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Laser generated air contaminants released during laser cutting of fabrics and polymers

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Environmental monitoring was conducted at an industrial facility to qualitatively identify the major contaminants generated while cutting fabrics and polymers with a 25 W CO_2 continuous beam laser. Carbon monoxide, hydrogen cyanide, and particulates were also assessed, and a bulk sample of residue from the laser exhaust duct was analyzed for inorganic acids, pH, and volatile organic compounds. Samples were collected while cutting vinyl, acrylics, woven fabrics, felt, Formica®, and Plexiglass®. The laser parameters were standardized to allow for meaningful comparison of results for each target material. The volatile organic compound samples were collected in multibed sorbent tubes with subsequent analysis via thermal desorption and gas chromatography/mass spectroscopy. Depending on the material being cut, a wide variety of compounds were detected. The highest relative concentrations of volatile compounds were found during laser cutting of felt fabrics. The lowest concentrations and fewest number of compounds were from woven fabrics. The compounds detected included hydrochloric acid, aldehydes, benzene, vinyl chloride, various acrylates, acrylonitrile, acetonitrile, styrene, furans, phenol, and butyl cellosolve. Methyl methacrylate was a significant peak detected during the laser cutting of acrylic ester polymers, Plexiglass, and polyvinyl chloride with adhesive backing. Carbon monoxide was not detected above background (2 ppm) during any of the laser cutting trials. Hydrogen cyanide was detected during the laser cutting of felt (15 ppm) and Formica® (8–10 ppm). Particles $\geqslant 0.3\,\mu m$ in diameter (μmd) generated during the laser cutting exceeded background particle levels by a factor of ten or more. Most compounds detected in the thermal desorption air samples were also detected in the bulk sample, and the residue was acidic (pH = 3). Area samples collected outside the laser enclosure suggested the local exhaust ventilation system sufficiently contained the air contaminants.

KEYWORDS: laser generated air contaminants (LGACs); laser safety; ventilation.

INTRODUCTION

As the laser industry continues to expand and mature, laser users are exposed to both laser beam and related (non-beam) hazards at what appears to be an increasing rate. One non-beam exposure area receiving much attention is occupational exposure to laser generated air contaminants (LGACs). Recently, the National Institute for Occupational Safety and Health (NIOSH) conducted an evaluation at a southeastern United States industrial facility that used 25 W carbon dioxide (CO_2) lasers to cut different fabrics and polymers. Workers at the facility had complained about the presence of objectional odors, visible smoke plume, and propagation of LGACs during the laser cutting processes. While no particular health complaints were cited, the concern about worker exposure to LGACs prompted NIOSH to perform a study at the facility.

BACKGROUND

During the intense interaction of laser energy with a target, a complex mixture of LGACs can be formed. The quantity and composition of the LGACs will greatly vary depending on the beam irradiance (power per area) and material undergoing the lasing action [1, 2]. Although research on the products of polymer pyrolysis has been conducted, with some exceptions (polyvinyl chloride) this data may not be applicable to the products generated when materials are irradiated with high power laser energy [2–4]. Research efforts to identify hazardous materials generated during specific laser operations has also been conducted, although information concerning LGAC formation is much less complete [5, 6]. Data regarding the compounds generated during the laser processing of specific materials under known operational parameters has been developed for some specific materials [6, 7]. However,

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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 reaches a given threshold, beginning at about 10^7 W cm^{-2} [1]. This level 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, carbon monoxide, hydrogen cyanide, etc.), and a particulate component (fumes, dust, re-condensation products) [2]. 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, Z136.1-1993.1 [1]. 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.

