO 624-83-9

CH_3NCO



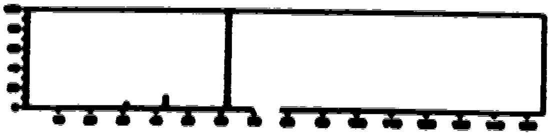
60
Hydrazine, ethyl- $C_2H_8N_2$ 624-80-6

$EtNHNH_2$



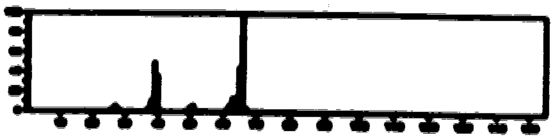
62
Ethyne, difluoro- C_2F_2 689-99-4

$FC≡CF$



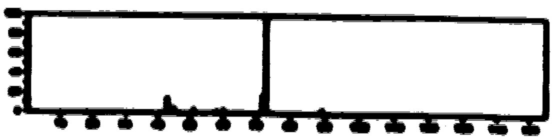
66
2-Penten-4-yne, (E)- C_5H_6 1574-40-0

$HC≡CCH=CHCH_3$

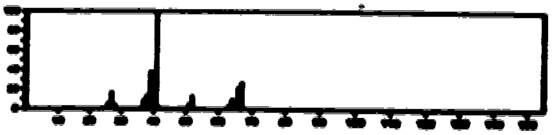


66
Acetic acid, lithium salt $C_2H_3O_2.Li$ 546-89-4

CH_3CO_2 • Li

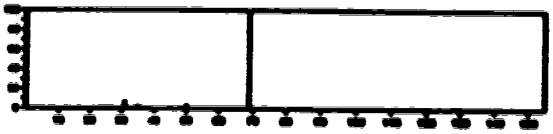


67
Cyclopropanecarbonitrile C_4H_5N 5500-21-0

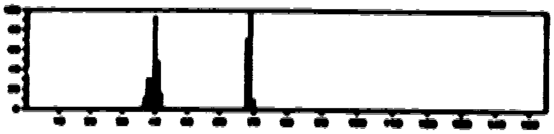


69
2-Propynenitrile, 3-fluoro- C_3FN [illegible]

$FC≡CCN$

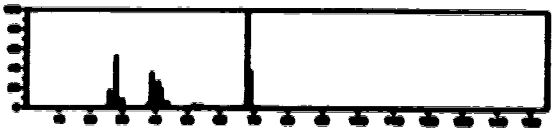


69
Isoxazole C_3H_3NO 288-14-2



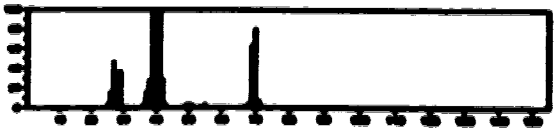
69
2-Propyn-1-amine, N-methyl- C_4H_7N 35161-71-6

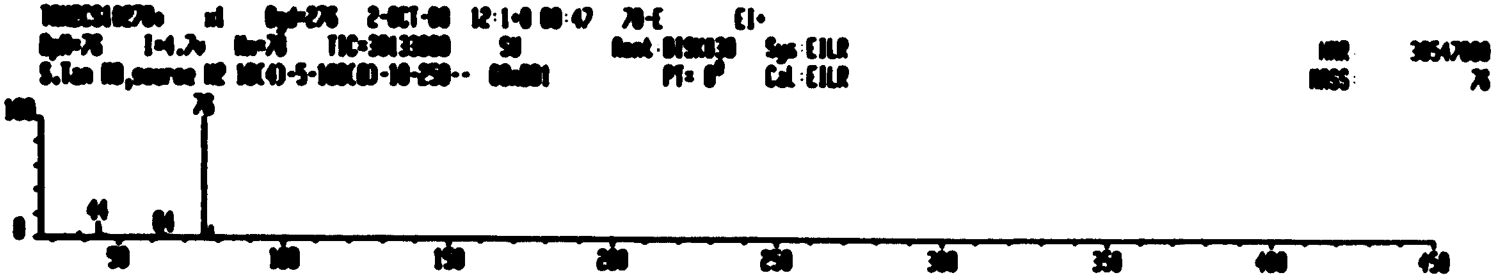
$HC≡CCH_2NHCH_3$

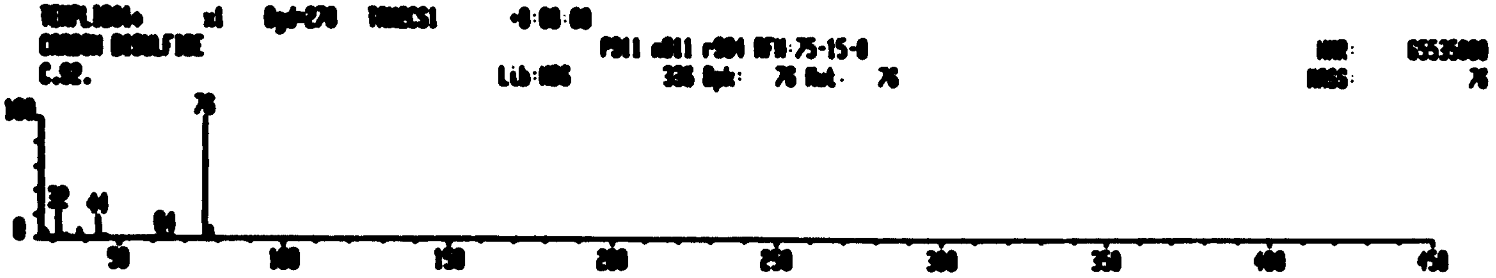


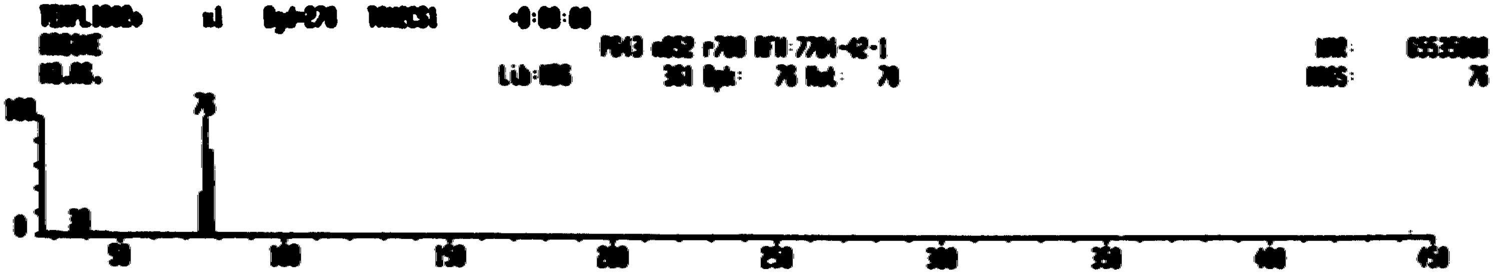
70
2-Butenal, (E)- C_4H_6O 123-73-9

$CH_3CH=CHCHO$




TANECS10270o xl Bgd=276 2-OCT-00 12:1+0 00:47 70-E EI+
BpM=76 I=4.7v Hm=76 TIC=30133000 SU Acnt:015K030 Sys:EILR
S.Tan 00,source 02 10(4)-5-100(0)-10-250-- 00a001 PT= 0° Cal:EILR
HHR: 30547000
MASS: 76
100
0
76
44
64
50
100
150
200
250
300
350
400
450


TEMPL1004o xl Bgd=270 TANECS1 +0:00:00
CARBON DISULFIDE P011 a011 r904 RFN:75-15-0
C.S2. Lib:NBS 336 Bpk: 76 Rmt: 76
HHR: 65535000
MASS: 76
100
0
76
32
44
64
50
100
150
200
250
300
350
400
450


TEMPL1002o xl Bgd=270 TANECS1 +0:00:00
ARSINE P043 a052 r700 RFN:7784-42-1
AS.H3. Lib:NBS 361 Bpk: 76 Rmt: 78
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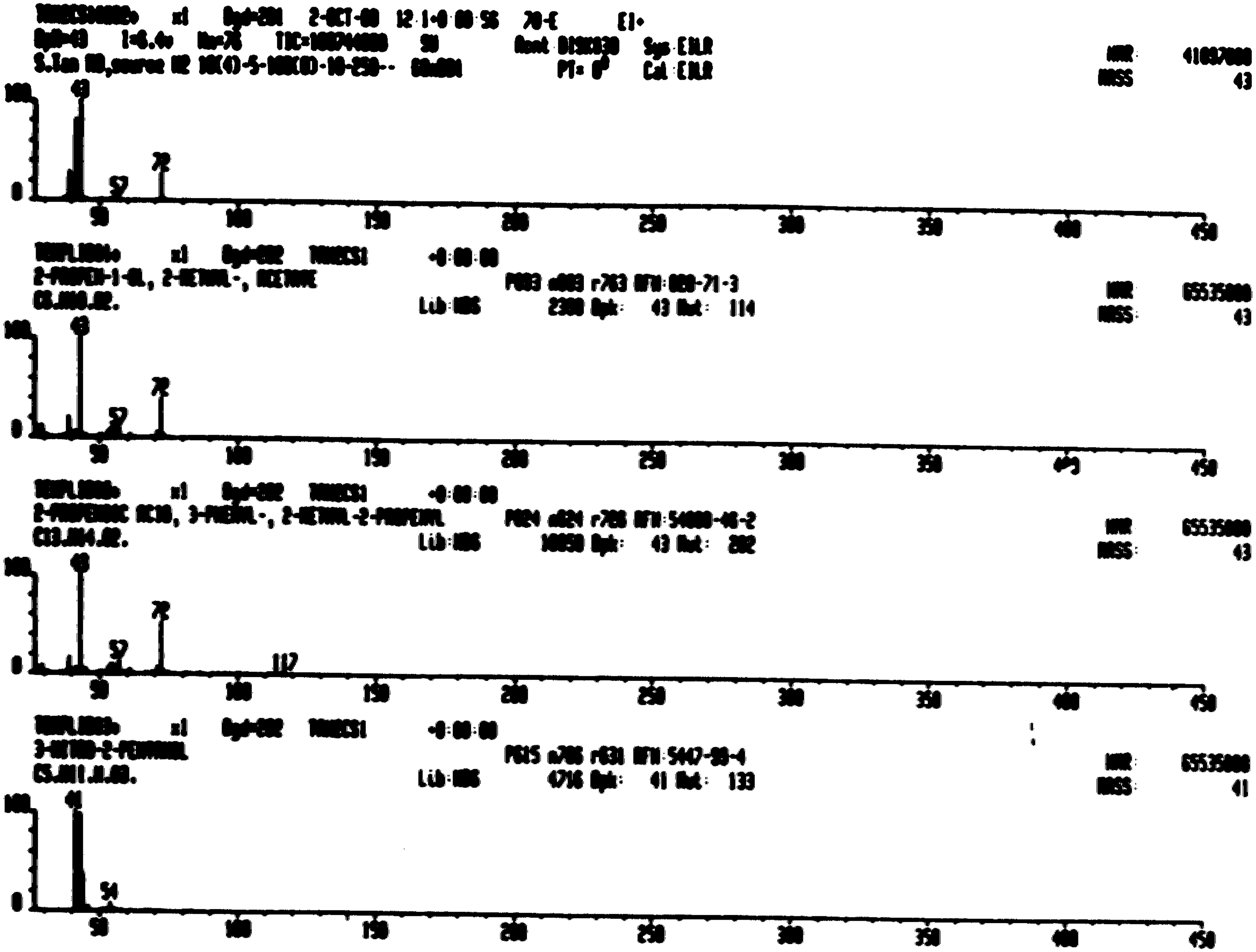
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MASS
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MASS
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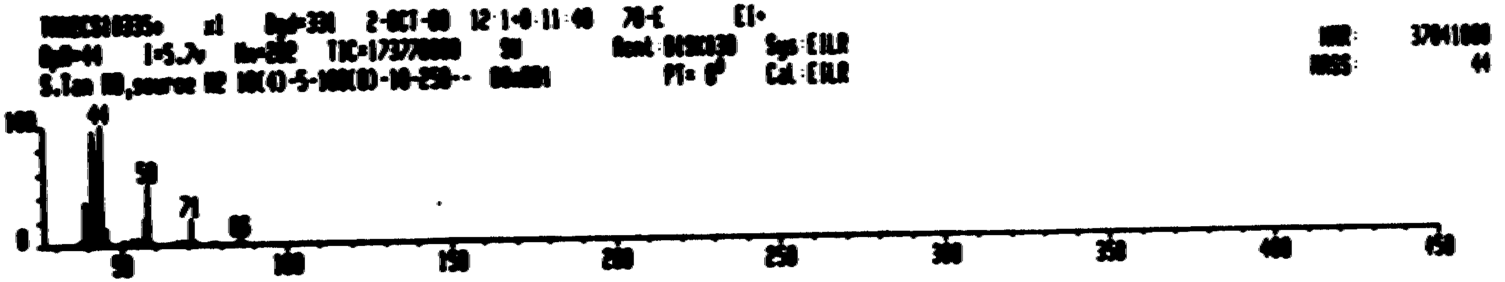
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Cal:EILR
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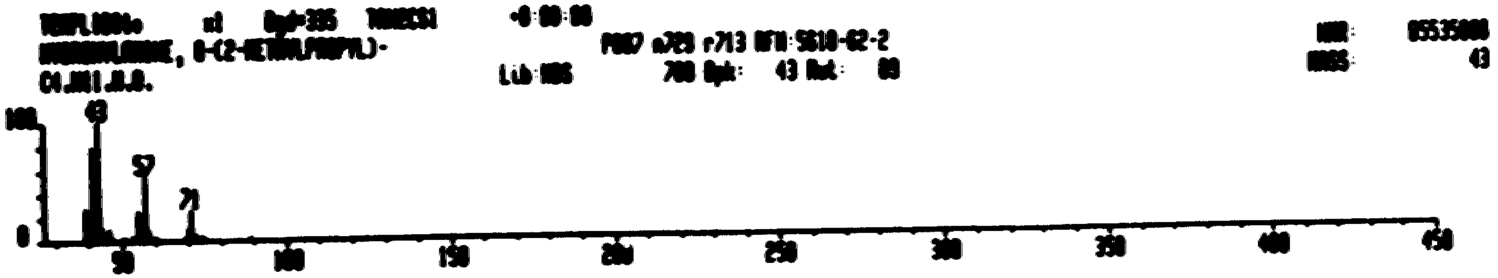
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700 Bpk: 43 Rnt: 80
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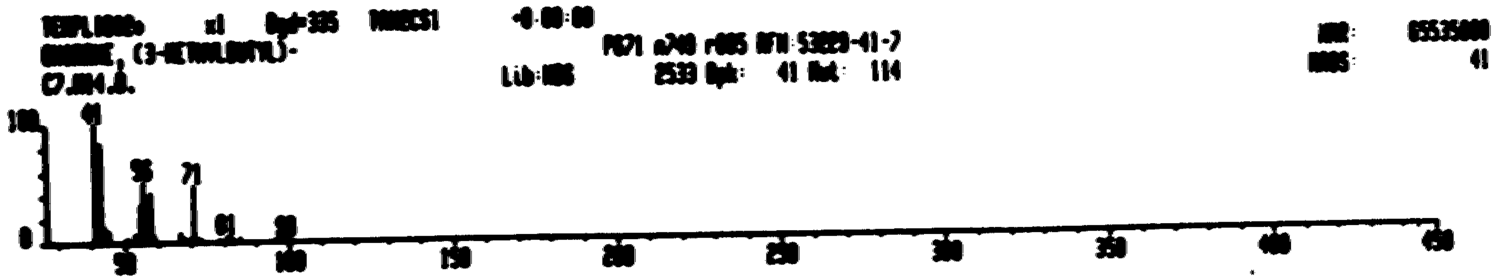
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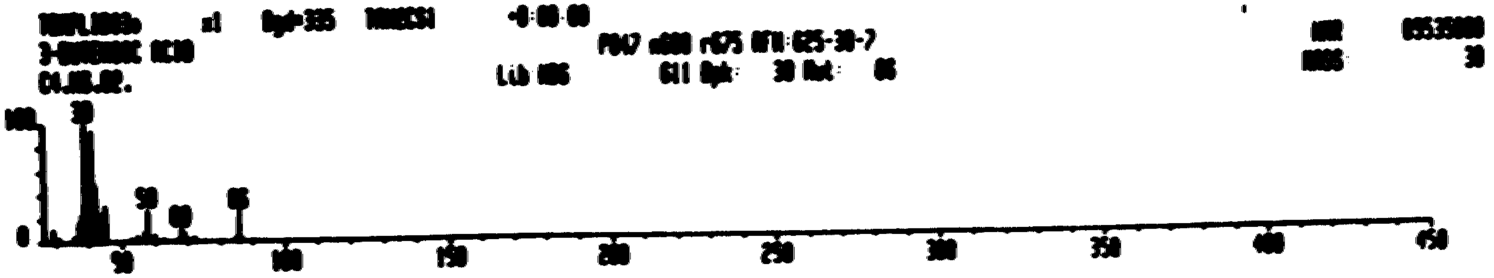
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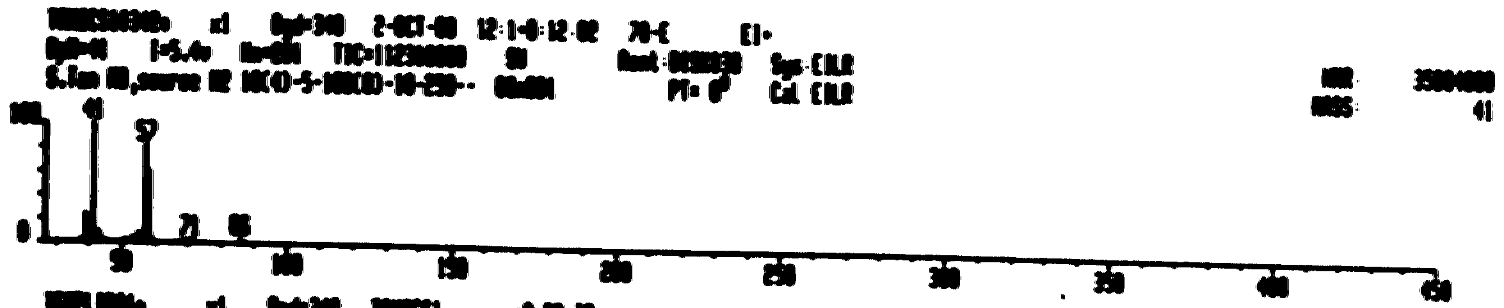
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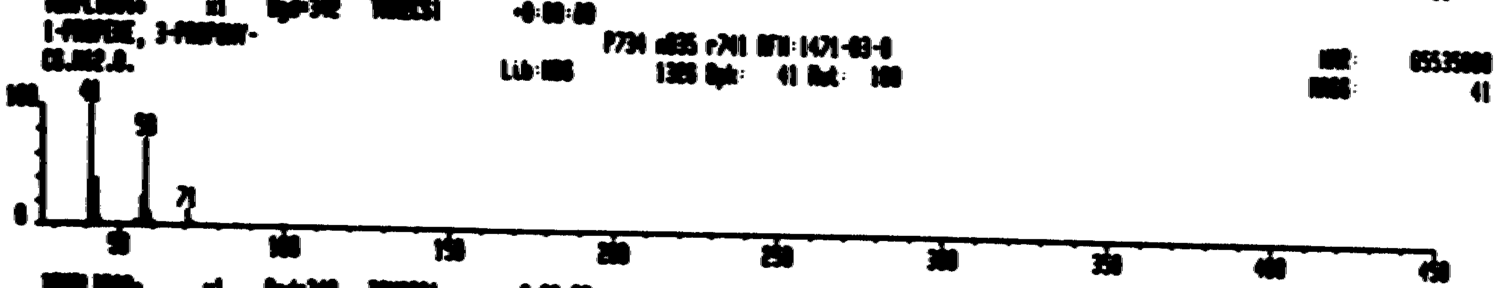
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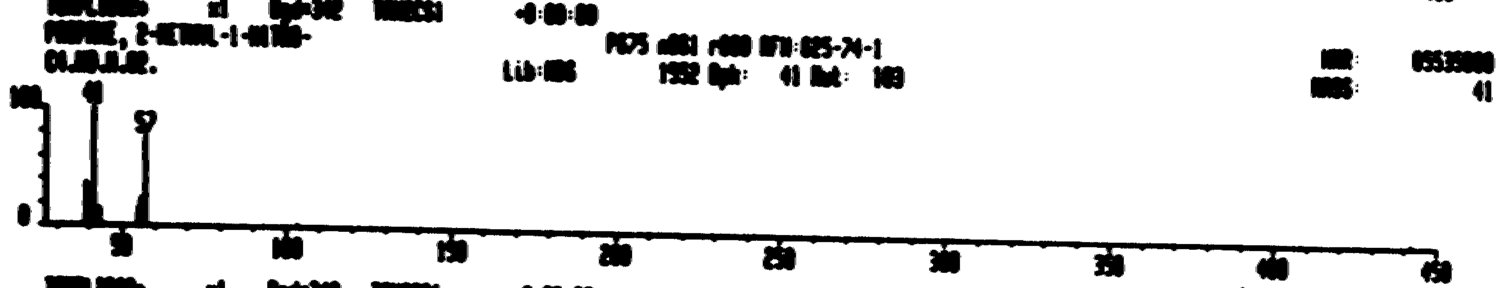
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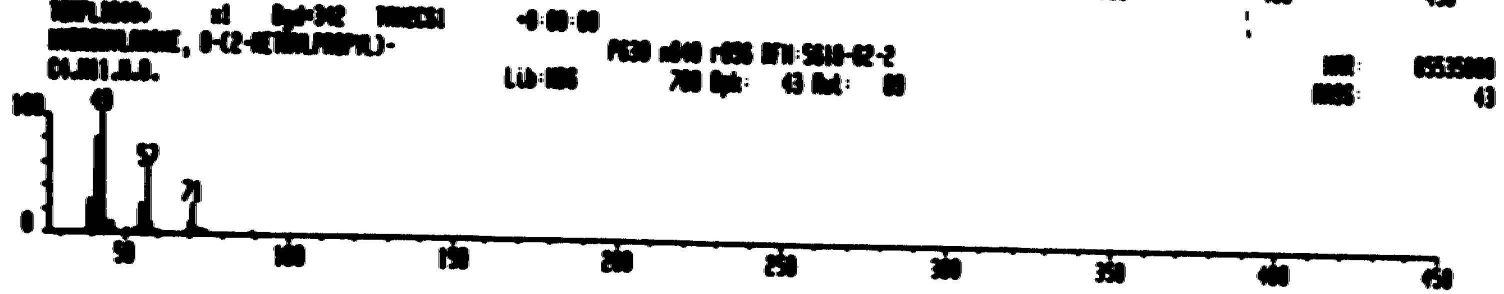
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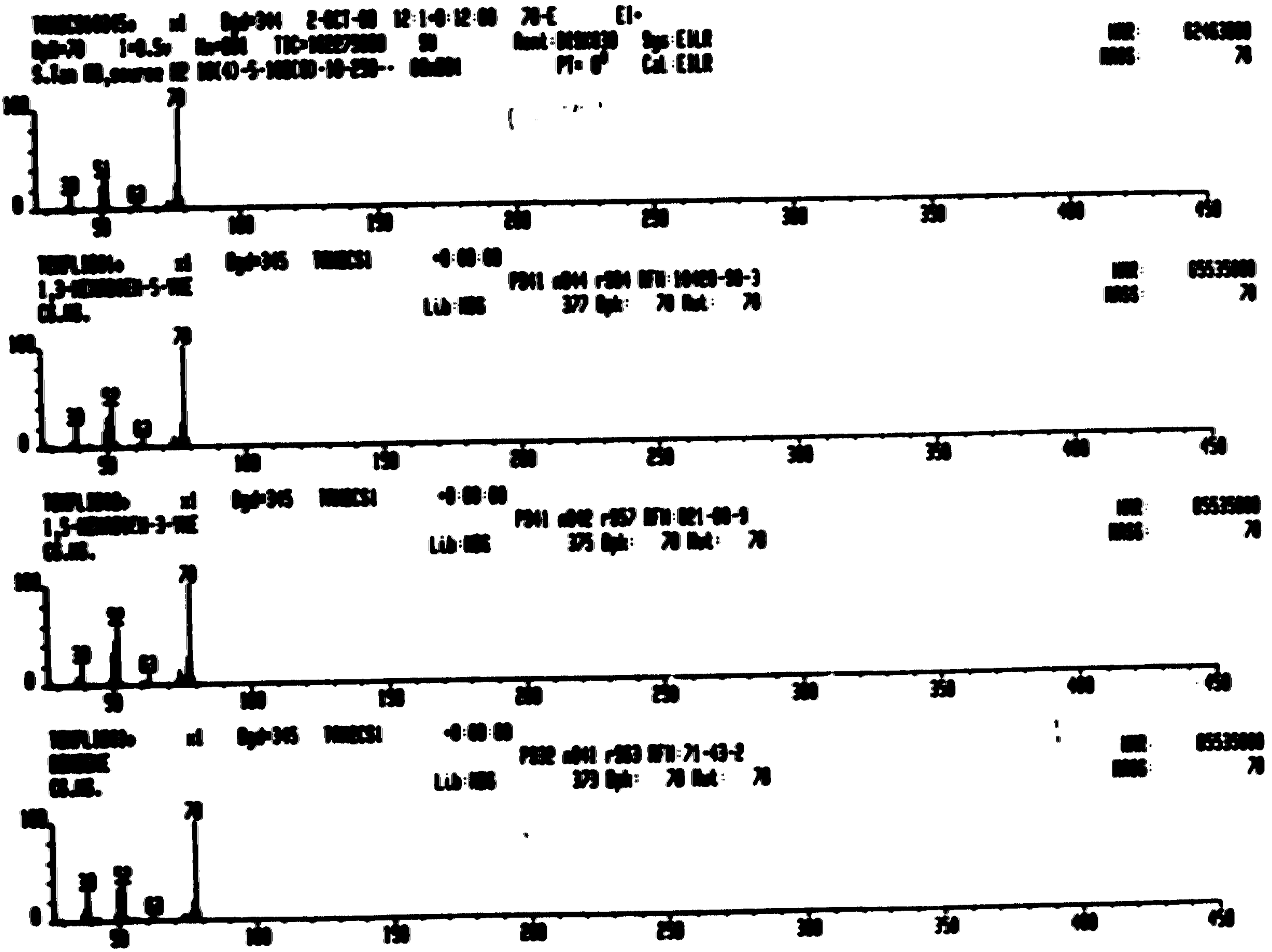
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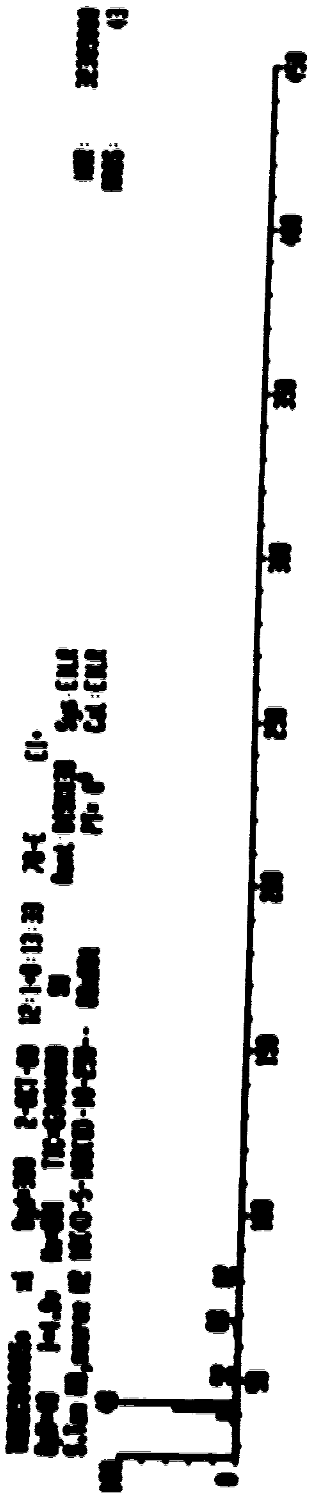

