HAZARD EVALUATION AND TECHNICAL ASSISTANCE REPORT
HETA 90-102-L2075
EBTEC EAST
AGAWAM, MASSACHUSETTS
OCTOBER 1990

Hazard Evaluations and Technical Assistance Branch
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I. BACKGROUND

On February 1-2, 1990, the National Institute for Occupational Safety and Health (NIOSH) made an evaluation at the Ebtec East Corporation located in Agawam, Massachusetts in response to a management request for a health hazard evaluation (HHE). This evaluation was performed to document potential exposures to emission products produced during the cutting of a Kevlar® composite material with a carbon dioxide (CO_2) laser.

Kevlar is a lightweight organic fiber with extremely high tensile strength and resistance of elongation.[1] It is an aromatic polyamide, more commonly referred to as an aramid fiver. It is formed in the reaction of aromatic diamines and aromatic diacid chlorides in an amide solvent, and consists of long polyamide chains attached to two aromatic rings.[2] Because of its dimensional stability, strength, heat and flame resistance, chemical inertness, and electrical resistivity, Kevlar has found many uses. It is currently used in bullet-resistant structures, filter bags for hot stack gases, insulation, protective clothing, tire cord, and in aerospace composites.[3]

A literature search failed to identify data on emissions generated during laser cutting of kevlar. Thermal degradation products generated during heating of Nomex®, another aramid fiver, and an unspecified aramid bating (without finish) at approximately 540° and 575°C, identified carbon dioxide, water, acetaldehyde, hydrogen cyanide and methylcyanide as thermal degradation products.[4] Thermal analysis of aramid fabric which contained an unidentified finish resulted in the evolution of additional decomposition products including aliphatic and aromatic hydrocarbons (including benzene), alcohols and several esters.[4] This emphasizes the fact that auxiliary chemicals applied to the fibers can affect the types of thermal degradation products formed. Although information regarding thermal degradation products of Kevlar composites having an epoxy matrix was not found, data from a material data sheet (MSDS) for the epoxy resin lists the following thermal decomposition products: carbon monoxide, carbon dioxide, ammonia, oxides of nitrogen, oxides of sulfur and/or hydrogen cyanide.

II. FACILITY DESCRIPTION

Ebtec East, a subsidiary of TI Group, is involved with development and processing techniques with metals, ceramics, and composite materials. In the conduct of such business, Ebtec East utilizes state-of-the-art laser and electron beam technology.

The composite material in use during this evaluation contained Kevlar fibers in an epoxy matrix. Sheets of the Kevlar composite were placed on a stand and a laser beam was used to cut a series of small holes in the sheet. Although the process was automated, it required periodic monitoring by a laser technician. The technician would set up the operation and return periodically to inspect the work, to determine if the size of the holes met specifications. The cutting operation was performed in an area approximately 8' x 10' which was enclosed with a plastic barrier. Local exhaust ventilation consisted of a down draft system which captured emissions from this process.

The CO_2 laser used by Ebtec East for this evaluation was a Coherent Radiation Inc. "Everlase" model operating in a pulsed mode. The laser is a class IV laser which operated at an average power of 350 watts at 10.6 microns (um) and used a five inch focussing lens. While a limited evaluation was made on the laser system, is is noted that this evaluation dealt mainly with emissions of gases/fumes since there had not been any reports of exposure to laser radiation. The only concern expressed to NIOSH investigators dealt with the nature of potential fume production.

Six laser technicians are trained to do this work, however, there is only one operator per shift. Although the laser cutting operation had been performed for approximately eight months, the type of composite used had been changed, and the new composite was just beginning to be used on a continuous production basis. Prior to this time, work had been performed on a Kevlar-graphite composite material. Reportedly, the odors from the Kevlar-graphite composite were much stronger and resulted in heavier soiling of the plastic barrier than emissions from the new composite material. Health complaints such as eye and skin irritation were also greater with the Kevlar-graphite material.

Two half-mask air purifying respirators with organic vapor and high efficiency particulate filter cartridges were available and were worn by the technicians when using the laser to finish the edges of the workpiece after the holes had been cut. This operation takes approximately 5 to 10 minutes. After the parts were completed, they were cleaned by the laser technician using Synasol, an alcohol-based solvent. The laser technician performed this cleaning activity in an area outside the booth, which was not supplied with local exhaust ventilation. Rubber gloves were used while cleaning the parts.