The laser used to cut fabrics and polymers at the facility studied was a Zeus Z-100 laser cutter developed for use in the textile industry. The laser used in the cutter was a Class IV 25 W sealed CO_2 operating in a continuous mode. All necessary paperwork has been filed with the Food and Drug Administration, Center for Devices and Radiological Health (FDA-CDRH) to classify the units as Class 1 laser systems (enclosed beam, keyswitch, emergency stop, interlocks, etc.). The laser was mounted vertically behind secured panels on the side of the system. Upon activation, the beam traveled upward and diverted horizontally onto a deflecting mirror on the movable laser head. The mirror then re-directed the focused and collimated beam down onto the fabric. The head moves the laser cutter in a horizontal direction across a one meter length cutting area. Very intricate patterns can be cut with this microprocessor-controlled system, as the software provides considerable versatility in graphics and lettering design. The cutting area can accommodate individual pieces of fabric or polymer (e.g., vinyl, glass, wood, other plastics, etc.), or rolls of fabrics. The cutting area was shielded by an interlocked tinted plastic enclosure to prevent beam access.

During the development of the laser system, it was observed that cutting events generated visible and occasionally irritating LGACs. Additionally, increased levels of noxious contaminants were liberated when the laser cut certain adhesive backings and materials. During the commercial marketing/development phase of the laser system, management became concerned about potential exposure to LGACs. In addition to the product safety concerns, the increased use of the lasers to cut fabrics and polymers during research and development resulted in a number of complaints from both employees and occupants in an adjacent business. Due to these complaints, a local exhaust ventilation (LEV) system to control emissions was installed at the facility where the laser was undergoing testing and development. NIOSH was asked to conduct an evaluation to characterize the composition of the LGACs, assess the potential for exposure, and review the LEV system. This LEV system consisted of a 2.5 cm diameter copper tube and flexible duct connected to an industrial vacuum cleaner. In an attempt to further control LGACs, management added a commercially available gas and vapor adsorbent (Purafil®) to the vacuum. A booster fan and ductwork were connected to the vacuum exhaust to vent emissions outside after filtration. The 2.5 cm exhaust inlet was connected to the movable laser head to scavenge contaminants at the point of generation. Observations indicated the ventilation was effectively capturing the generated contaminants. Problems occurred, however, as the vacuum clogged rapidly (1–2 h), probably due to re-condensed volatilized material. The re-condensed material had also caused the copper tube to corrode with time. Finally, during cutting of large sections of fabric, because of the speed of the laser head in moving to a new location, the area previously cut could still emit contaminants since they were not completely captured by the ventilation system. The cutting area enclosure, however, appeared to contain these fugitive emissions, and continued operation of the ventilation system for a short period after cutting seemed to provide sufficient control.

METHODS AND MEASUREMENTS

During the survey, specific laser operating parameters were reviewed, and environmental monitoring was conducted to qualitatively identify major contaminants generated during the cutting of different fabrics and polymers. Instantaneous samples for carbon monoxide (CO), hydrogen cyanide (HCN), and particulates were also collected using direct reading instrumentation, and a bulk sample of residue from the laser exhaust duct was obtained for analysis.

During the monitoring, the laser parameters were standardized as much as possible to allow for the comparison of results for each cut material. The same laser cutting pattern was used for each material, and the cutting time was fixed at 1 min for each trial. The cut speed varied from 2–60% of the maximum cutting speed (61 cm s^{-1}). This varied because different materials require different cut times, and some trials included deeper cuts into the adhesive backing while others did not. The laser output was measured with a SynRad Power Wizard 250® and found to be 25.9 W. When the smallest beam diameter was used, the irradiance was approximately 2×10^6 W cm^{-2}.

Qualitative air and bulk sampling

Qualitative air monitoring was conducted to characterize volatile organic compounds (VOCs) and help determine if emissions generated during the laser cutting process warrant further evaluation. Area air samples were obtained utilizing reusable thermal desorption (TD) tubes configured for the Perkin-Elmer ATD 400 thermal desorption system as the collection media. Each stainless steel TD tube contained three beds of Supelco sorbent materials, a front layer of Carbopack Y ($\approx$90 mg), a middle layer of Carbopack B ($\approx$115 mg), and a back section of Carboxen 1003 ($\approx$150 mg). Prior to field use, each tube was cleaned by conditioning at 375 °C for 2 h. 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).

