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VideoJet Systems, International
Wood Dale, Illinois

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PREFACE

The Hazard Evaluations and Technical Assistance Branch of the National Institute for Occupational Safety and Health (NIOSH) conducts field investigations of possible health hazards in the workplace. These investigations are conducted under the authority of Section 20(a)(6) of the Occupational Safety and Health Act of 1970, 29 U.S.C. 669(a)(6) which authorizes the Secretary of Health and Human Services, following a written request from any employer or authorized representative of employees, to determine whether any substance normally found in the place of employment has potentially toxic effects in such concentrations as used or found.

The Hazard Evaluations and Technical Assistance Branch also provides, upon request, technical and consultative assistance to Federal, State, and local agencies; labor; industry; and other groups or individuals to control occupational health hazards and to prevent related trauma and disease. Mention of company names or products does not constitute endorsement by NIOSH.

ACKNOWLEDGMENTS AND AVAILABILITY OF REPORT

This report was prepared by Max Kiefer and C. Eugene Moss, of the Hazard Evaluations and Technical Assistance Branch, Division of Surveillance, Hazard Evaluations and Field Studies (DSHEFS). Analytical support was provided by Ardith Grote, NIOSH Measurement Support Branch. Desktop publishing was performed by Ellen Blythe. Review and preparation for printing were performed by Penny Arthur.

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Highlights of the NIOSH Health Hazard Evaluation

Emissions generated from the laser marking of different products

In March 1999, NIOSH investigators conducted a health hazard evaluation (HHE) at the request of VideoJet Systems, Chicago, Illinois. We looked at air contaminants produced during the laser marking of various materials such as plastics and ink-coated products and how well the local exhaust ventilation system contained these emissions.

What NIOSH Did

- # Air samples were collected during the marking of different materials with an 80 watt carbon dioxide laser.
- # Measured levels of carbon monoxide and hydrogen cyanide.
- # The sizes of the particles generated by the laser marking were measured.
- # The laser safety program was evaluated.

What NIOSH Found

- # Over 250 different compounds were identified from the air samples. The laser marking of plastic substances produced the largest number of potentially hazardous compounds.
- # Laser marking produced carbon monoxide but not hydrogen cyanide.
- # Very small particles were generated during laser marking. These levels were greater than background levels.
- # The laser safety program was found to be adequate.

- # The local exhaust ventilation system was effective.

What VideoJet Systems Managers Can Do

- # Tell laser workers that a potential exists in the laboratory for exposure to air contaminants created during laser marking.
- # Require local exhaust ventilation in the laboratory to reduce worker exposure to laser marking emissions.

What VideoJet Systems Employees Can Do

- # Laser personnel shall wear protective eye wear and be trained in laser safety.
- # Insure that the local exhaust ventilation system in the laboratory properly operates during all laser procedures.



What To Do For More Information:
We encourage you to read the full report. If you would like a copy, either ask your health and safety representative to make you a copy or call 1-513/841-4252 and ask for HETA Report # 99-0109-2754



Health Hazard Evaluation Report 99-0109-2754
VideoJet Systems, International
Wood Dale, Illinois
October 1999

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SUMMARY

On February 17, 1999, the National Institute for Occupational Safety and Health (NIOSH) received a management request for a health hazard evaluation at VideoJet Systems International, Inc., (VSI) in Wood Dale, Illinois. The request asked NIOSH to characterize laser-generated air contaminants (LGAC) and evaluate the potential hazards during the laser marking of various materials and ink-coated products. No health problems had been reported, however the laser developers were concerned about potential exposures to VSI research and maintenance personnel, as well as end users (product stewardship). Additionally, NIOSH was asked to evaluate a ventilation system and recommend appropriate safety measures.

An initial site visit was conducted on March 15, 1999, to review the laser marking process and develop an appropriate evaluation strategy. A follow-up visit to collect air samples during the laser marking of different substrates, and evaluate the ventilation system, was made on May 18-19, 1999. During this follow-up visit, environmental monitoring was conducted to qualitatively identify major contaminants generated during the marking of 13 different substrates. Instantaneous samples for carbon monoxide (CO), hydrogen cyanide (HCN), and particulate were also collected using direct reading instrumentation, and a bulk sample of the filter used in the laser exhaust system was analyzed.

Approximately 250 different compounds were qualitatively identified on the thermal desorption tubes and filter extracts. The highest relative concentrations of volatile compounds were found on the plastic materials, the lowest from materials such as glass, cardboard, and ceramic. Compounds including hydrochloric acid, benzene, styrene, methyl methacrylate, and vinyl chloride were detected from the laser marking of polyvinyl chloride; alkyldienes, alkenes, and alkanes were detected from the marking of high density polyethylene bottles. Phenols and cresols were the major compounds detected from marking plastic integrated circuits. Laser marking on the polyethylene terephthalate (PET) plastic materials generated benzene, toluene, styrene, benzoic acid, phenol, and acetophenone. Traces of polycyclic aromatic hydrocarbons were detected on several samples (i.e., plastic integrated circuit).

No HCN was detected in the plume of any materials marked. In general, the number of particles ≥ 0.3 micrometers in diameter (μm) and $\geq 1.0 \mu\text{m}$ generated during the laser marking exceeded background particle levels by a factor of 10 or more for the polymer products. Particles were also higher than background for the other test materials (cardboard, glass, ceramic), but not to the same degree as the plastics. CO was detected at higher than background levels on 77% of the materials tested. The highest CO levels (90-100 parts per million) were measured during the laser marking of PET.

Finally, the monitoring results indicated that the exhaust ventilation being used in-place on the laser marking system was adequately controlling the LGACs generated during the marking trials for this evaluation.

A wide variety and complex composition of LGACs were measured during experimental trials using the LaserProDM system to mark various substrates. Although these results are not indicative of personnel exposure under “worst-case” conditions they do suggest a potential for generating hazardous air contaminants. The composition of the LGACs varied significantly depending on the material being coded. The polymer-based materials generated the highest number and relative concentrations of LGACs. Many of the detected compounds can have toxic and irritating effects if exposure is high enough, which confirms the need to provide sufficient ventilation to capture the emissions.

Keywords: SIC 3699 (Electrical Machinery, Equipment, and Supplies, Not Elsewhere Classified). Laser Generated Air Contaminants, Laser Marking, Class IV CO₂ Laser, Carbon Monoxide, Hydrogen Cyanide.

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INTRODUCTION

In response to a management request for a health hazard evaluation (HHE), National Institute for Occupational Safety and Health (NIOSH) investigators conducted an initial site visit at VideoJet Systems International (VSI) in Wood Dale, Illinois, on March 15, 1999. A follow-up site visit to VSI was conducted on May 18–19, 1999. The request asked NIOSH to evaluate the potential for laser generated air contaminants (LGACs) during the laser coding of various substrates under experimental (research) conditions using a high power carbon dioxide laser. No health problems were reported.

During the initial site visit, background information about the laser coding process was obtained, and an evaluation strategy determined. During the follow-up site visit, environmental monitoring was conducted to qualitatively identify gaseous or vapor LGACs, collect instantaneous samples for carbon monoxide (CO) and hydrogen cyanide (HCN), and evaluate particulate LGACs. Monitoring was conducted under controlled conditions during the laser marking of 13 substrates.

BACKGROUND

VSI manufactures and markets industrial, graphic, imaging, and postal coding systems for a wide variety of industries in over 80 different countries. VSI specializes in high-speed barcoding of products utilizing ink jet technology, and has recently begun developing and marketing laser-based marking and coding equipment. The Wood Dale, Illinois, facility is the VSI corporate headquarters, and both manufacturing and research and development is conducted at this location. The company has been in business for 30 years and employs approximately 400 engineers, chemists, and service technicians.

The VideoJet LaserPro DM is a laser system designed to print messages onto products. The system is typically used to provide high speed industrial marking and coding of dot matrix images

on a wide variety of substrates, including glass, plastics, coated cardboard, circuit boards, ceramics, semiconductors, etc. The liquid-cooled laser system contains an embedded Class IV 100 watt (W) sealed carbon dioxide (CO₂) [10.6 micrometer wavelength] continuous beam laser and can code products on an assembly line at speeds in excess of 825 feet per minute. The laser can also operate in the pulsed mode at a maximum power of 350 W (pulse repetition frequency = 2 [kilohertz] kHz, 300 microsecond pulse width), but this has limited applications. The laser operates as a Class 1 system and is vertically mounted within secured panels on the side of the system. Upon activation, the beam travels straight up and then diverts horizontally to a fixed laser head, which reflects the collimated beam to focus the laser at the coding point. A programmable microprocessor controlled solid state beam deflection system is used to deliver the beam to the product and mark the appropriate code. The software provides considerable versatility in graphics and lettering design, including high-speed sequential numbering and coding.

During the development of the laser system, VSI personnel were concerned that potentially harmful concentrations of LGACs could result from the marking and coding process. Information characterizing potential contaminants from this type of laser process is sparse, and the developers requested NIOSH assistance to determine the types of contaminants that may be generated. VSI was also interested in NIOSH recommendations regarding appropriate measures to control exposure to any contaminants generated from the coding process.

METHODS

Background information about the laser marking process, the various materials used, and the ventilation system, was obtained during an initial site visit by NIOSH investigators on March 15, 1999. On May 18–19, 1999, a follow-up visit to VSI was made to review specific laser operating parameters, and conduct environmental monitoring to

qualitatively identify major contaminants generated during the marking of 13 different substrates. Instantaneous samples for CO, HCN, and particulate were also collected using direct reading instrumentation, and a bulk sample of the filter used in the laser exhaust system was obtained for analysis. Sampling was conducted for CO and HCN because these are common byproducts of combustion and are amenable to measurement via direct reading instrumentation. Particulate monitoring was conducted to help evaluate the aerosol fraction of the laser plume. All monitoring was conducted at the VSI facility. Prior to operating the laser, background samples were collected both inside and outside the laser-marking room to check humidity and for control, or comparison purposes. Additionally, room air samples were collected during the course of the laser-marking trials to evaluate general room conditions and measurements of room exhaust were made.

Qualitative Air Sampling

Qualitative air monitoring was conducted to characterize emissions generated during the laser-marking process under fixed conditions in a controlled (non-production) setting. These area air samples were obtained utilizing reusable multibed thermal desorption (TD) tubes as the collection media. These stainless steel tubes contain three beds of sorbent materials – a front layer of Carboxen 1003 (150 mg), a middle layer of Carboxen 1003 (115 mg), and a back section of Carboxen 1003 (90 mg [milligrams]). This technique is designed to trap a wide range of organic compounds for subsequent qualitative analysis via thermal desorption and gas chromatography/mass spectrometry (GC/MS). Prior to sampling, the tubes were conditioned by heating at 375°C for two hours.

Low-flow air sampling pumps (SKC Pocket Pump™) were used to collect the air samples. The SKC pumps are constant-flow sampling devices and were pre- and post-calibrated using a primary standard (BIOS® Dry Cell) to verify the flow rate. The total volume of air sampled is the product of flow rate and time sampled. Prior to the laser coding

trials, background samples were collected from the laser room and manufacturing area. Area samples in the laser room were also collected during the laser coding trials. During the trials, short-term (0.5–1 minute) samples from each material being coded were obtained by sampling directly from the plume produced by the laser interaction with the substrate. Flow rates of 100 cubic centimeters per minute (cc/min) were used for the plume sampling; flow rates of 20–50 cc/min were used for the room monitoring. After each sampling event, a clearance time of approximately 5 minutes was allowed to pass prior to conducting the next event.