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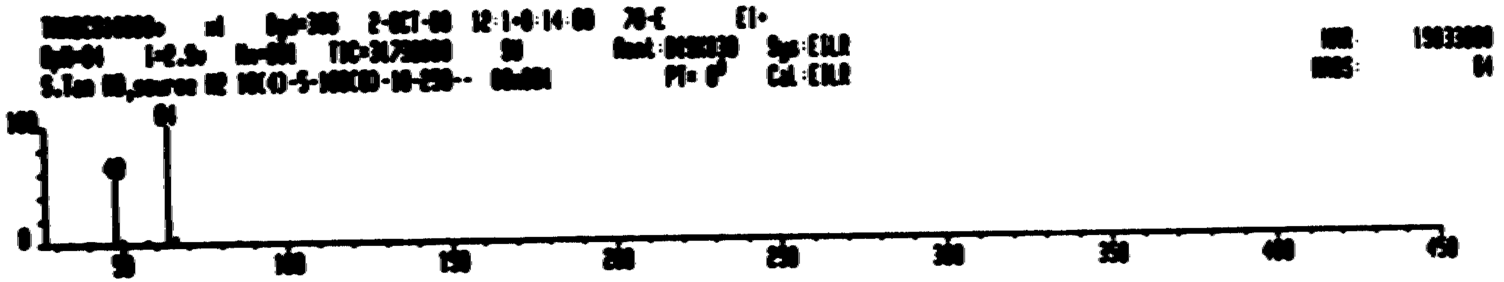
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HIRS:
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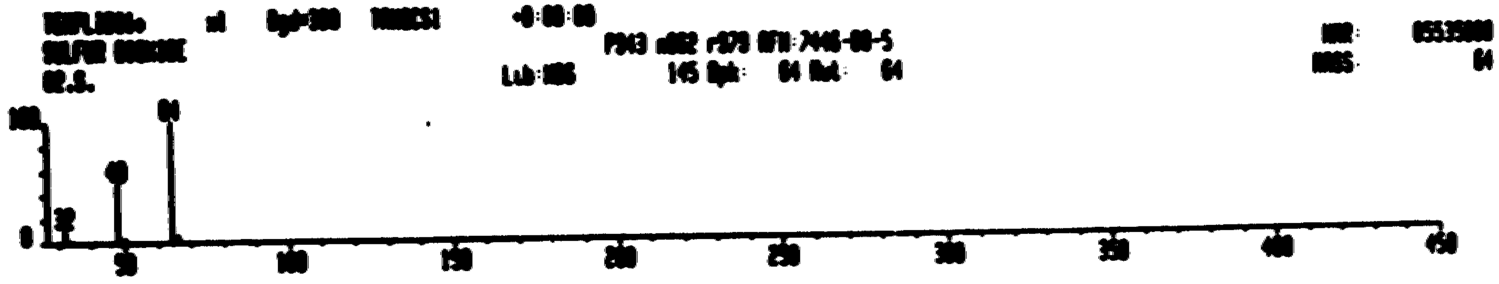
SULFUR DIOXIDE
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HIR:
HIRS:
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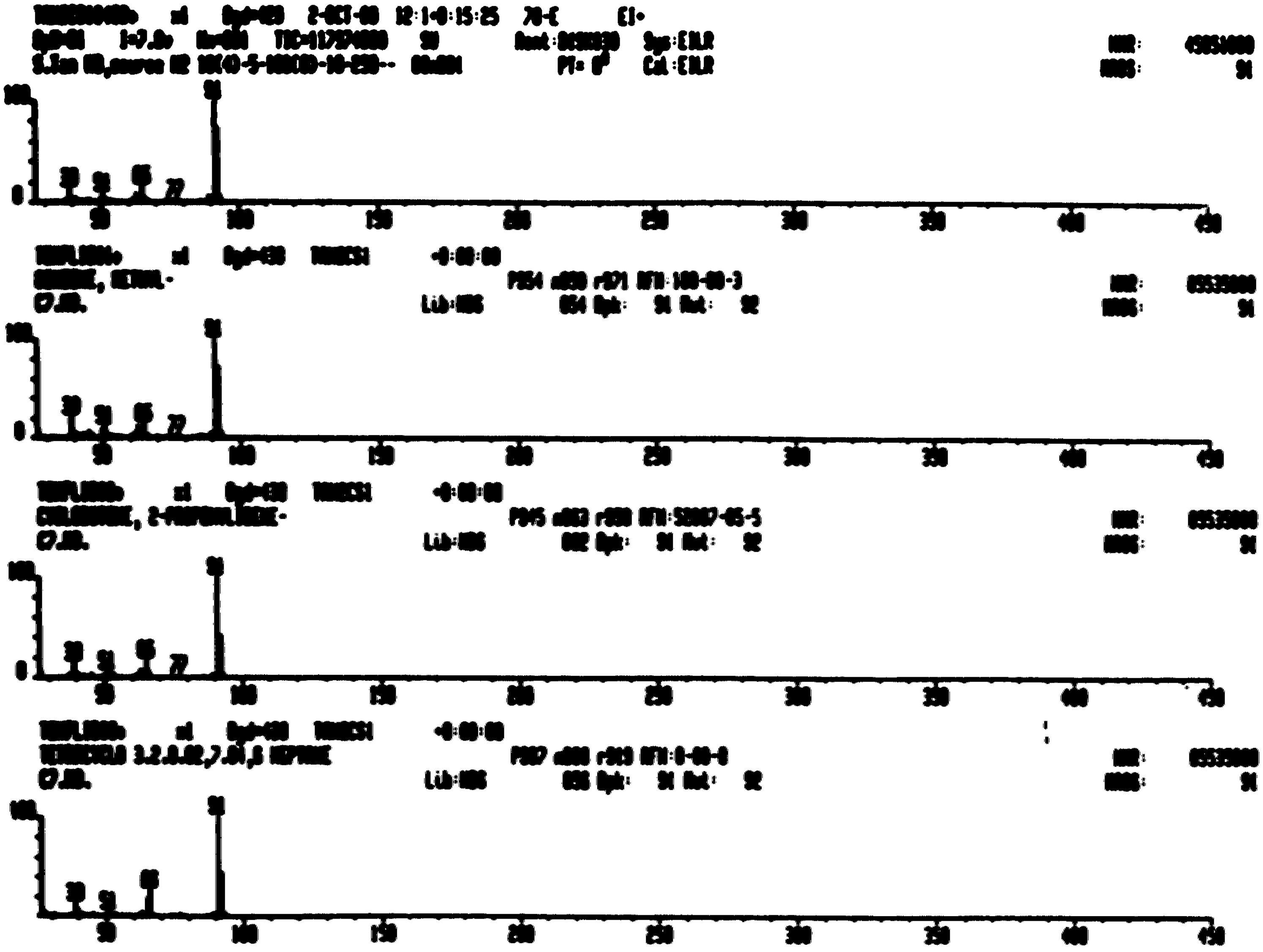
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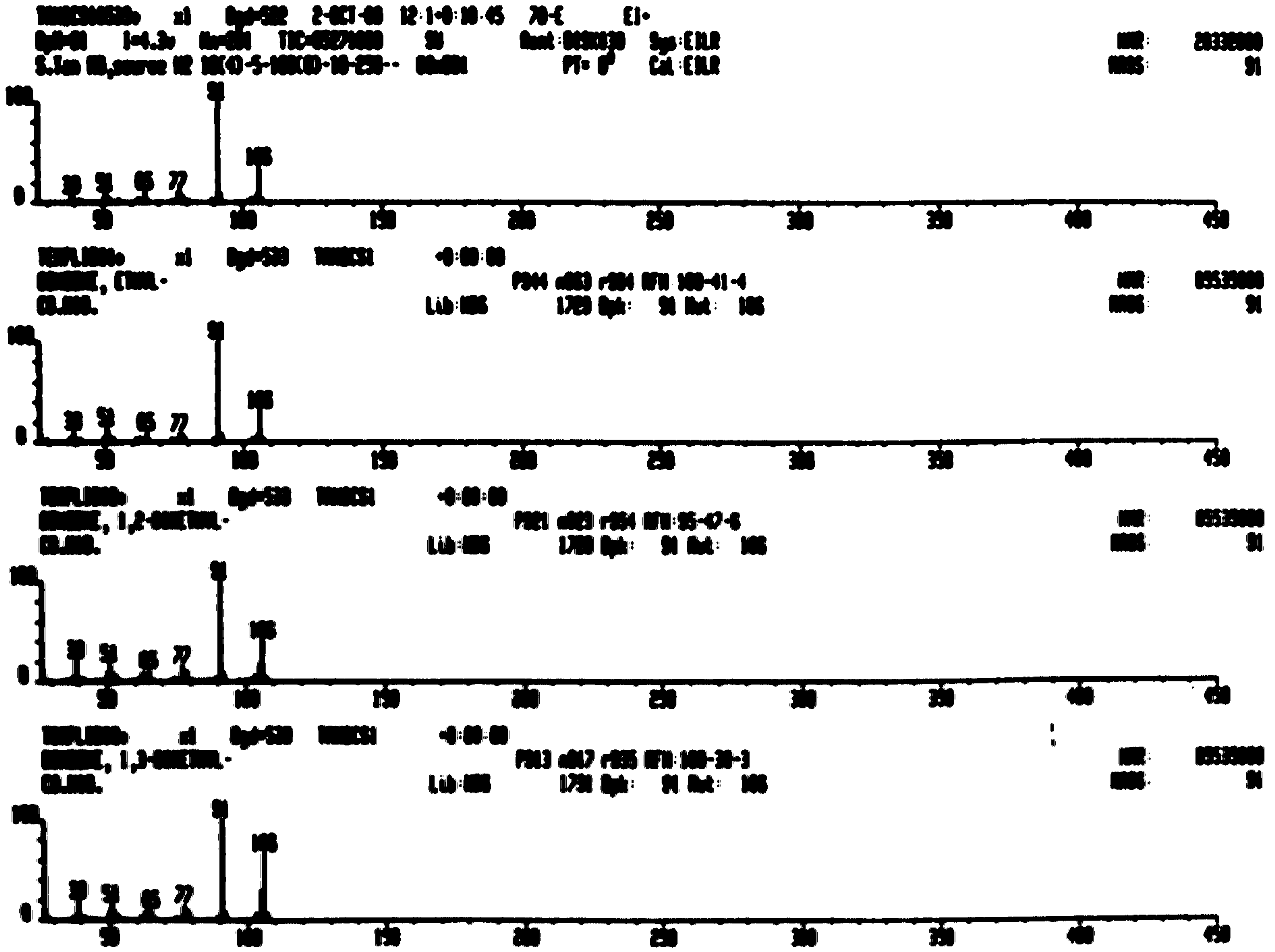
2-OCT-88
70-E
EI+
91
100-41-4
95-47-6
108-38-3
Lib:
Rat: 106
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106
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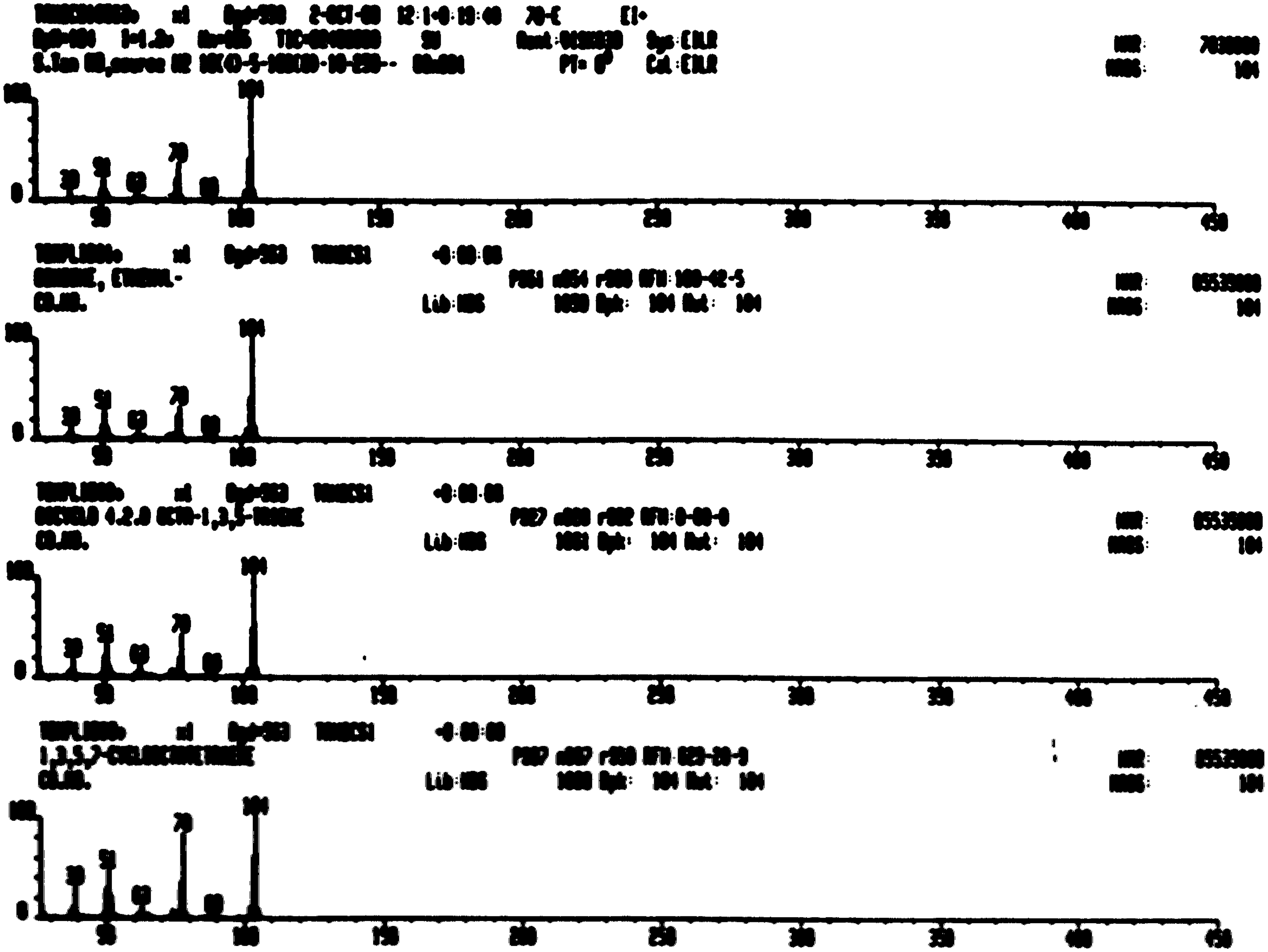
EI+
BENZENE, ETHENYL-
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Lib:NBS
BICYCLO 4.2.0 OCTA-1,3,5-TRIENE
Lib:NBS
1,3,5,7-CYCLOOCTATETRAENE
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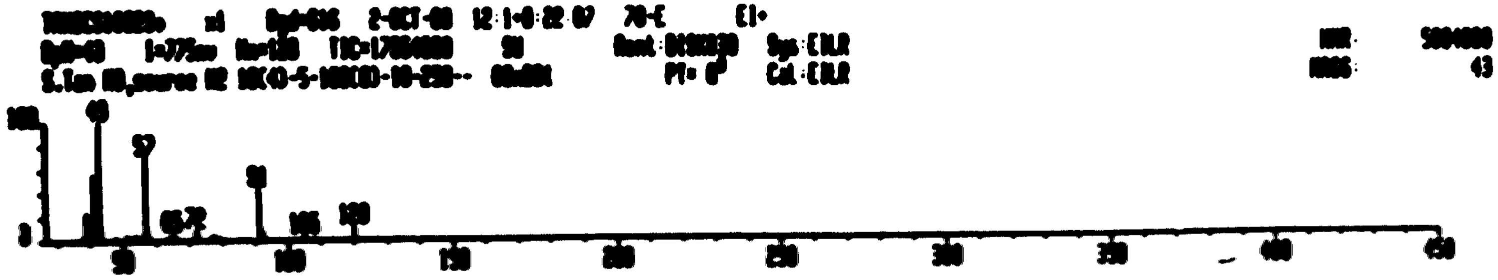
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EI+
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Cal:EILR
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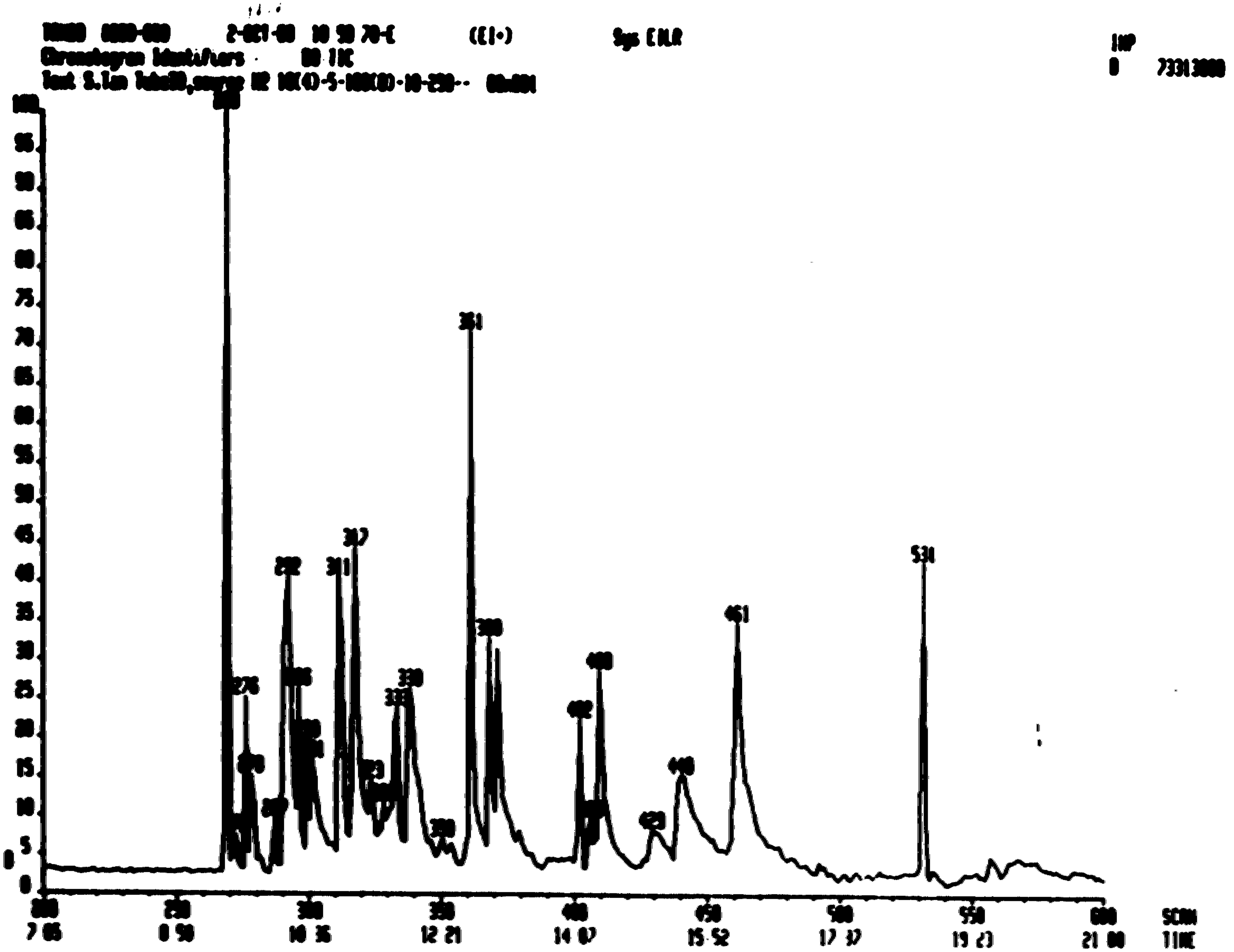
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(EI+)
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317
330
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402
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531
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SCAN
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8 50
10 36
12 21
14 07
15 52
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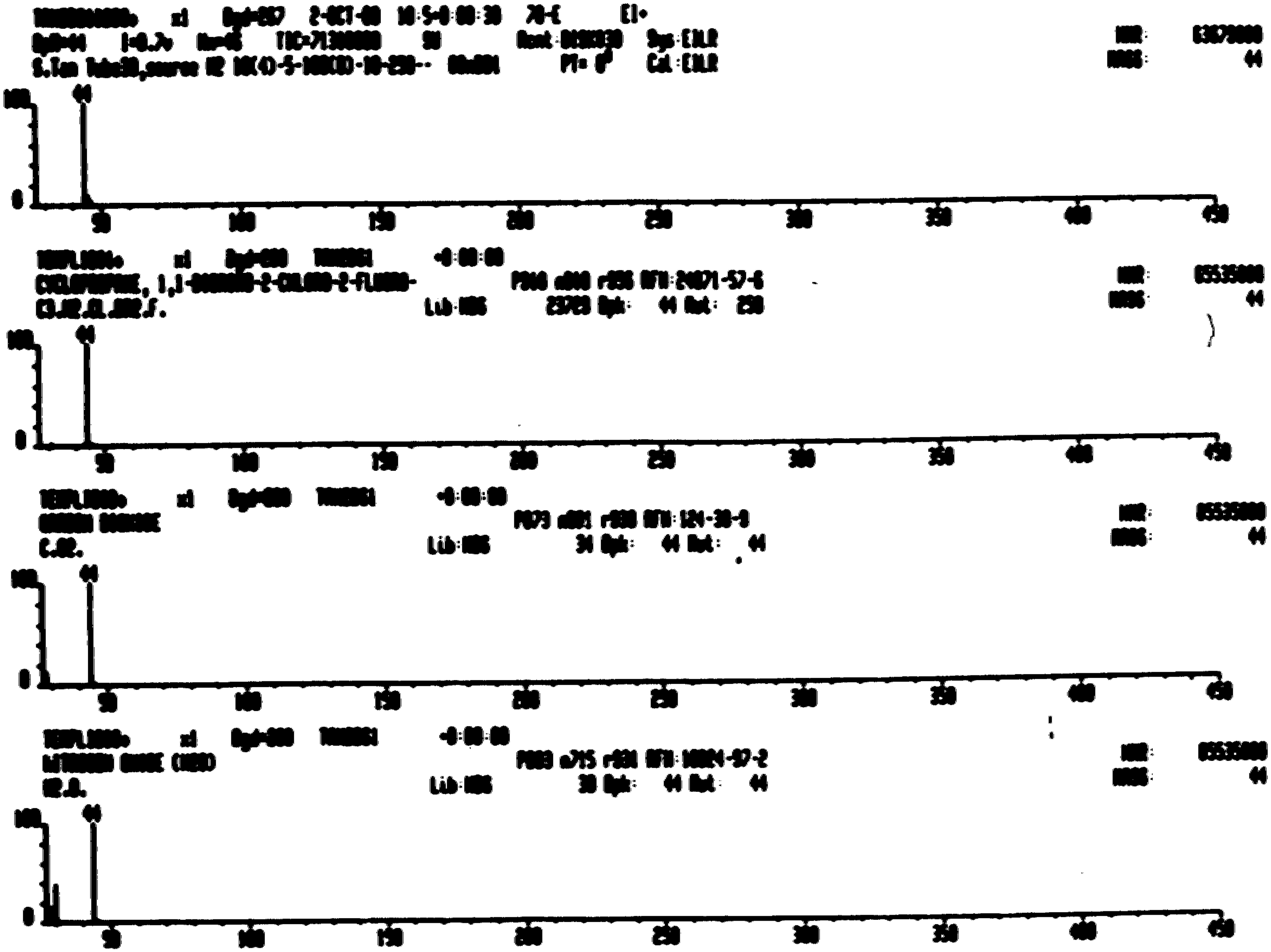
19 23
21 08
TIME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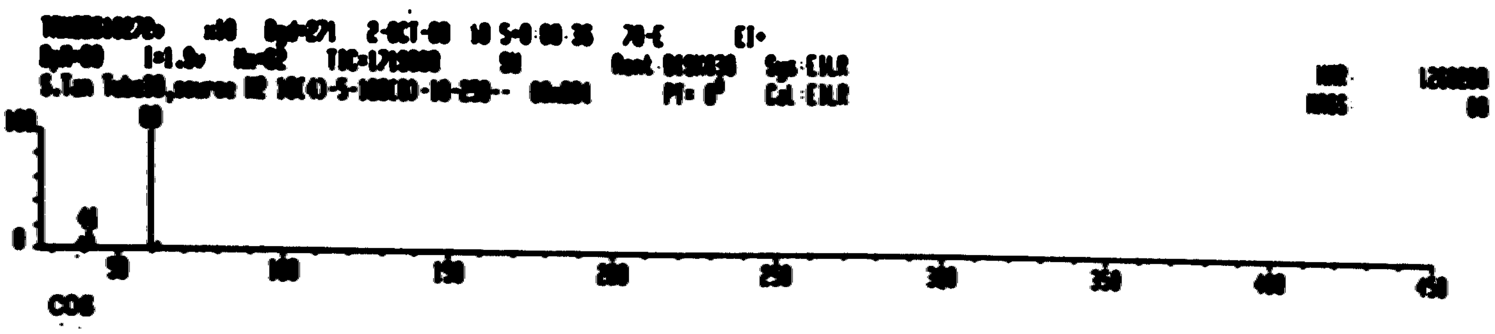
70-E
EI+
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Cal:EILR
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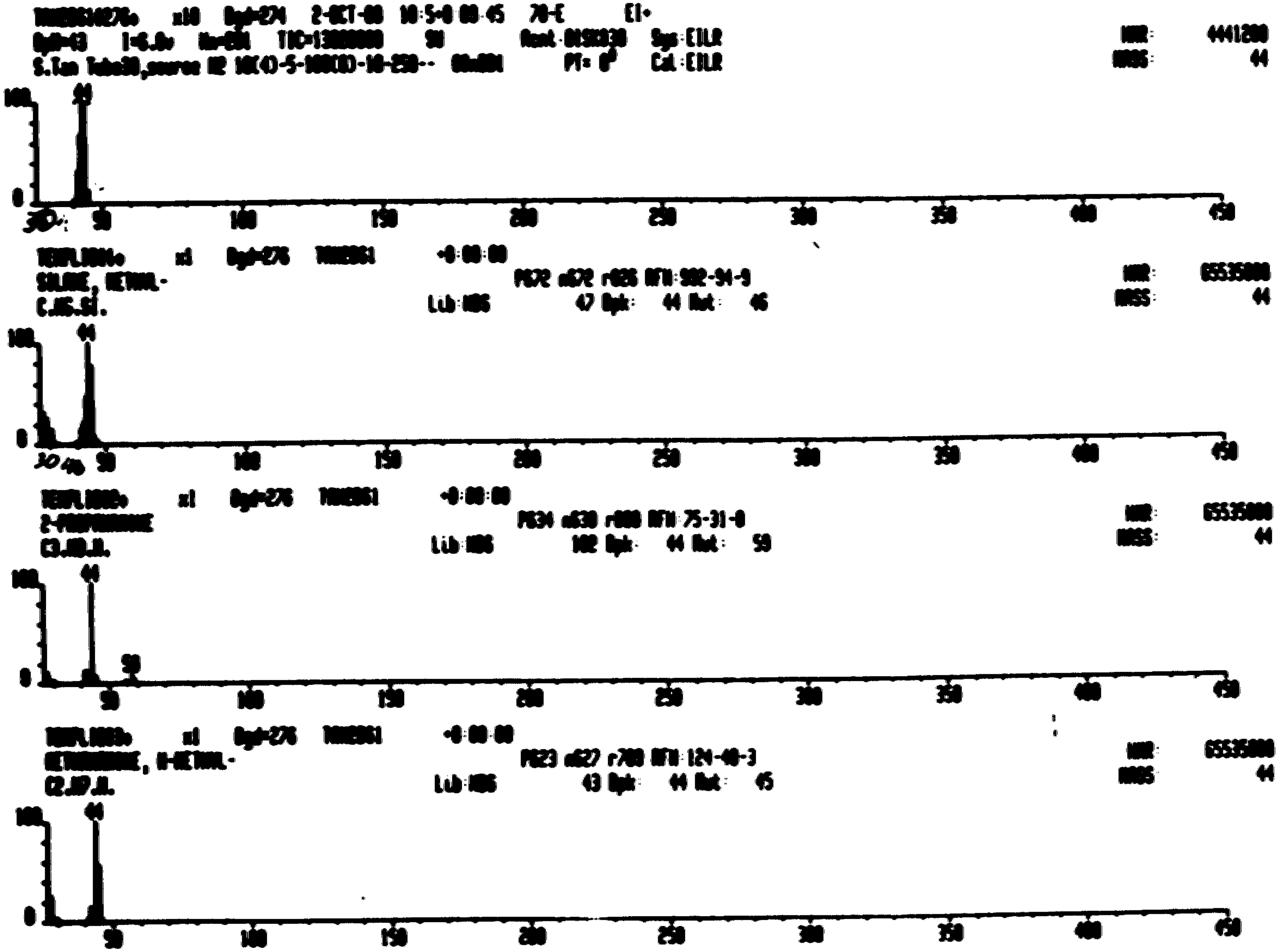
2-OCT-88
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EI+
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PI: 0
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MASS:
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+0:00:00
47
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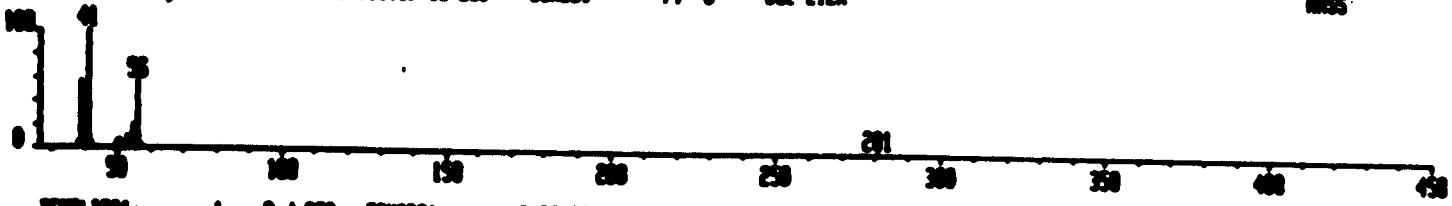
46
Lib:NBS
CAS: 75-31-0
102
44
58
CAS: 124-40-3
43
44
45

[illegible] x10 [illegible] 2-OCT-[illegible] 10:5+0:00:40 70-E EI+
[illegible] I=4.5v [illegible] TIC=[illegible] SU Acnt:[illegible] Sys:EILR
S.Tan Tube30,source [illegible] 10(4)-5-100(0)-10-250-- [illegible] PI= 0° Cal:EILR
MMR: 2950000
MASS: 41



TEMPL.1004+ x1 [illegible] [illegible] +0:00:00
1-PROPENE, 2-METHYL-
C4.H8.
P007 a007 r978 RFN:115-11-7
Lib:NBS 77 Bpk: 41 Nxt: 56
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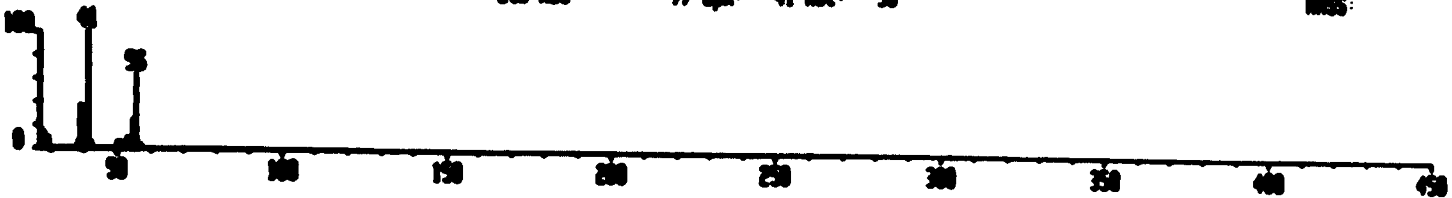
MASS: 41