The samples were collected using constant-volume SKC model 222 low-flow sampling pumps set at flow rates of 20–100 cc min^{-1}. The pumps were equipped with a pump stroke counter and the number of strokes necessary to pull a known volume of air was determined. This information was used to calculate the pump's volume of air per pump-stroke K factor. The pump-stroke count was recorded before and after sampling and the difference used to calculate the total volume of air sampled.

At the laboratory, the samples were analyzed using the ATD 400 automatic thermal desorption system containing an internal focusing trap packed with Carbopack/Carboxen 1000 sorbents. The thermal unit was interfaced directly to an HP5890A gas chromatograph and HP5970 mass selective detector. The mass spectrometer was operated in full scan mode (20–300 amu). A 30 m DB-1 fused silica capillary column was used for the analyses. Each sample was analyzed separately by directly inserting the tube into the ATD thermal desorber unit with no other sample preparation. A desorption time of 10 min at 300 °C was used. The reconstructed total ion chromatogram for each sample was scaled to the same extent to enable comparisons. Each peak in the chromatogram was identified by the use of Wiley® and the National Institute of Standards and Technology (NIST) mass spectral libraries.

The bulk sample of dry residue from the exhaust port was analyzed to compare compounds detected in the air samples with those found in the bulk sample. The sample was analyzed for inorganic acids and pH, as well as by GC/MS. After weighing the sample, 2.0 ml of deionized water was added and the sample sonicated for 10 min. The mixture was then filtered and measured with a pH meter. An aliquot was injected into a Dionex series 4500 ion chromatograph equipped with an AS4A anion separator column, an anion micro-membrane suppressor, and a conductivity detector. Analyses were conducted in accordance with NIOSH methods 7903 (inorganic acids) and 2011 (formic acids). For the GC/MS analysis, a 1 mg portion of the residue was placed in a glass tube configured for the ATD. Pre-cleaned glass wool plugs were placed at both ends, and the sample heated at 200 °C for 10 min prior to the analysis.

After first collecting a background sample to check humidity, short-term (1–2 min) samples from each material being cut were obtained by sampling within the enclosure during the cut. Samples were collected from the same location inside the enclosure during each trial. The laser exhaust system was throttled down during cutting to ensure sufficient LGACs for sample collection were present inside the enclosure. Reducing the exhaust ventilation is not normally done during routine laser operation and represents 'worst-case' conditions for the purpose of this evaluation. The exhaust was then turned up and the enclosure cleared prior to the next laser cut. One sample was collected with the ventilation system fully operational to help assess the effectiveness of the exhaust. A control, or background, area sample was collected at the front of the facility prior to any laser cutting. Two area samples were also collected at a height of about 1.5 m directly in front of the laser and outside the enclosure during the cutting operations.

Carbon monoxide

A calibrated Metrosonics PM-7700® toxic gas monitor with an electrochemical carbon monoxide (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. After first collecting background samples, readings were obtained outside the cutting area enclosure, directly in front of the laser system. Instrument sensor repeatability was $15 \pm 2\%$ between -5 and -40 °C and the sensitivity is 0.5 ppm.

Particle monitoring

The particle monitor used by NIOSH in this evaluation was a factory-calibrated Met One, Inc. Model 227B® hand-held laser particle counter. This unit is capable of simultaneously monitoring two particle size ranges, and was set to monitor all particles $\geqslant 0.3$ umd and those $\geqslant 1.0$ μmd. The instrument was set to continuously monitor particles on a 1 min cycle time period. A primary standard was used to determine the monitor's flow rate ($2.83 \times 10^{-3}\ \mathrm{m}^3\,\mathrm{min}^{-1}$), and the total number of particles $\geqslant 0.3$ umd and those $\geqslant 1.0$ umd measured in each cycle were determined.