After collection, the samples were shipped via overnight delivery to the NIOSH laboratory for analysis. At the NIOSH laboratory, each sample was analyzed by directly inserting the tube into a thermal desorber unit (Perkin Elmer ATD 400 thermal desorption system) with no other sample preparation. Samples with collection volumes greater than 5 liters were dry purged with helium for 30 minutes at 100 cc/min to remove water. A desorption time of 10 minutes at 300°C was used. The thermal desorber was directly connected to a HP6890A GC and HP5973 MS detector. Reconstructed total ion chromatograms were obtained for each sample, and all were scaled the same for comparison. Each peak in the chromatogram was identified.

Laser Coding Trial Conditions

The trials were conducted in the laser research and development center at VSI, which allowed for manipulation of the laser to accommodate experimental needs. During the sampling trials, the laser shielding was removed and the substrate positioned approximately 4 inches (") from the beam exit; the substrate was moved by hand during the marking to prevent the beam from penetrating through the material. The laser exhaust system was operational during the experiments. Note that during normal use, the beam shielding is intact, which provides for a ventilated enclosure to scavenge emissions. Filtered shop air is discharged onto the

surface of the marking area during coding. Because the interlocks were defeated and the shielding removed (allowing open beam firing), the laser was re-designated a class IV system requiring precautions to protect users from beam hazards. As such, all personnel in the room wore laser-protective eyewear (optical density = 5) designed for the CO₂ laser wavelength while the laser was operating. The laser room door was also shut and locked during operation.

During the trials, the laser was operating with a 2.5" focal lens which produced a final beam spot size of 350 micrometer (µm). The lasing area is fixed with a beam stop in the event the laser is fired without a substrate to code or mark. Measurement of laser power with a SynRad Power Wizard 250 found that the laser was operating at an average power of 80 W. For the two trials using the cardboard substrate, the laser power was reduced to 2 W to prevent igniting the substrate. Using the smallest beam diameter, the irradiance was estimated to be approximately 8.32 X 10⁴ W per square centimeter (W/cm²) for most trials, and 2.0 X 10³ W/cm² for the cardboard substrates.

During the air monitoring, the laser parameters were standardized as much as possible to allow for the comparison of results for each material marked. When possible, the same laser pattern was used for each material, and the cutting time was fixed at either 0.5 seconds or 1 minute for each trial. The decision to modify the sample time was based on observation of visible plume generation during the marking of certain substrates and judgement regarding the sample volume necessary to ensure sufficient analytical sensitivity yet not overload the collection media.

Filter Analysis

A portion of used and unused filter from the laser exhaust system was submitted to the NIOSH laboratory for analysis. A portion of each filter was first extracted with methylene chloride and then concentrated by evaporation prior to analysis. The methylene chloride extract was then analyzed by GC/MS.

Carbon Monoxide

A Metrosonics PM-7700 toxic gas monitor with a CO sensor was used to measure CO during laser cutting activities. The instrument was pre-calibrated prior to use with a known concentration of CO. Instrument sensor repeatability is ± 2% at an operating temperature of -5 to 40° C. After first collecting background samples, readings were obtained directly from the plume during marking.

Particle Monitoring

The particle monitor used was a factory calibrated Met One, Inc. Model 227B hand held laser particle counter. This unit is capable of monitoring two particle size ranges simultaneously, and was set to monitor all particles ≥ 0.3 micrometers in diameter (µmd) and those ≥ 1.0 µmd. For background samples, the instrument was set to provide a 1-minute average particle count from two 1-minute sampling cycles with a 1-minute off time between cycles at a flow rate of 0.1 cubic feet per minute (cfm). During the laser coding trials, 1-minute samples were obtained (total particle count for both size ranges) from a fixed position directly adjacent to the laser-substrate marking area.

Hydrogen Cyanide

Sampling for hydrogen cyanide (HCN) was conducted using Dräger Hydrocyanic Acid 2/a direct reading colorimetric indicator tubes and a bellows pump. With this sampling technique, a known volume of air is drawn through the tube and the media inside the indicator tube will change color in proportion to the concentration of contaminant. According to the manufacturer, the relative standard deviation for this particular sampling method is 10-15%.¹ Samples were collected directly from the LGACs plume.

Ventilation

Ventilation rates were determined by measuring air velocity across the face of the laser exhaust duct and the room exhaust grille. Multiple measurements of air velocity were taken and the results averaged to obtain the exhaust rate in feet per minute. The product of the air velocity and the ventilation opening in square feet provides the ventilation rate in cubic feet per minute (cfm). Instrumentation consisted of a factory-calibrated TSI, Inc. model 8360 VelociCalc® thermal anemometer with a digital readout. This instrument was also used to obtain dry bulb temperature and relative humidity (RH) levels in the laser room. This unit is battery operated and has humidity and temperature sensors on an extendable probe. The temperature range of the meter is 14 to 140° F and the humidity range is 20–95%.

EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by workplace exposures, NIOSH field staff employ environmental evaluation criteria for the assessment of a number of chemical and physical agents. These criteria are intended to suggest levels of exposure to which most workers may be exposed up to 10 hours per day, 40 hours per week for a working lifetime without experiencing adverse health effects. It is, however, important to note that not all workers will be protected from adverse health effects even though their exposures are maintained below these levels. A small percentage may experience adverse health effects because of individual susceptibility, a pre-existing medical condition, and/or a hypersensitivity (allergy). In addition, some hazardous substances may act in combination with other workplace exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled at the level set by the criterion. These combined effects are often not considered in the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially

increases the overall exposure. Finally, evaluation criteria may change over the years as new information on the toxic effects of an agent become available.

The primary sources of environmental evaluation criteria for the workplace are: (1) NIOSH Recommended Exposure Limits (RELs),² (2) the American Conference of Governmental Industrial Hygienists' (ACGIH®) Threshold Limit Values (TLVs®),³ and (3) the U.S. Department of Labor, Occupational Safety and Health Administration (OSHA) Permissible Exposure Limits (PELs).⁴ Employers are encouraged to follow the OSHA limits, the NIOSH RELs, the ACGIH TLVs, or whichever are the more protective criterion.

OSHA requires an employer to furnish employees a place of employment that is free from recognized hazards that are causing or are likely to cause death or serious physical harm.⁵ Thus, employers should understand that not all hazardous chemicals have specific OSHA exposure limits such as PELs and short-term exposure limits (STELs). An employer is still required by OSHA to protect their employees from hazards, even in the absence of a specific OSHA PEL.

A time-weighted average (TWA) exposure refers to the average airborne concentration of a substance during a normal 8-to-10-hour workday. Some substances have recommended STELs or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from higher exposures over the short-term.

Laser Generated Air Contaminants

During the intense interaction of laser energy with a target, a wide variety and complex mixture of LGAC can be formed. The quantity and composition of the LGAC will vary greatly depending on the beam irradiance (power per area) and material undergoing the lasing action.^{6,7} Although research on the products of polymer pyrolysis and combustion has

been conducted, this data may not be applicable to the products generated when materials are irradiated with high power laser energy. Information concerning LGAC formation is much less complete, although some data is available.^{8,9,10,11,12} Predicting the composition and quantity of LGACs that may be generated during any laser situation is not possible. However, it is known that toxic airborne contaminants can be liberated from materials such as plastics, composites, metals, wood, etc., when the target irradiance (power per area) reaches a given threshold, beginning at about 10^3 W/cm^2 .⁶ These can be generated from certain Class 3b and 4 lasers.

Emissions from laser interaction with matter can include both a gaseous or vapor fraction (aldehydes, benzene, CO, HCN, etc.), and a particulate component (fumes, dust, re-condensation products). Information and guidelines for the control of LGAC have been developed and are found in the American National Standards Institute (ANSI) *Safe Use of Lasers standard, Z136.1-1993*.⁶ This consensus standard contains information concerning LGAC formation and hazard control methods. The primary method for controlling exposure to LGAC is local exhaust ventilation that captures contaminants at the point of generation. Health hazard information on specific compounds and known products of combustion, CO and HCN, are presented below.

Carbon Monoxide

CO is a colorless, odorless gas that is a product of incomplete combustion. Engine exhaust, tobacco smoking, and inadequately ventilated heaters that use hydrocarbon fuel are sources of exposure to CO. CO exposures can result from the reduction of carbon dioxide used for shielding in gas metal arc welding, and has been reported during flame cutting of primed steel in confined spaces.¹³ Overexposure to CO may cause initial symptoms such as headache, dizziness, drowsiness, and nausea. These symptoms may progress to vomiting, loss of consciousness or collapse if high exposures are encountered.¹⁴ The NIOSH REL for CO is 35 parts per million (ppm) as a TWA for up to 10 hours per day. NIOSH also recommends a ceiling level of 200 ppm for CO.²

Hydrogen Cyanide

HCN is a colorless gas that can be produced by the incomplete combustion of carbon–nitrogen containing materials, including natural fibers (wool, silk), and synthetic polymers (polyurethane, polyacrylonitrile, nylon, etc.).¹⁵ HCN is one of the fastest-acting lethal agents encountered in clinical toxicology and can cause rapid death due to chemical asphyxiation by inhibition of the important enzyme cytochrome oxidase.^{14,15} HCN is often attributed as the cause of death in smoke-inhalation fatalities. Symptoms of exposure can include headache, nausea, disorientation, and seizures.^{14,15} The NIOSH REL for HCN is 4.7 ppm as a 15 minute STEL.²

RESULTS

Qualitative Air Sampling

Twenty thermal desorption tube air samples collected at VSI on May 18 and 19 were submitted for analysis. Thirteen samples were collected during the marking and coding of various substrates (Table 1). Prior to using the laser, area samples were obtained (one inside the laser room and one in the manufacturing area [May 18 only]) for control, or background, purposes. During the laser trials, area samples were collected inside the laser room. Two blanks (unsampled media) were submitted with the samples.

Table 1
Materials Evaluated: VSI, May 18–19

Sample #	Description
AO3428	PET Soft Drink Bottle (clear)
AO3700	HDPE Shampoo Bottle with laser additive
AO4575	Plastic Integrated Circuit
AO4130	Cardboard Cereal Box, Red Dye
AO 3003	Printed Circuit Board
AO 3679	Ink Coating Sample B
AO5013	Rubber with Aluminum Insert
AO3722	PET Soft Drink Bottle (green)
AO3124	Ceramic Integrated Circuit
AO3798	Cardboard Cereal Box, Blue Dye
AO5505	Glass Wine Bottle
AO5090	Ink Coating Sample A
AO3181	Polyvinyl Chloride Card

PET = polyethylene terephthalate

HDPE = high density polyethylene

Approximately 250 different compounds were identified on the thermal desorption tubes and filter extracts. Appendix A contains the reconstructed total ion chromatograms from these analyses. All chromatograms were scaled the same for comparison (time and abundance). Also included in Appendix A is a list depicting each peak number with its corresponding identification. These results do not provide quantitative information concerning the compounds detected other than on a relative comparison basis. However, those materials emitting the greatest number of compounds and the magnitude of the signal response was determined.