III. ENVIRONMENTAL EVALUATION AND METHODS

To characterize the emissions generated during the laser cutting operation, air samples for various gases, vapors, and particulates, were collected.

The following gases were monitored using the Drager gas detection system: carbon monoxide (CO), oxides of nitrogen (NO_x), formaldehyde, petroleum hydrocarbons, and hydrogen cyanide (HCN). This technique allows for instantaneous measurement of gases using colorimetric detector tubes specific for the gases of interest. Measurements were made in the morning and again in the afternoon during the cutting operation. Additionally, battery-operated air sampling pumps calibrated at 0.2 liters per minute (Lpm) were used to collect full-shift and short-term air samples for HCN. Air samples were collected in the laser booth and on the laser technician. Analysis of the air samples was performed using NIOSH Method 6010.[5]

Air samples were collected for analysis of volatile organic compounds (VOCs) using two different media: activated charcoal tubes and Carbotrap 300 thermal desorption tubes. The Carbotrap tubes contain three different sorbent materials for trapping organic compounds over a wide range of volatility. Air samples obtained inside the laser booth were collected on a cart located as close as possible to the laser, approximately 2.5 feet away. Both types of VOC samples were collected by drawing air through the sorbent tubes at a known flowrate using battery-operated air sampling pumps. The charcoal tube air samples were collected at a flowrate of 0.05 to 0.8 Lpm and the thermal tubes were sampled at 0.1 Lpm. Short-term and full-shift charcoal tube air samples were obtained. Sequential one-hour air samples were collected using the thermal tubes, to avoid overloading the sampling media.

Preliminary analysis of the thermal tubes and three charcoal tube samples was performed using gas chromatography to qualitatively identify the VOCs present on the tubes. The charcoal tubes were desorbed with carbon disulfide and the thermal tubes with a thermal desorption unit. Analysis was performed using a gas chromatograph equipped with a mass selective detector (GC-MSD). Additional charcoal tube area air samples and one personal breathing zone air sample obtained on the laser technician were subsequently quantitatively analyzed for the major compounds identified in the GC- MSD analyses.

Personal breathing zone and area air samples were also analyzed for aldehydes. One area air sample obtained inside the booth was used as a qualitative screening sample. The remaining air samples were quantitated for the specific aldehydes identified in the preliminary screening. Air samples were collected on ORBO-23 tubes at a flowrate of 0.5 Lpm. Analysis was performed using gas chromatography with flame ionization detection.

A bulk sample of the Kevlar composite was analyzed by transmission electron microscopy (TEM) to characterize fiber size and shape. An area air sample of the particulate material collected during the cutting operation was then analyzed by TEM to determine if Kevlar fibers were present. The area air sample was collected over the entire workshift using a mixed cellulose ester filter as the collection media and an air sampling pump operating at 2 Lpm.

IV. EVALUATION CRITERIA

As a guide to the evaluation of the hazards posed by work place 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 if 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 work place exposures, the general environment, or with medications or personal habits of the worker to produce health effects even if the occupational exposures are controlled to the level set by the evaluation criterion. These combined effects are not often considered by the evaluation criteria. Also, some substances are absorbed by direct contact with the skin and mucous membranes, and thus potentially increase 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 work place are: 1) NIOSH Criteria Documents and Recommended Exposure Limits (RELs), 2) the American Conference of Governmental Industrial Hygienists' (ACGIH) Threshold Limit Values (TLVs), and 3) the U.S. Department of Labor (OSHA) Permissible Exposure Limits (PELs). The OSHA PELs may be required to take into account the feasibility of controlling exposures in various industries where the agents are used; the NIOSH-recommended exposure limits, by contrast, are based primarily on concerns relating to the prevention of occupational disease. In evaluating the exposure levels and the recommendations for reducing these levels found in this report, it should be noted that industry is legally required to meet those levels specified by an 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 short-term exposure limits or ceiling values which are intended to supplement the TWA where there are recognized toxic effects from high, short-term exposures.

At present, there is limited information from OSHA on exposure criteria for workers exposed to physical agents, such as lasers. Criteria for physical agents not covered by OSHA come from either ACGIH, NIOSH, or in some cases, from consensus standards promulgated by the American National Standards Institute (ANSI).