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. Samples were collected within the enclosure where the LGAC plume was produced.

RESULTS

Qualitative air sampling

Eighteen thermal desorption tube air samples were collected during the laser cutting of poly vinyl chloride, acrylics, woven fabrics, felt, Formica®, Plexiglass®, and some of these materials had adhesive backings. Appendix A provides additional structural information regarding these materials. Figures 1–4 are the reconstructed total ion chromatograms from these analyses. All the chromatograms are scaled to the same extent to enable comparisons. Table 1 lists the identification of selected peaks found on the chromatogram. These results do not provide quantitative information concerning the compounds detected other than on a relative comparison basis.

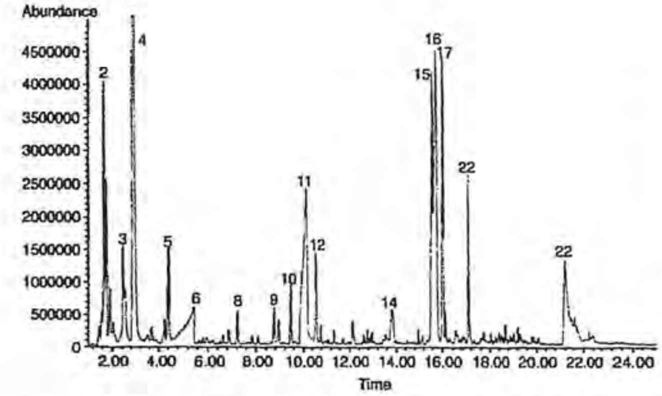

FIGURE 1. Selected chromatogram showing LGACs produced during cutting of felt.

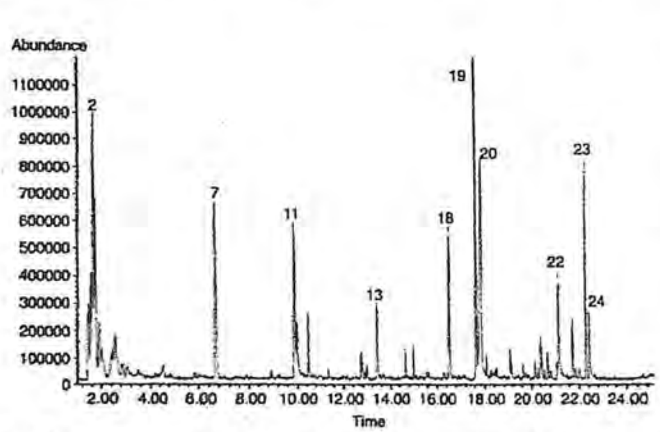

FIGURE 2. Selected chromatogram showing LGACs produced during cutting of woven fabric.

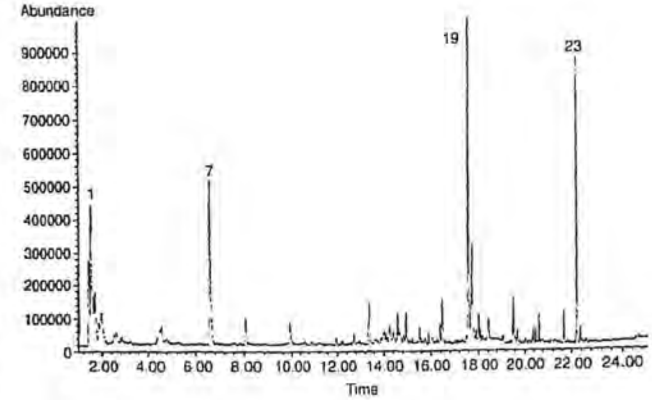

FIGURE 3. LGACs produced when cutting woven fabric with backing and no ventilation controls applied.