The number and quantity of compounds identified on the thermal desorption tubes varied with the matrix that was coded. Table 2 lists the total number of compounds detected and the ten largest peaks on the corresponding chromatogram for each material tested. The highest relative concentrations of volatile compounds were found on the plastic materials. The lowest concentrations and fewest number of compounds were from materials such as glass, cardboard, and ceramic. Compounds including hydrochloric acid (HCL), benzene, styrene, methyl methacrylate, and vinyl chloride were among the compounds detected from the marking of polyvinyl chloride (PVC); alkylidienes, alkenes, and alkanes were detected from the marking of high density polyethylene bottles. Phenols and cresols were major compounds detected from another of the plastic products (plastic integrated circuit). Laser marking on the polyethylene terephthalate (PET) plastic materials generated benzene, toluene, styrene, benzoic acid, phenol, and acetophenone. Traces of polycyclic aromatic hydrocarbons (PAHs) were detected on several samples (i.e, plastic integrated circuit).

If exposures are high enough, many of these compounds can result in adverse health effects. Some of these compounds are considered primary irritants (e.g., HCL), pulmonary irritants (e.g., acetophenone), central nervous system depressants (e.g., styrene and other solvents), and carcinogens (e.g., benzene, vinyl chloride, polyaromatic hydrocarbons). Note that these results are not indicative of personal exposure, as the samples were collected directly from the laser generated plume under "worst-case" conditions. However, the results do indicate the potential for generating hazardous air contaminants from laser coding of these substrates, and confirm the need for proper exhaust ventilation to control emissions.

Hydrochloric acid was a major constituent detected in the LGAC plume from the laser marking of PVC, (sample #A03181). Additionally, methyl methacrylate, indene, naphthalene, and benzene were also among the 10 largest peaks identified in the PVC sample. These compounds were also among

the major compounds identified in a previous study that evaluated LGAC formation from the laser cutting of PVC with a CO₂ laser.¹¹ Similarly, PAHs such as naphthalene have been previously detected during CO₂ laser processing of PVC.¹⁰

Ambient Air Monitoring

Prior to conducting the laser marking trials, air samples were collected inside the laser room (AO4210, AO3941) and in the manufacturing area (AO4620) to identify background levels of volatile materials. During the laser coding trials, integrated air samples (AO3074, AO5518) were collected in the laser room on both days. These sample results were compared with the results of the control, or background, samples collected prior to using the laser and are depicted in the attached chromatograms in Appendix A.

The number of compounds detected, and the 10 largest peaks for each sample are summarized in Table 3. The control (background) samples collected prior to using the laser contained a number of volatile solvents, including methanol, ethanol, acetone, methyl-ethyl-ketone (MEK), methyl-isobutyl-ketone (MIBK), ethyl acetate, and propyl acetate. This suggests that the volatile compounds detected on these samples are from sources other than the laser marking process. Potential sources of volatile materials include fabrics, office supplies (e.g., correction fluid), caulk, paint, and activities associated with manufacturing and maintenance of the ink-jet machines.

These results indicate that, in general, there were no substantive differences in compounds detected or relative concentrations between the control samples and the samples collected in the laser room during the marking trials. As such, these results suggest that the laser exhaust ventilation was sufficiently containing the LGACs. During some of the trials, however, a visible plume that was not captured by the exhaust system and noticeable odors associated with the marking trial were observed. As this observation was not reflected by the air sampling results, it is possible that the uncaptured emissions

were either particulate in nature or were significantly diluted to below the sensitivity limit of the sampling method. Note, however, that the exhaust system was not operating as intended in a production operation and that the marking trials were not typical of routine applications for this laser. Under intended use (production) conditions, it would be expected that the laser enclosure would enhance the performance of the ventilation exhaust system (more effective scavenging and containment) and further reduce the potential for worker exposure to emissions from this process.

Low to trace levels of approximately 15 compounds were found on the field blanks. Compounds detected included hexamethylcyclotrisiloxane, toluene, methanol and acetaldehyde.

Carbon Monoxide, Hydrogen Cyanide, Particle Monitoring

The results of the monitoring conducted with direct reading instrumentation (CO, HCN, particulate) are shown in Table 4.

In general, the number of particles $\geq 0.3 \mu\text{m}$ and $\geq 1.0 \mu\text{m}$ generated during the laser marking exceeded background particle levels by a factor of 10 or more for the PET high density polyethylene (HDPE) products. Particles were also higher than background for the other test materials (cardboard, glass, ceramic), but not to the same degree as the plastics. The specific chemical constituents of these particles are not determined by this technique; however, it is likely these particles comprise a large fraction of the overall LGACs produced. Visible smoke was observed during the laser trials with the polymer materials.

CO was detected at higher than background levels on 10/13 (77%) of the materials tested. The highest levels (90–100 ppm) were measured during the laser marking of PET.

Filter Sample Results

Analysis of the filters found only trace amounts of any contaminants that were detected in the qualitative air monitoring. These include fatty acids, nicotine, and amines. The filter is designed to capture particulate and not gaseous components; as such this was not a surprising result.

Ventilation

Because of the concern regarding generation and exposure to LGACs, an in-line local exhaust ventilation system to control emissions was installed, consisting of a 3" diameter duct positioned 8" to 12" from the lasing action is connected to a commercially available pollution control system (Fumex Model 2A) that consists of an exhaust fan and filtering system. The Fumex system contains approximately 10 pounds of activated charcoal (gas and vapor adsorbent), a pleated filter, and a terminal high efficiency particulate air (HEPA) filter. After filtration, the Fumex system is subsequently vented to an exhaust duct that discharges the exhaust air directly outside (roof level). During normal operation (i.e., in production mode) the exhaust duct is connected to one side of the laser enclosure. An average of four measurements across the face of the exhaust duct found a velocity of 2200 feet per minute (fpm), which corresponds to an exhaust volume of 110 cfm.

General room exhaust in the laser room is accomplished by a floor level exhaust grille that is ducted to a roof-mounted fan. Air is supplied to the laser room by two ceiling mounted supply air diffusers. Comfort fans are also used in the laser room. The dimensions of the laser room are: 9 foot (') (ceiling height) x 18' x 20', room volume = 3240 cubic feet. An average of 10 measurements across the exhaust grille (14" X 16", 1.56 [square feet] ft²) found an average velocity of 246 fpm and a room exhaust volume of 383 cfm.

Procedural/Beam Hazards

VSI has developed procedures to ensure safe operation and protection against optical and LGAC hazards. There is good awareness and concern for safety and health issues, and this is reflected in the LaserPro DM manual. Calculations to determine the nominal hazard zone (NHZ) were conducted to assess the potential ocular hazard of the laser. The NHZ describes the space within which the level of direct, reflected, or scattered laser radiation exceeds the applicable maximum permissible exposure (MPE) limit.⁶ Exposures beyond the boundary of the NHZ are below the MPE. These calculations indicate the diffuse NHZ for this laser under the most conservative conditions (100% reflectance) for 80 W and a MPE of 0.1 W/cm², is approximately 16 centimeters. Workers would not be located closer than this distance without appropriate eye and skin protection. Note that this NHZ applies to the diffuse beam, and not direct beam viewing.

DISCUSSION

A wide variety and complex composition of LGACs can be produced from the interaction of high power CO₂ laser energy with various substrates using the LaserPro DM system. The composition of the LGACs varies significantly depending on the material being coded. The polymer-based materials generated the highest number and relative concentrations of LGACs. Because these compounds have potential toxic and irritating effects, ventilation to capture the emissions is warranted. The monitoring results indicated that the exhaust ventilation in-place on the system used in the laser coding trials was sufficiently containing the LGACs.

Note that to ensure that sufficient emissions were generated to allow for adequate sample collection, each substrate was marked for a considerably longer time period than would be experienced during the normal marking and coding process. As such, the results from this study should only be interpreted qualitatively; conclusions regarding exposure or anticipated concentrations during routine use of the

laser cannot be made from this data. Since defining the composition and relative amounts of degradation products is not possible, ventilation to control emissions is warranted.

It appears that some of the compounds (e.g., methanol, acetaldehyde, methyl-ethyl ketone, acetone, and ethanol) detected on the thermal desorption tubes were not LGACs but were from other sources (e.g., manufacturing processes at VSI) or artifacts of the analytical procedure. In fact, for materials with relatively little LGAC formation, the largest relative peaks on the chromatograms were apparently non-LGAC compounds.

CO is a product of incomplete combustion. It is probable that the CO was formed from incomplete burning of the test materials after initial heating by the laser. A previous study, which evaluated CO during the laser cutting of fabrics and polymers, did not find CO generation above background levels.¹¹ One possible explanation is that in the previous referenced study, the laser cut was complete in a relatively short time period, and the prolonged interaction with the substrate during this project resulted in higher CO generation.

The effect of various compounds that may have been present in some of the materials tested (e.g., unrecorded coatings, plasticizers, color additives, etc.) on LGAC formation was not determined. Additionally, because the laser trials involved a marking time that was considerably longer (30–60 seconds) than would be encountered during routine production (< 1 second), the effect of extended laser/substrate interaction on additional LGAC formation, or the relative concentrations of specific LGACs, is not known. For example, it is not known if the additional laser interaction resulted in further decomposition (e.g., additional breakdown of higher molecular weight LGACs) than would have occurred during normal use, or if formation of some of the detected LGACs required longer laser/substrate interaction times and may not have formed during routine use. Monitoring during the use of the laser in a production setting is likely necessary to answer these questions.

CONCLUSIONS

A wide variety and complex composition of LGACs were measured during experimental trials using the LaserPro DM system to mark various substrates. The composition of the LGACs varied considerably depending on the material being coded. The polymer-based materials generated the highest number and relative concentrations of LGACs. Many of the detected compounds can have toxic and irritating effects if exposure concentrations are high enough and confirms the need to provide sufficient ventilation to capture the emissions. Because these trials were not typical of intended-use applications for the laser, and the air monitoring was qualitative, these results can not be used to draw conclusions regarding exposure. The room air monitoring results indicated that exhaust ventilation used during the trials was containing the LGACs.

RECOMMENDATIONS

Consider incorporating the use of a low-power visible laser (e.g., helium-neon) for laser alignment to improve the safety of this activity. This would negate potential harmful outcomes in the event the present laser beam was off-target and missed the mirrors or beam stop.

Protective laser goggles sufficient to protect users should be worn whenever maintenance is conducted or the laser is fired with the shielding removed or interlocks defeated. When the laser is operating, the door should be locked and a warning lamp or sign to indicate that testing is in progress. Although workers are not normally inside the NHZ, this will help ensure untrained employees from entering the area while the laser is activated.