V. RESULTS

Direct-reading measurements for CO, HCN, formaldehyde, petroleum hydrocarbons, and NO_x were made between 8:45-9:15am, and between 12:50-1:15pm. Formaldehdye and HCN were not detected; the limit of detection (LOD) for both gases was 0.2 parts per million (ppm). Petroleum hydrocarbons also were not detected, however, the LOD for this class of substances is fairly high, at 100 ppm. Carbon monoxide was measured at 30-35 ppm in the morning and at 10 ppm in the afternoon. The current NIOSH REL for CO is 35 ppm as an 8- hour TWA, and 200 ppm as a ceiling limit. Oxides of nitrogen (nitric oxide and nitrogen dioxide) were measured at 5 ppm in the morning and were not detected in the afternoon (LOD = 0.5 ppm). The current NIOSH REL and OSHA PEL for nitric oxide is 25 ppm as a TWA over the workshift, and for nitrogen dioxide is 1 ppm as a 15-minute ceiling limit. Although the measurements made during this survey do not distinguish between the different nitrogen oxide forms, NO is converted spontaneously in air to NO_2.

Time-weighted average air concentrations of HCN (measured as CN) in the laser cutting area ranged from 0.03 to 0.08 milligrams per cubic meter (mg/m^3) in four short-term air samples of 15 to 60 minutes duration. The concentration of HCN in the laser cutting area was 0.05 mg/m^3, as a TWA over the entire workshift. The personal air sample obtained on the laser technician gave a concentration of 0.01 mg/m^3. All HCN concentrations were well below the current exposure guidelines established by NIOSH (5 mg/m^3 as a 10-minute ceiling) and OSHA (5 mg/m^3 as a 15-minute short-term exposure limit).

Gas chromatograms from four air samples analyzed for VOCs are shown in Figures 1 and 2. In Figure 1, chromatograms from the two different media (charcoal and thermal tubes) are shown. These chromatograms are very similar, both having ethanol, 1,1,1-trichloroethane, methyl isobutyl ketone (MIBK), and ethyl acetate as the major peaks. A few additional substances are present on the thermal tubes (such as methanol) due to the different types of sorbent materials present in this sampling media. Figure 2 shows the GC chromatograms from thermal tube air samples obtained outdoors and in the general plant area outside the laser booth. The outdoor air sample shows only water and a trace of 1,1,1-trichloroethane. The chromatogram from the general room air sample is quite similar to those obtained inside the laser booth, showing major peaks for ethanol, ethyl acetate, 1,1,1-trichloroethane, MIBK, and dichloroethylene.

One full-shift personal breathing zone air sample obtained on the laser technician and two full-shift area air samples (one inside and one outside the laser booth) collected on charcoal tubes were quantitated for nine specific VOCs. The analysis included determination of 1,1,1-trichloroethane, ethyl acetate, ethanol, trichloroethylene, dichloroethylene, MIBK, toluene, p-dioxane, and benzene. With the exception of benzene, these particular VOCs were chosen based on the preliminary analyses which indicated that these substances were present in the highest concentrations. Benzene was quantitated because previous air sampling data collected by Ebtec using 3M passive organic vapor monitors had indicated benzene TWA concentrations of 0.35 and 0.92 ppm during laser cutting operations performed on the Kevlar-graphite composite material. Similar results were obtained for all three air samples. No benzene or dichloroethylene were detected on any of the air samples; the LOD for benzene and dichloroethylene were approximately 0.08 and 0.05 ppm, respectively. The remaining VOCs were present in very low or trace levels, with all concentrations less than 3% of the most protective evaluation criteria established by NIOSH and OSHA.

The aldehyde screening sample indicated the presence of formaldehyde and acetaldehyde, however, the concentrations of these aldehydes in the area air sample obtained in the laser booth and the personal sample obtained on the laser technician were below the limit of detection (<0.06 ppm).