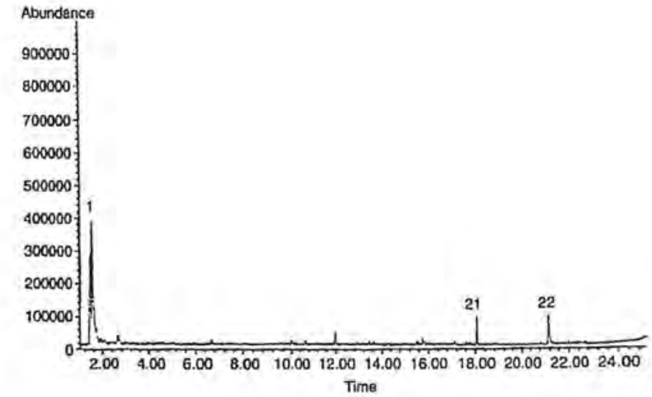

FIGURE 4. LGACs produced when cutting woven fabric with backing and full ventilation controls applied.

Depending on the material being cut, a wide variety of compounds were detected. The highest relative concentrations of volatile compounds were found on the felt fabric. The lowest concentrations and fewest number of compounds were from the woven fabrics. Table 2 lists the total number of compounds detected and the identification of the ten largest peaks for each material tested. Compounds detected included hydrochloric acid (HCl), HCN, formaldehyde, acetaldehyde, acrolein, nitrogen-containing compounds, benzene, vinyl chloride, acetic acid, methyl methacrylate, ethyl acrylate, methyl acrylate, benzoic acid, acrylonitrile, acetonitrile, formic acid, styrene, furans, benzaldehyde, phenol, and butyl cellosolve. If concentrations are high enough, exposure to many of these compounds can result in adverse health effects [8, 9]. Some of these compounds are considered primary irritants (e.g., HCl, sensitizers and pulmonary irritants (e.g., formaldehyde, acrolein), central nervous system depressants (e.g., styrene), and carcinogens (e.g., benzene) [10, 11]. Note that these results are not indicative of exposure, as the

TABLE 1. Identification of selected GC/MS peaks noted on Figs 1–4

(1)	CO_2
(2)	Formaldehyde
(3)	Acetonitrile
(4)	Acrylonitrile
(5)	Methyl propene nitrile
(6)	Acetic acid
(7)	Benzene
(8)	Methylene butane nitrile
(9)	Pentadienenitrile
(10)	Butenedinitrile
(11)	Cyanomethanol
(12)	Cyanomethyl acetate
(13)	Styrene
(14)	Butanedinitrile
(15)	Aliphatic, nitrogen compound
(16)	Acrylonitrile dimer (methylene glutaronitrile)
(17)	Nitrogen-containing compound
(18)	Acetophenone
(19)	1-Phenyl-1,2-propanedione
(20)	Benzoic acid
(21)	Siloxane compound (system contaminant)
(22)	Acrylonitrile oligomer
(23)	Nitrogen containing compound
(24)	Phthalic acid ester

samples were collected directly from the laser generated plume or from within the enclosure. Furthermore they were collected under 'worst-case' conditions. However, the results do explain the noticeable irritating odors that occurred prior to installing the ventilation, and confirm the need for proper exhaust ventilation to control emissions.

Figures 3 and 4 show the results obtained during the cutting of the same material (woven fabric), with and without ventilation controls (extraction). Figure 4 clearly shows that the number and magnitude of the compounds detected were significantly less when ventilation controls were operational. Figure 4 shows the importance of using a properly operating ventilation system as a means to effectively control LGACs.