As these units are commercially sold, inform customers and other laser users of the LGAC potentially formed during cutting, and the need for proper exhaust ventilation during laser operation. Customer training and the operations manual should include this information. Customers should be made

aware that applications using different substrates will result in different rates and characteristics of LGAC formation

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Table 2
Material Testing Summary: Number of Compounds Detected and Ten Largest Peaks
VideoJet Systems International, Inc.
HETA 99–0109

Sample # and Material	# of Compounds Detected	Identification of the Ten Largest Peaks
A05090 Ink Coating Sample A on Glass	37	*Ethanol, *Acetone, MEK, *Methanol and Acetaldehyde**, Styrene, 3-Buten-2-one, *Diethylphthalate, *Dimethylphthalate, *Toluene, *Benzene
A04130 Red Dye on Cardboard	36	*Ethanol, MEK, *Methanol and Acetaldehyde**, Styrene, *Cellosolve acetate, *Hexamethylcyclotrisiloxane, *Toluene, *Benzene, *Acetone, Isoamyl acetate
A03428 PET Plastic Bottle	64	*Benzene, *Toluene, Ethyl benzene/xylene isomers, Styrene, Phenol, Benzoic acid, Biphenyl, Acetophenone, Isobutyrophenone, Substituted acetophenones
A03722 PET Plastic Bottle (green)	58	Biphenyl, Methyl phenyl penten-1-one, Benzoic acid, Benzoyl methyl ketone, Phenol, Substituted acetophenones, *Benzene, *Toluene, Styrene, Acetophenone
A03124 Ceramic Integrated Circuit	38	MEK, Methanol and Acetaldehyde**, *Cellosolve acetate, *Chlorodifluoromethane, *Diethylphthalate, Heptanal, Propane *Hexamethylcyclotrisiloxane, *Propanoic acid ester, *Toluene
A04575 Plastic Integrated Circuit	82	Methyl butadiene, *Toluene, *Benzene, Styrene, Phenol, Cresol isomers, Dimethyl phenol, Phenylacetylene, Benzofuran, Naphthalene
A03798 Blue Dye on Cardboard	31	Ethanol, MEK, *Methanol and Acetaldehyde**, Styrene, α -methyl styrene, *Hexamethylcyclotrisiloxane, *Benzene, *Acetone, Methylene diphenyl, Methylene bis (methylphenol)
A05505 Glass Bottle	36	*Methanol and Acetaldehyde**, *Ethanol, MEK, *Hexamethylcyclotrisiloxane, 3-Buten-2-one, *Dimethylphthalate, *Octamethylcyclotetrasiloxane, *Diethylphthalate, Ethanediol, *Acetone
A03003 Printed Circuit Board	24	Methanol and Acetaldehyde**, *Ethanol, MEK, *Acetone, *Benzene, *Hexamethylcyclotrisiloxane, *Octamethylcyclotetrasiloxane, Benzoic acid, Phthalate ester, Phthalic anhydride
A03679 Ink Coating Sample B on Glass	44	Methanol and Acetaldehyde**, *Ethanol, MEK, *Acetone, *Benzene, Methyl methacrylate, Styrene, α -methyl styrene, *Diethylphthalate
A03700 HDPE Shampoo Bottle	65	Decene, Undecene, *Octamethylcyclotetrasiloxane, Nonene, Heptene, Hexene, Butadiene, Dodecene, Tridecene, Tetradecene
A03181 Polyvinyl Chloride	83	Hydrochloric acid, Butadiene, *Benzene, Methyl methacrylate, Styrene, Indene, Aliphatic chlorocompounds, Methyl Indene, Naphthalene, Biphenyl
A05013 ABS Rubber Gasket	38	Propene, Propadiene, Butadiene, *Ethanol, *Acetone, MEK, *Benzene, *Toluene, Naphthalene, Diethyl phthalate

* = Detected on some media/field blanks and background control samples (prior to laser coding)

** = May be present as impurities or decomposition products of methanol and ethanol

MEK = methyl ethyl ketone

MIBK = methyl isobutyl ketone

Table 3
Room Monitoring Summary
Number of Compounds Detected and Ten Largest Peaks
VideoJet Systems International, Inc.
HETA 99-0109

Sample # and Material	# of Compounds Detected	Identification of the Ten Largest Peaks
A04210 Inside Laser Room Prior to Coding ¹	46	*Ethanol, *Acetone, MEK, *Methanol and Acetaldehyde**, 3-Buten-2-one, *Decamethylcyclopentasiloxane, Ethyl acetate, 1-methoxy-2-propanol, n-propyl acetate, MIBK
A04620 Outside Laser Room Prior to Coding ²	36	*Ethanol, MEK, *Methanol and Acetaldehyde**, *Ethanol, *Acetone, n-Propyl acetate, Ethyl acetate, Butanol, Butyl Cellosolve, MIBK
A03941 Inside Laser Room Prior to Coding ³	49	*Chlorodifluoromethane, *Methanol and Acetaldehyde**, 3-Buten-2-one, *Ethanol, *Acetone, MEK, Ethyl acetate, Butanol, n-Propyl Acetate, *Decamethylcyclopentasiloxane,
AO3074 Inside Laser Room During Coding ⁴	43	*Methanol and Acetaldehyde**, 3-Buten-2-one, *Ethanol, *Acetone, MEK, Ethyl acetate, MIBK, *Dimethylphthalate, *Diethylphthalate
AO5518 Inside Laser Room During Coding ⁵	38	*Methanol and Acetaldehyde**, 3-Buten-2-one, *Ethanol, *Acetone, MEK, Ethyl acetate, MIBK, Isopropyl acetate, Propyl acetate

* = Detected on some media/field blanks and background control samples (prior to laser coding)

** = May be present as impurities or decomposition products of methanol and ethanol

MEK = methyl ethyl ketone

MIBK = methyl isobutyl ketone

1. May 18, 1999, 12:49-2:33 p.m.

2. May 18, 1999, 12:54-4:55 p.m.

3. May 19, 1999, 7:57-9:45 a.m.

4. May 18, 1999, 2:35-4:53 p.m.

5. May 19, 1999, 9:43-11:06 a.m.

Table 4
Carbon Monoxide, Hydrogen Cyanide, Particulate Results
VideoJet Systems International, Inc.
HETA 99-0109, May 18-19, 1999

Sample # and Material	Sample Time (seconds)	HCN (ppm)	CO (ppm)	Particulate	
				>0.3 µmd	>1.0 µmd
A05090 Ink Coating Sample A on Glass	60	ND	7	101,627	3559
A04130 Red Dye on Cardboard	60	ND	1-2	92,460	3161
A03428 PET Plastic Bottle (clear)	30	ND	>100	745,712	115,056
A03722 PET Plastic Bottle (green)	30	ND	90	822,568	87,608
A03124 Ceramic Integrated Circuit	60	ND	21	not recorded	not recorded
A04575 Plastic Integrated Circuit	60	ND	15	737,800	118,084
A03798 Blue Dye on Cardboard	60	ND	1-2	110,463	2241
A05505 Glass Bottle	60	ND	1-2	68,107	2686
A03003 Printed Circuit Board	60	ND	35	86,446	2462
A03679 Ink Coating Sample B on Glass	60	ND	7	101,627	3559
A03700 HDPE Shampoo Bottle	30	ND	18	895,179	105,759
A03181 Polyvinyl Chloride	30	ND	21	257,382	13,564
A05013 ABS Rubber Gasket	30	ND	65	137,357	2889
Background	60	ND	1	53,164	1211

ppm = parts of gas or vapor per million parts air

CO = carbon monoxide

µmd = diameter of particle in micrometers

HCN = hydrogen cyanide

Sample ID# refers to the thermal desorption sample number corresponding to that material. Except for samples A04130 and A03798, the laser was operating in continuous wave mode, 80 Watts, 350 micrometer beam size, 2.5 inch lens. The power was backed down to 2 Watts for the other two samples. The ventilation system was on for all trials.

Particulate refers to the total number of particles measured during the sampling interval, not concentration.

Background conditions (prior to any laser marking):

CO = 1 ppm

HCN = < 2 ppm

Temperature = 75°F

Relative Humidity = 45%

APPENDIX A

Qualitative Air Monitoring Contaminants Identified and Chromatograms

**THERMAL DESORPTION TUBES
PEAK IDENTIFICATION**

Page 1 of 4

(#s match peaks on subsequent chromatograms)

- | | |
|---------------------------------|-----------------------------------|
| 1) Air*/CO ₂ * | 36) Hexene |
| 2) Formaldehyde** | 37) Methyl furan |
| 3) Hydrochloric acid | 38) Hexane |
| 4) Vinyl chloride | 39) 1,1,1-Trichloroethane |
| 5) Chlorodifluoromethane* | 40) Hexadien-yne? |
| 6) Propene | 41) Methylcyclopentadiene |
| 7) Propane | 42) Methyl dioxolane |
| 8) Propadiene | 43) Cyclohexadiene |
| 9) Methanol*+acetaldehyde** | 44) Methyl cyclopentane |
| 10) Butane | 45) Isopropyl acetate |
| 11) Butadiene | 46) Benzene* |
| 12) Butene/butyne | 47) Butanol |
| 13) Ethanol* | 48) Methyl 3-buten-2-one |
| 14) Acrolein | 49) 1-Methoxy-2-propanol |
| 15) Acetone* | 50) Methylene bromide. |
| 16) Isopentane* | 51) Hexatriene |
| 17) Isopropanol | 52) Cyclohexene |
| 18) Methyl butadiene (isoprene) | 53) Heptadiene |
| 19) Methyl butene | 54) Ethyl acrylate |
| 20) Allyl alcohol | 55) Heptene |
| 21) Furan | 56) Chlorobutanone |
| 22) Formic acid | 57) Heptatriene |
| 23A) Pentene | 58) Methyl methacrylate |
| 23) Pentane* | 59) Heptane |
| 24) Cyclopentadiene | 60) 2-Ethoxyethanol |
| 25) Pentadiene | 61) n-Propyl acetate |
| 26) Methacrolein | 62) Pyridine |
| 27) 3-Buten-2-one | 63) Propylene glycol |
| 28) Methyl ethyl ketone (MEK) | 64) Methyl isobutyl ketone (MIBK) |
| 29) 1-Methyl-1-propanol | 65) Dimethoxybutane |
| 30) Hexadiene | 66) Cyclopropylamine? |
| 31) Chlorobutane | 67) 2-Methyl furan |
| 32) Butenal | 68) Chlorocyclopentene |
| 33) Acetic acid | 69) Toluene* |
| 34) Chlorobutadiene | 70) Dimethylene cyclohexane? |
| 35) Ethyl acetate | 71) Cycloheptatriene |

**THERMAL DESORPTION TUBES
PEAK IDENTIFICATION**

Page 2 of 4

- | | |
|---|---|
| 72) C ₈ aliphatics | 110) Limonene |
| 73) Hexanal* | 111) Indene |
| 74) Octadiene | 112) Acetophenone |
| 75) Octene | 113) C ₈ -C ₁₀ aliphatic aldehydes* |
| 76) Furfural | 114) Octamethylcyclotetrasiloxane* |
| 77) Butyl acetate | 115) Methyl pyrrolidinone |
| 78) Perchloroethylene | 116) p-Dichlorobenzene |
| 79) Octane | 117) 2-Ethyl-1-hexanol |
| 80) Vinylcyclohexadiene | 118) Hydroxybenzaldehyde* |
| 81) Aliphatic, chloro- compounds | 119) Camphor* |
| 82) Hexamethylcyclotrisiloxane* | 120) Dimethylbenzene methanol |
| 83) 4-Vinylcyclohexene | 121) Chloroalkane |
| 84) Chlorobenzene | 122) Chlorostyrene |
| 85) Methyl pyridine | 123) Methyl indenenes/divinylbenzene |
| 86) Propylene glycol methyl ether acetate | 124) C ₁₀ H ₁₆ terpene |
| 87) Ethyl benzene/xylene isomers | 125) Cresol isomers |
| 88) Isoamyl acetate | 126) Indene |
| 89) Styrene | 127) Terpinene |
| 90) Heptanal | 128) Methyl benzaldehyde |
| 91) Cellosolve acetate* | 129) Dimethyl phenol (xylenol) |
| 92) Butyl cellosolve | 130) Methyl benzofuran |
| 93) Nonene | 131) Methyl benzoate |
| 94) Amyl acetate | 132) Ethyl styrene/methyl indan |
| 95) Anisole | 133) Azulene |
| 96) Phenyl acetylene | 134) Vinyl styrene |
| 97) 2-Heptanone (MAK) | 135) Isobutyrophenone |
| 98) C ₉ H ₁₂ alkyl benzenes | 136) Benzoyl methyl ketone |
| 99) Bromobenzene | 137) Benzoic acid |
| 100) Methyl furanone | 138) Methyl acetophenone |
| 101) Benzaldehyde | 139) Cinnamaldehyde |
| 102) 2-Ethylhexanal | 140) Decamethylcyclopentasiloxane* |
| 103) Pinene | 141) Naphthalene |
| 104) Phenol | 142) Trimethyl phenol |
| 105) α-Methyl styrene | 143) Dimethylbenzofurans |
| 106) Benzyl chloride | 144) Caprolactam |
| 107) Benzofuran | 145) 2-Ethylhexyl acrylate |
| 108) Methyl styrene isomers | 146) Dimethylbenzaldehyde |
| 109) Dihydronaphthalene/methylene indan | 147) Benzothiazole |