The TEM analysis of the Kevlar bulk revealed curved, wispy fibers and bundles of fibers of varying diameters. The largest fiber was about 2.5 um thick while individual fibers and those at the end of the bundle ranged to well under 0.1 um thick. The air sample obtained within a few feet of the laser contained yellow particulate material that was largely devoid of fibers. Those few that were present were all in the 0.15 to 0.25 um diameter range and less than 10 um in length. Although evaluation criteria have not been established for Kevlar fibers by NIOSH, OSHA, or ACGIH, the DuPont Company (the U.S. manufacturer of these fibers) has established an acceptable exposure limit of five respirable fibrils per cubic centimeter of air as an 8-hour TWA.[6]

ANSI Z136.1 specifies the 8-hour maximum permissible exposure (MPE) for CO_2 lasers as 100 mW/cm^2. Using equations derived in the ANSI standard one can calculate the space within which the level of direct, reflected, or scattered radiation exceeds the MPE for that laser. This space is designated the nominal hazard zone (NHZ). The NHZ perimeter is the envelope of MPE exposure level produced by a specific laser in a given application. The space within the NHZ usually requires control measures, such as laser eye-protectors, ventilation, and restricted access. Using the laser operating parameters, it was determined that the NHZ was less than two feet. Since the laser was installed inside an 8' X 10' area then the MHZ was not exceeded.

VI. CONCLUSIONS AND RECOMMENDATIONS

The environmental data collected during this survey indicates the presence of low levels of several VOCs including aliphatic, aromatic, and chlorinated hydrocarbons, alcohols, and aldehydes in air samples taken both inside and outside the laser booth. These low levels are not considered a health hazard for employees working in these area. Based on the types of substances seen and their presence in other areas of the plant, it appears that these VOCs are being volatilized from solvents used in the plant rather than being evolved from the laser cutting operation. The MSDS for Synasol lists the following ingredients: ethanol, methanol, ethyl acetate, aliphatic hydrocarbons, MIBK, and acetaldehyde, all of which were present in air samples taken inside and outside of the laser booth. Although VOCs such as 1,1,1-trichloroethane and trichloroethylene were also found in low levels on these air samples, these substances are commonly found in air samples as a result of their use in many cleaning and degreasing products, and would not be expected to be generated during the laser cutting operation.

Gases such as CO and NO_x were detected inside the booth during the laser cutting operation. The concentration of CO measured in the morning was 30 to 35 ppm, approaching the NIOSH REL for CO of 35 ppm as an 8-hour TWA. Exposure to carbon monoxide can result in symptoms of headache, nausea, weakness, and dizziness by preventing blood from carrying sufficient oxygen. Nitrogen oxides are respiratory irritants. Exposure to NO_2 at 25 ppm has resulted in eye, nose, throat, and respiratory irritation and chest pain.

Generation of Kevlar fibers from the laser cutting process does not appear to be a concern, as an air sample obtained a few feet from the laser was largely devoid of fibers. While a yellowish particulate material was collected on the filter, efforts to identify the components by high pressure liquid chromatography (following a chloroform extraction of the filter sample) were not successful.

Based on the data obtained and observations made during this survey, the following recommendations are offered. These recommendations are made in an effort to improve environmental conditions in the laser cutting area and to minimize health complaints of eye and skin irritation experienced by laser technicians.

1. The most serious problem was the wearing of Nd-YAG laser eye protection designed for Nd-YAG lasers rather than CO_2 lasers. Unless the eye protectors are rated and state their optical density values for both CO_2 and Nd-YAG, then it is inappropriate to wear laser eye protectors not designed or labelled for the given laser.

2. The lack of interlocks or warning signs on the entrance way leading to the laser area in both directions should be addressed immediately in order to conform to the ANSI Z136.1 standard.

3. A more permanent enclosure should be constructed for the laser cutting operation. The plastic enclosure which is currently being used has some tears and is heavily soiled. An enclosure which can be cleaned more easily is recommended. In addition, air pressure differential should be maintained in the booth so that air flows into the booth from the surrounding areas. Flexible laser barriers that would serve as an appropriate control measure are currently available on the market.

4. Although the local exhaust ventilation system appears to do an adequate job in capturing emissions generated in the middle of the workpiece, the exhaust is least effective on the edges where emissions were observed to be escaping from the workpiece. Efforts should be made to improve the ventilation system so that emissions are more effectively captured at the source. The use of a partial enclosure around the laser system may help contain emissions.

5. While this survey did not document worker overexposures to organic vapors or particulates that would require respiratory protection, workers may continue to utilize respiratory protection, if desired, to minimize symptoms of irritation. The use of respiratory protection should only be considered as a temporary measure, however, until engineering controls are improved.

   Whenever respiratory protection is offered to employees, a respirator program consistent with the requirements of the OSHA Respiratory Protection Standard, 29 CFR 1910.134 must be implemented.