Two samples were collected outside the laser enclosure in front of the laser system and were compared with the results of the control sample, which was collected prior to using the laser. These results indicate that, with one exception, there were no substantive differences in the compounds detected or relative concentrations between the control sample and the samples collected in front of the laser during cutting operations. This suggests that the VOCs detected in these samples are from sources other than the laser cutting process. Other potential sources of VOCs may include fabrics, office supplies (e.g., correction fluid), caulk, paint, copying machines, etc. The one exception noted was methyl methacrylate, which was detected outside the enclosure. Methyl methacrylate was a significant peak detected on samples obtained during the laser cutting of the sheet of acrylic, Plexiglass®, and poly (vinyl chloride) with an adhesive backing. It is likely that during the trials with these materials, insufficient clearance time was allowed prior to opening the enclosure after a cut, resulting in LGAC escaping into the workroom, or during the throttling of the exhaust system. Both acrylic ester polymers and Plexiglass® are thermoplastics that contain methacrylate acrylate monomers [12, 13]. The detection of methacrylate monomer on the poly (vinyl chloride) was an unexpected

TABLE 2. Material testing summary: total compounds detected and ten largest peaks

Material	Number of compounds detected	Identification of the ten largest peaks
Felt	40	formaldehyde, hydrogen cyanide, acetonitrile, acrolein, acrylonitrile, formic acid, methyl propene nitrile, cyanomethanol, cyanomethyl acetate, nitrile oligomer
[a]Woven fabric	34	formaldehyde, hydrogen cyanide, benzene, cyanomethanol, acetophenone, 1-phenyl-1,2-propanedione, benzoic acid, nitrile oligomer, phthalic acid esters, styrene
[a]Woven fabric	26	carbon dioxide, formaldehyde, cyclopropene, vinyl chloride, benzene, 1-phenyl-1,2-propanedione, benzoic acid, phthalic anhydride, butyl acrylate, acetic acid
Formica®	25	formaldehyde, hydrogen cyanide, methanol, cyanomethanol, cyanomethyl acetate, acetonitrile, acrolein, 2-methyl furan, furfural, furan
[a]Poly (vinyl chloride)	39	benzene, methyl methacrylate, nitrile oligomer, methylheptyl acrylate, styrene, naphthalene, hydrochloride acid, vinyl chloride, acetic acid, indene
Plexiglass®	28	methyl butadiene, methyl acrylate, methyl methacrylate, limonene, phthalic acid ester, carboxylic acid methyl esters, methanol, formaldehyde, ethyl acrylate, acrolein
Acrylic	27	methyl methacrylate, methanol, carboxylic acid, methyl esters, phthalic acid esters, styrene, methyl butadiene, chloromethane, formaldehyde, acrolein, limonene

[a] = material had an adhesive backing

finding; the source may have been the adhesive backing and not the polymer.

Carbon monoxide and hydrogen cyanide particulate monitoring

The results of the monitoring conducted with direct reading nstrumentation (CO, HCN, particulates) are listed in Table 3. CO was not detected above background (2 ppm) during any of the laser cutting trials. One possible explanation for the absence of CO is that the intense heat of the laser and readily available oxygen does not lend itself to CO generation. HCN was detected during the laser cutting of felt (15 ppm) and Formica® (8–10 ppm), and trace amounts (2 ppm) were found on the sample obtained during the cutting of one of the woven fabrics. These results correlate with the results of the hermal desorption tube monitoring. Both felt and Formica® ontain nitrogen compounds.

n general, concentrations of particles ⩾0.3 μmd generated uring the laser cutting exceeded background particle levels y a factor of ten or more. Note that the particle samples ere collected immediately after and not during the laser utting. The specific chemical constituents of these particles not determined by this monitoring technique.

ulk sample results

Most of the compounds detected in the thermal desorption air amples were also detected in the bulk sample. Acetate, ormate, chloride, and sulfate anions were found in the mple. The sample solution, however, was acidic with a pH of 3, suggesting that the material is corrosive. GC/MS analysis of the residue, after heating at 200 °C for 10 min, shows the presence of hydrochloric, formic, and acetic acids. The presence of these acids explains the corrosive nature of this residue.