THERMAL DESORPTION TUBES

PEAK IDENTIFICATION

Page 3 of 4

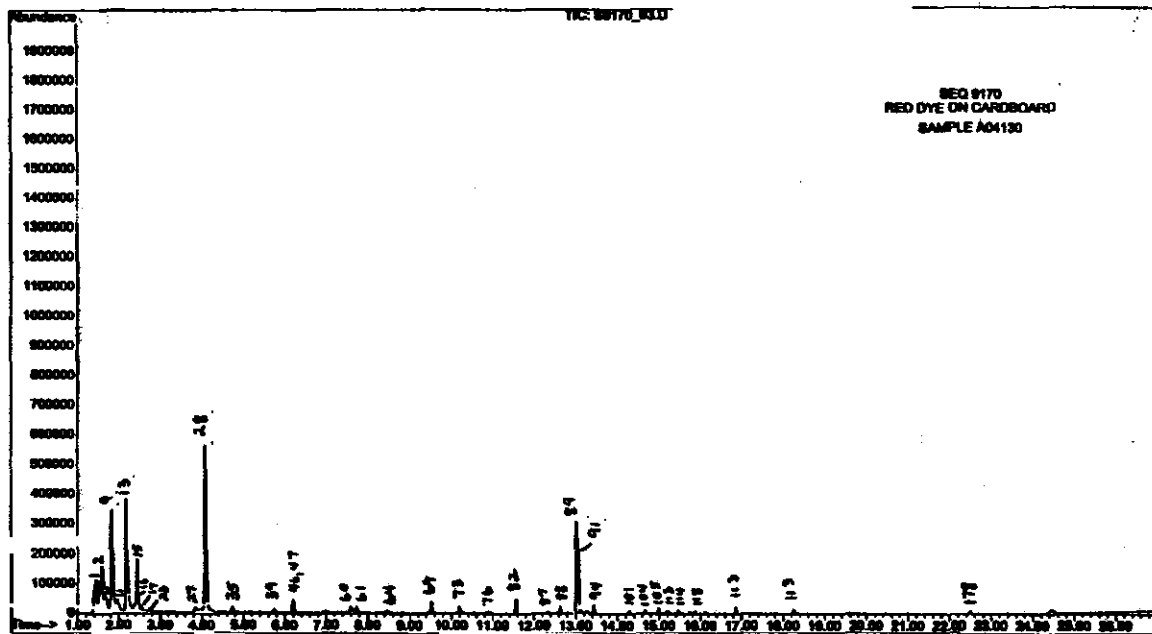
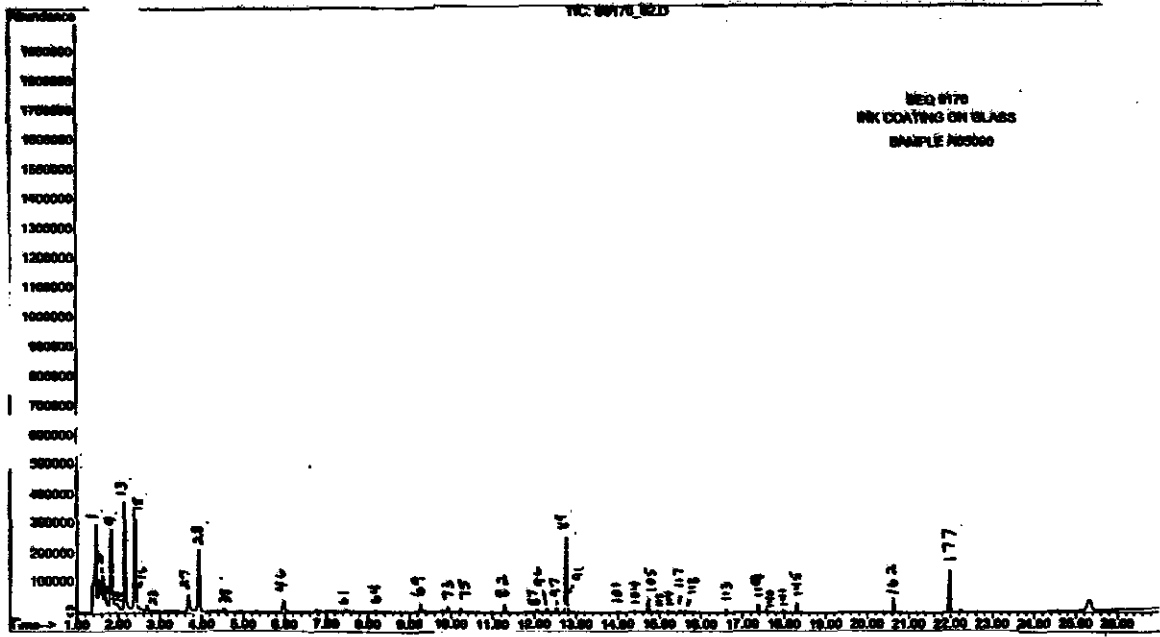
- | | |
|------------------------------------|-----------------------------------|
| 148) Hydroquinone | 186) Methyl benzyl phenol |
| 149) Methyl benzoic acid | 187) Phenyldivinylcyclohexane |
| 150) Ethyl acetophenone | 188) Stilbene |
| 151) Methyl phenyl butene | 189) Diphenylcyclopropane |
| 152) Methyl phenyl penten-one? | 190) Anthracene/phenanthrene |
| 153) Vinyl benzoic acid | 191) Vinyl anthracene |
| 154) Dibromobicyclooctatriene? | 192) Phenyl acetophenone |
| 155) Trimethyl benzofuran | 193) (Acetylphenyl)phenyl methane |
| 156) Methyl naphthalenes | 194) Phenyl compounds |
| 157) Diacetyl benzene | 195) Phenyl naphthalene |
| 158) Dihydromethylnaphthalene | 196) Methyl phenanthrene |
| 159) Phenyl cyclohexadiene | 197) Phenyl ethyl phenol |
| 160) Biphenyl | 198) Xanthone |
| 161) Phthalic anhydride | 199) Fluorene/pyrene |
| 162) Dimethyl phthalate* | 200) Methylenediphenyl |
| 163) Acetylacetophenone | 201) Methylenebis(methylphenol) |
| 164) Diphenylmethane | 202) Ethanediol, dibenzoate? |
| 165) Methylhydroxybenzoate | 203) Octadiene |
| 166) Substituted acetophenones? | 204) Octene |
| 167) Biphenylene/acenaphthylene | 205) Octane |
| 168) Anisyl acetone | 206) Nonadiene |
| 169) Methyl biphenyl | 207) Nonene |
| 170) Dihydrobiphenyl | 208) Nonane |
| 171) Acenaphthene | 209) Decadiene |
| 172) Benzyl benzene | 210) Decene |
| 173) BHT(butylated hydroxytoluene) | 211) Decane |
| 174) Dibenzofuran | 212) Undecadiene |
| 175) Dihydrostilbene | 213) Undecene |
| 176) Bibenzyl | 214) Undecane |
| 177) Diethyl phthalate* | 215) Dodecadiene |
| 178) Propanoic acid ester* | 216) Dodecene |
| 179) Phthalate ester | 217) Dodecane |
| 180) Butyl biphenyl | 218) Tridecadiene |
| 181) Fluorene | 219) Tridecene |
| 182) Xanthene | 220) Tridecane |
| 183) Benzyl phenol | 221) Tetradecadiene |
| 184) Vinyl biphenyl | 222) Tetradecene |
| 185) Fluorenone | 223) Tetradecane |

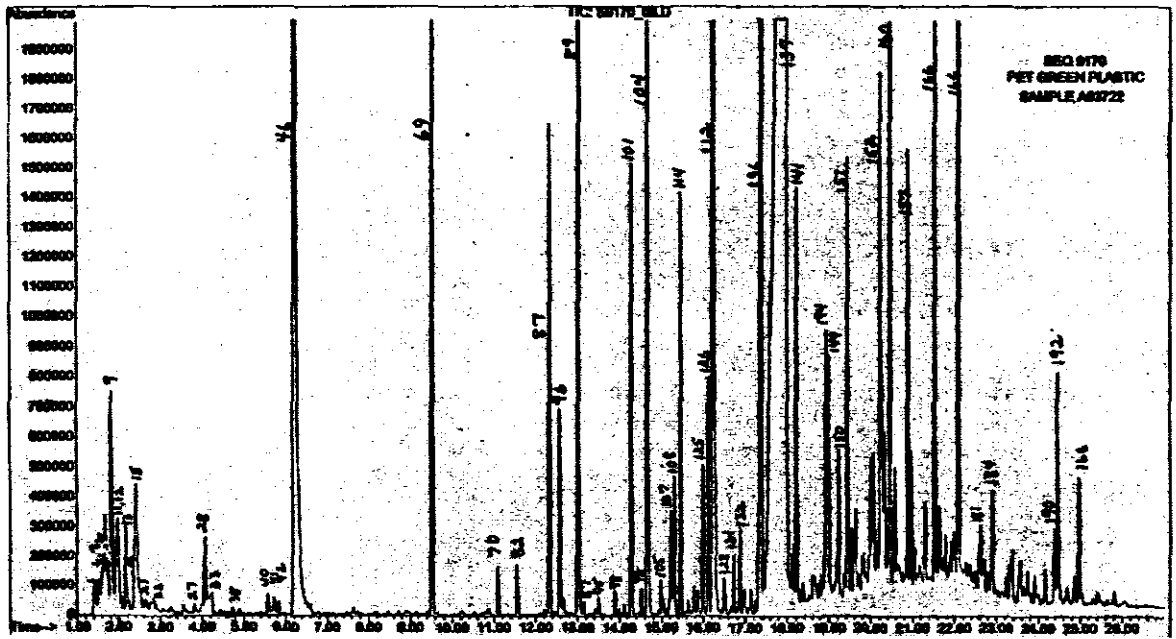
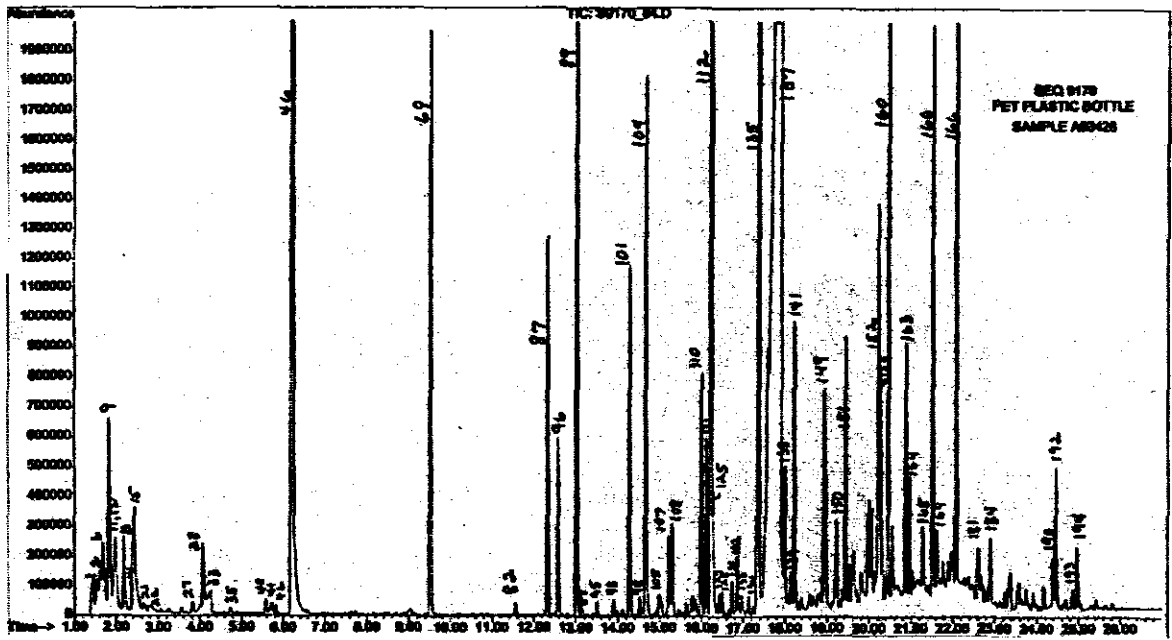
**THERMAL DESORPTION TUBES
PEAK IDENTIFICATION
Page 4 of 4**