6. Periodic monitoring for carbon monoxide and oxides of nitrogen is recommended. Exposure monitoring should also be conducted if different materials are used (such as the Kevlar-graphite composite) or if process changes are made which could affect employee exposures.

7. The presence of the encoder on the floor by the entrance to the laser booth presents a safety hazard and should be moved.

8. Material Safety Data Sheets (MSDSs) for all new products used at this facility should be obtained at the time of purchase, or preferably, before purchase to evaluate potential hazards associated with their use.

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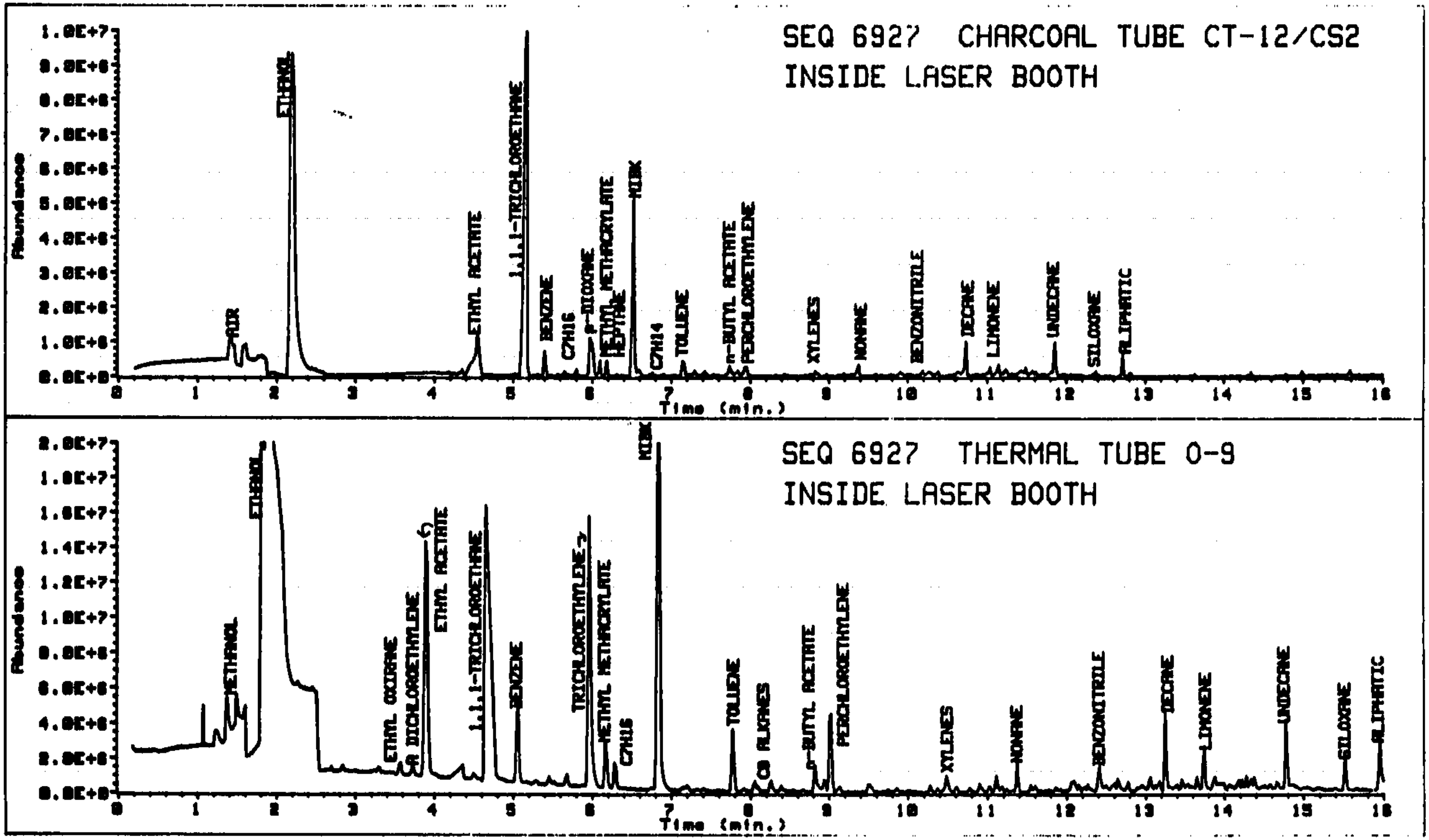

Figure 1-- Gas chromatograms for air samples obtained in the laser booth.