DISCUSSION AND CONCLUSIONS

A wide variety of LGAC's are produced during the cutting of various fabrics and polymers with the laser system. The composition of the LGACs is complex and significantly varies depending on the material being cut, irradiance, and time of cut. Many of these compounds can have toxic and irritating effects if exposure concentrations are high enough. The monitoring indicated that the exhaust ventilation contained the LGACs within the enclosure. However, modifications to the ventilation system design would enhance the performance of the exhaust and improve the control of LGACs. One suggested design is to install a top mounted slot-type hood which could be fixed behind the laser head track. The slot should extend the width of the cutting area to ensure adequate coverage. A centrifugal exhaust fan designed for industrial ventilation systems should be used, and the system should be vented outside and above the roofline. The hood and ductwork should be constructed of corrosion-resistance material (e.g., PVC, coated aluminum, etc.). The effectiveness of the adsorbent is questionable and may not be necessary. As these laser units are commercially sold, manufacturers must inform 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.

TABLE 3. Carbon monoxide, hydrogen cyanide, particulate monitoring results

Material	Cut speed (%)	HCN (ppm)	CO (ppm)	Particles ⩾0.3 μmd
Felt	15	15	2	1100
Woven fabric with backing	27 (Kiss cut)	<2	2	1795
Woven fabric with backing	8 (Deep cut)	<2	2	1368
Woven fabric with backing	27 (Kiss cut)	<2	2	1702
Woven fabric with backing	8 (Deep cut)	<2	2	1766
[a]Woven fabric with backing	27 (Kiss cut) extraction on	<2	2	287
Woven fabric, no backing	12	2	2	1000
Formica®	8 (Deep cut)	8–10	2	1358
Plastic	10	<2	2	2248
Vinyl with backing	60	<2	<2	3307
0.32 cm Acrylic	2 (Deep cut)	<2	1–2	1812
Plexiglass®	2 (Deep cut)	<2	1–2	1596

Kiss cut refers to laser cutting sufficient to penetrate the material but not protective or adhesive backing.
[a]Sample was taken from inside the laser enclosure with the ventilation extraction system fully operational.
Background concentrations (prior to any laser cutting):
CO = 2–3 ppm
HCN = <2 ppm
Particles ⩾0.3 μmd = 88–137

It is noted that the findings in this evaluation are consistent with previous results that show that when the target irradiance exceeds $10^7\ \mathrm{W\,cm^{-2}}$, the LGACs liberated are toxic, noxious, and pose occupational concern. Moreover, the amount of LGAC may be greater for lasers that have most of their energy absorbed at the surface of the material, as in this evaluation. In general, there are three major control measures available to reduce the LGAC concentrations to acceptable levels: exhaust ventilation, respiratory protection, and process isolation. The reader is advised to refer to basic industrial hygiene references for further information on which control measure is advisable.

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APPENDIX A

Descriptive information: materials evaluated

Poly (vinyl chloride): A flexible and elastic polymer that has widespread use because of a high degree of chemical resistance and ability to be mixed with additives. Poly (vinyl chloride) is produced by the free-radical polymerization of vinyl chloride. Vinyl chloride is often copolymerized with a wide variety of monomers, and poly (vinyl chloride) is always mixed with other ingredients before processing. Other ingredients may include thermal stabilizers, lubricants, plasticizers, initiators, and suspending agents.

Felt: A homogeneous fibrous structure of interlocking fibers of wool or combined wool and synthetic fibers. Felts may be combined with resins or chemicals.

Formica^{TM}: High pressure laminated sheets of melamine (formaldehyde and malanine resin) and phenolic plastics.

Acrylic: An acrylic ester polymer represented by the generic formula $CH_2{=}CHC(O)OR$. The nature of the R group determines the specific properties and formula. These are thermoplastic polymers or copolymers of acrylic acid, acrylonitrile, or esters. Typical acrylic ester monomers are methyl acrylate, ethyl acrylate, and other acrylates.

Plexiglass^{TM}: Thermoplastic poly (methyl methacrylate)-type polymers.