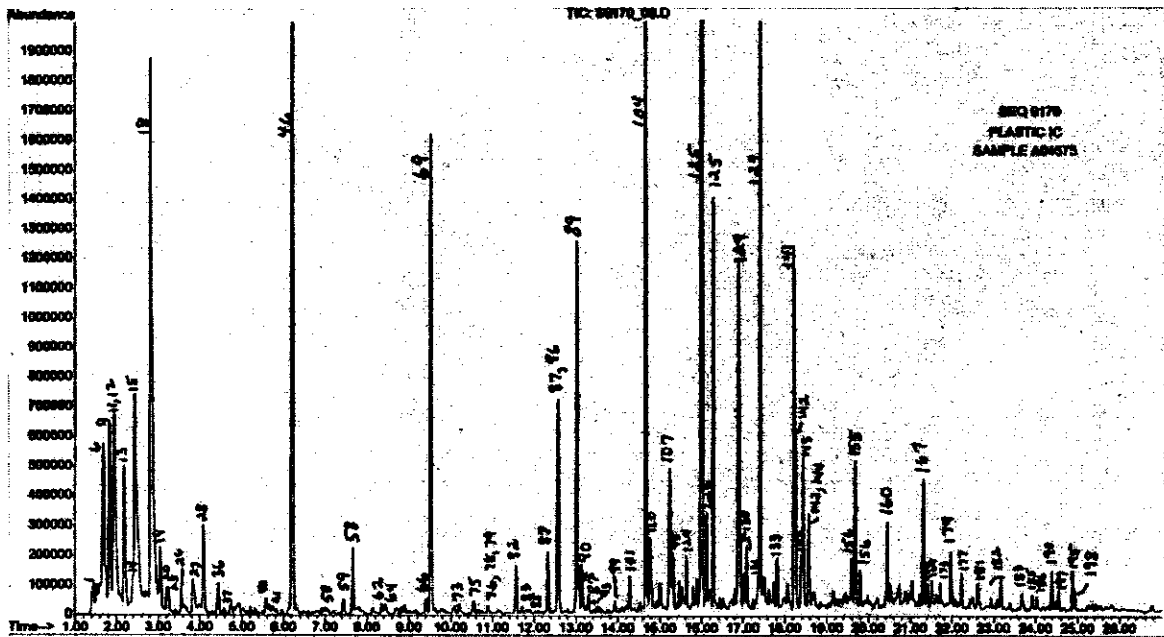
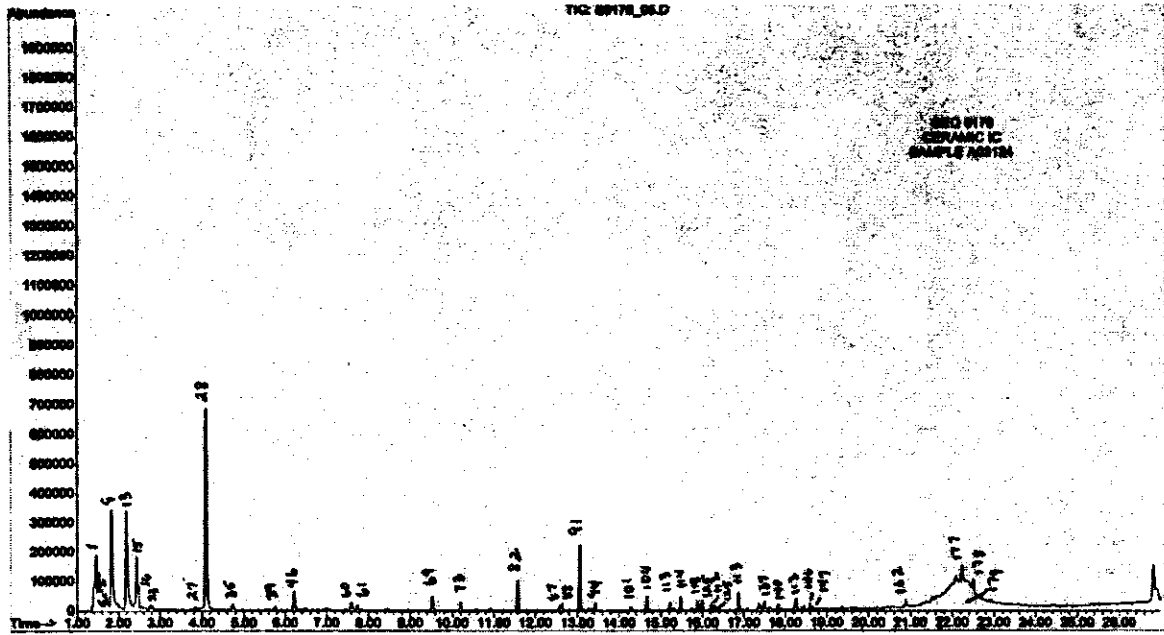
224) Pentadecadiene	235) Octadecene
225) Pentadecene	236) Nonadecadiene
226) Pentadecane	237) Nonadecene
227) Hexadecadiene	238) Nonadecane
228) Hexadecene	239) Eicosadiene
229) Hexadecane	240) Eicosene
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234) Octadecene	