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P020 a030 r970 RFN:107-01-7
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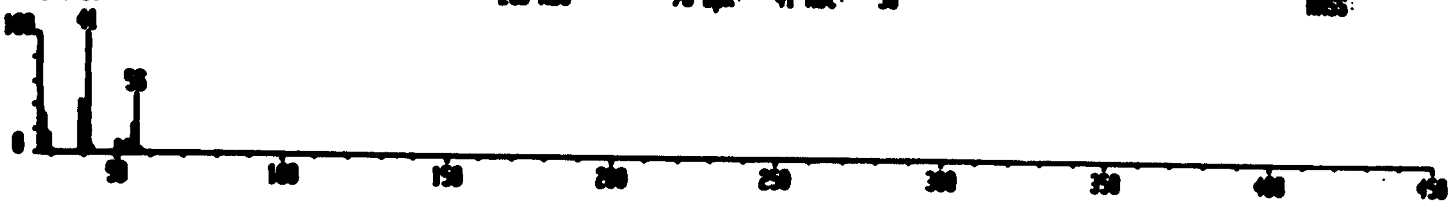
MASS: 41



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[illegible], 5-HYDROXY-
C5.H11.N.O2.
P000 a000 r754 RFN:29806-12-2
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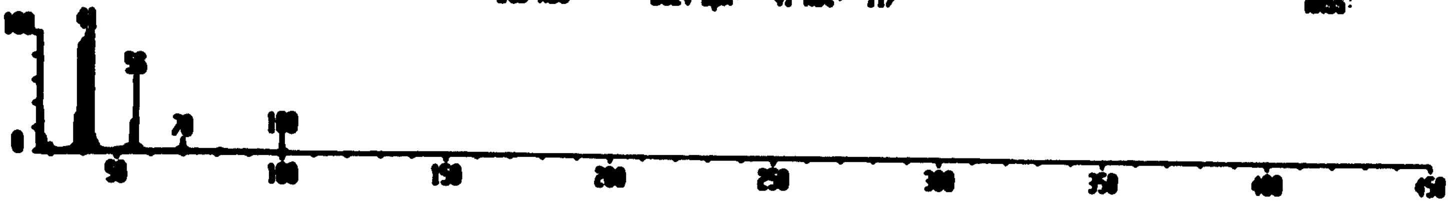
MMR: 65535000
MASS: 41



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BpM=55 I=2.7v Hm=800 TIC=4000000 50 Acnt:DISK030 Sys:EILR
S.Tan Tube30,source HZ 10(C)-5-100(D)-10-250-- 00x004 PI= 0° Cal:EILR
HRR: 1792000
MASS: 55

TEMPL.0004+ x1 Bpd=007 T000001 +0:00:00
CYCLOPROPANE, 1,1-DIMETHYL- P000 n027 r012 RFN:1630-94-0
C5.H10. Lib:NBS 207 Bpk: 55 Mwt: 70
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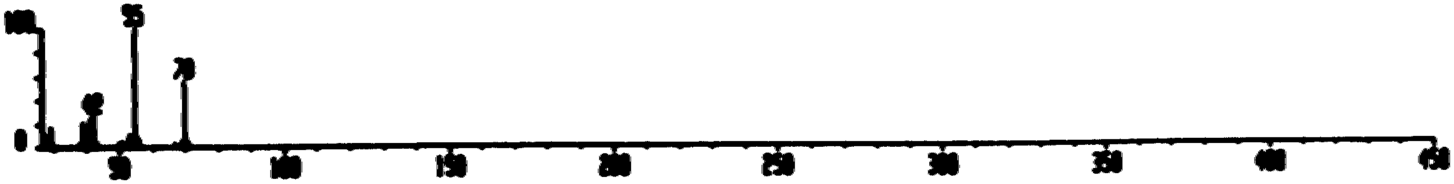
MASS: 55



TEMPL.0006+ x1 Bpd=007 T000001 +0:00:00
CYCLOBUTANE, 1,1,2,3,3-PENTAMETHYL- P030 n030 r706 RFN:57905-86-9
C9.H18. Lib:NBS 3700 Bpk: 70 Mwt: 126
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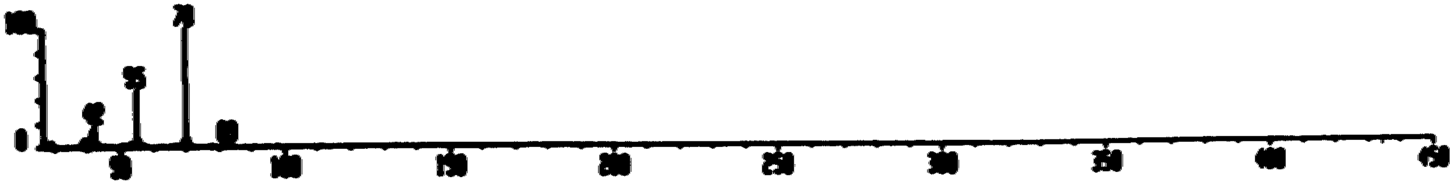
MASS: 70



TEMPL.0008+ x1 Bpd=007 T000001 +0:00:00
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C7.H14. Lib:NBS 1155 Bpk: 41 Mwt: 98
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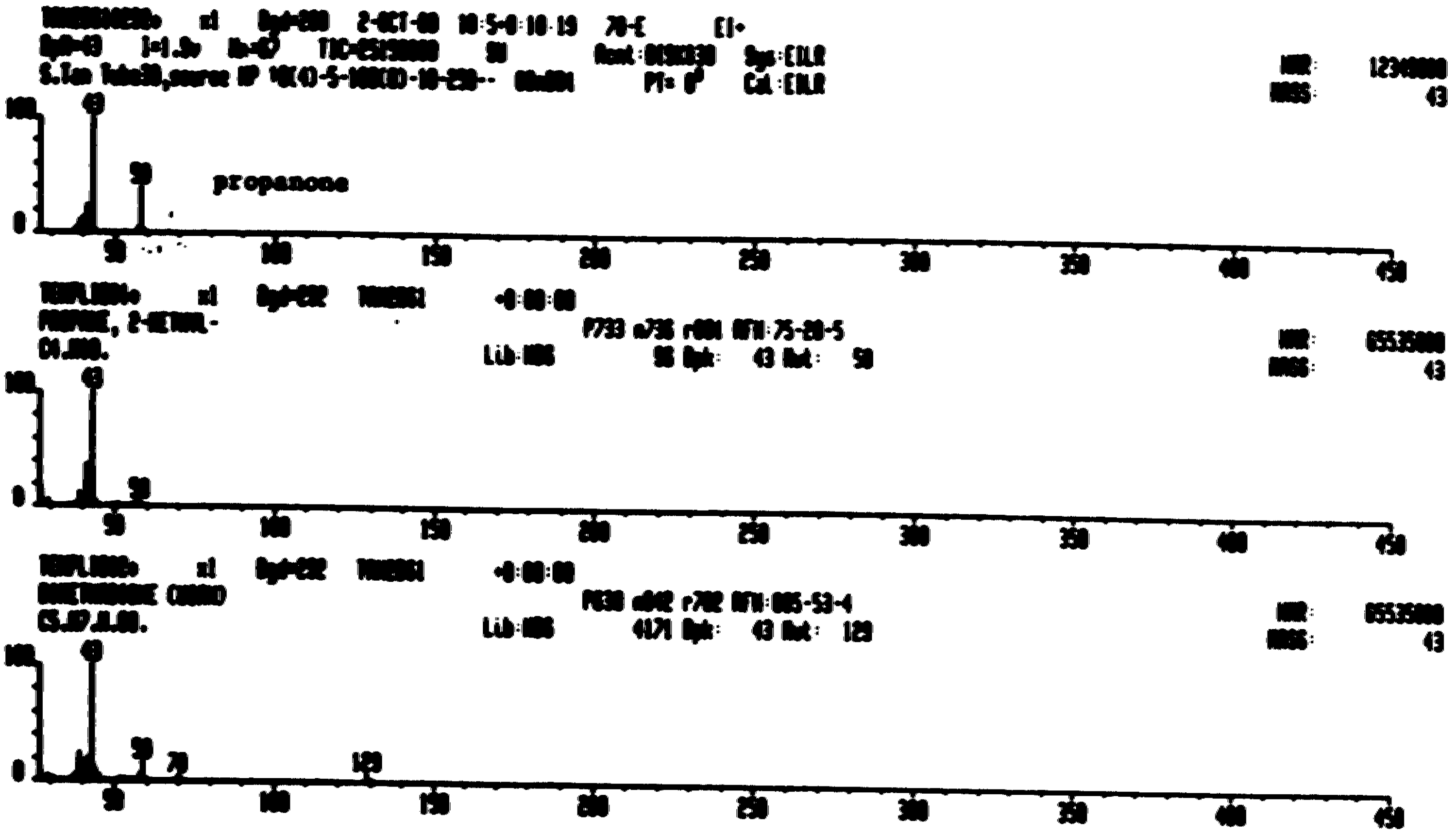
MASS: 41


EI+
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Cal:EILR
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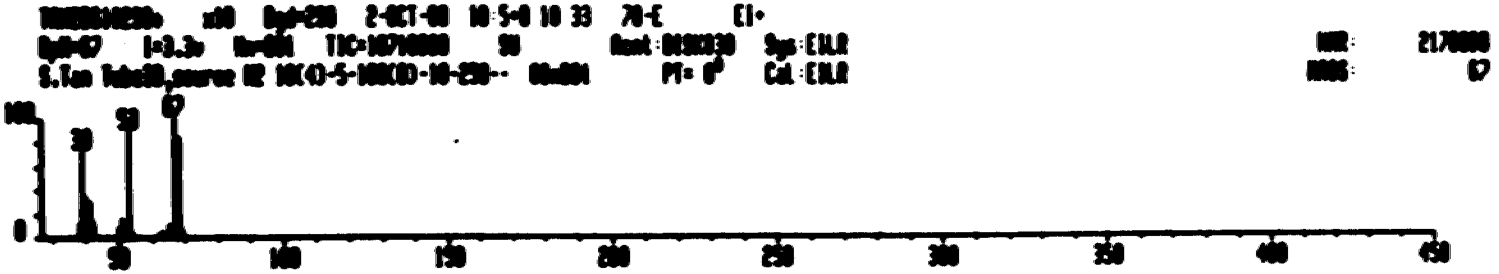
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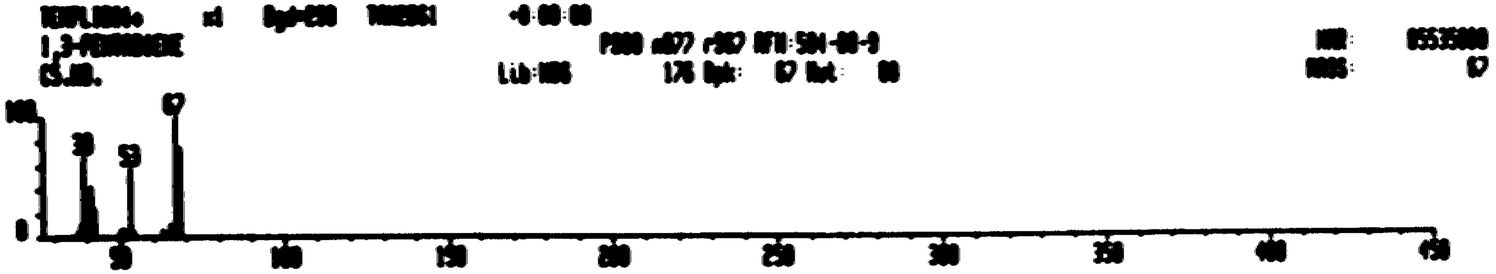
1,3-PENTADIENE
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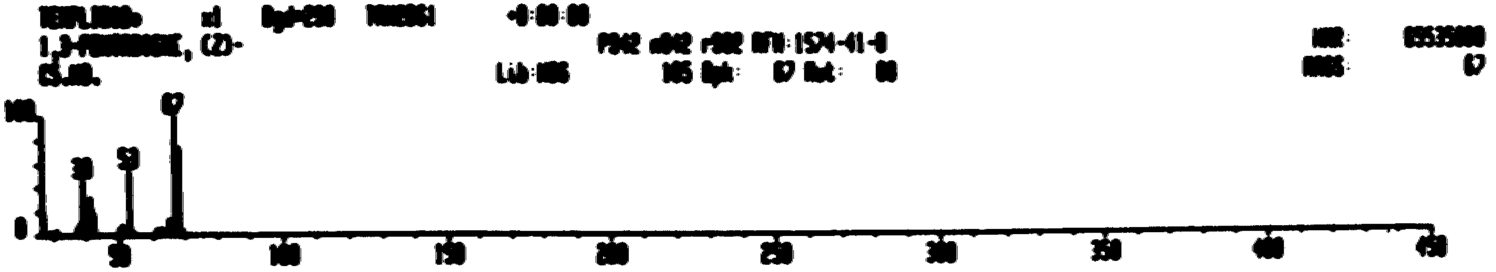
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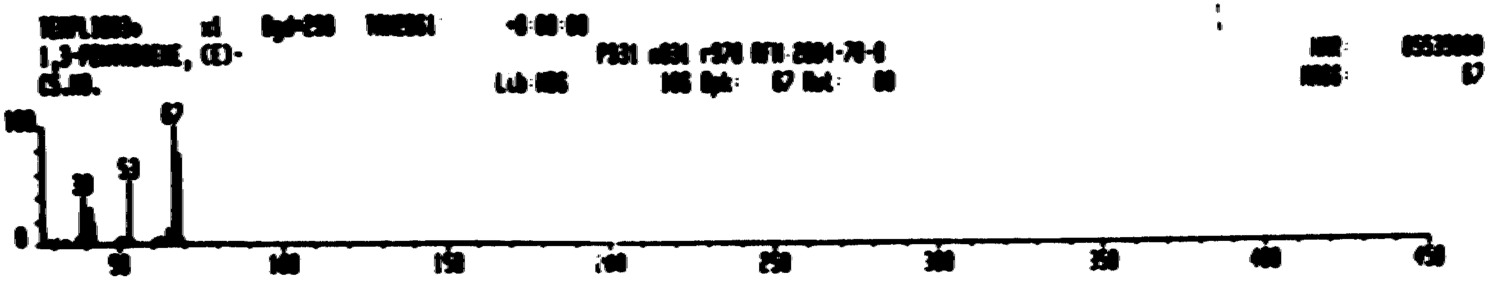
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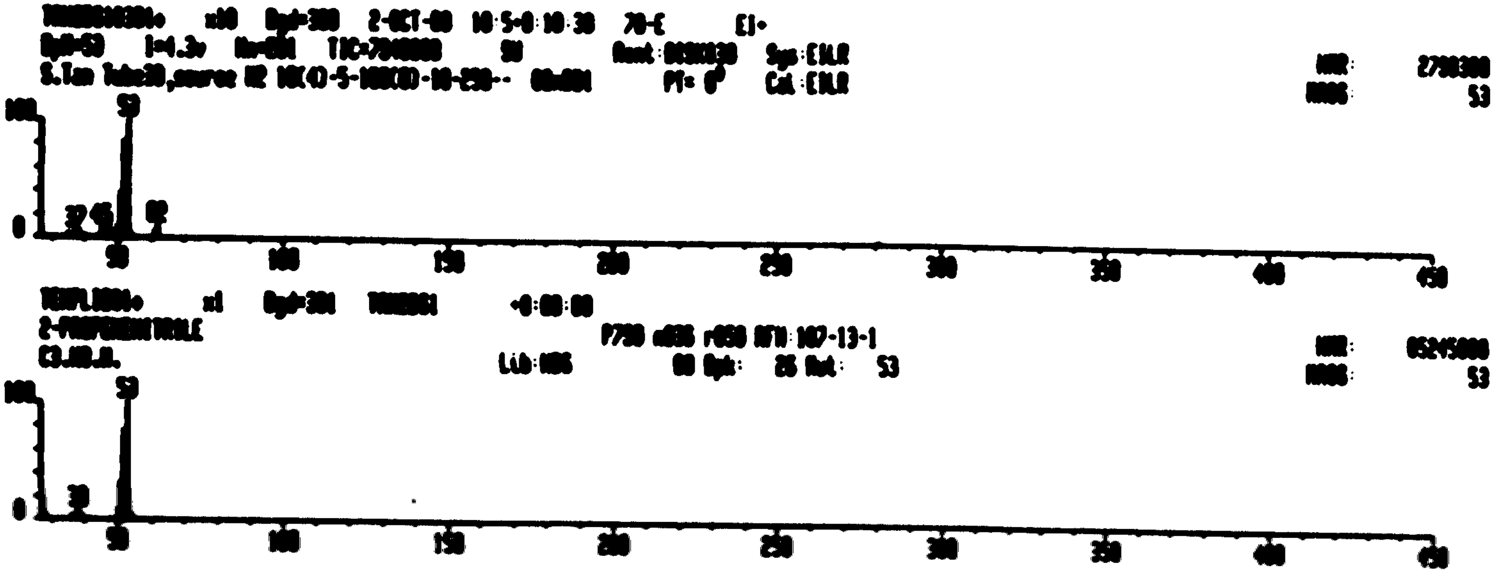
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x1
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107-13-1
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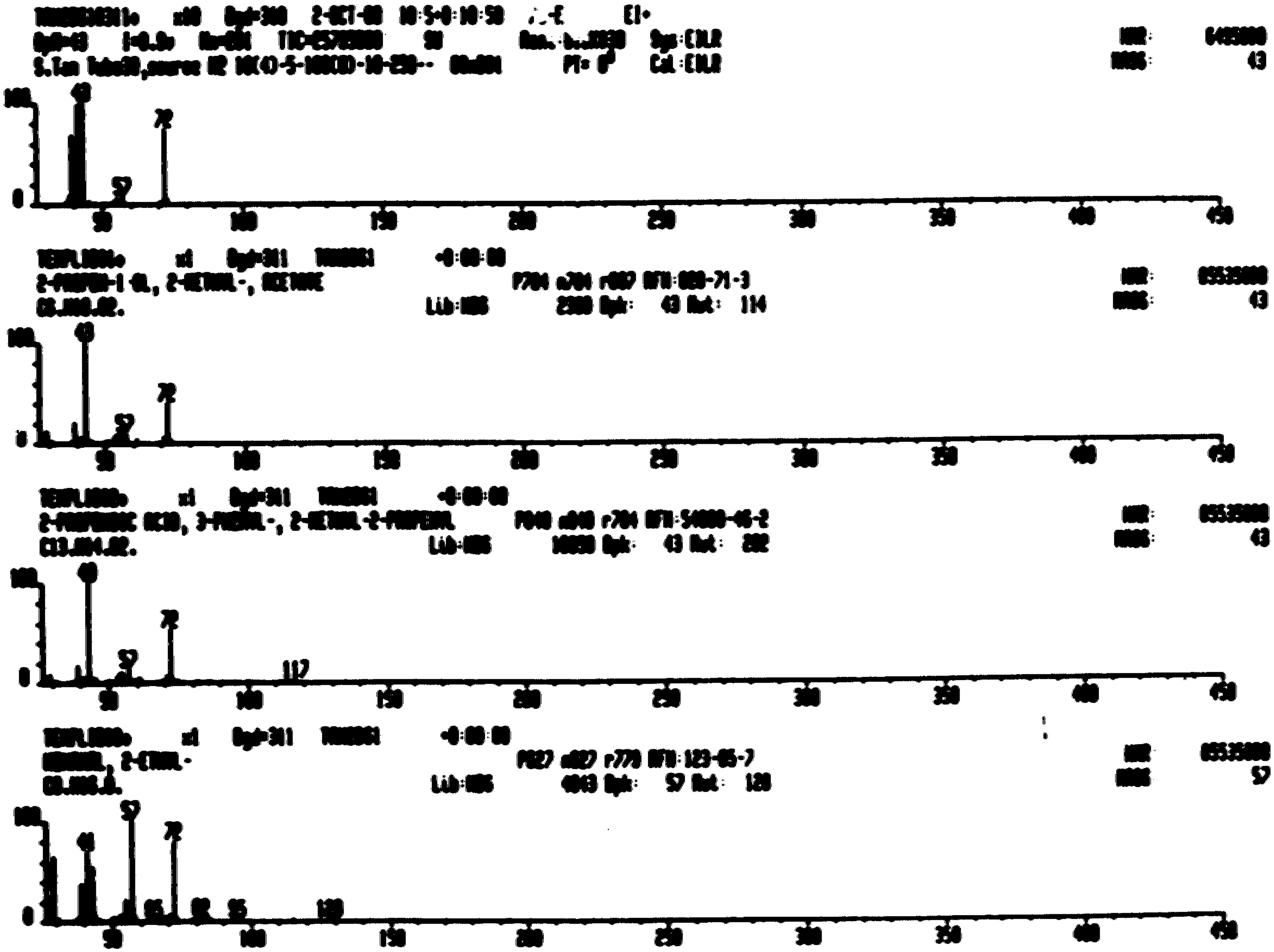