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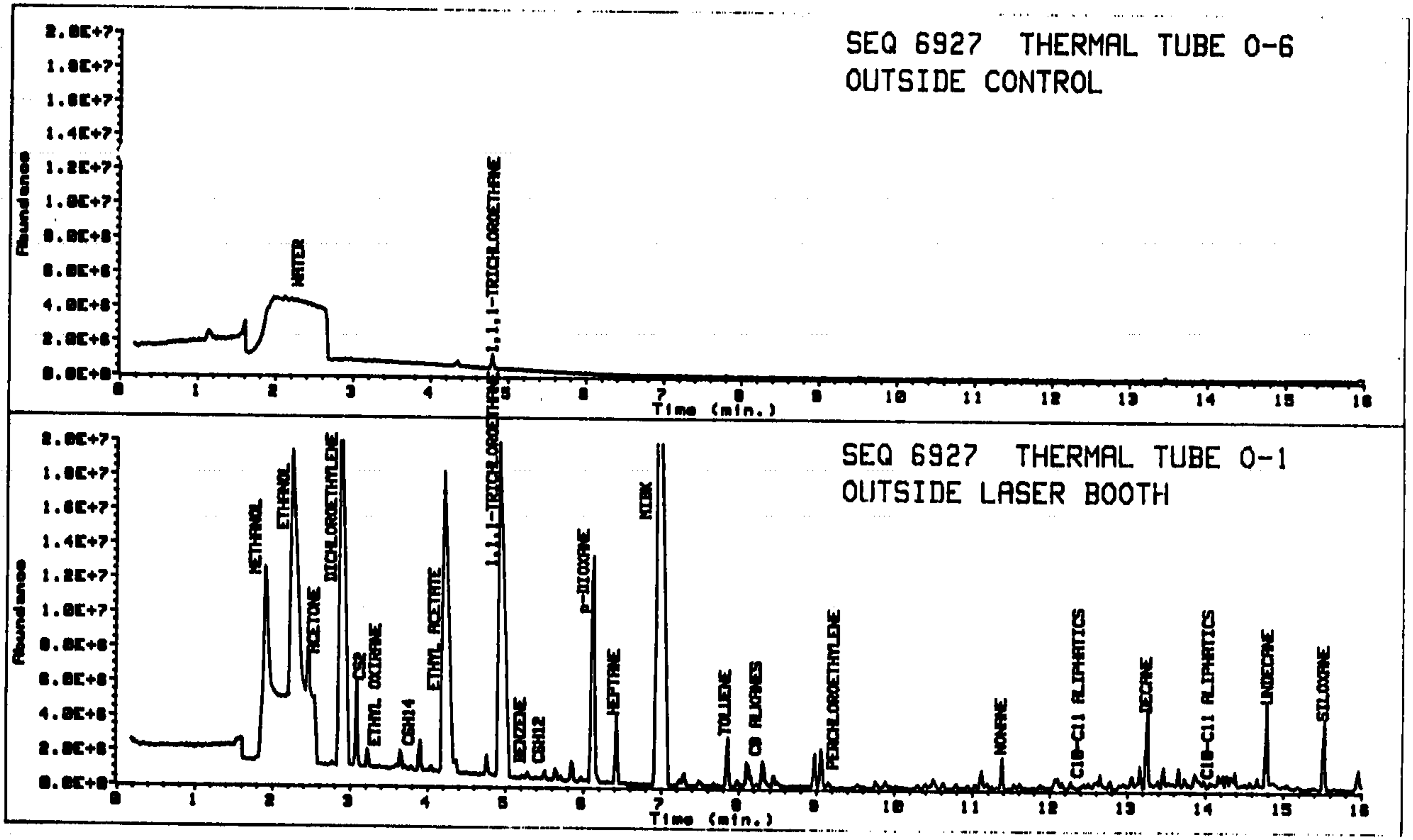
SEQ 6927 THERMAL TUBE O-6
OUTSIDE CONTROL

SEQ 6927 THERMAL TUBE O-1
OUTSIDE LASER BOOTH

Figure 2-- Gas chromatograms for air samples obtained outdoors and outside the laser booth.