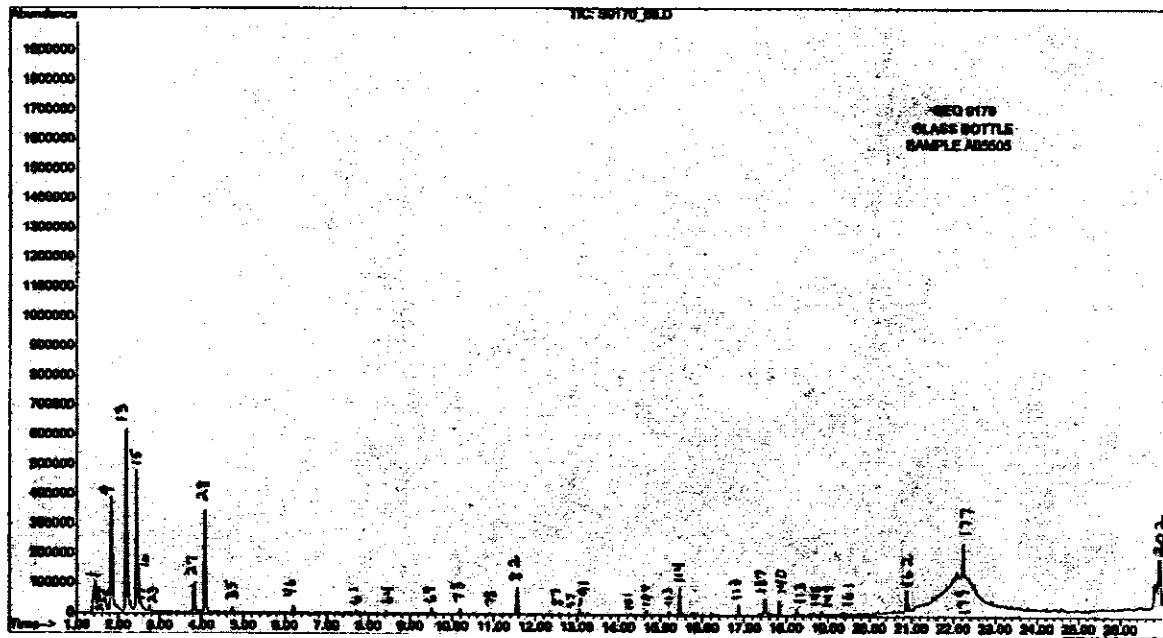
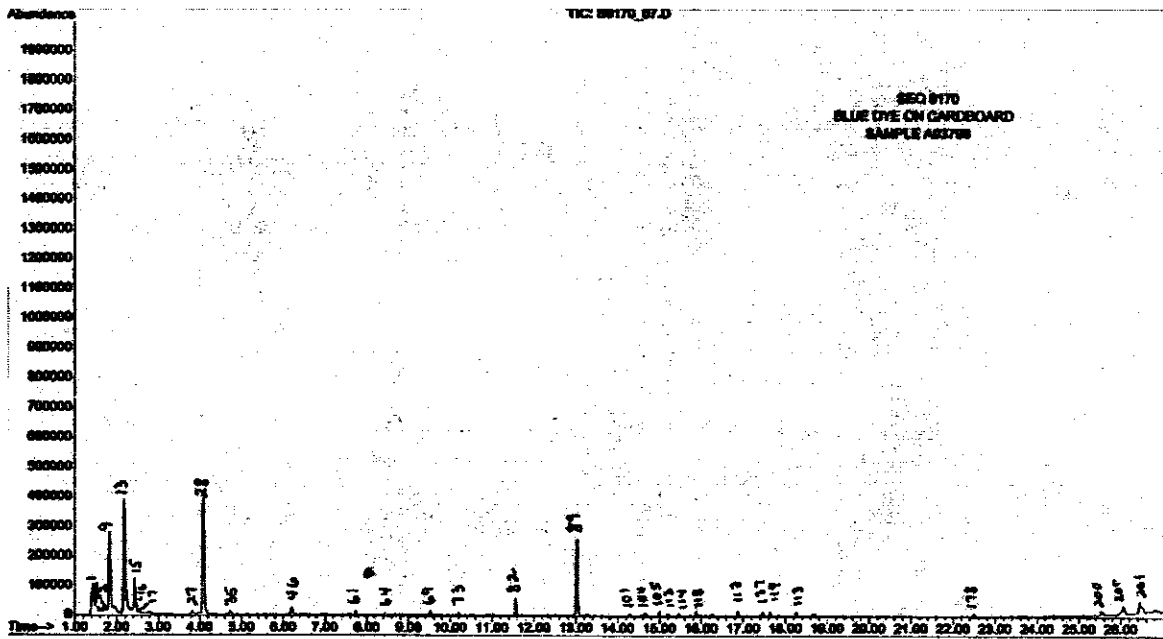
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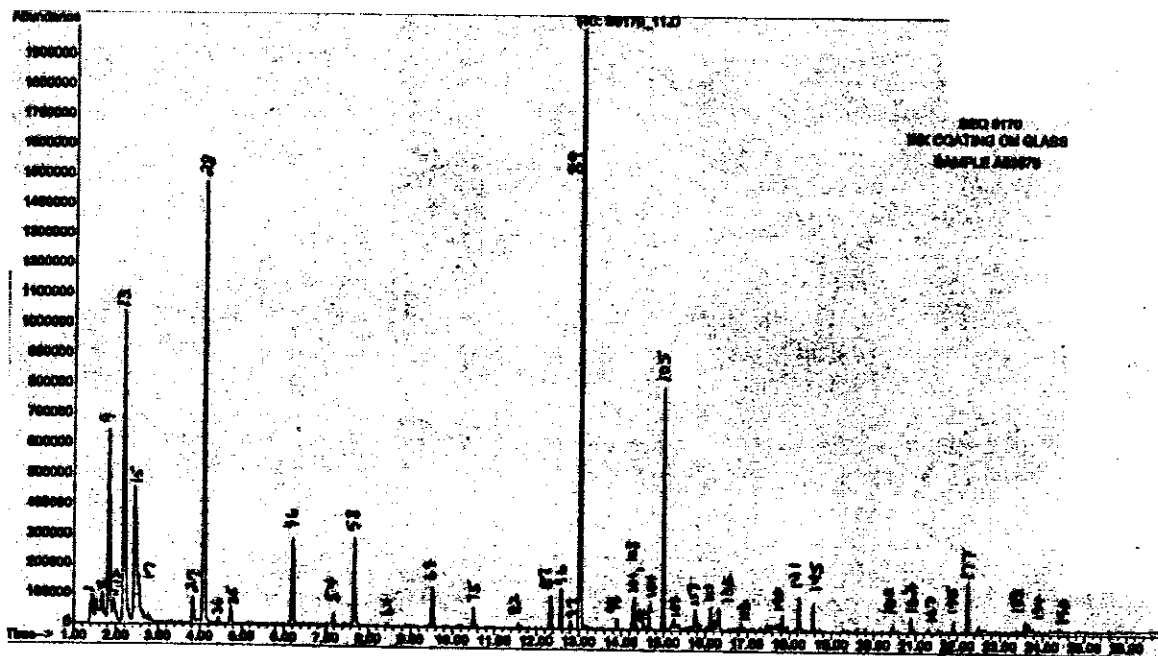
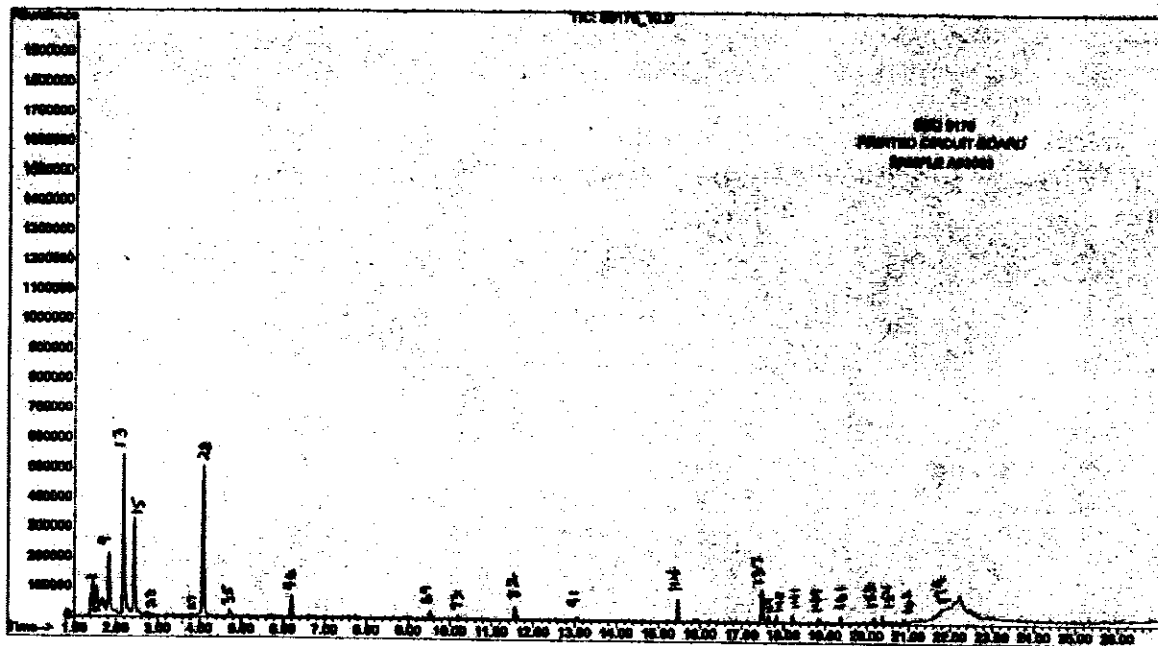
****May be present as impurities and/or decomposition products of methanol and ethanol.**

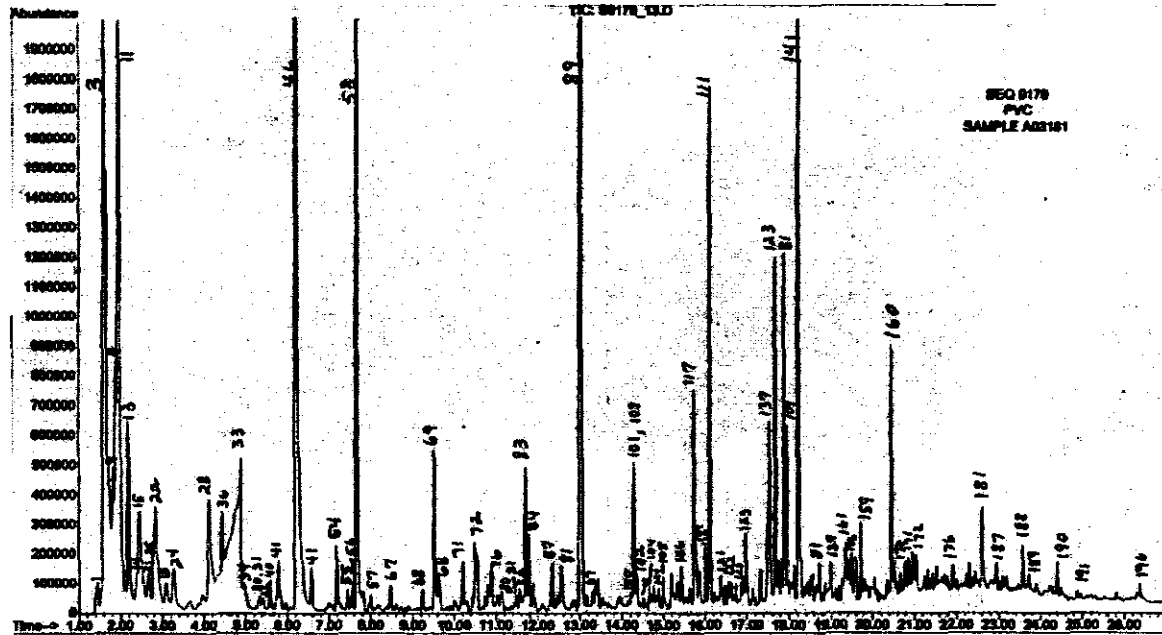
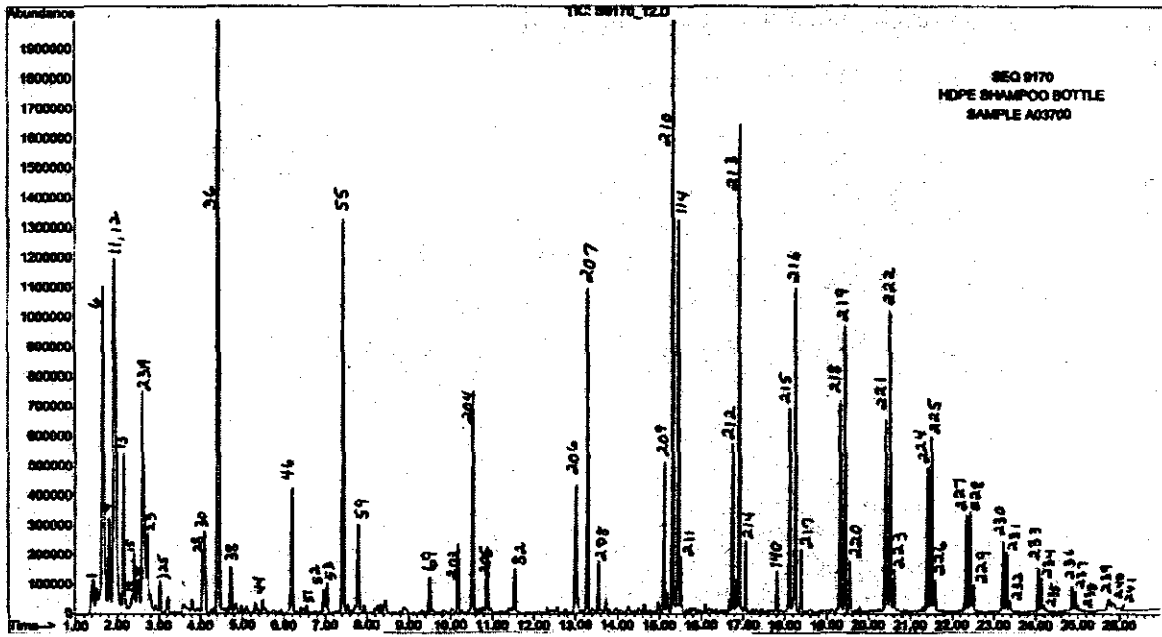