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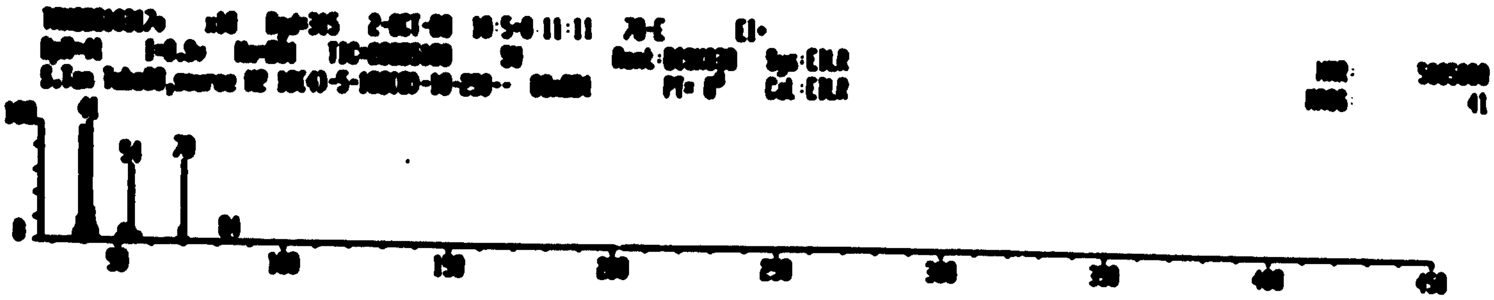
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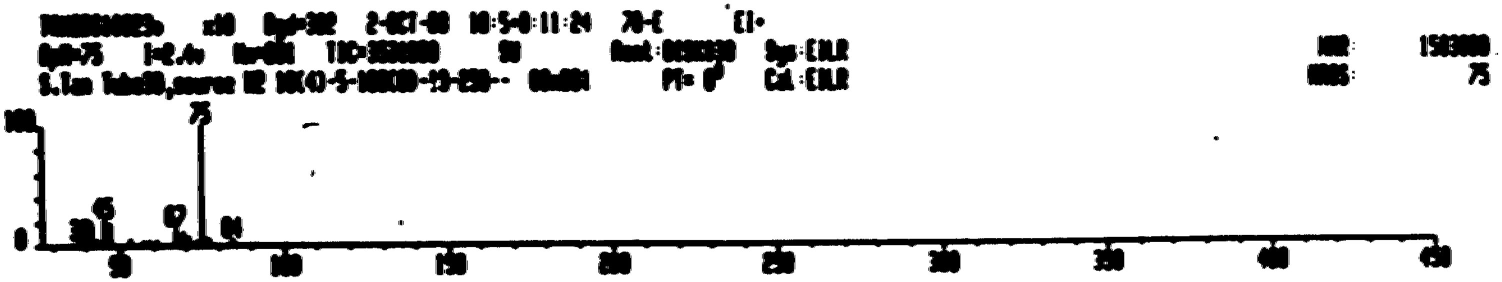
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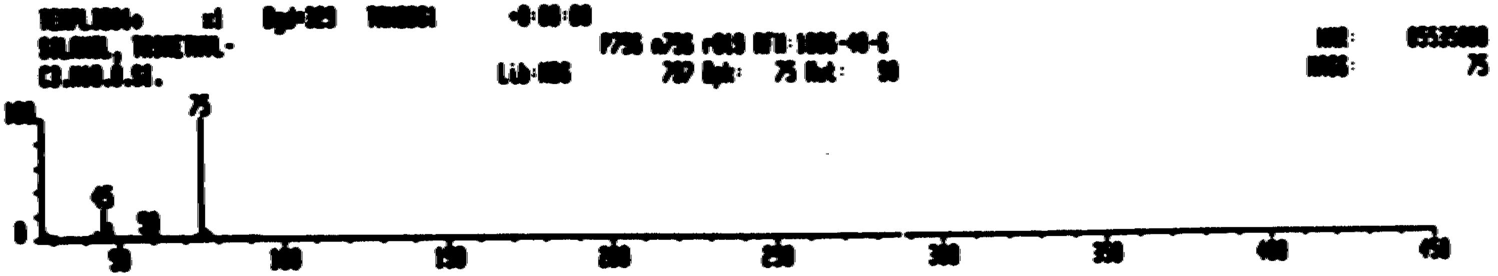
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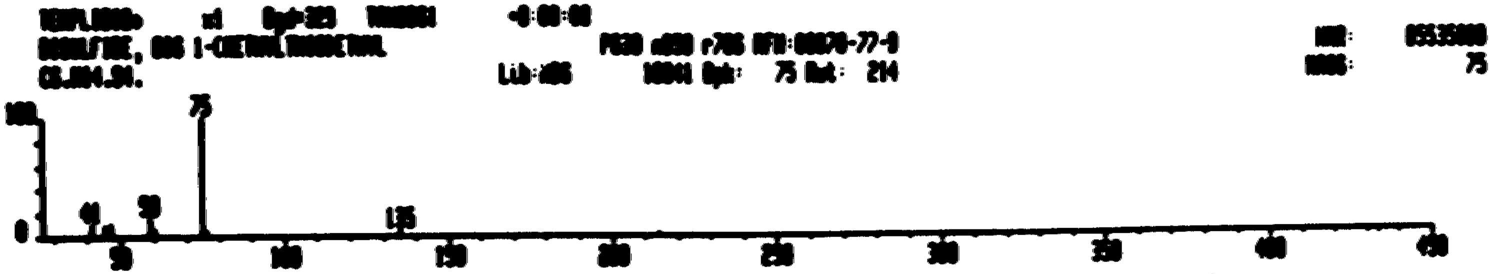
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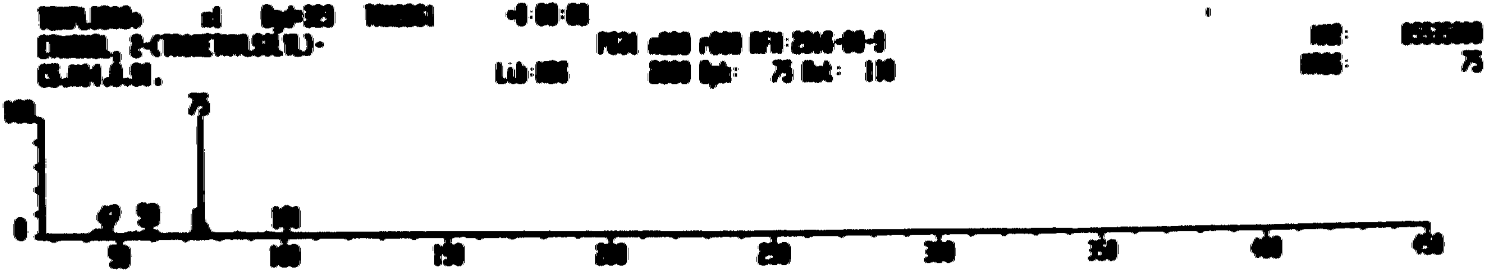
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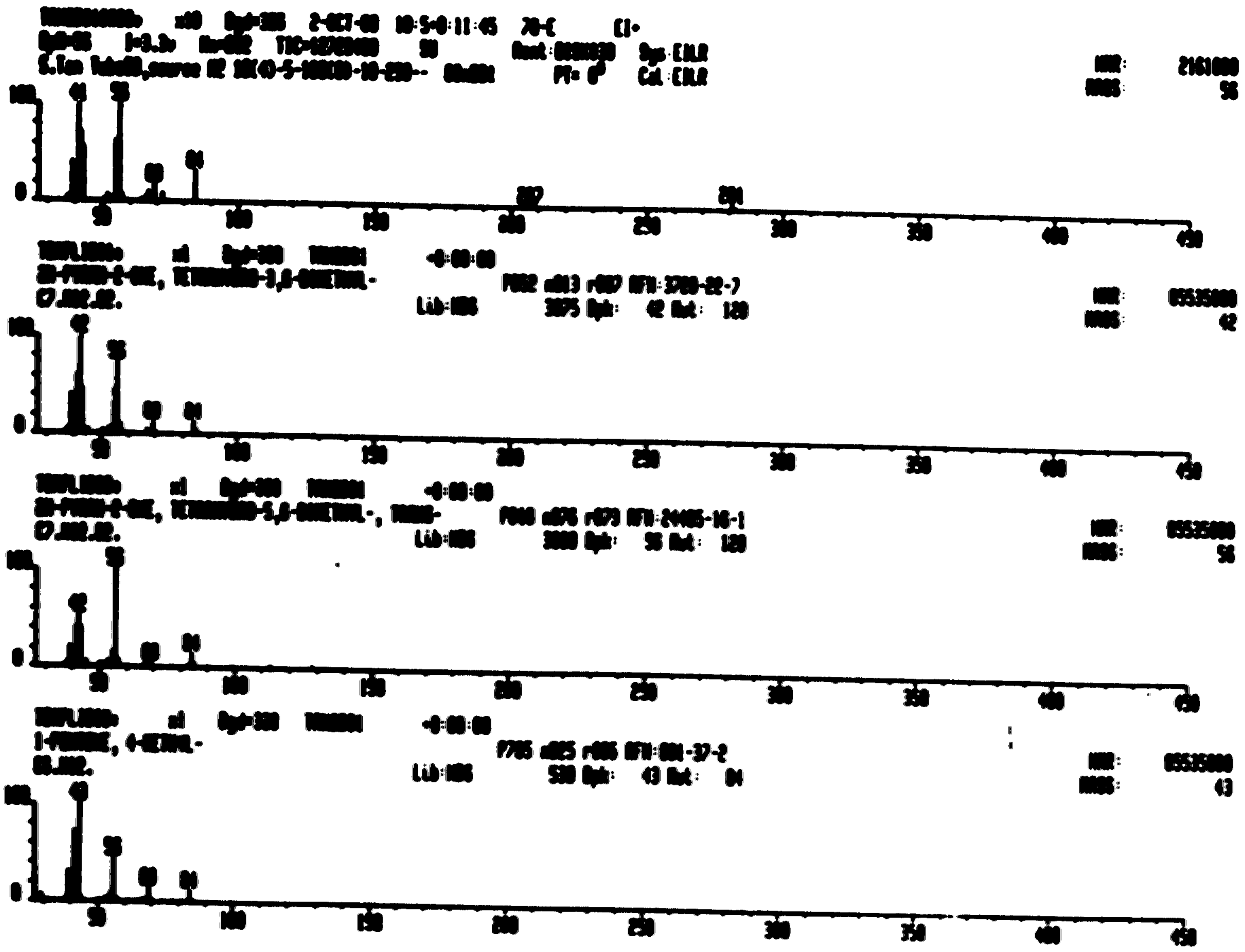
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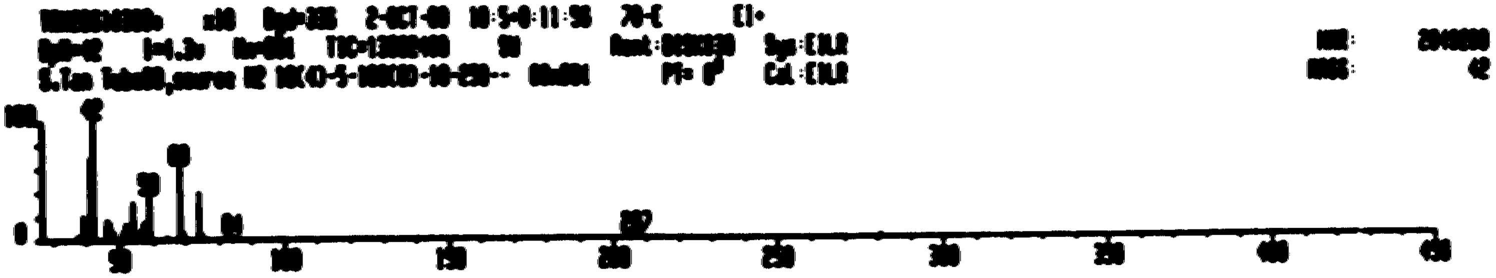EI+
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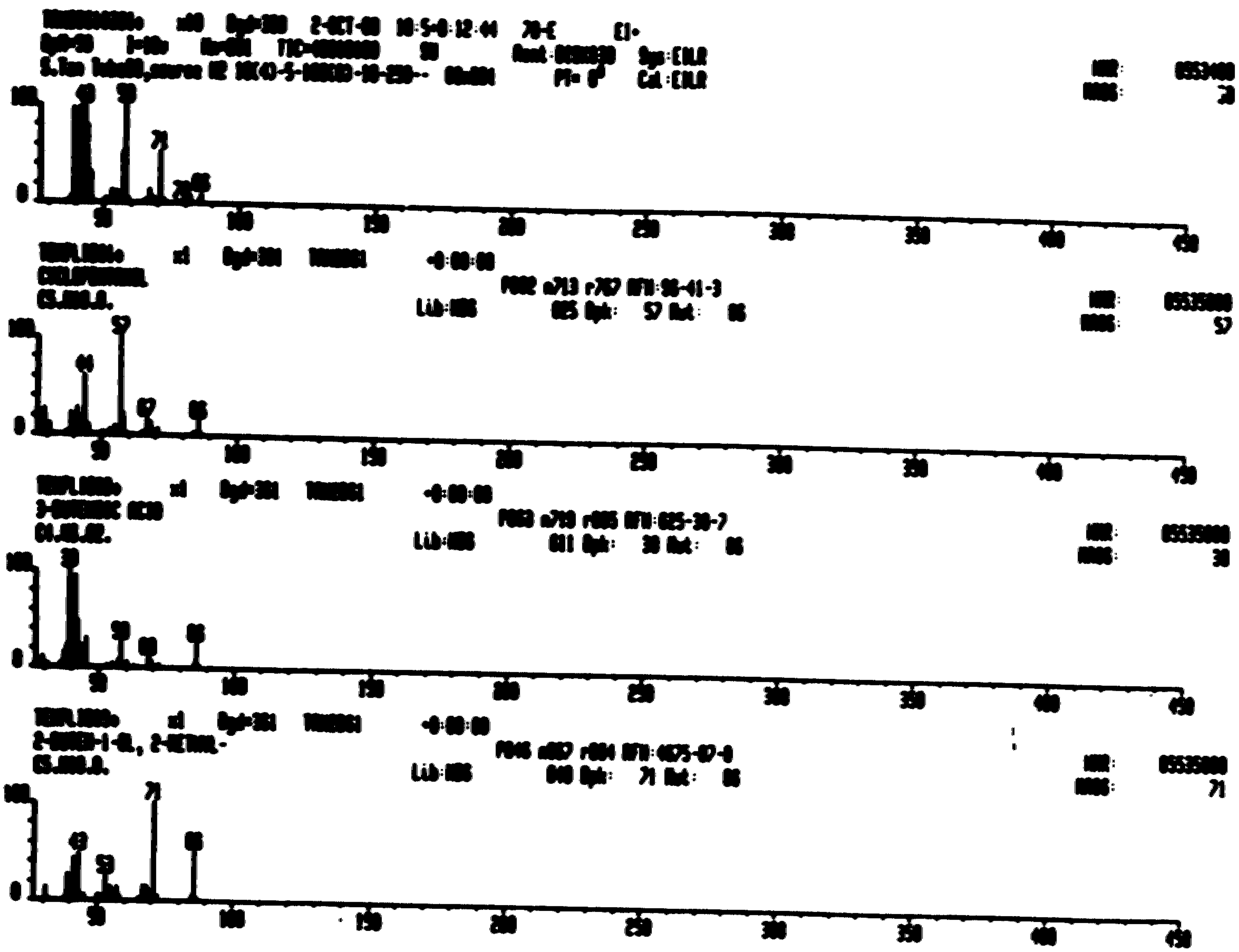
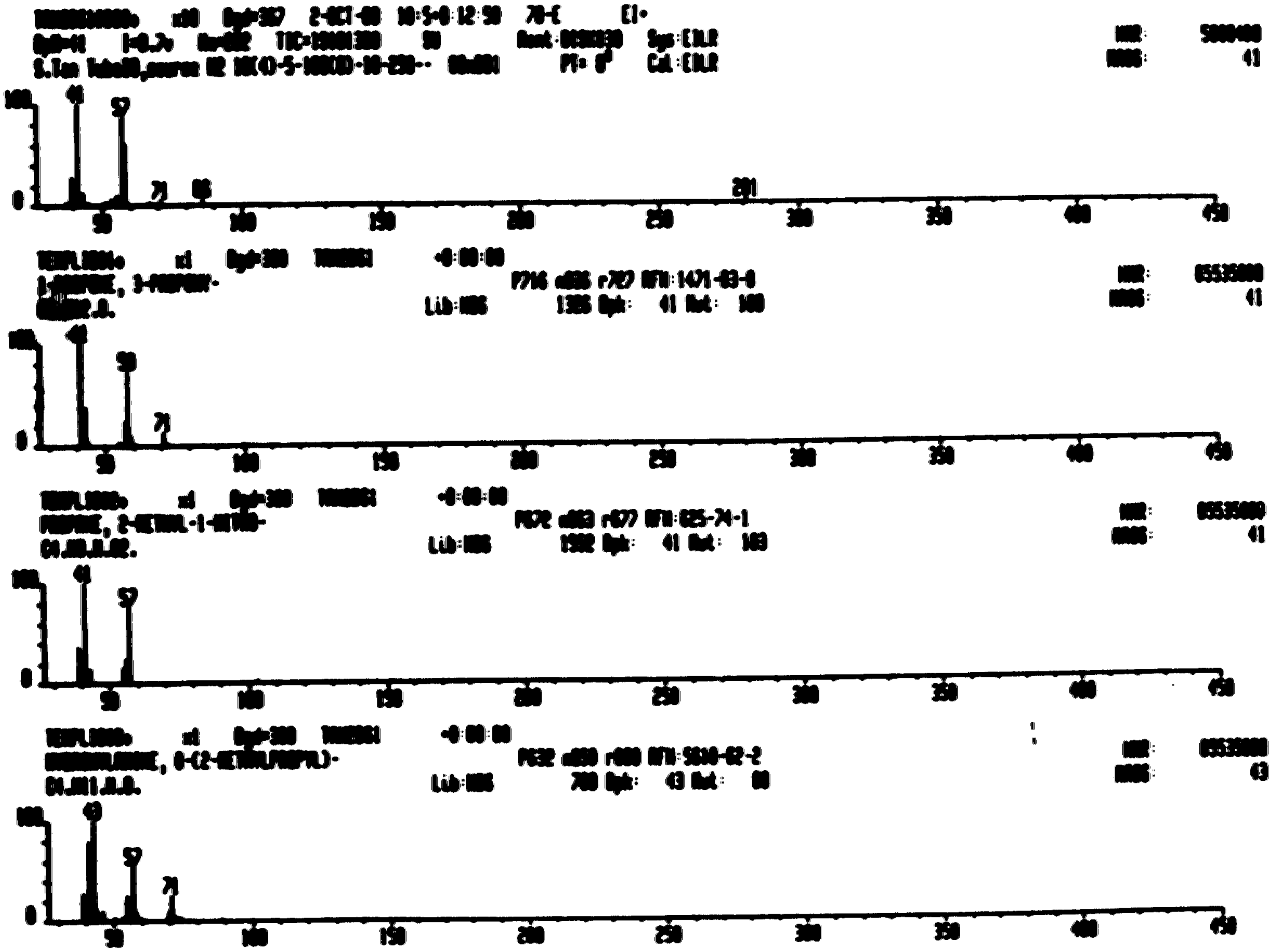
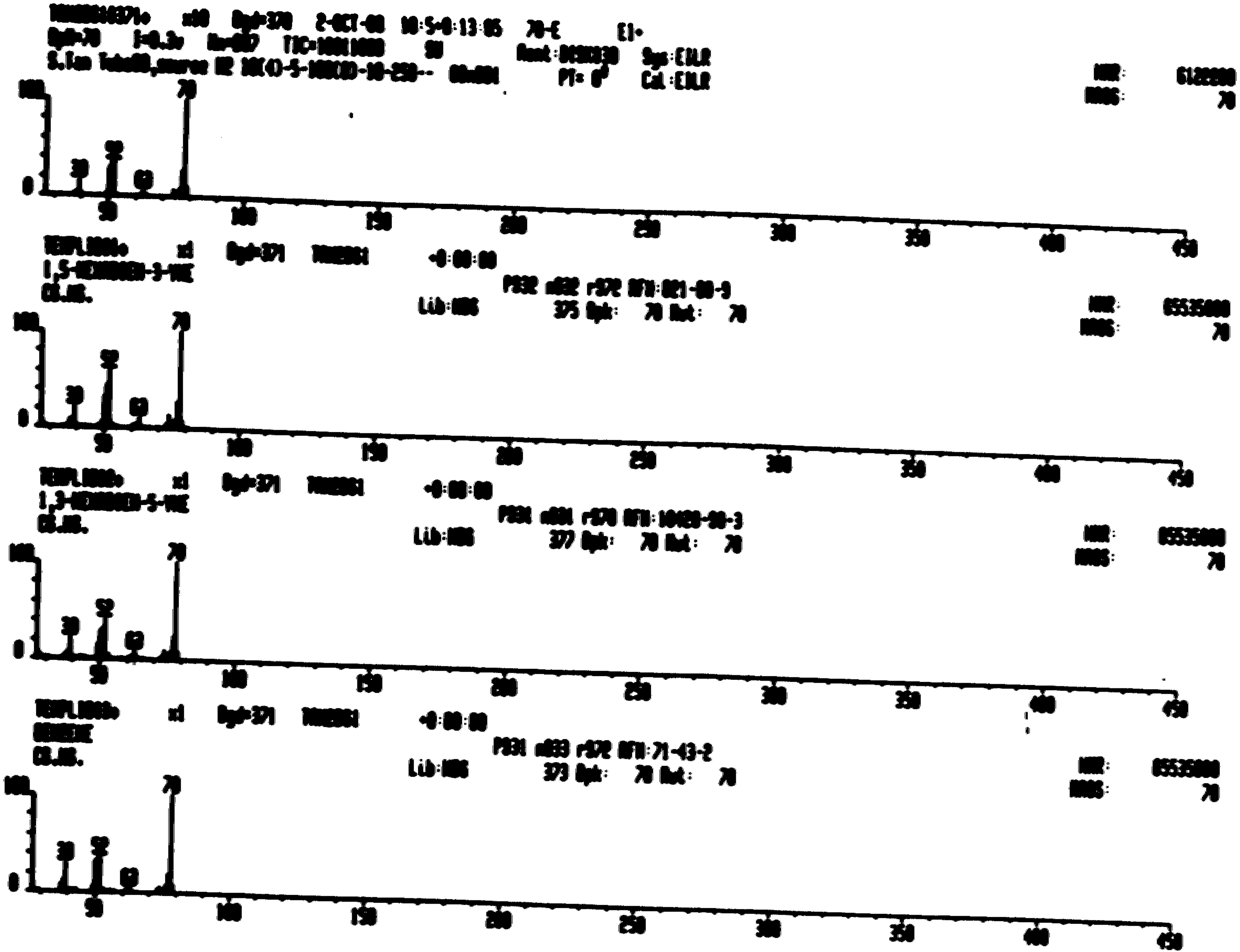
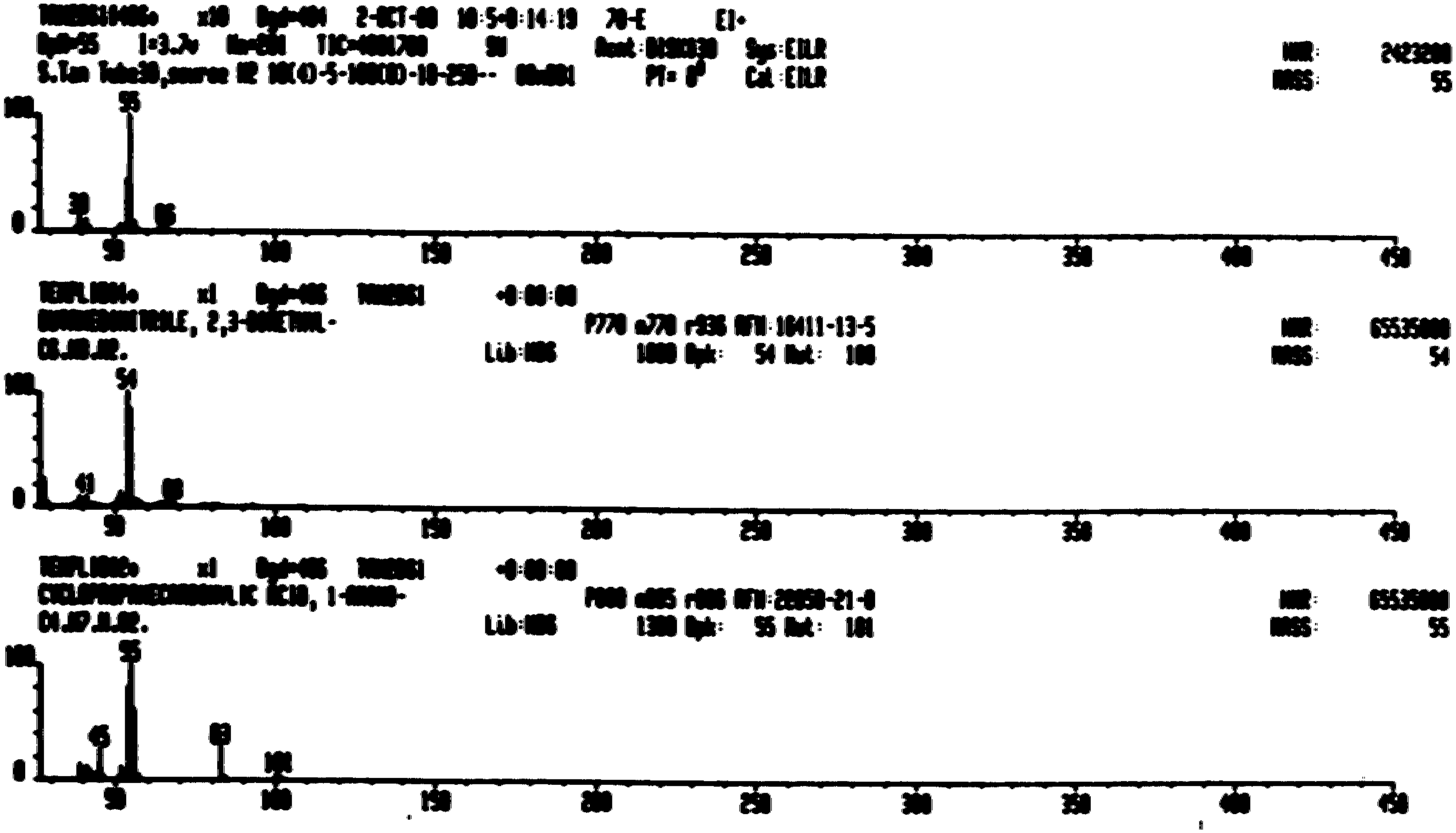
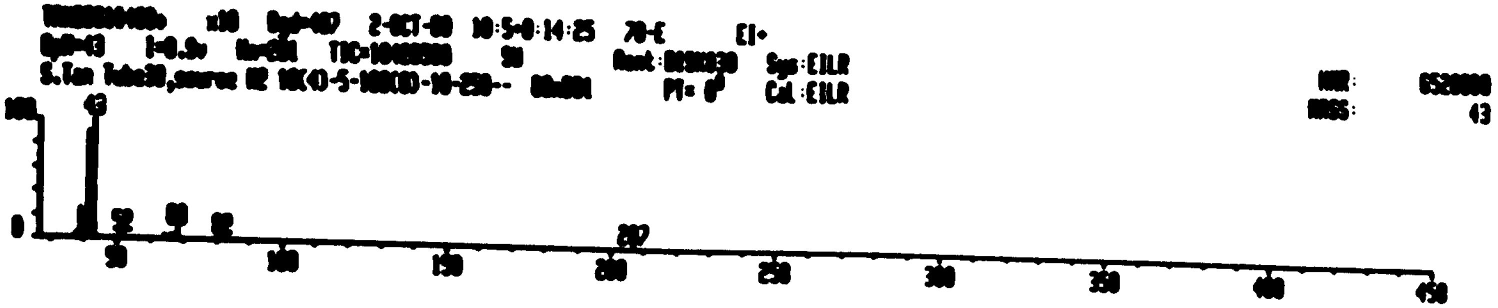
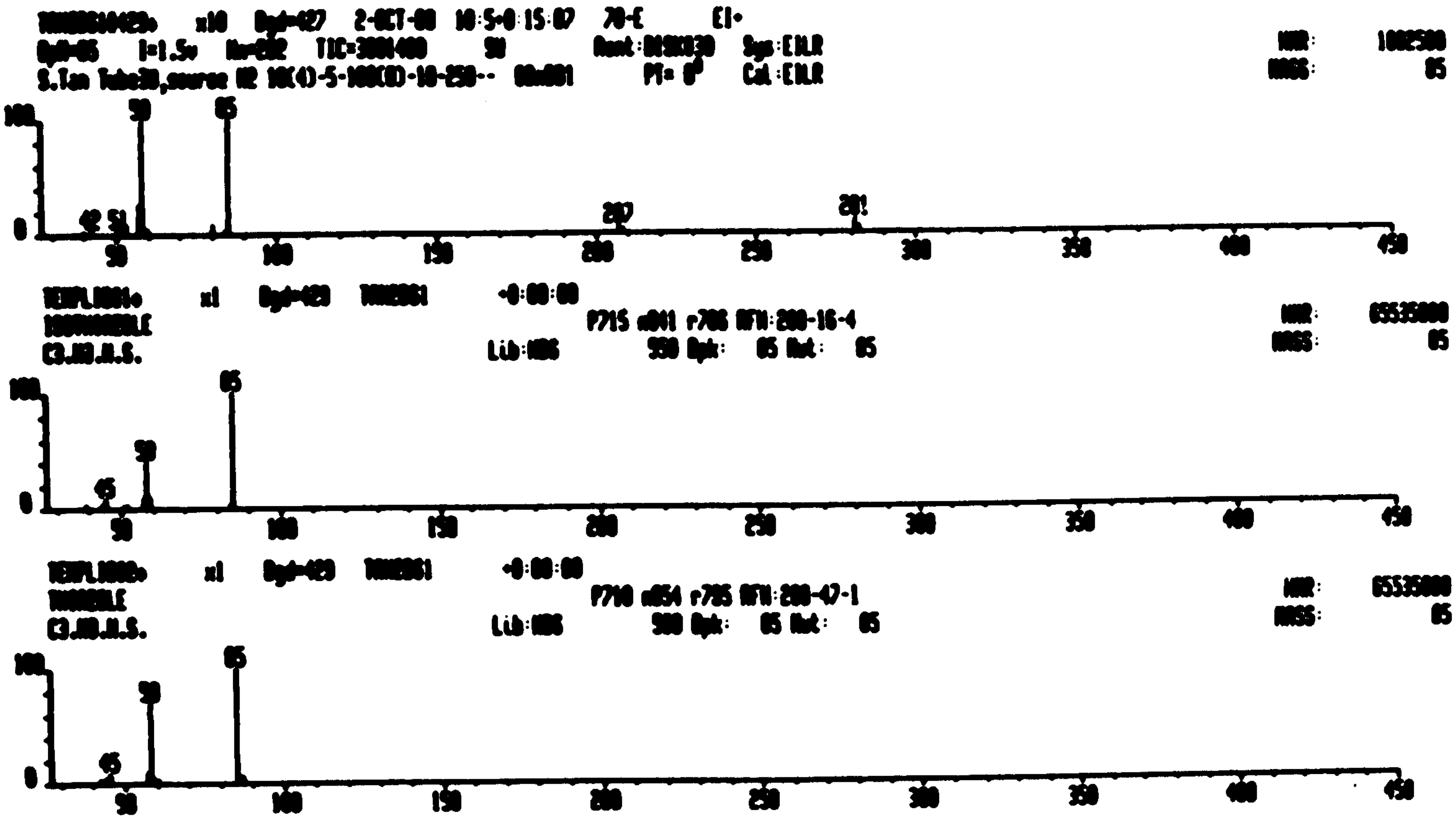

EI+
CYCLOPENTANOL
C5.H10.O.
96-41-3
3-BUTENOIC ACID
C4.H6.O2.
625-38-7
2-BUTEN-1-OL, 2-METHYL-
C5.H10.O.
4675-87-0
Lib:NBS
100
0
50
100
150
200
250
300
350
400
450
57
71
86


100
0
41
57
71
85
281
50
100
150
200
250
300
350
400
450
100
0
41
58
71
100
0
41
57
100
0
43
57
71
Lib:NBS
Lib:NBS
Lib:NBS


EI+
Lib:NBS
375 Rpk: 70 Rvt: 70
377 Rpk: 70 Rvt: 70
373 Rpk: 70 Rvt: 70
100
0
39
52
63
70
50
100
150
200
250
300
350
400
450


EI+
70-E
Sys:EILR
Cal:EILR
BMR: 2423200
MASS: 55
100
0
55
30
86
50
100
150
200
250
300
350
400
450
BUTANEDINITRILE, 2,3-DIMETHYL-
Lib:NBS
CAS:10411-13-5
BMR: 6553600
MASS: 54
54
41
80
CYCLOPROPANECARBOXYLIC ACID, 1-AMINO-
Lib:NBS
CAS:22059-21-8
BMR: 6553600
MASS: 55
55
45
83
101

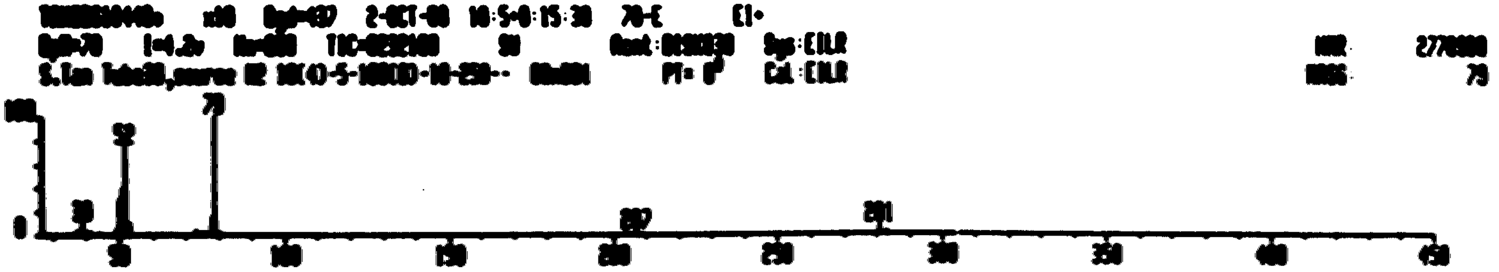

x10
70-E
EI+
S.Tan
Sys:EILR
Cal:EILR
MASS:
652000
43
100
0
43
52
80
92
207
50
100
150
200
250
300
350
400
450

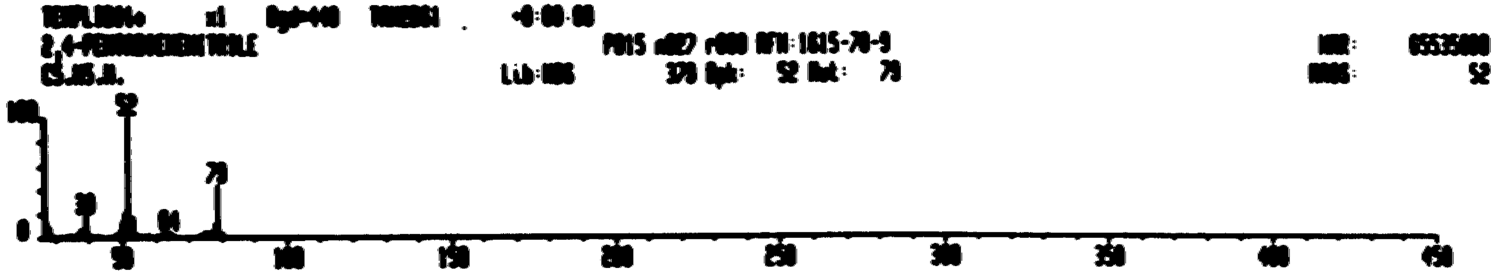


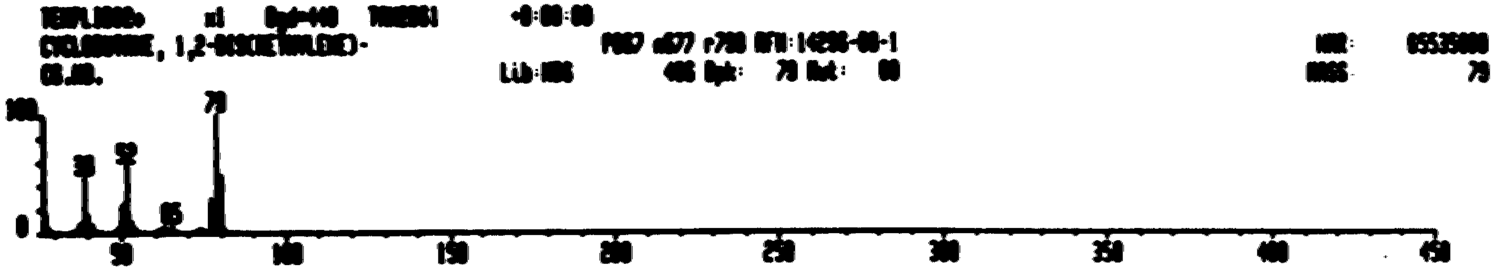
[illegible] x10 [illegible] 2-OCT-[illegible] 10:5+0:15:07 70-E EI+
[illegible] I=1.5v [illegible] TIC=[illegible] [illegible] Sys:EILR
S.Tan Tube[illegible],source [illegible] 10(1)-5-100(1)-10-250-- [illegible] PT= 0 Cal:EILR
[illegible]: 1002500
MASS: 85

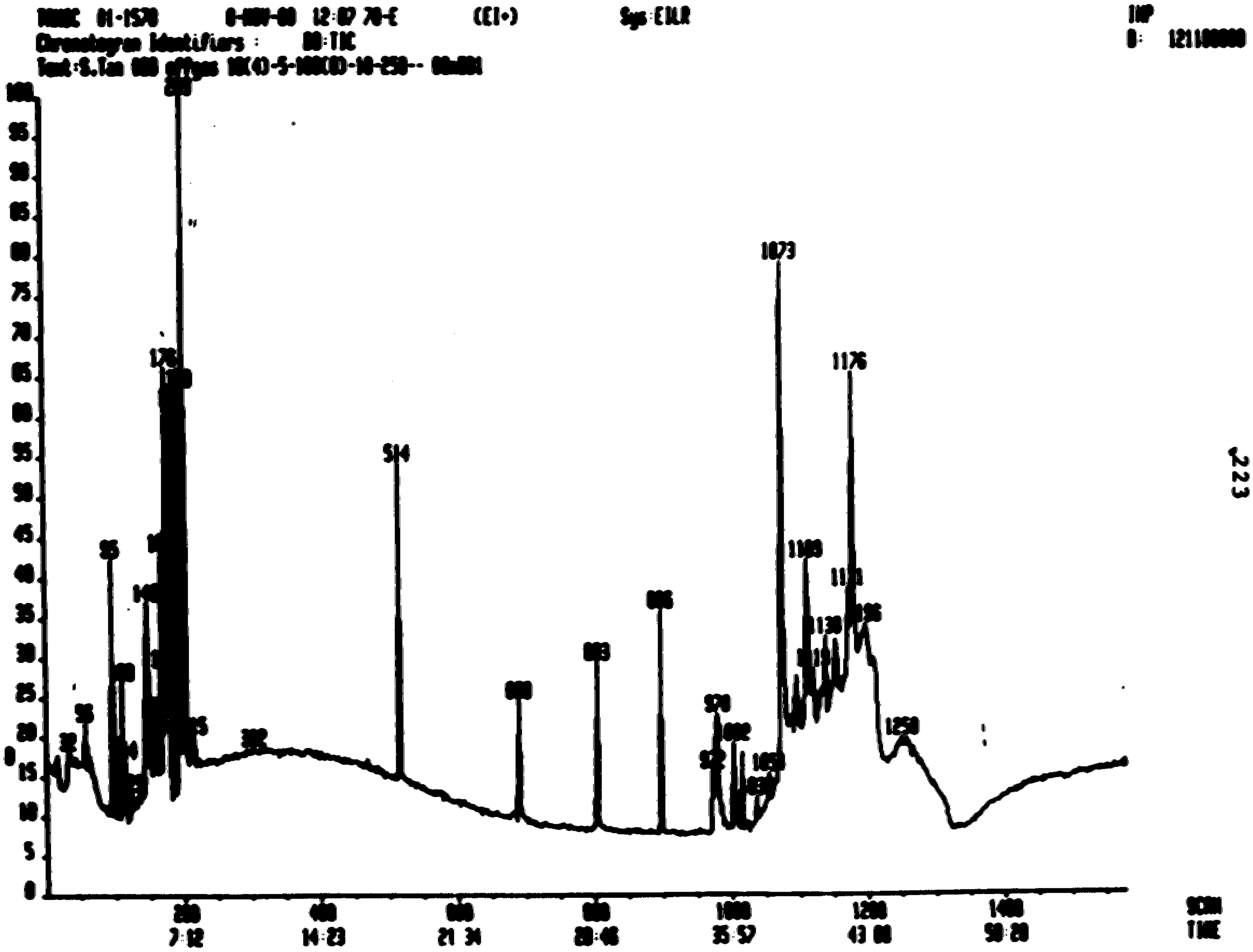
TEMPL.[illegible] x1 [illegible] [illegible] +0:00:00
[illegible] P715 [illegible] r706 [illegible]:280-16-4
C3.[illegible] Lib:[illegible] 550 [illegible]: 85 [illegible]: 85
[illegible]: 65535000
MASS: 85

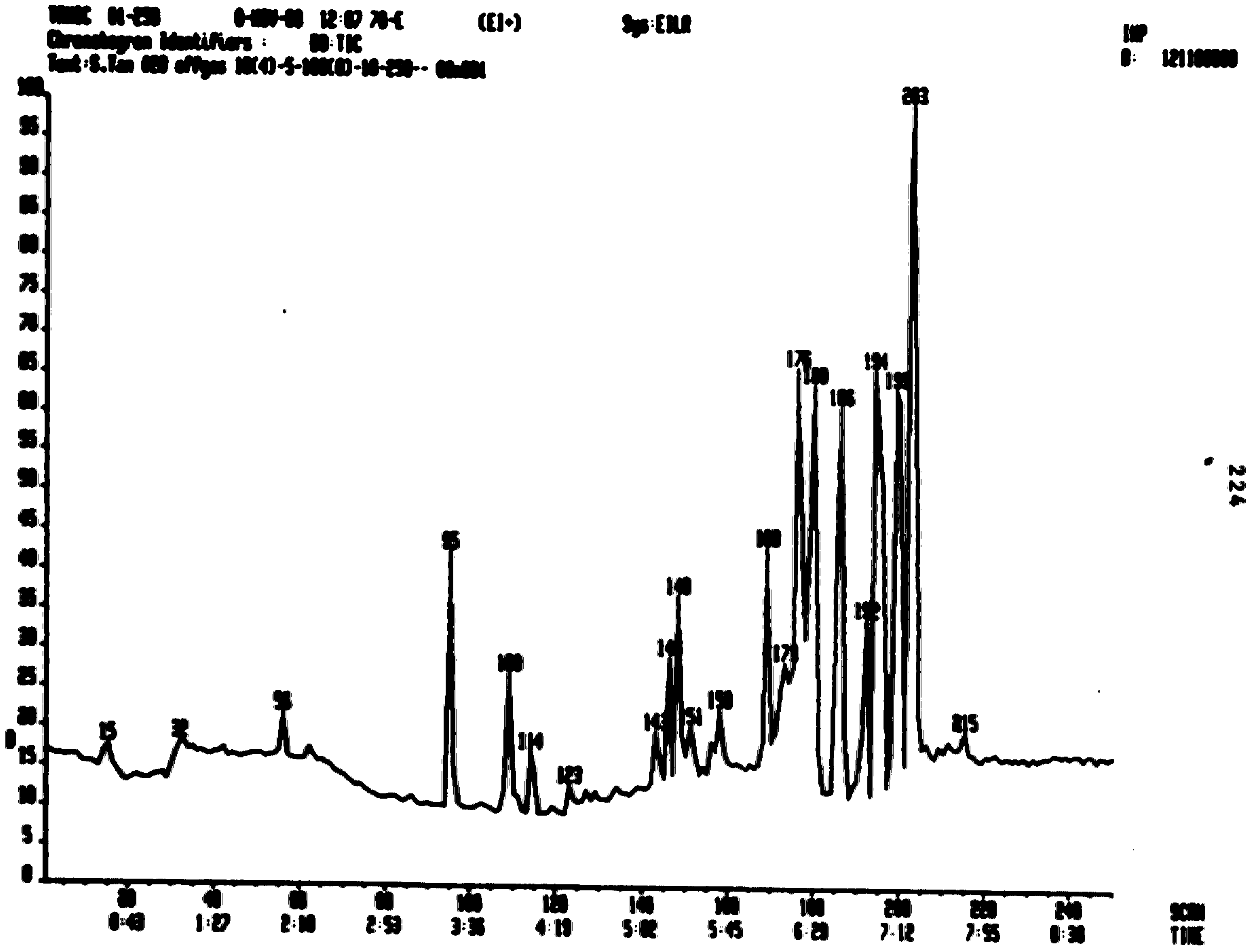
TEMPL.[illegible] x1 [illegible] [illegible] +0:00:00
[illegible] P710 [illegible] r705 [illegible]:280-47-1
C3.[illegible] Lib:[illegible] 500 [illegible]: 85 [illegible]: 85
[illegible]: 65535000
MASS: 85

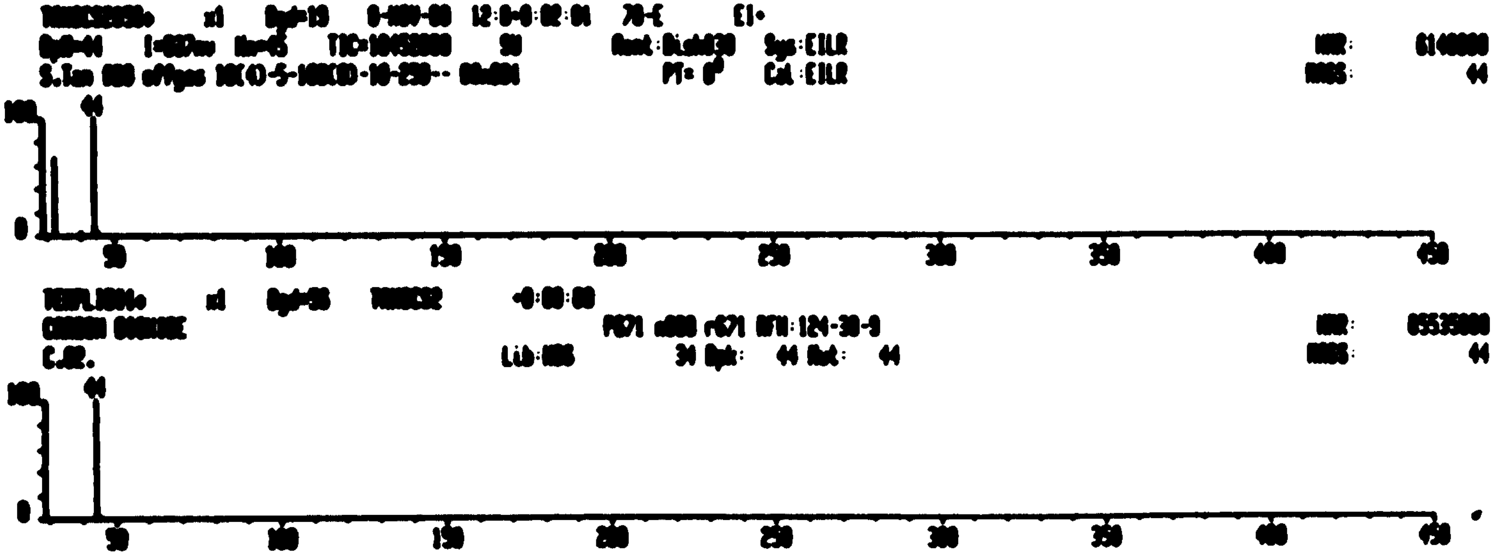

2-OCT-00
EI+
Sys:EILR
Cal:EILR
HRR:
2770000
79
100
0
30
52
79
207
281
50
100
150
200
250
300
350
400
450


2,4-PENTADIENENITRILE
Lib:NBS
RN:1615-70-9
370
52
79
HRR:
6553600
52
100
0
30
52
64
79
50
100
150
200
250
300
350
400
450

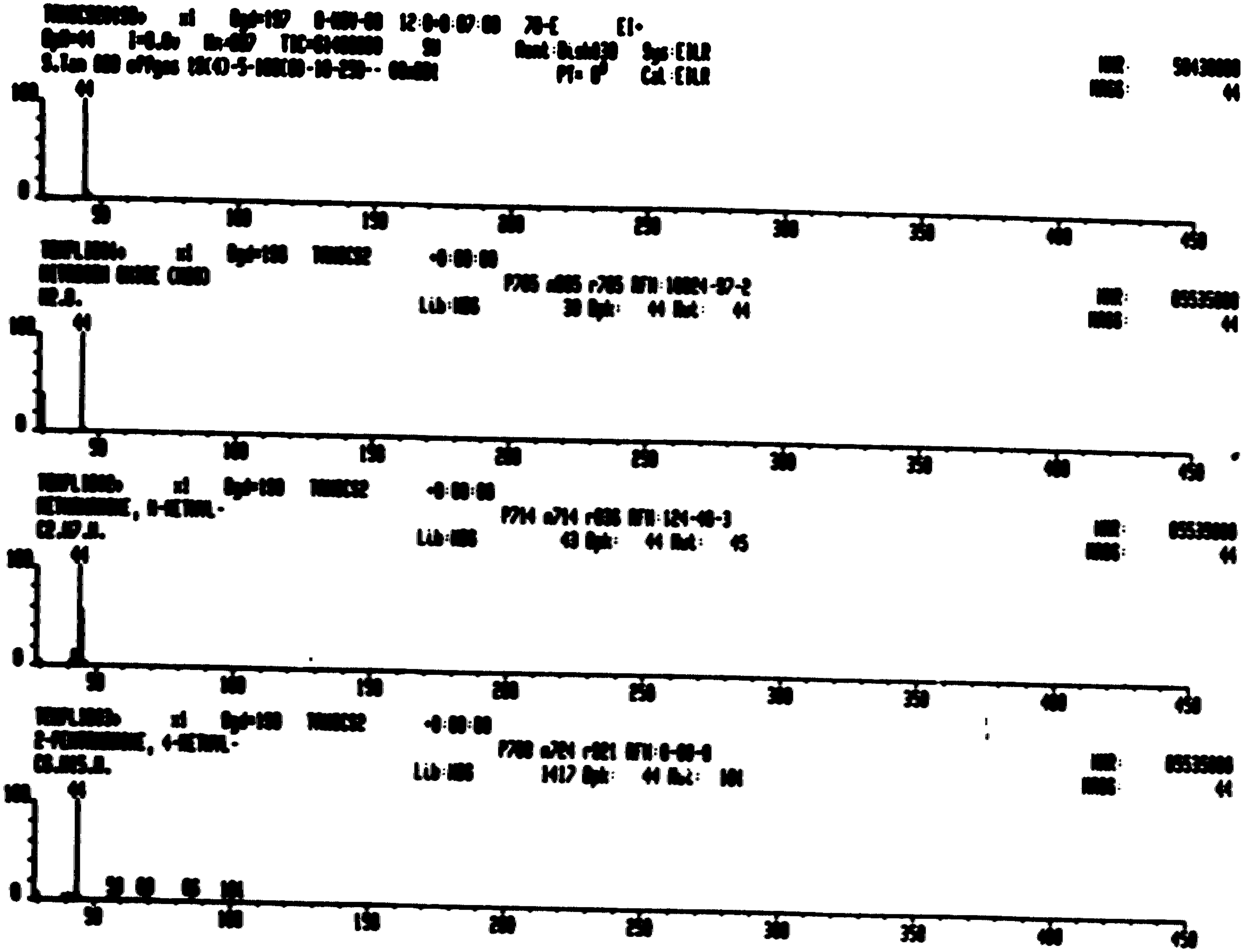

CYCLOBUTANE, 1,2-BIS(METHYLENE)-
Lib:NBS
RN:14296-80-1
406
79
HRR:
6553600
79
100
0
39
52
65
79
50
100
150
200
250
300
350
400
450

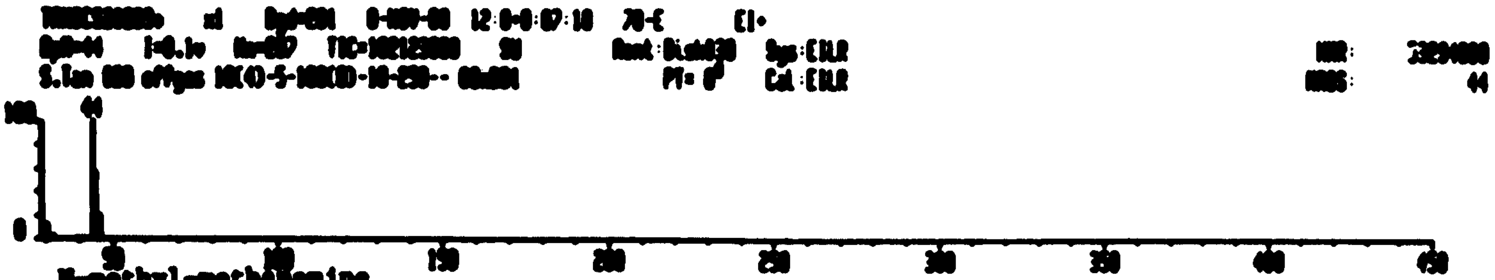

(EI+)
Sys:EILR
Chromatogram Identifiers : 00:TIC
0: 121100000
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
178
95
514
1073
1176
1100
1136
1250
908
806
698
978
1002
1050
302
200
7:12
400
14:23
600
21:34
800
1000
35:57
1200
43:08
1400
50:20
SCAN
TIME


TOMIC 01-250 0-NOV-00 12:07 70-C (EI+) Sys:EILR
Chromatogram Identifiers : 00:TIC
Text:S.Tan 000 offgas 10(4)-5-100(0)-10-250-- 00x004
TIC
0: 121100000
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
0
15
32
56
95
108
114
123
143
146
148
151
158
168
173
176
180
186
192
194
198
203
215
20
0:43
40
1:27
60
2:10
80
2:53
100
3:36
120
4:19
140
5:02
160
5:45
180
6:29
200
7:12
220
7:55
240
8:38
SCAN
TIME

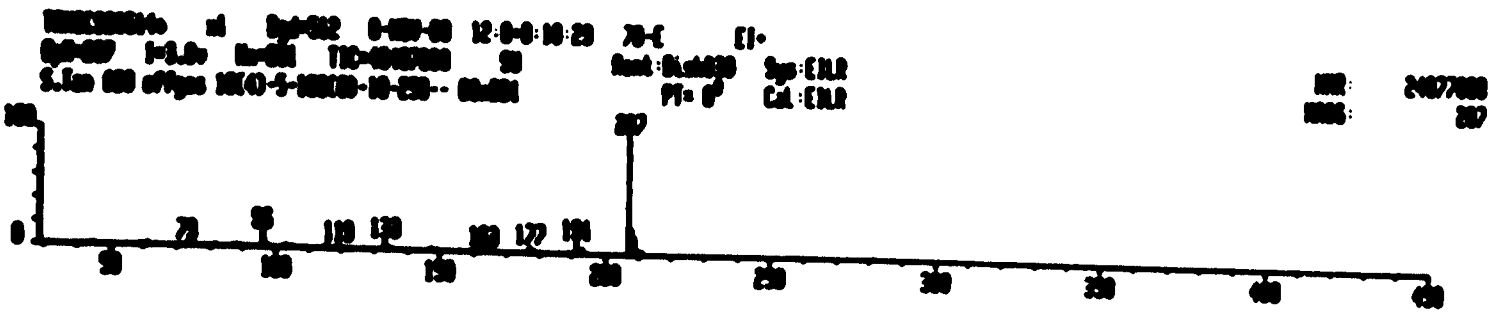


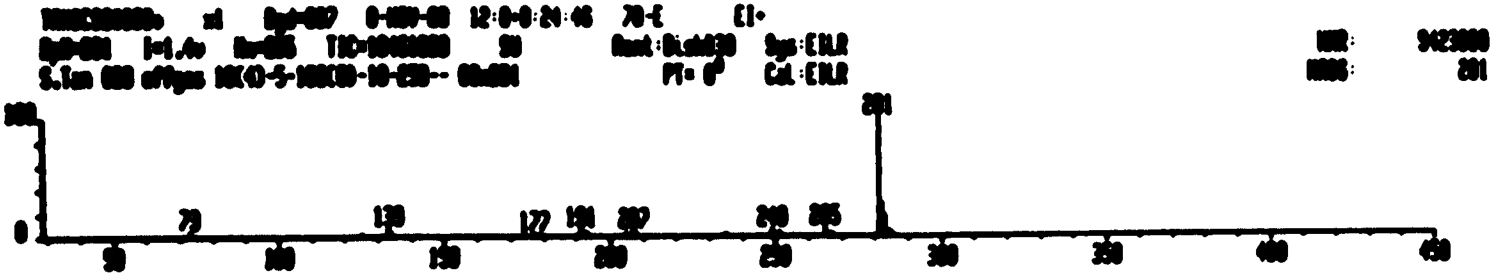
Note: peaks #32 to 199 all have a similar mass spectrum as #199.

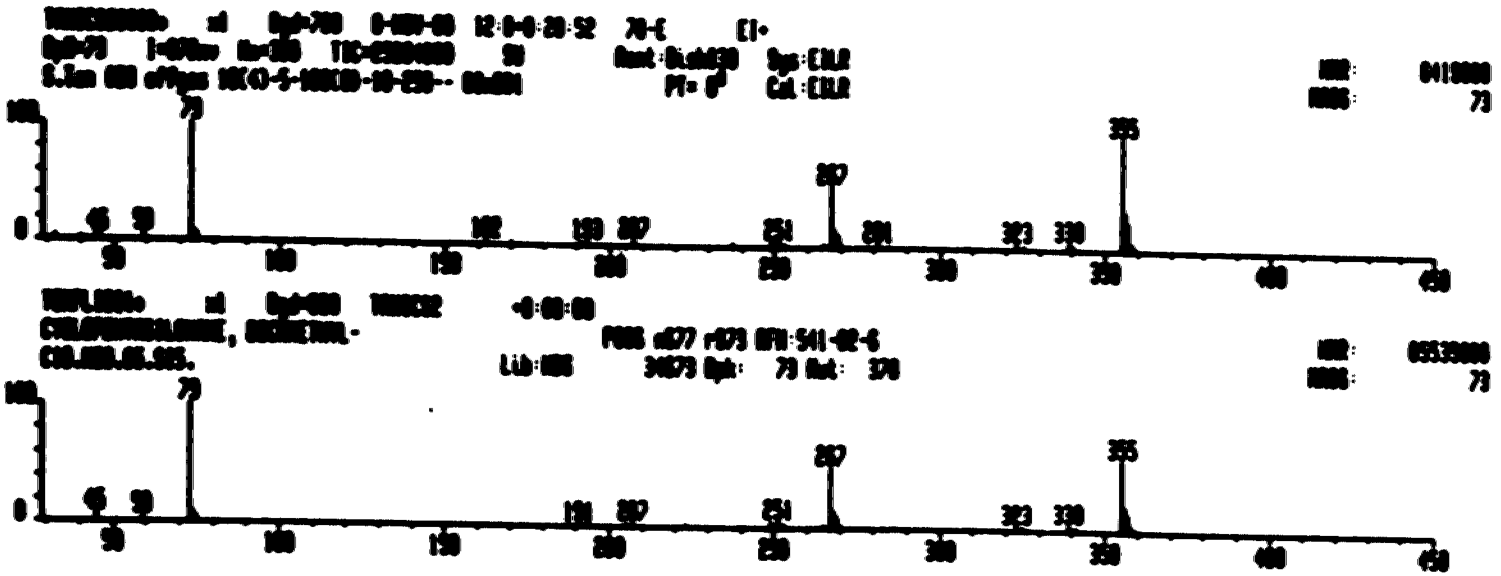

EI+
100
0
44
50
100
150
200
250
300
350
400
450
NITROUS OXIDE
METHANAMINE, N-METHYL-
10024-97-2
124-40-3
50
60
65
101

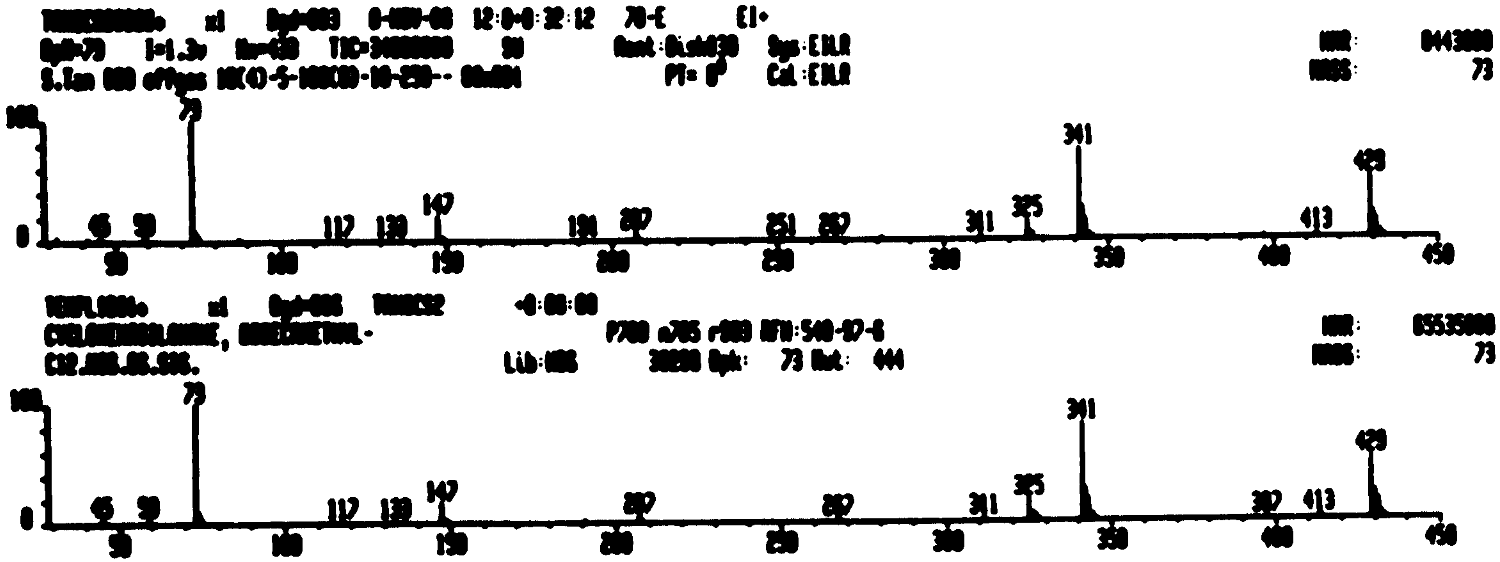


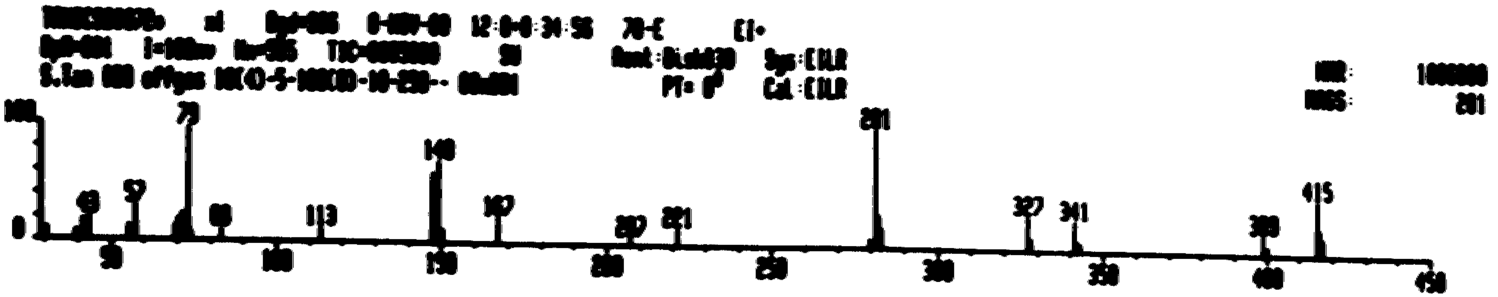
N-methyl-methanamine

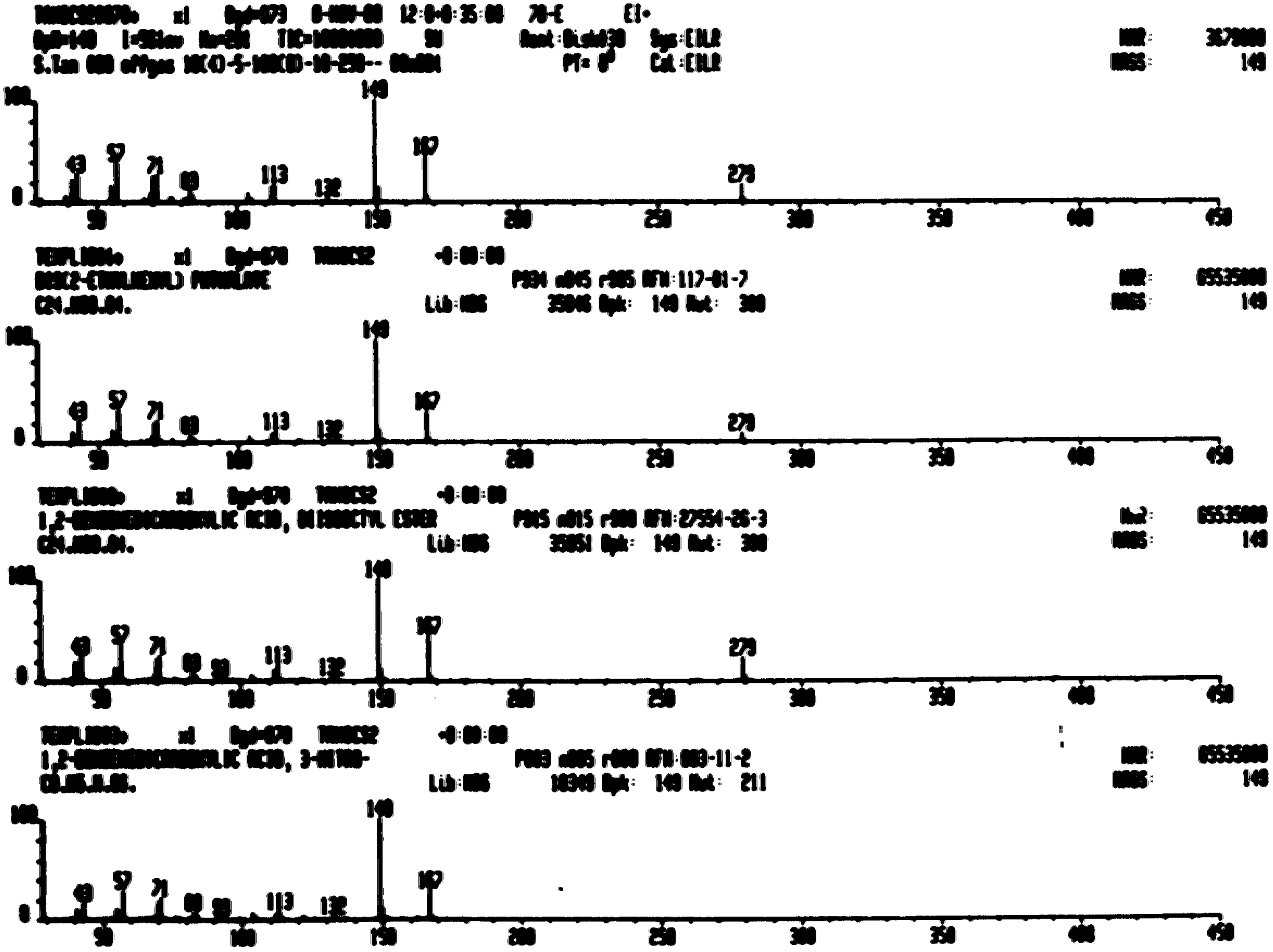

EI+
100
0
73
96
119
130
160
177
194
207
50
100
150
200
250
300
350
400
450
207

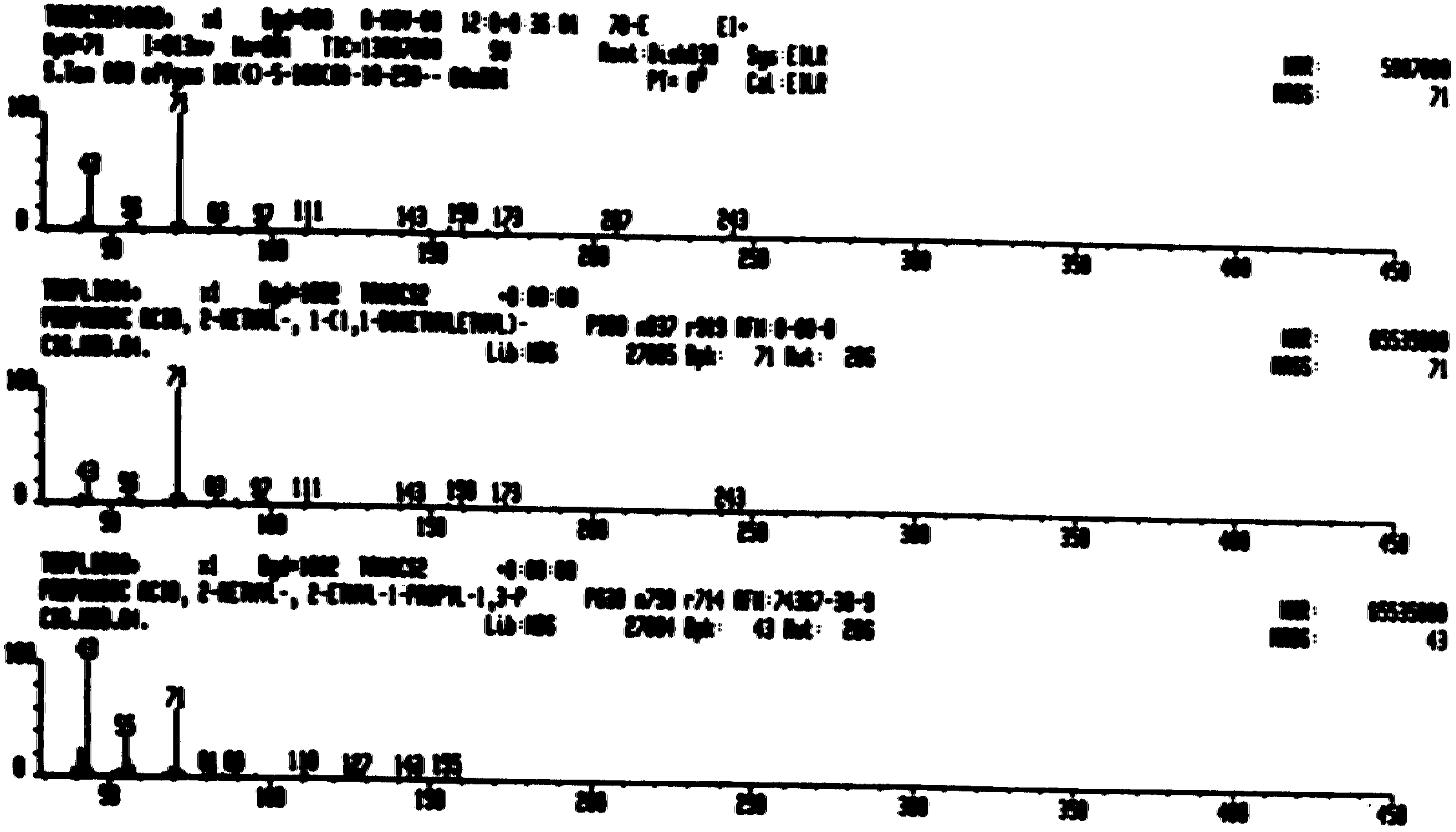

x1
EI+
9423000
201
100
0
79
130
177
191
207
240
265
281
50
100
150
200
250
300
350
400
450