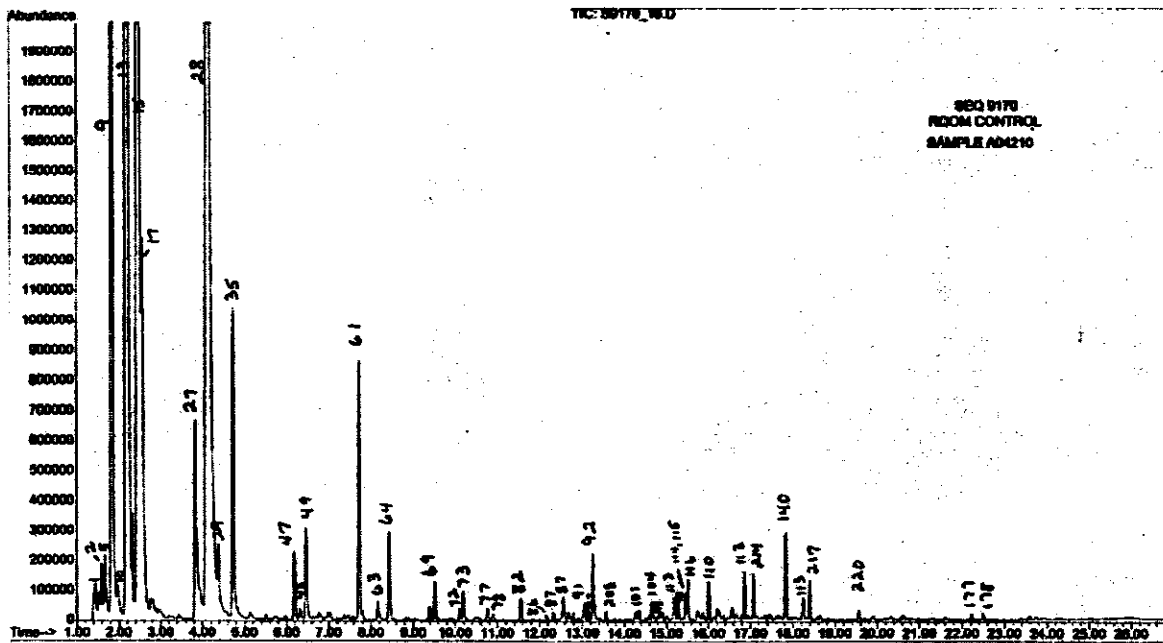
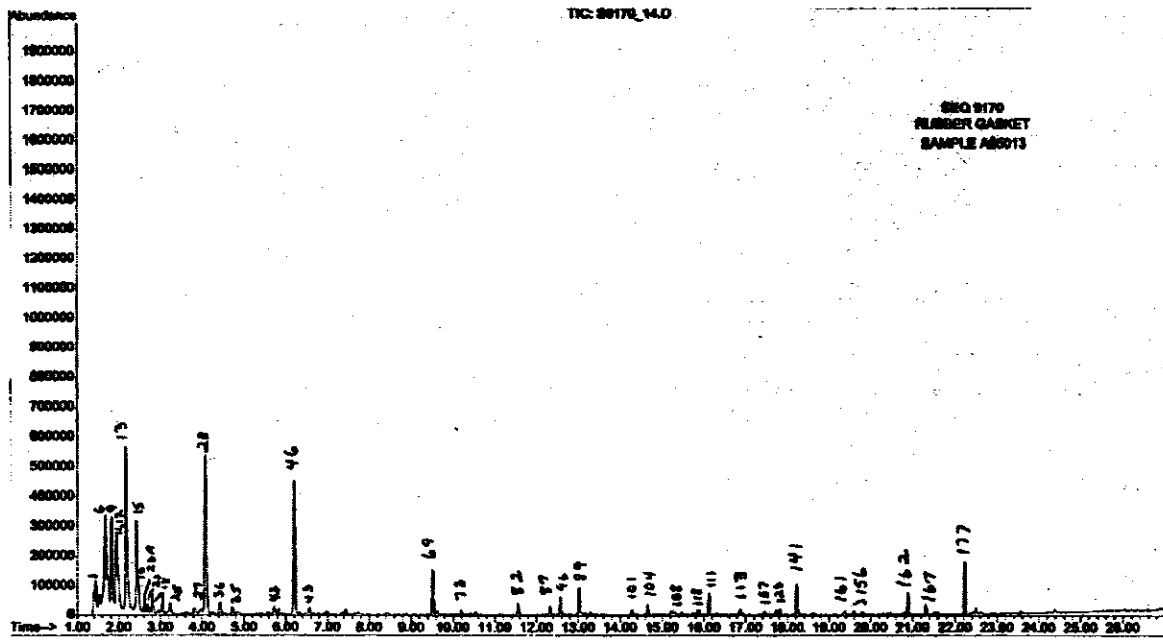


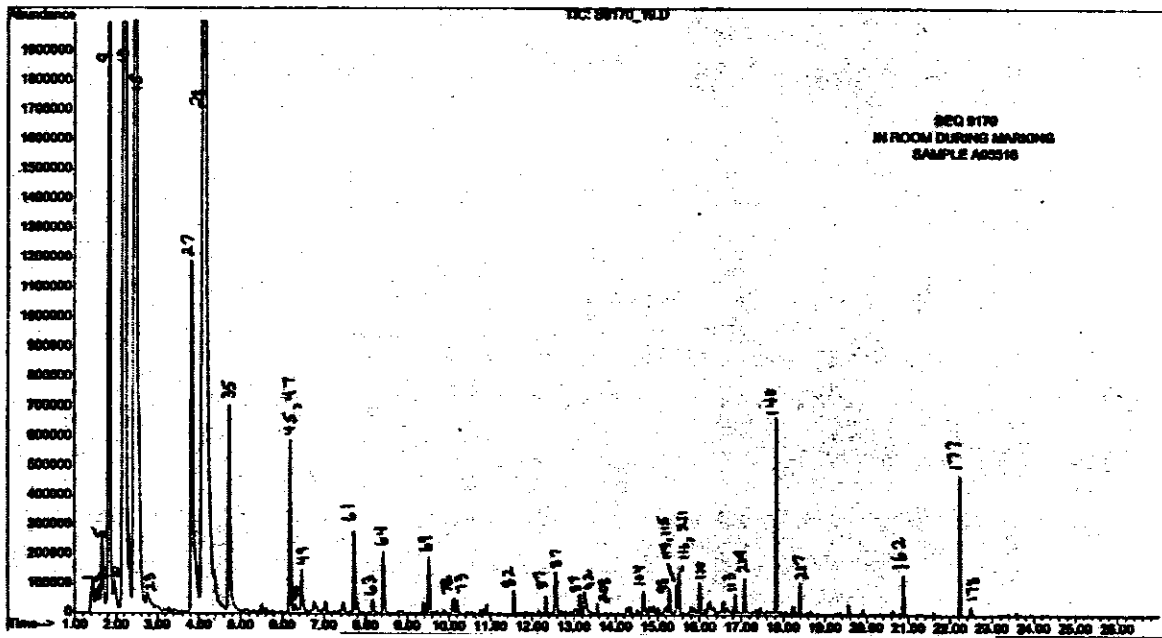
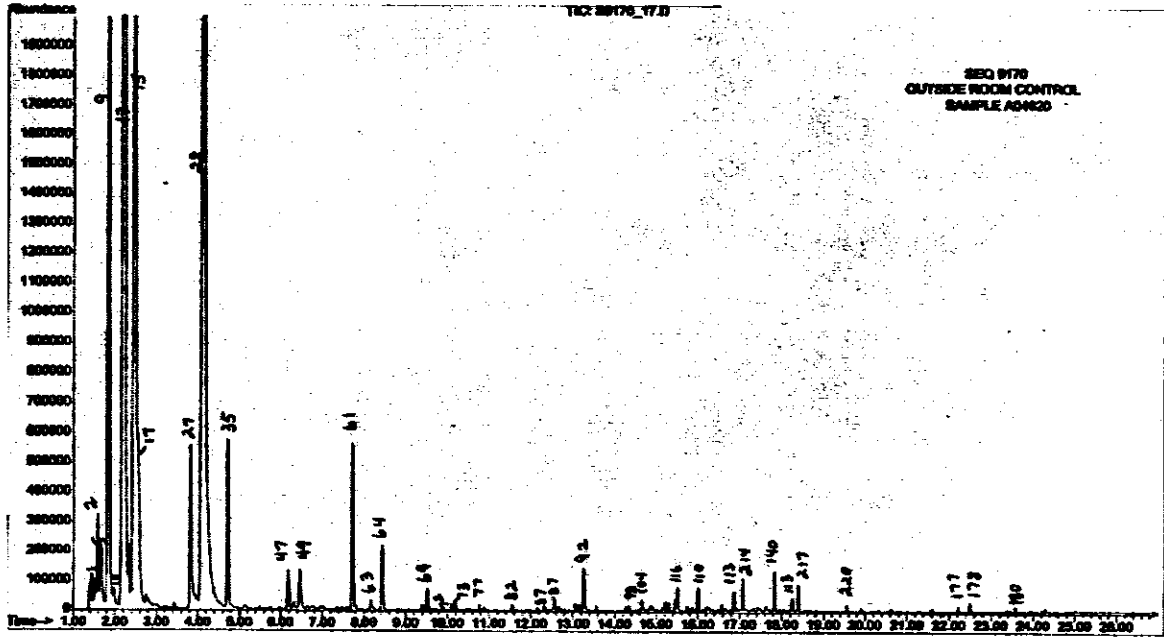


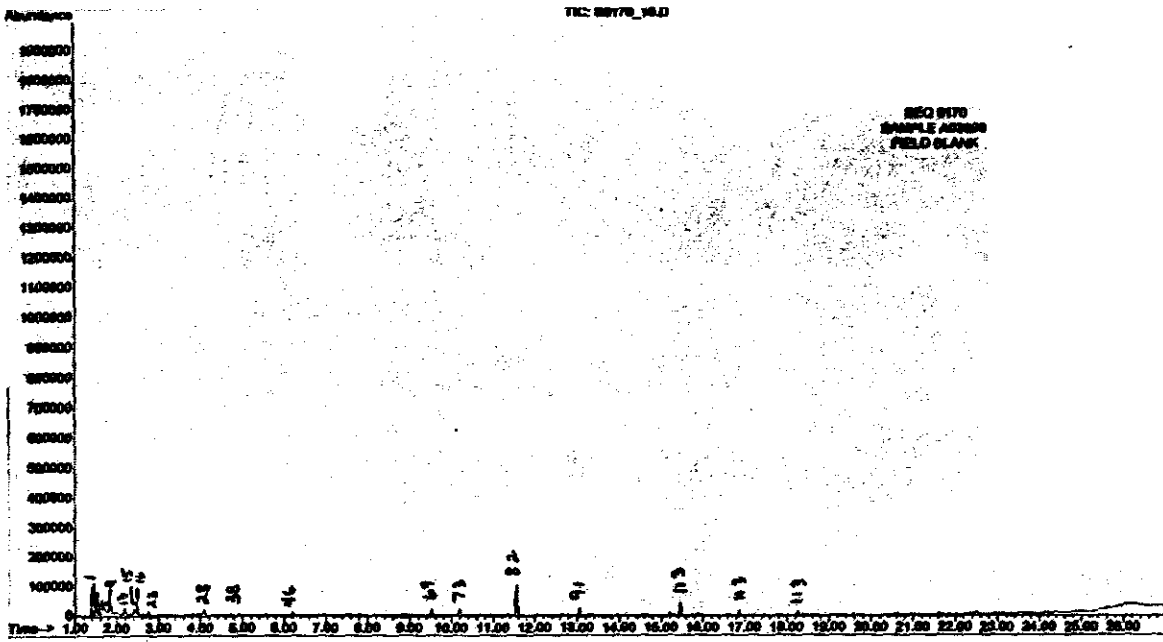












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