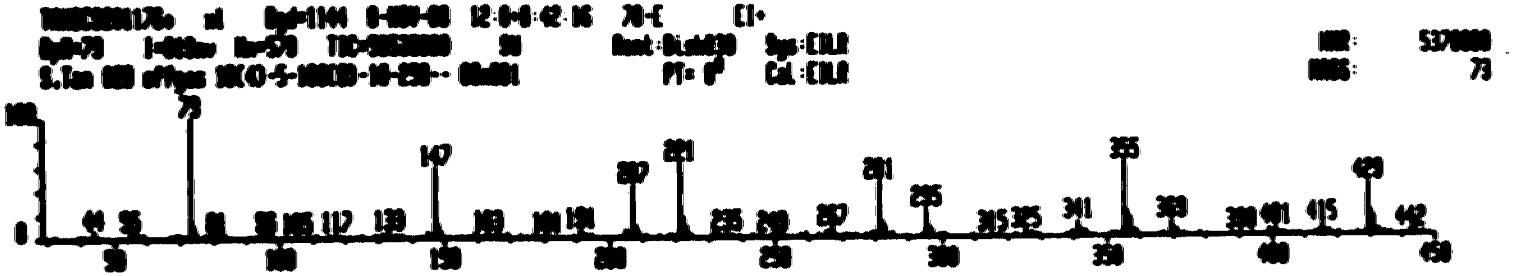

EI+
100
73
45
59
182
190
207
251
267
281
323
339
355
0
50
100
150
200
250
300
350
400
450
541-02-6
100
73
45
59
190
207
251
267
323
339
355
0
50
100
150
200
250
300
350
400
450


x1
12:0-0:32:12
70-E
EI+
Sys:EILR
PI= 0
Cal:EILR
73
100
0
73
45
59
112
133
147
191
207
251
282
311
325
341
413
429
50
100
150
200
250
300
350
400
450
x1
-0:00:00
CYCLOHEXASILOXANE, DODECAMETHYL-
P700 a765 r909 RFN:540-97-6
C12.H36.O6.SI6.
Lib:NBS
73
444
73
100
0
73
45
59
112
133
147
207
282
311
325
341
397
413
429
50
100
150
200
250
300
350
400
450


70-E
EI+
Sys:EILR
Cal:EILR
281
100
0
43
57
73
113
140
167
207
221
281
327
341
415
50
100
150
200
250
300
350
400
450

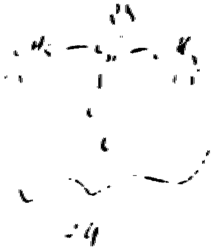

EI+
Sys:EILR
PT: 8°
Cal:EILR
RIC: 3679000
MASS: 149
TEMPL.1004 x1 TAKEC32 +0:00:00
BIS(2-ETHYLHEXYL) PHTHALATE
RN:117-81-7
Lib:NBS Bpk: 149 Rmt: 390
MASS: 149
TEMPL.1005 x1 TAKEC32 +0:00:00
1,2-BENZENEDICARBOXYLIC ACID, DIISOOCTYL ESTER
RN:27554-26-3
Lib:NBS Bpk: 149 Rmt: 390
MASS: 149
TEMPL.1003 x1 TAKEC32 +0:00:00
1,2-BENZENEDICARBOXYLIC ACID, 3-NITRO-
RN:603-11-2
Lib:NBS Bpk: 149 Rmt: 211
MASS: 149
100
0
43
57
71
83
93
113
132
149
167
279
50
100
150
200
250
300
350
400
450

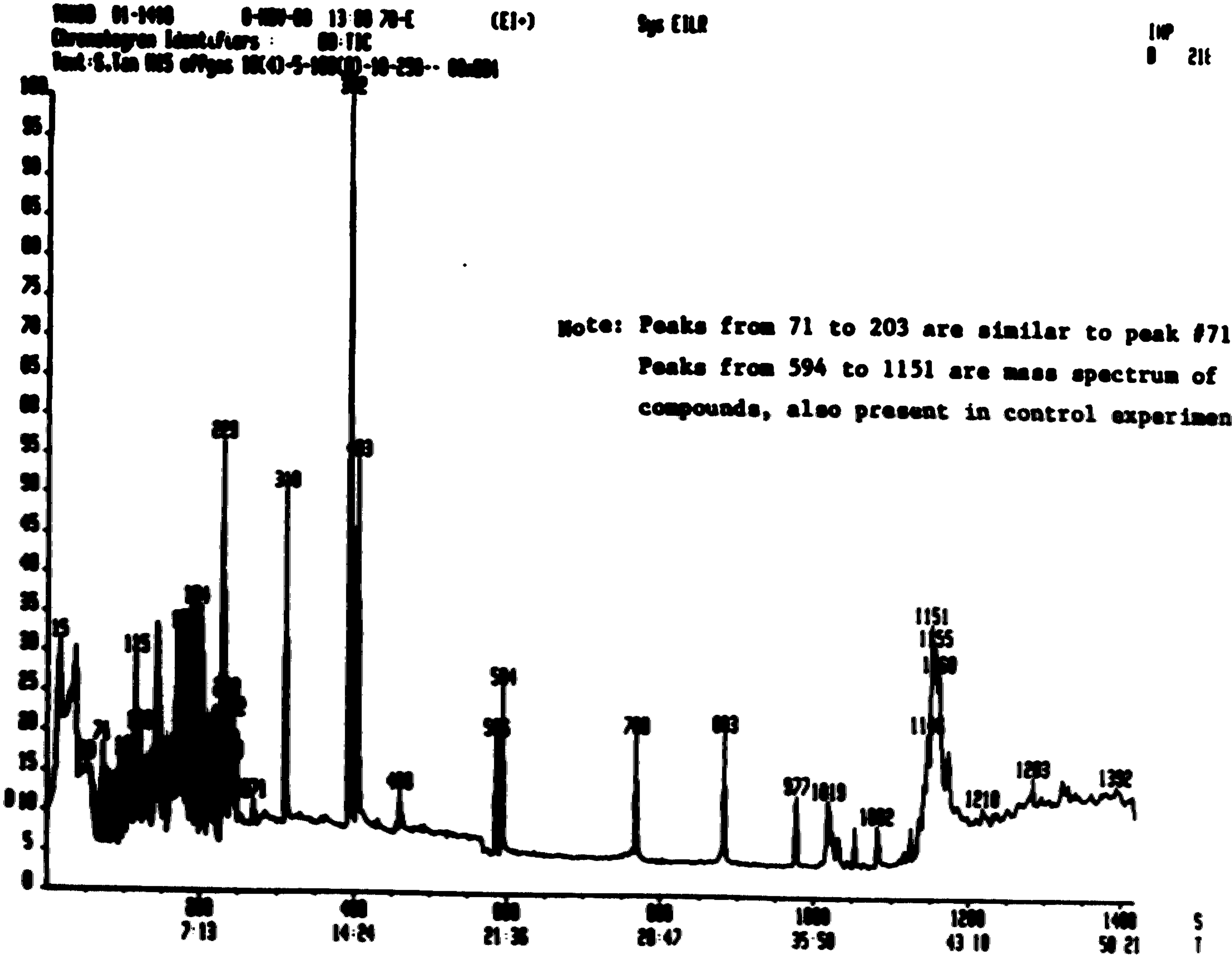

100
0
43
55
71
83
97
111
143
159
173
207
243
50
100
150
200
250
300
350
400
450
100
0
43
55
71
83
97
111
143
159
173
243
50
100
150
200
250
300
350
400
450
100
0
43
55
71
110
127
143
155
50
100
150
200
250
300
350
400
450
71
71
43


EI+
Cal:EILR
537000
73
100
0
73
44
55
147
207
221
281
295
355
429
442
415
401
341
369
390
183
191
235
249
267
315
325
98
105
112
130
50
100
150
200
250
300
350
400
450

[illegible]

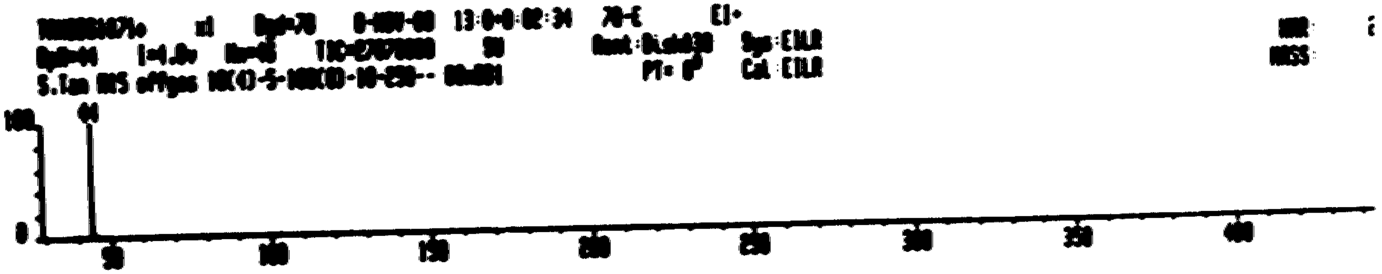
[illegible]

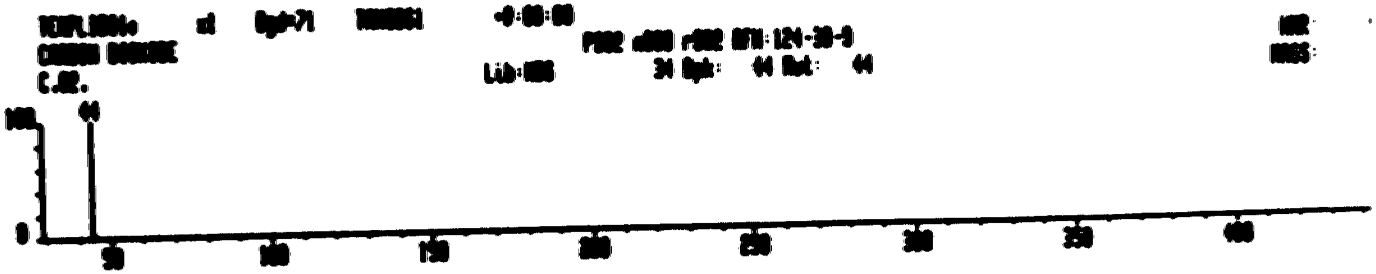


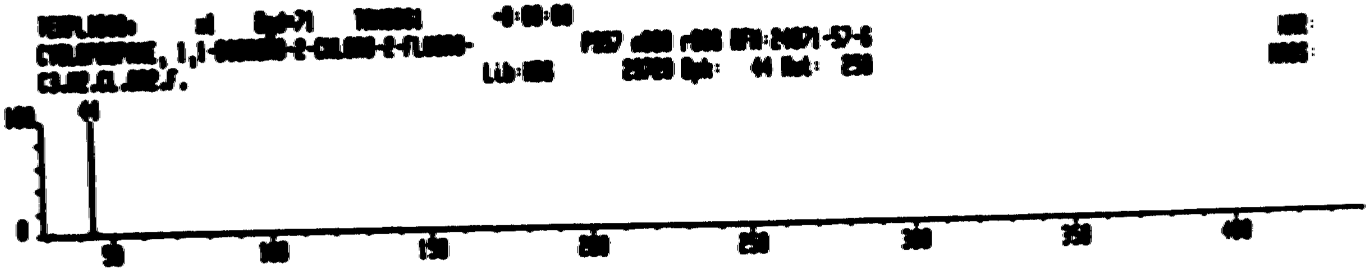


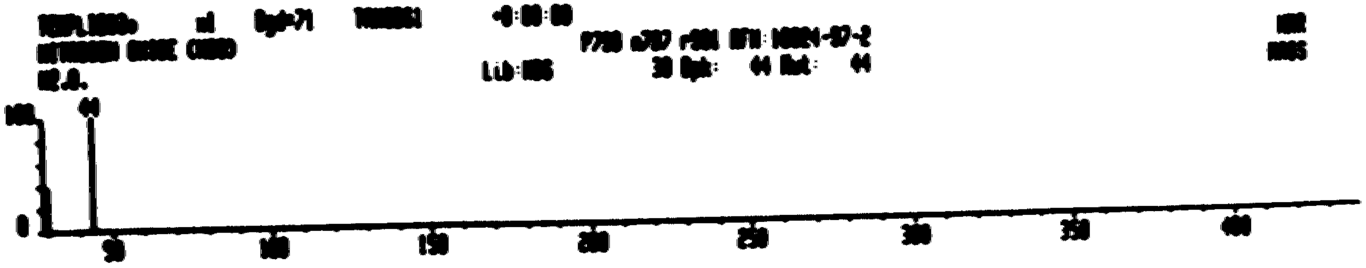
Note: Peaks from 71 to 203 are similar to peak #71.

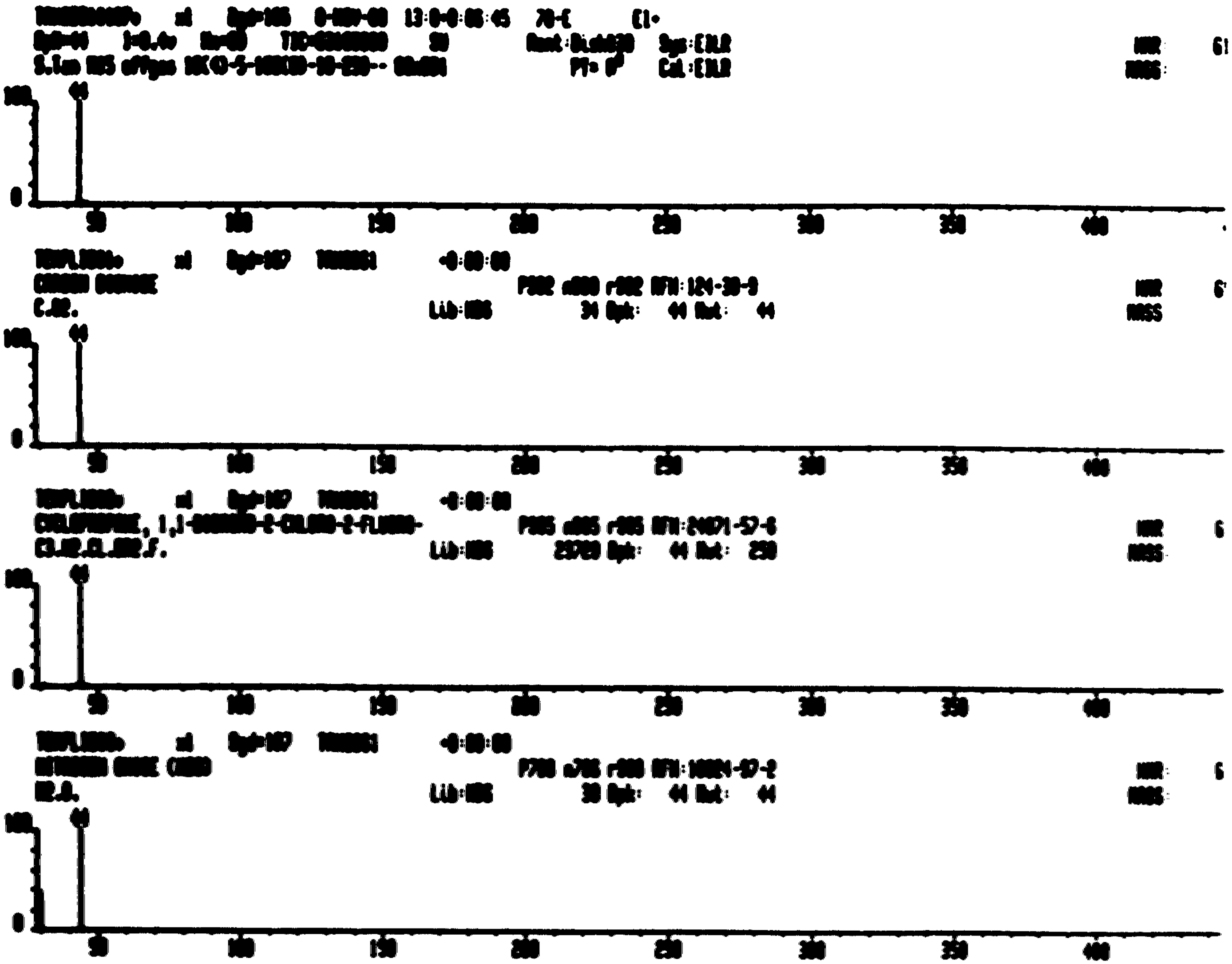
Peaks from 594 to 1151 are mass spectrum of siloxane compounds, also present in control experiment.

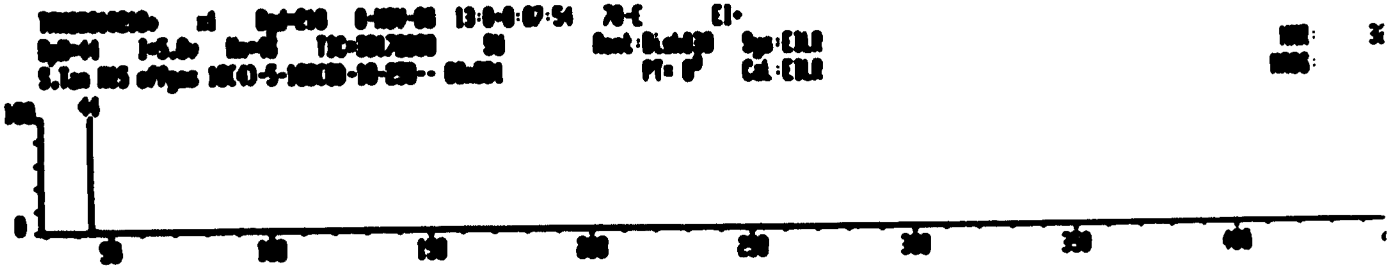

13:0+0:02:34 70-E EI+
TIC=27079000
Sys:EILR
Cal:EILR
S.Tan MS offgas 10(4)-5-100(0)-10-250--
HRR:
MASS:
100
0
44
50
100
150
200
250
300
350
400

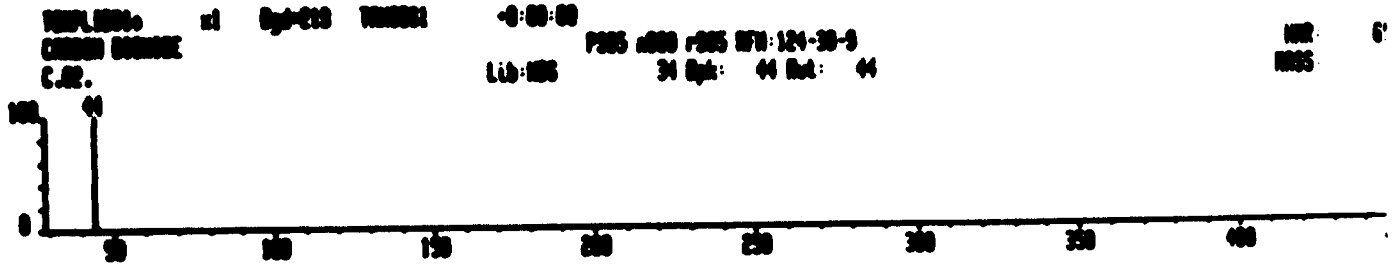

-0:00:00
RFN:124-38-9
CARBON DIOXIDE
C.O2.
Lib:NBS
34 Bpk: 44 Rmt: 44
HRR:
MASS:
100
0
44
50
100
150
200
250
300
350
400

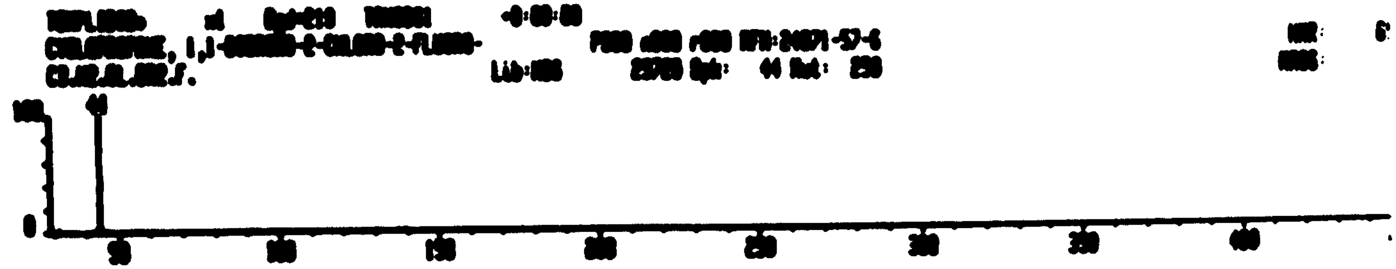

-0:00:00
CYCLOPROPANE, 1,1-DIBROMO-2-CHLORO-2-FLUORO-
C3.H3.CL.BR2.F.
Lib:NBS
Bpk: 44 Rmt: 250
HRR:
MASS:
100
0
44
50
100
150
200
250
300
350
400

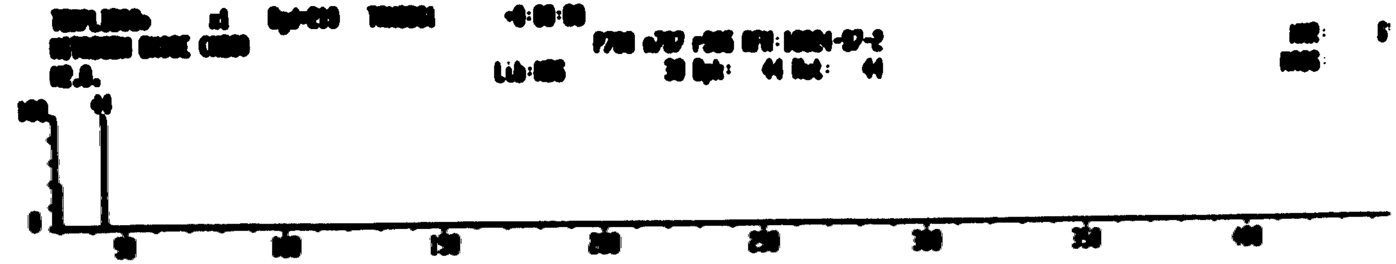

-0:00:00
NITROGEN OXIDE (N2O)
N2.O.
Lib:NBS
30 Bpk: 44 Rmt: 44
HRR
MASS
100
0
44
50
100
150
200
250
300
350
400

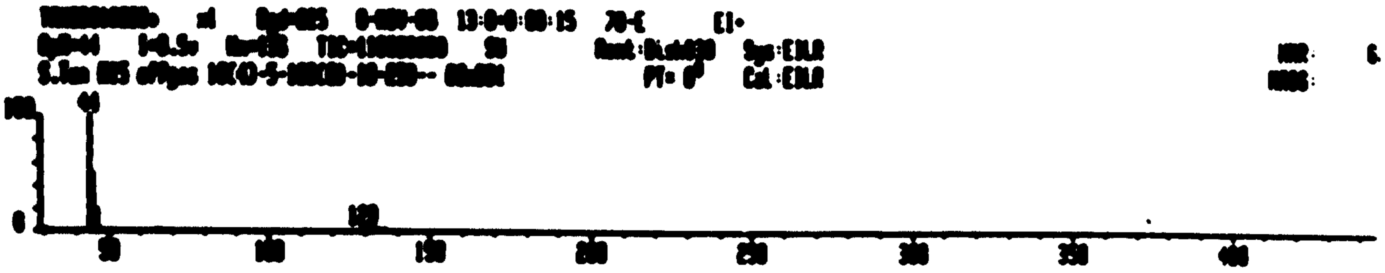

13:0-0:08:45
EI+
Lib:NBS
RFN:124-38-9
C.O2.
34 Bpk: 44 Rnk: 44
CHLOROPROPANE, 1,1-
RFN:24071-57-6
Lib:NBS
23700 Bpk: 44 Rnk: 250
RFN:10024-97-2
Lib:NBS
30 Bpk: 44 Rnk: 44
100
0
44
50
100
150
200
250
300
350
400


13:0-0:07:54
EI+
100
0
44
50
100
150
200
250
300
350
400

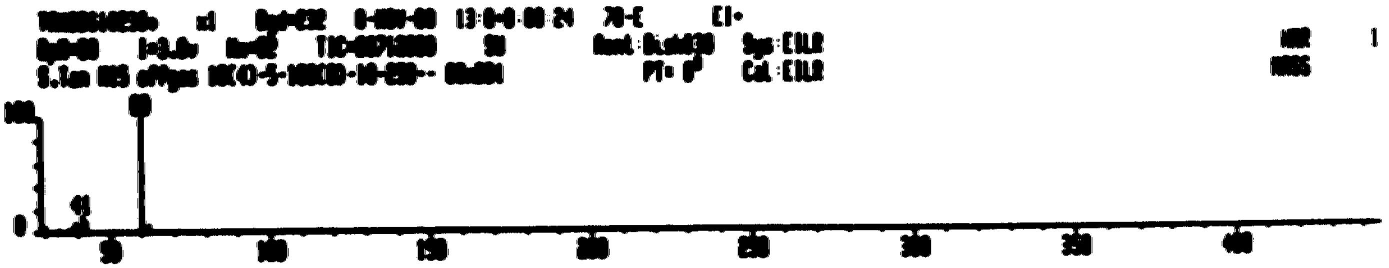

-0:00:00
124-38-9
Lib:NBS
44
100
0
44
50
100
150
200
250
300
350
400

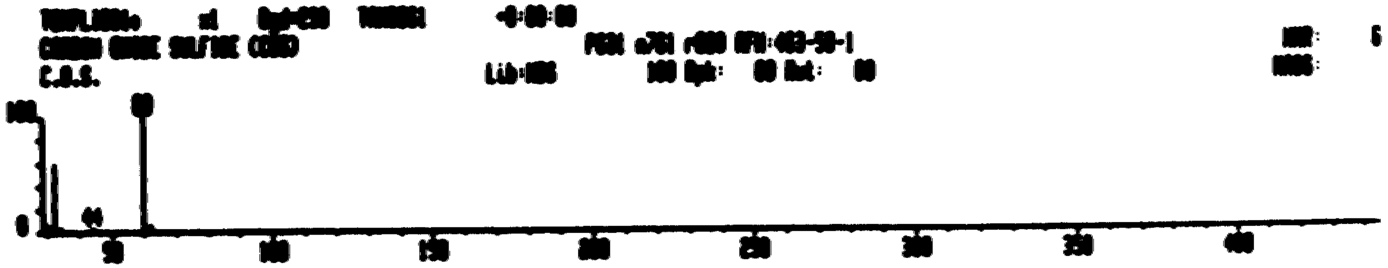

-0:00:00
Lib:NBS
44
100
0
44
50
100
150
200
250
300
350
400

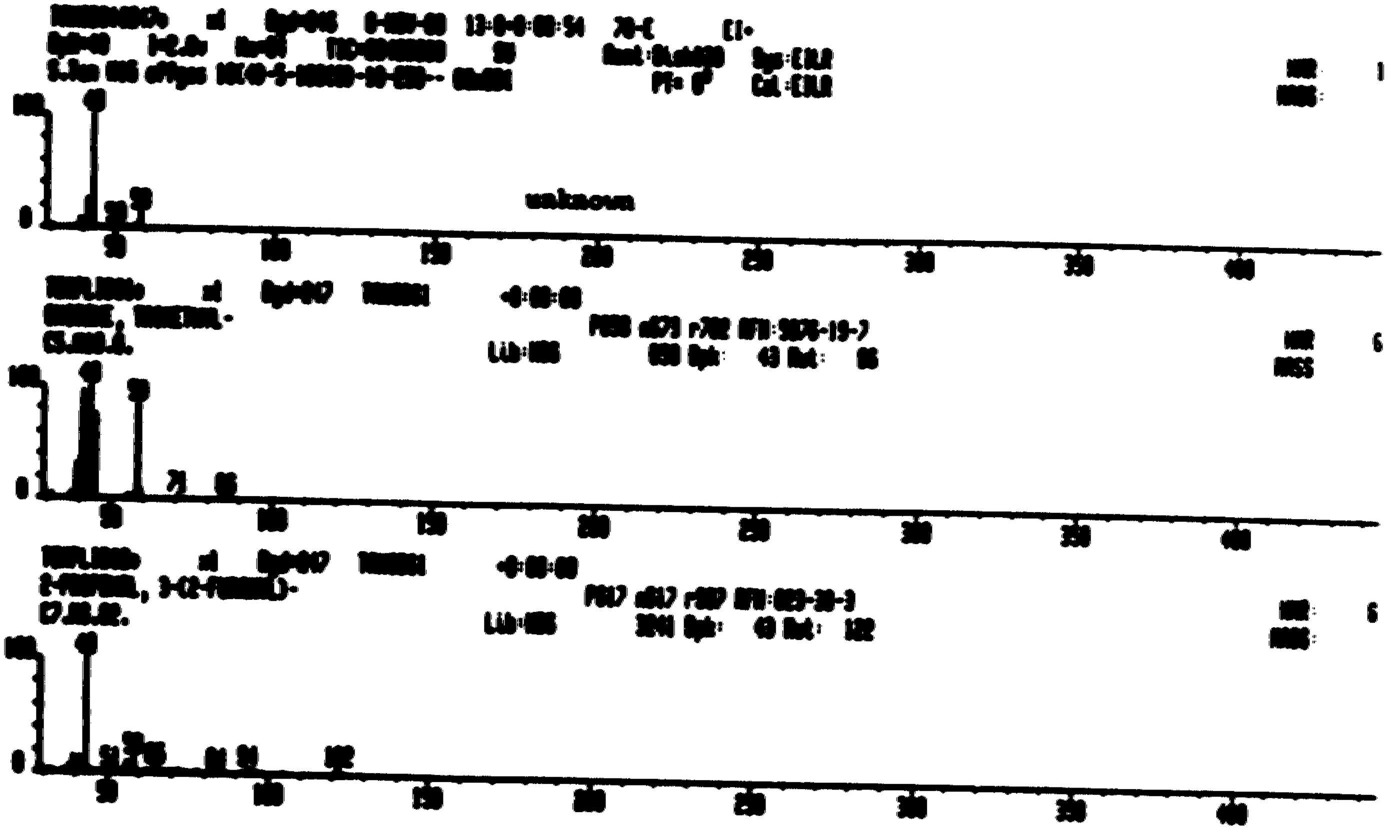

-0:00:00
Lib:NBS
44
44
100
0
44
50
100
150
200
250
300
350
400

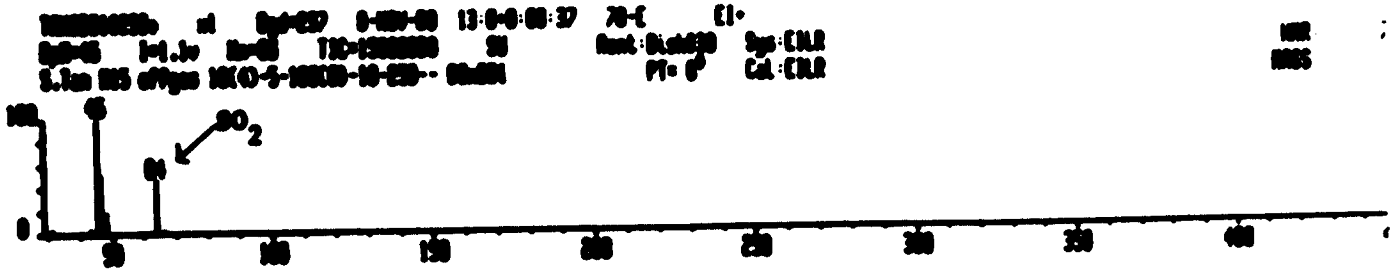


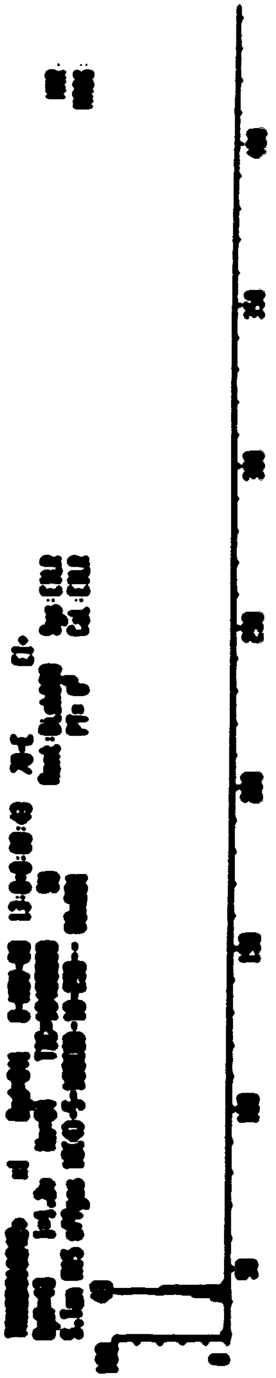
70-E
EI+
Sys:EILR
Cal:EILR
PT: 0
100
0
44
120
50
100
150
200
250
300
350
400

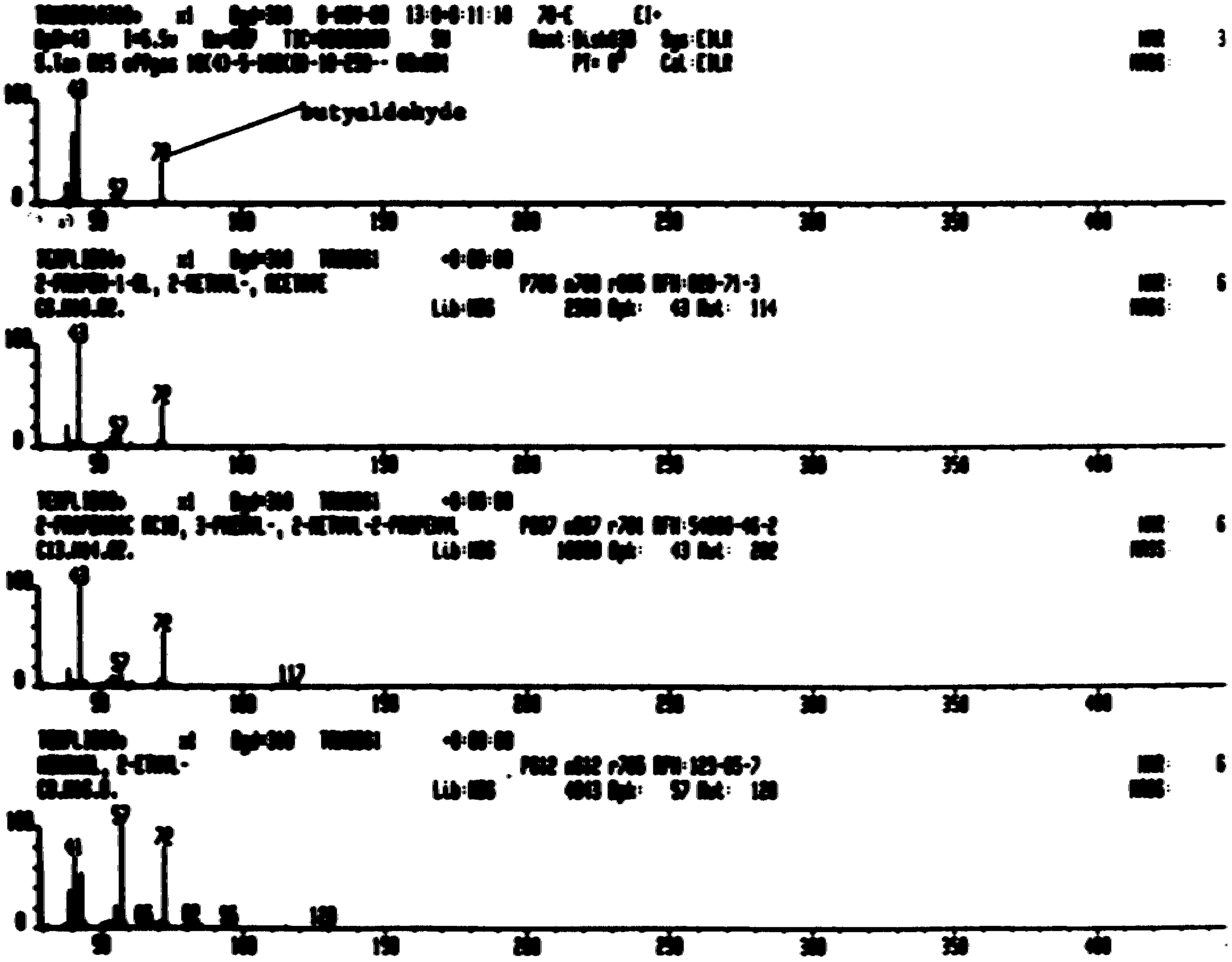

EI+
1
100
0
41
50
100
150
200
250
300
350
400


C.O.S.
463-58-1
5
100
0
44
50
100
150
200
250
300
350
400


unknown
EI+
Lib:NBS
Lib:NBS
100
0
41
59
71
86
102
50
100
150
200
250
300
350
400


EI+
100
0
64
SO_2
50
100
150
200
250
300
350
400

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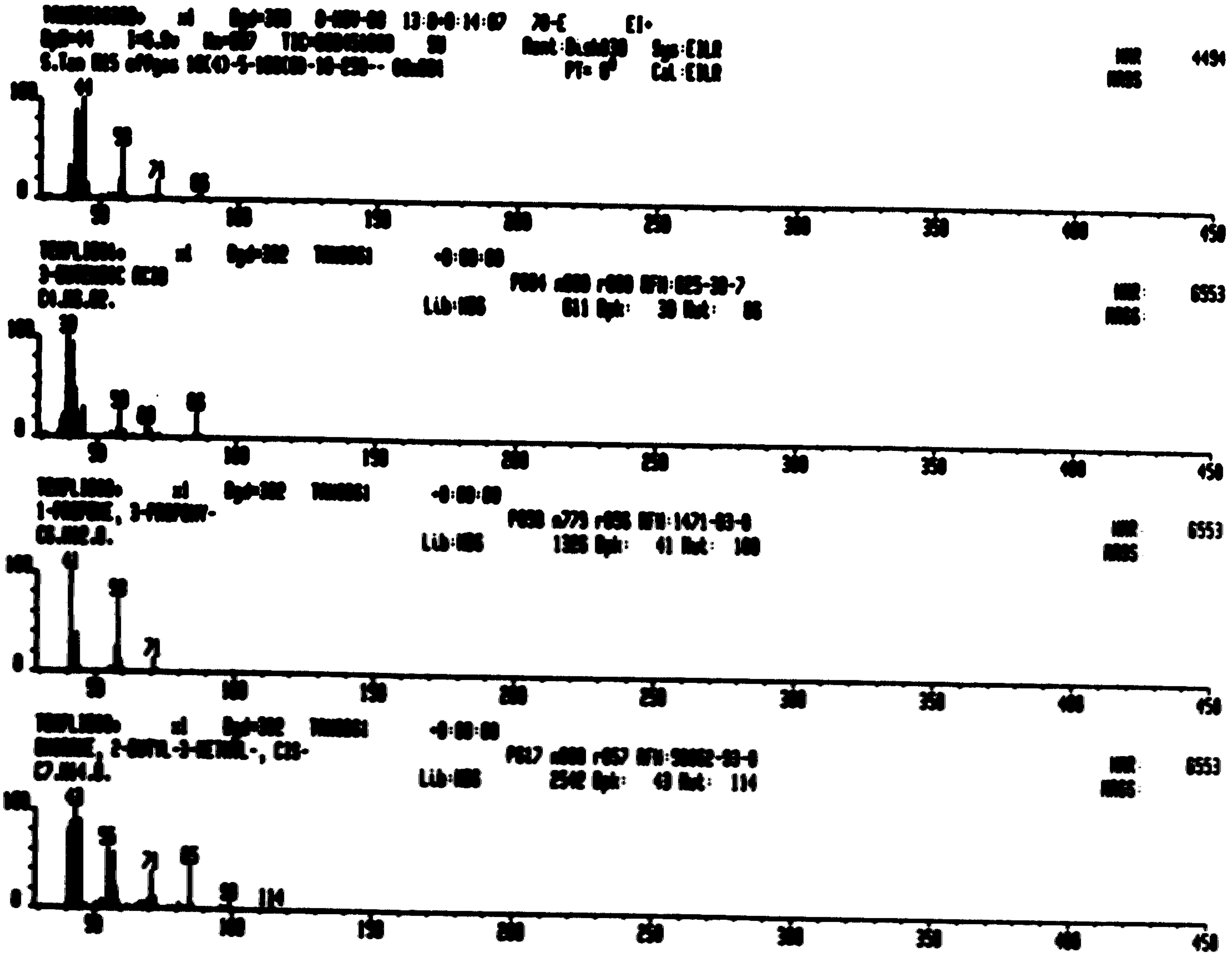
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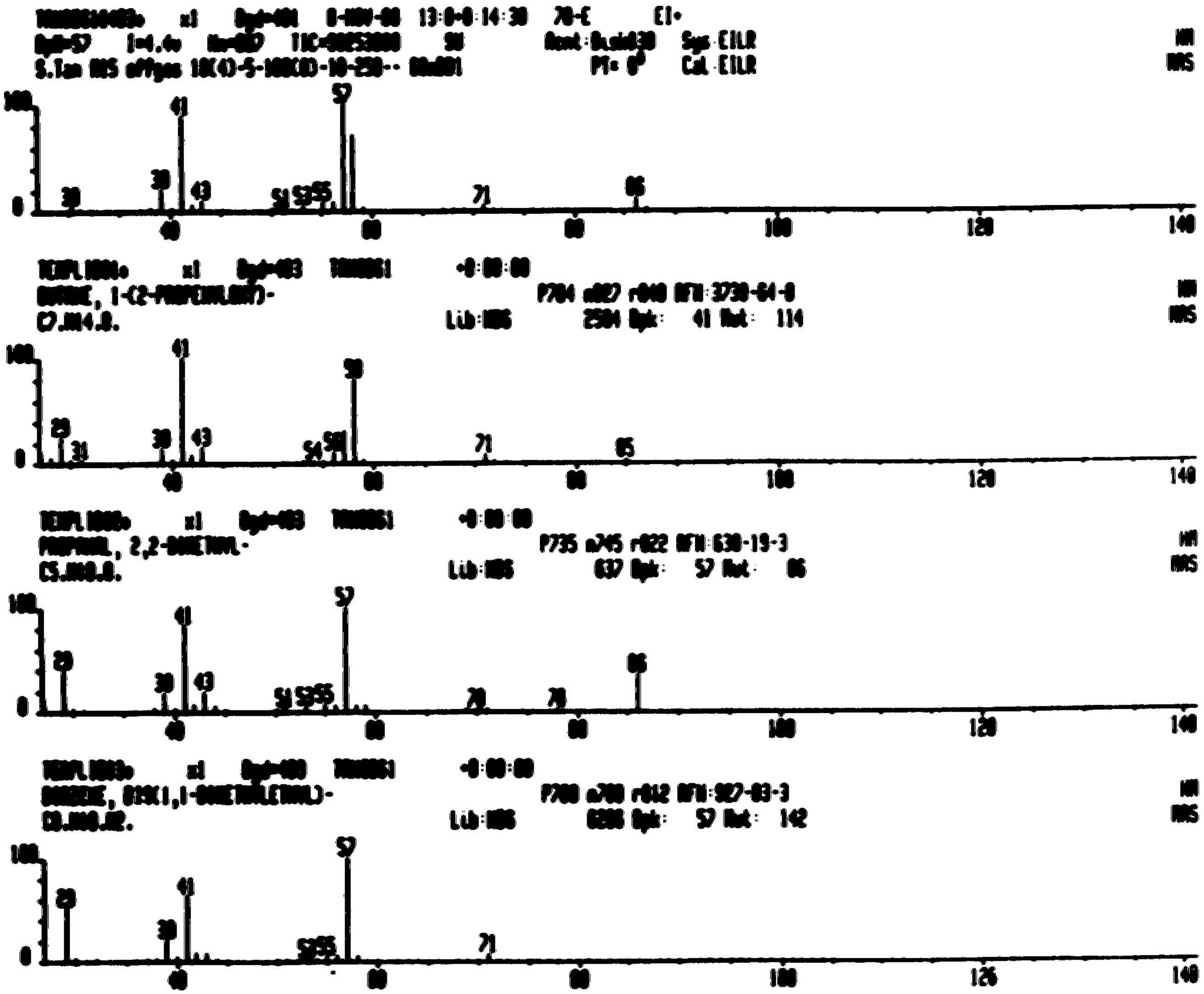
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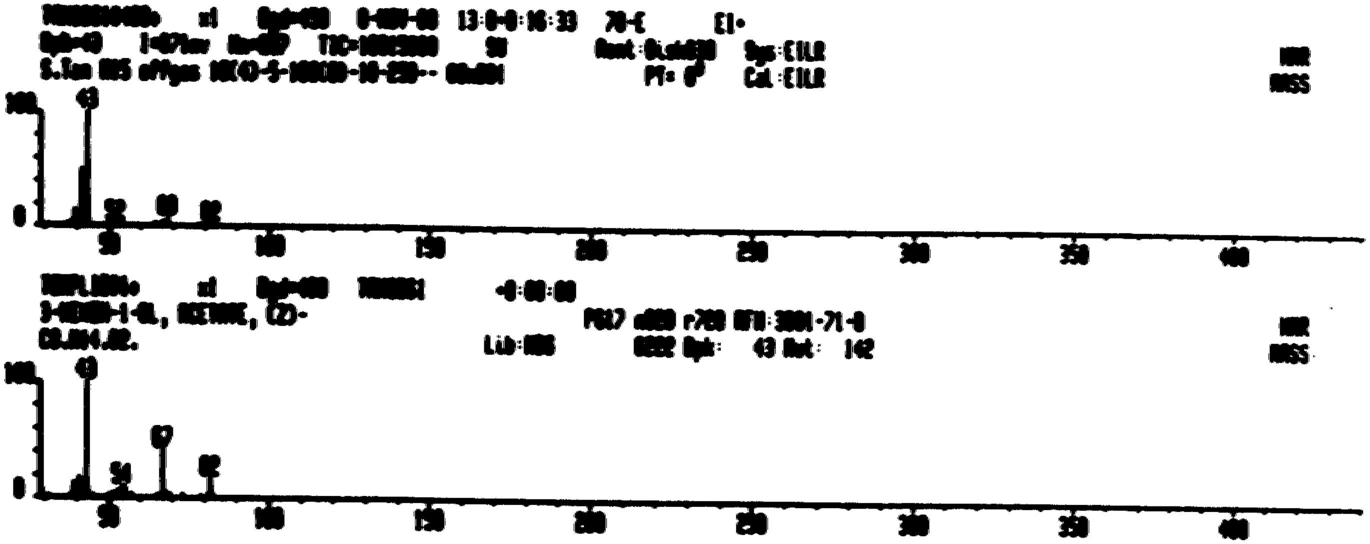
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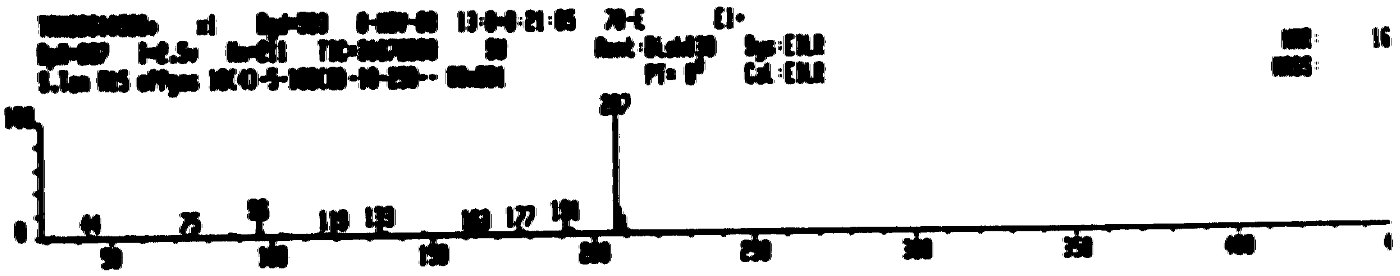
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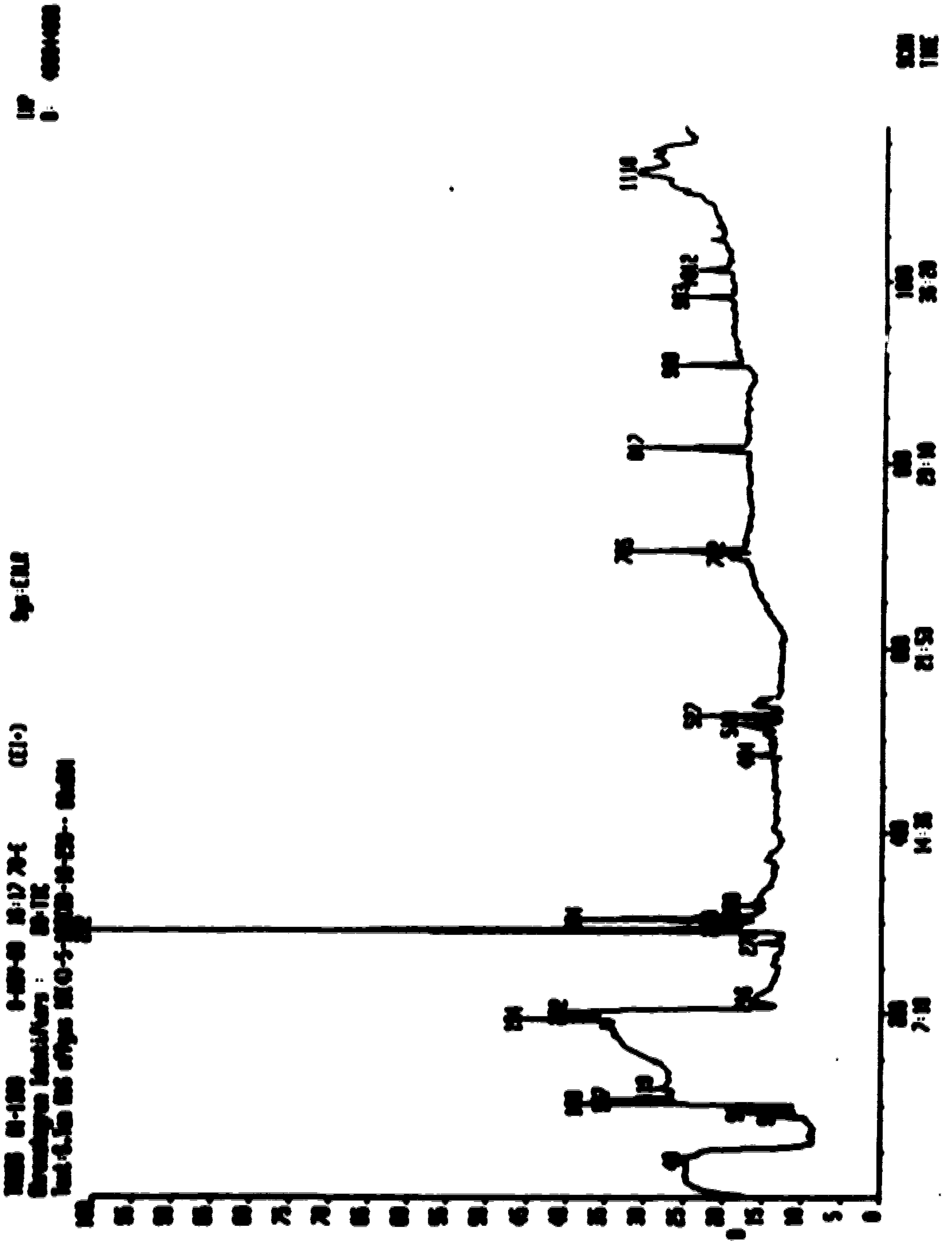
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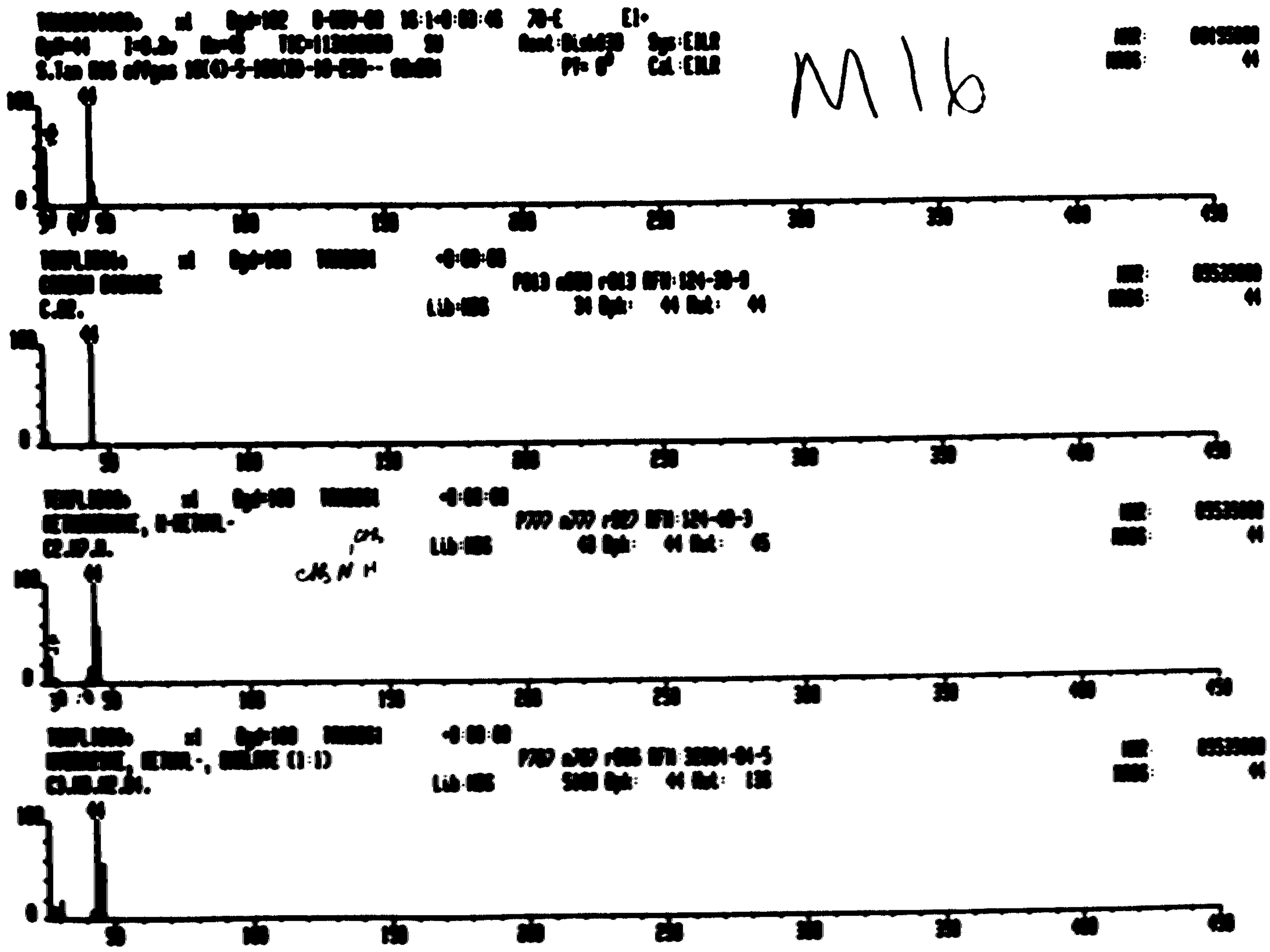

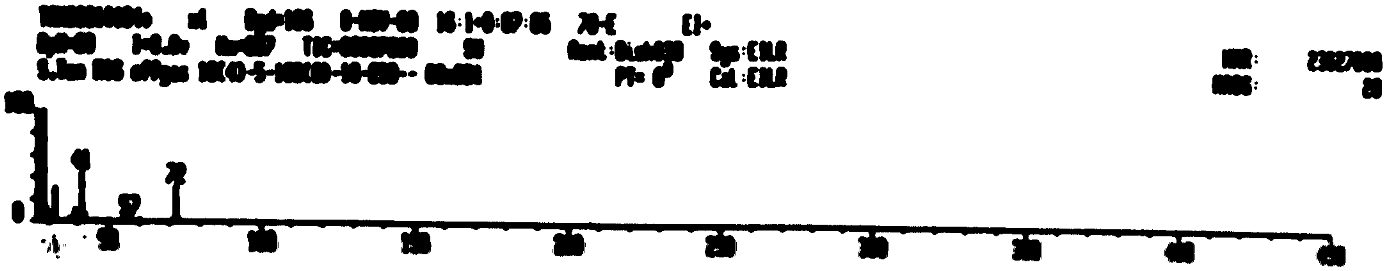

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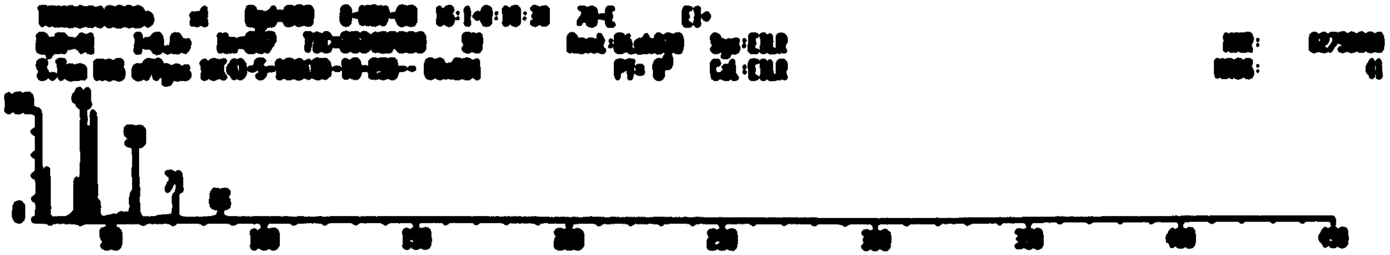
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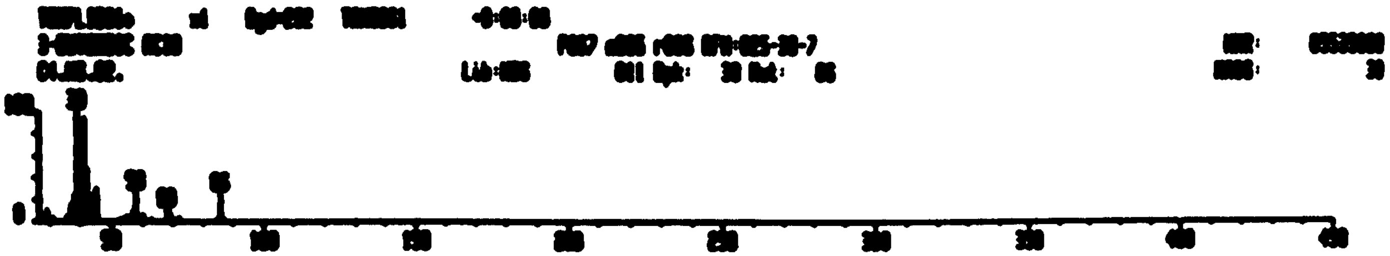
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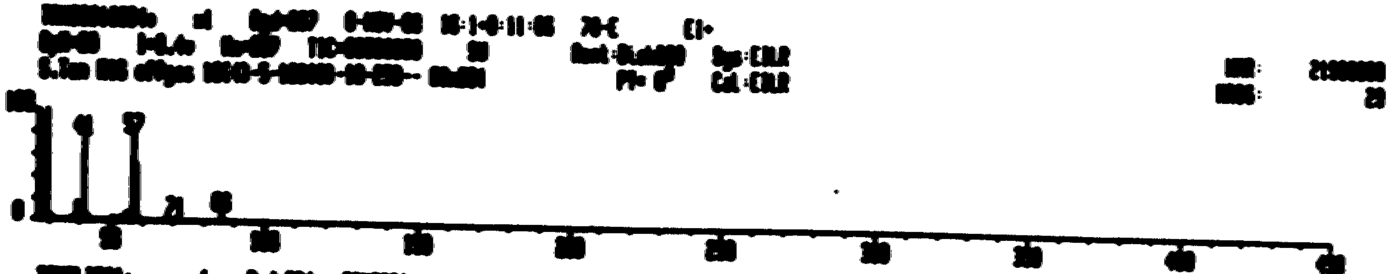
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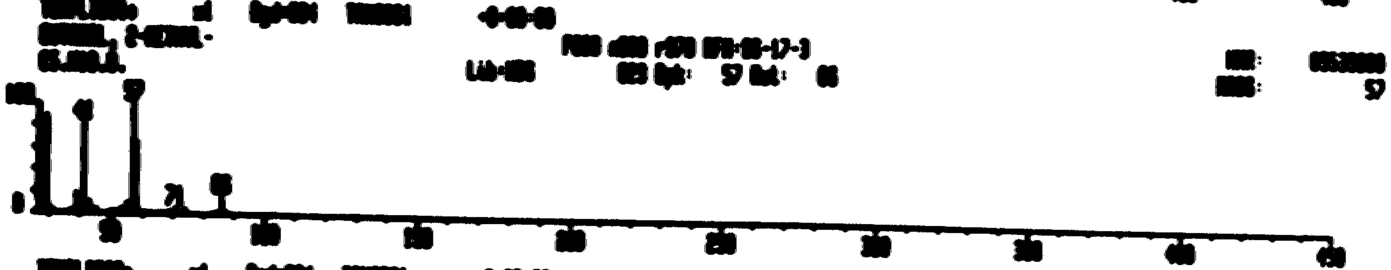
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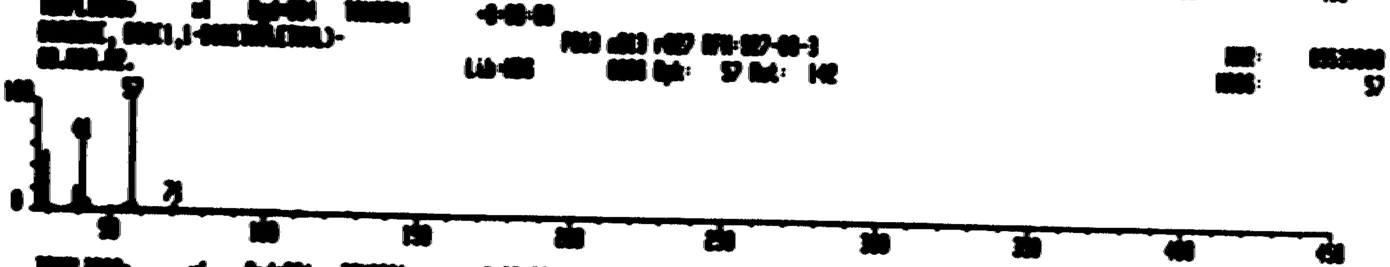
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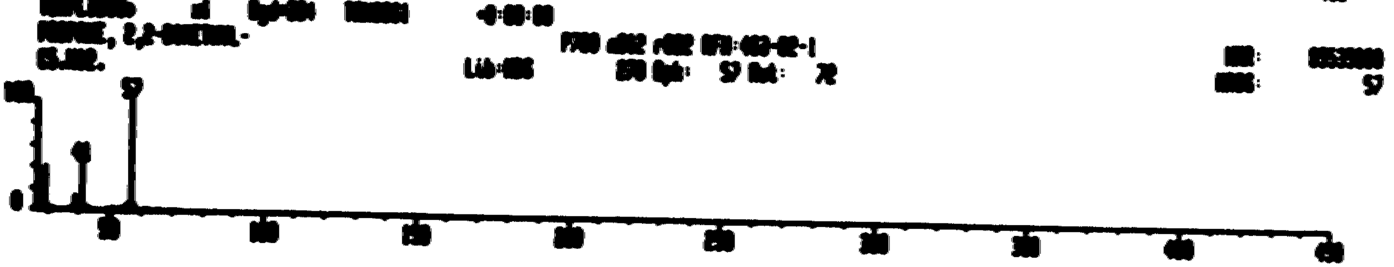
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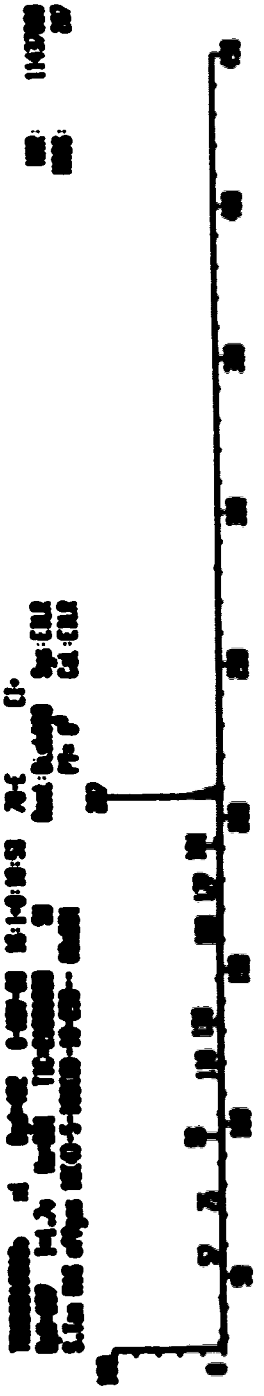
CI+
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APPENDIX E

E1. QUANTITATIVE ANALYSIS BY GC/FPD

A Tracor 560 GC/FPD fitted with a 610 mm by 3 mm acetone washed porapak QS column was used. A Varian 4270 integrator was connected to this apparatus. The electrometer setting of this machine were input=10, polarity = +ve, filter = F, output = auto and zero range = LO. The injector port temperature of the GC was set to 125 °C. The temperature of the FPD was set to 150 °C. The flow rate of the hydrogen was usually set at 60 mL/min. The oxygen flow rate was between 170 mL/min to 220 mL/min. The oxygen flow was frequently adjusted to higher values in order to light the flame. The GC temperature programs were varied for different set of experiments.

Two experiments were conducted to gain quantitative measurement of the sulfur species for the source samples and the out-gas samples. The first step was to determine whether direct injection into the GC/FPD would be concentrated enough to obtain quantitative measurements. Two source samples were obtained with the S1 sampling method. A 5 L Tedlar bag was used to sample the fumes generated from 3 g of 100% wool material. The flow rate of sampling was 3 mL/min. The laser was operating at a power of 200 watts and a cutting speed of 70 mm/s. The sample was obtained at room temperature and at atmospheric pressure.

The second experiment used thermal desorption sampling and GC/FPD analysis. Type OG-3 out-gas sampling method and S3 source sampling method were employed to collect samples via sodium sulfate drying agent onto molecular sieve 5A adsorbent. The sample flow rate was 750 mL/min. The sampling times were between 4.4 to 6.5 minutes. The absolute amount of wool cut by laser varied from sample to sample between 3.5 to 5.2 g for source samples. The amount of cut wool used for out-gas sampling ranged from 13.0 g to 14.4 g. The out-gases were purged out at 1.7 L/min. A pressure of 52.5 to 175 kPa was required to achieve this flow rate.

APPENDIX F

F1. METHOD L1

Two types of solvents were used in this procedure namely acetone and dichloromethane. A small quantity of dichloromethane was weighed and transferred into a 2 mL disposable glass vial. This vial was placed at the bottom of the vacuum pan. Sampling was achieved as described in system S2. A slight variation of this procedure was also experimented with, which involved replacement of the glass probe with a glass funnel. This funnel was suspended 20 mm above the cutting surface. The modification was implemented in order to improve the efficiency of gas collection.

F2. METHOD L2

A modified approach to Method L1, involved positioning the vial of solvent into a heated metal ring. The heat from the metal ring would increase the vaporization of the solvent in the vial. The metal ring was heated in the oven at about 80 °C. This metal ring was then transferred into the metal box prior to the introduction of the vial of solvent. The sampling was similar to the one used in Method L1.

F3. METHOD L3

In this method a known quantity, approximately 4 mL of a volatile compound was placed in a gas sampling trap. The trap was weighed before and after the experiment to determine the exact quantity of compound evaporated. To ensure that no vapors were lost during the weighing and transfer process from the analytical balance to laser testing station, all openings to the trap were completely sealed with rubber septums. A steady flow of air was slowly introduced into this trap. In this way a vapor concentration of solvent is constantly produced. Sampling was performed as described in method L1 and L2. The experimental conditions are recorded in Table F3-1. A diagram of the vapor generation and sampling set-up is shown in Figure F3-1.

Gas standards were prepared by syringe injection of known quantities of compounds into a 1 L calibration glass bulb. The syringe was weighed before and after the injection. The differences in the weight was thus determined. Several different quantities of this calibration mixture was then injected into the GC. A graph was then plotted of the integration area versus the number of grams of the analyte injected. The calculations for the percentage recovered are as reported in Table F3-2.

TABLE F3-1 EXPERIMENTAL CONDITIONS FOR RECOVERY TEST USING METHOD L3 AND ONE TENAX TUBE

Acetone Used (g)	Qt (L/min)	Qs (L/min)	Ts (mins)	Recovery (%)
0.8287	0.75	0.60	5.5	3.9 E-6
1.0209	0.75	0.60	5.0	7.5 E-4
0.8016	0.75	0.60	5.0	2.2 E-4
0.2916	1.00	0.50	5.0	1.5 E-4
0.4042	2.00	0.50	5.0	0.4 E-4
0.4164	2.00	0.50	5.0	0.5 E-4
0.3136	2.00	0.50	5.0	0.4 E-4

Qt Purge rate through gas trap containing solvent

Qs Sampling flow rate

Ts Total sampling time

FIGURE F3-1 DIAGRAM SHOWING THE GENERATION OF ORGANIC VAPOR AND SAMPLING SET-UP FOR METHOD L3

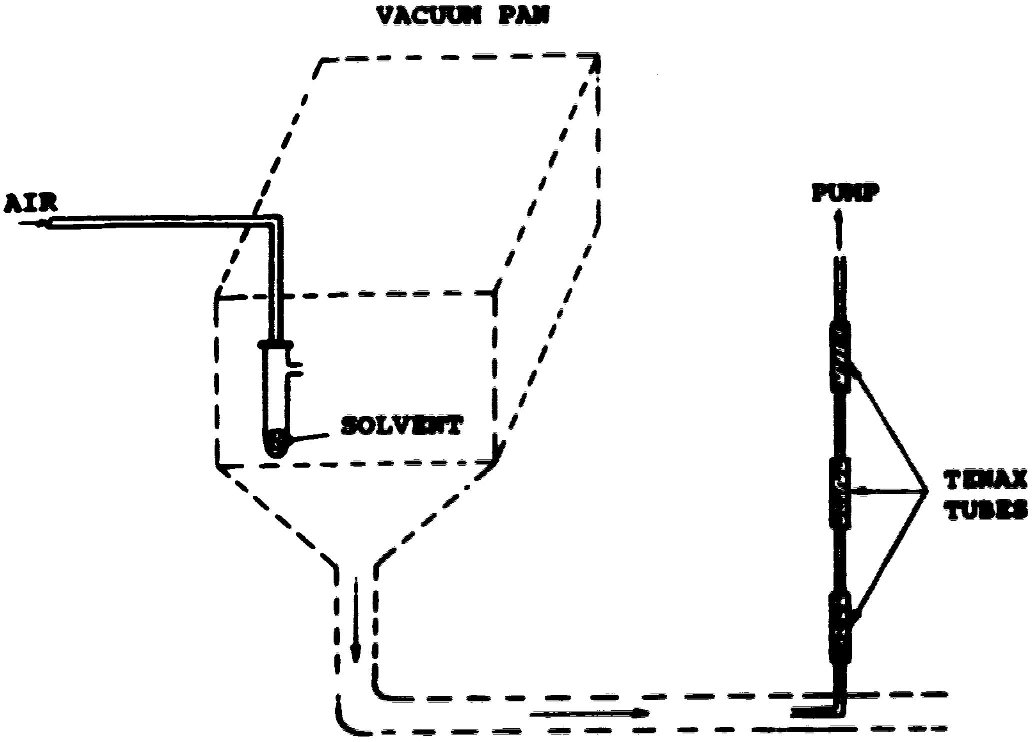

TABLE F3-2 CALCULATION OF PERCENTAGE RECOVERY FROM VERIFICATION EXPERIMENT USING METHOD L4

Vf = v * Ts

%R = 100 * (Vf*A) / (Vs*G)

Where:

Vf = volume of total effluent exhausted (L)

Vs = volume of sample collected (L)

v = velocity of flow (L/s)

Ts = sampling time (s)

%R = % of the vapor generated that was recovered

G = amount of compound generated (g)

A = amount of compound recovered (g)

Appendix G

G1. TROUBLE SHOOTING THE THERMAL DESORBER

The portable thermal desorber was tested by desorption chromatograms of empty adsorbent tubes and blank Tenax tubes. Two problems were encountered:

a) The desorber contaminated the GC system.
b) A leak was found in the septum needle assembly which was connected to the cryogenic-heating coil. This leak was difficult to find because it would only occur when the coil was heated and not before.

The first problem was solved by disassembling the entire thermal desorber and GC system. All parts in the desorber were washed with methanol and baked at 250°C for an hour. The injector parts of the GC were completely cleaned with soap and water and solvents, baked dry and reassembled. In addition the GC system was baked for several days.

The second problem was solved by adding a piece of 3 mm (O.D.=3.2 mm) copper tubing between the needle and the base of the brass cap. This applied an upward pressure on the septum against the base of the cryogenic coil securing a better seal.

Having solved the two major problems, the desorption chromatograms of blanks and odor samples were as expected. The odor samples showed many peaks and the control samples had clean baseline. It was then concluded that the portable thermal desorber was operating well. The next step was to interface it with the GC/MS system and obtain an analysis of the odors. Results from this experiment revealed the presence of carbon dioxide, silicone and phthlates. One would expect the presence of carbon dioxide from the cutting process but the silicone and phthlates were attributed the septum and column in the GC/MS system. These disappointing results were attributed to one of the following reasons:

a) The gas samples were too dilute and the sampling protocols were not sufficiently sensitive;
b) The wrong types of samples were obtained. It was possible that the odors were adsorbed onto the fine particulates generated during the laser cutting operations and were not present in the gas phase;
c) The Tenax adsorbent used was not effective in sampling the type of chemical compounds present in the laser fumes; and
d) The detectors used were not sensitive to the

chemical species found in the laser fumes.

Sampling system S2, described in Appendix A, was developed to obtain a more concentrated sample. This however did not solve the above problems. An experiment to check whether the odors were adsorbed in the particulates was conducted. The particulates generated during the laser cutting of wool was collected on a Sartotius glass fiber prefilter. A total of 0.01409 g of fine dust was then transferred into a 2 mL vial containing 1 mL of HPLC grade dichloromethane and shaken in an ultrasonic bath. To prevent the vapors from escaping while the solvent was allowed to desorb the odors from the particulates, the vial was cooled in dry ice for about an hour. The sample was filtered and the extract was analyzed on the GC/FID system and no peaks were found. It was thus concluded that odors were not found in the particulate matter but was in the gas phase as was originally suspected.

The next step was to try a different pre-concentration technique. Cryogenic trapping of the out-gas vapors was experimented with. A U-shaped pyrex tube with O.D. 6 mm and I.D. 4 mm was used as a cryogenic trap. This was attached to the sampling system III using Teflon tubing. The cryogenic trap was immersed in liquid nitrogen for an hour of sampling. Half millilitre of dichoromethane was used to wash out the condensate in the cryogenic tube out. The extract was analyzed on the GC/FID and found to contain traces of three compounds. These were very much smaller than those from adsorbent sampling. It was concluded that the adsorbent type of sampling was superior to this.

Having concluded that adsorbent preconcentrated technique was still the better method, it was thought that the adsorbent used, Tenax, was not efficient at adsorbing the odors. This was tested by sniffing the effluent gas for odors after it had passed through the Tenax tube. Indeed it was discovered that odorous sulfur type of gas was not completely adsorbed. A literature survey indicated the following:

a) Chromosorb 102 was used successfully in sampling odors generated from diesel exhaust fumes;
b) activated charcoal was good for sampling very volatile compounds with low boiling points; and
c) XAD 2 resin has been used successfully in sampling of sulfurous odors in pulp mill effluents.

Many studies on diesel exhaust odors reported the use Chromosorb 102 to sample for the odors followed by solvent desorption in cyclohexane. Thus, an experiment was carried out using Chromosorb 102 In this investigation, the odors were adsorbed onto Chromosorb 102 by using sampling method S3. The results indicated that very few peaks were detected. However when the sampling method S2 was used the chromatogram showed the presence of many compounds. This method was successful and a detailed account of it is reported in Appendix A.

Although S2 sampling with Chromosorb 102 was successful, there were three major shortcomings:

a) It was unable to detect the volatile odors that were masked under the cyclohexane solvent peak;
b) It could not be quantified using the S2 sampling method; and
c) It could not be used on the out-gas type of sampling.

Attempts to overcome these shortcomings were thought to lie in using activated carbon and XAD 2 adsorbents. Charcoal tubes obtained from SKC company were too large to fit the desorber. The charcoal was removed and repacked in tubes as described in Appendix A. When blank activated charcoal adsorption tubes were desorbed into GC/FID, it contaminated the entire system for about three weeks. The contamination was a result of some fine charcoal particulates that went into the column and also block the splitless valve. This type of experimentation was therefore abandoned.

An S2 source sample was adsorbed onto XAD 2 and Tenax resins. These were analyzed on a GC/FID. The chromatogram of blank and odor sample were identical. Both showed a single large peak with small shoulder peaks. Tests with odor sample on Tenax showed a series of small peaks. Literature review indicated that gaseous hydrogen sulfide, carbonyl sulfide, sulfur dioxide and carbon disulfide were evolved from the combustion of wool. It is known that the FID detector cannot detect traces of the above compounds. However the FPD was capable of detecting these compounds at ppb levels. More samples were obtained on Tenax, Chromosorb 102 and XAD 2 resins. This time the analysis were performed on a GC attached to both a FPD and a FID detectors. Results from Chromosorb 102 indicated that only tiny peaks were obtained on the FID trace and none on FPD trace. Spikes of authentic carbon disulfide were obtained by pulling a vacuum held directly over a carbon disulfide bottle for exactly 10 minutes for each of the adsorbents. These results were all as expected. A single large peak was seen on the FPD chromatograms and a very small peak was seen on the FID traces. In comparing the size of the peaks on these chromatograms, it was observed that

Chromosorb 102 had the largest peak and XAD 2 had the smallest. It was concluded that XAD 2 was not a very effective adsorbent for sulfur compounds and that Tenax and Chromosorb 102 were better. Another inference made was that the odor samples were simply not concentrated enough.

More experiments were conducted with S2 sampling on Tenax with GC/FID. The chromatograms showed no peaks. It was observed that odorous emissions were leaking out of the front end of the portable desorber when the thermal desorption was in progress. This was very puzzling because one would expect a helium flow carrying the desorbed odors to flow in the opposite direction. One possible explanation was the pressure in the injector port of the GC was much higher than the thermal desorber. To verify that a sample was desorbed on the commercial thermal desorber, Envirochem 850 that was permanently hooked up to a GC. Huge peaks were observed on the chromatogram.

APPENDIX H

H1. PROBLEMS ENCOUNTERED IN GC/FPD ANALYSIS

The retention times and areas from 3 syringe injections of the same calibration mixture consisting of 10 ppm of carbon disulfide are shown in Table H1-1. The results indicated that the retention times and areas are inconsistent. The reason for this was the large size of the needle on the syringe and small leaks through the injector port septum can change the results drastically. After the septum was changed the results improved dramatically as shown by retention times and area counts of sample 4 and 5 in Table H1-1.

Results showing the integration and retention times of 10 ppm of methyl mercaptan and hydrogen sulfide are recorded in Table H1-2. Only one peak was obtained with fairly consistent retention time and integration values. Since only one peak was observed, it was inferred from the long retention time that only methyl mercaptan was detected. The FPD detector was more sensitive to methyl mercaptan than hydrogen sulfide. To verify the above conclusion, syringe injection of a calibration containing 10,000 ppm of hydrogen sulfide was carried out. The results listed in Table H1-3 confirmed this. The retention time of the hydrogen sulfide peak was 0.6 minutes indicating that indeed the peak detected in earlier experiment was methyl mercaptan. Reproducible retention times and integration values were obtained.

Having accomplished obtaining reproducible results from syringe injections, the next step was to spike these calibration mixtures onto molecular sieve 5A. A comparison of the areas and retention times between syringe injections and thermal desorption of the same calibration mixture onto molecular sieve 5A is reported in Table H1-4. This comparison shows that the results from syringe injection was consistent. However both the retention times and the integration from the adsorbent techniques were very variable. The retention times of the adsorbent method were longer than those from syringe method by 3.5 to 4 minutes because of 3 minutes of cryofocussing and 0.5 to 1 min of flash heating. Thus, the retention times were expected to vary between 3.9 minutes to 4.4 minutes. The integration values were expected to be more consistent and have a desorption efficiency of 87 % according to Black et al.(1978). The desorption efficiencies of sample not dried by sodium sulfate was 0.3 % and those dried with sodium sulfate as 0.2 %. It was initially thought that the way of introducing the spiking onto the adsorbent was a problem. These samples were later spiked with a commercial thermal desorber. The calibration mixture used this time was 10,000 ppm H_2S, 10,000 ppm CH_3SH and 8 ppm CS_2. The

TABLE H1-1 RETENTION TIME AND AREAS VALUES FROM 1 ML SYRINGE INJECTION INTO TRACOR 560 (GC/FPD)

SAMPLE NO	RETENTION TIME (MIN)	AREA OF PEAKS
1	3.3	1027379
2	5.6	2282349
3	6.9	4094414
4*	2.8	2145383
5*	2.7	2187054

* Samples injected after changing septum.

TABLE H1-2 RETENTION TIME AND AREAS VALUES FROM SYRINGE INJECTION OF 10 PPM METHYL MERCAPTAN AND 10 PPM OF HYDROGEN SULFIDE

SAMPLE NO	RETENTION TIME (MIN)	AREA OF PEAKS
1	6.4	1120570
2	6.4	1154364
3	7.2	1293704

TABLE H1-3 RETENTION TIMES AND AREAS OF 10,000 PPM OF HYDROGEN SULFIDE

SAMPLE NO	RETENTION TIME (MIN)	AREA OF PEAKS	INJECTION VOLUME
1	0.6	120204	1
2	0.6	127498	1
3	0.6	131191	1
4	0.6	59520	0.5
5	0.6	59353	0.5
6	0.7	62122	0.5

TABLE H1-4 COMPARISON OF RETENTION TIMES AND AREAS OF SYRINGE AND ADSORBENT METHOD

	SYRINGE METHOD		ADSORBENT METHOD	
SAMPLE NO.	AREAS	RETENTION TIME (MIN)	AREAS	RETENTION TIME (MIN)
1	2.624*107	0.4	1.304*105	4.3
2	2.701*107	0.4	1.818*105	5.2
3	2.753*107	0.4	1.749*104	3.6
4	2.479*107	0.4	4.563*104	4.8
5	2.648*107	0.4	1.055*105	3.9
6	2.870*107	0.4	9.256*104	4.5
7	2.624*107	0.4	7.013*104	5.7
8	-	-	3.981*104	5.1
9	-	-	0	-
control	-	-	-	-
blank	-	-	-	-

concentration of CS_2 is about a thousand times smaller than the other two because it is a liquid at room temperature and the FPD detector was very much more sensitive to it than gaseous H_2S, and CH_3SH. The results are recorded in Table H1-5. These results were variable and three distinct peaks could not be identified from the chromatograms. The huge discrepancy between literature and experiments lies in the amount of sulfur compound used for spiking. The amount of hydrogen sulfide adsorbed on molecular sieve 5A according to Black et al. was 40 ng. In this study the spikes were with 14 mg of H_2S for one experiment and a mixture of 7mg H_2S, 15mg CH_3SH and 25 ng of CS_2. Large amounts of break throughs must have occurred. Concentrations of hydrogen sulfide and methyl mercaptan in the nanograms range could not be detected by the faulty FPD detector. However, in retrospect, calibration of only carbon disulfide should have been used for this test.

The FPD detector is a flow sensitive detector. Optimum sensitivity can only be achieved by the correct proportion of air and hydrogen. The amount of air should be 1.5 times the amount of hydrogen. The detector was not working at it's most sensitive setting because it was impossible to light the flame of the FPD detector at the correct setting. In order to light the flame, the flow of air was sometimes regulated to 3 times the hydrogen flow. On occasions the flame would light at the optimum condition but no compound would be detected. Calibrations values of 10 ppm and 1000 ppm of hydrogen sulfide injected would show no peaks detected. Finally 10,000 ppm calibration was used to just get a reading. It was known from literature review that this type of GC/FPD can measure sulfur gases in 10 to 100 ppb concentration. All routine checks for leaks could not solve the sensitivity problem. Finally a diagnostic check was conducted and this indicated that the photomultiplier tube may have been damage At this point the experiments were discontinued.

H2. RESULTS FROM RECOVERY TESTS ON LASER TESTING STATION

Recovery tests using Method L1 and L2 were unsuccessful because no spiked compound was detected. The results from the recovery of acetone introduced into the laser effluent station are reported with their experimental conditions in Tables F3-1, Table 3.7.2-1 and Table 3.7.2-2. The percentage recoveries were very low. The poor recoveries were due to the type of solvent used and the sampling method used. Acetone is very reactive and had probably reacted with the walls and ducts of the testing station. The sampling method did not allow for all the spiked substance to be completely recovered because

TABLE H1-5 COMPARISON OF RETENTION TIMES AND AREAS OF SYRINGE AND ADSORBENT METHOD

Sample No.	Syringe Method		Adsorbent Method	
	Areas	Retention Time (MIN)	Areas	Retention Time (MIN)
1	4.862 E6	0.4	8.804 E5	5.3
	6.885 E6	2.1	8.951 E5	6.5
	6.990 E6	5.1	2.179 E5	8.4
2	6.021 E6	0.9	3.376 E4	4.0
	8.240 E6	2.5	9.515 E5	5.5
	7.900 E6	5.0	1.225 E5	8.0
			4.017 E4	8.9
3	4.753 E6	0.4		
	5.973 E6	1.1	3.480 E5	9.4
	5.704 E6	3.2	1.673 E5	13.5
4			2.304 E5	5.5
			6.028 E5	8.4

the sampling stopped at the same time as the vapor generation was stopped.

The recoveries using two and three adsorbent tubes with Method L4 are reported in Table H2-1. Only two adsorbent tubes were used in samples 1,2 and 3 while three adsorbent tubes were used to sample the rest. The average percent recovery of sample 1,2 and 3 was 0.2 %. The average percent recovery of the last 5 samples was 12.4 ± 4.3. The discrepancies between these two results may be caused by different concentrations of cyclohexane generated. The concentrations of cyclohexane generated in the first three samples range from 20 ug/L to 27 ug/L. The concentrations of cyclohexane generated for the last five sample was about 10 to 20 times smaller being 1 ug/L to 3 ug/L. It was possible when the concentrations of the generated vapor was low, less condensation of vapors occurs and more of the vapor can be recovered. Therefore, the average percent recovery of 12.4±4.3 was deemed as the more relevant result.

TABLE H2-1 RECOVERIES OF CYCLOHEXANE FROM THE EXPERIMENTAL LASER TESTING STATION

Sample No	Concentration* (ug/L)	TR** (%)	% of TR Adsorbed on Tubes 1st	 2nd	 3rd
1	20	0.3	61.0	39.0	NA
2	20	0.1	62.0	38.0	NA
3	27	0.1	46.0	54.0	NA
4	3	7.8	47.0	33.9	19.1
5	1	17.1	58.8	35.9	5.3
6	2	12.0	39.7	29.2	31.2
7	1	13.7	50.8	23.4	25.8
8	1	11.5	68.4	27.0	4.7

* Concentration of Cyclohexane in the flue

**Total Recovery of Cyclohexane on all adsorbent tubes