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13. Type of Report & Period Covered

14.

15. Supplementary Notes

16. Abstract (Limit: 200 words) This study was undertaken to define the nature and magnitude of laser material processing uses and to examine the potential respirable hazards that might be released as part of the interaction plume from some of the more commonly used industrial materials. A workforce of greater than 14,000 people were to some extent using lasers on a daily basis for material processing applications on over 70 different materials. Lasers were used in the areas of drilling or welding of metals, ceramics, plastics, and diamonds. They were used for material cutting and scribing on natural and synthetic fabrics, paper, metals, and plastics. They were used in electronic component controlled fracturing of crystals and glass and material heating of metals, chemicals, and other substances. Eighteen laser beam related accidents that were related to ocular and skin hazards were reported. A general synopsis of current laser safety practices at industrial laser installations was also included. Laboratory experiments confirmed that hazardous gases can be produced in carbon-dioxide (124389) cutting of plastics. In addition, respirable particulates were released in sufficient quantities in ruby laser drilling of metals to constitute a hazard. The authors conclude that proper ventilation of laser material processing systems is essential.

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OCCUPATIONAL HAZARDS OF  
LASER MATERIAL PROCESSING

FINAL REPORT

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MAY 21, 1976

FINAL PROGRESS REPORT

- I. RESEARCH GRANT NUMBER: R01 OH 00371
  1. TITLE: OCCUPATIONAL HAZARDS OF LASER MATERIAL PROCESSING
  2. NAME OF PRINCIPAL INVESTIGATOR: R. JAMES ROCKWELL, JR.
  3. NAME OF SPONSORING INSTITUTION: COLLEGE OF MEDICINE OF THE  
UNIVERSITY OF CINCINNATI
  4. PERIOD COVERED BY THE REPORT: OCTOBER 1, 1972 - JANUARY 31, 1975
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The survey conducted at the onset of this study established that a workforce of greater than 14,000 people are, to some extent, using lasers on a daily basis for material processing applications on over seventy different materials. The principal laser types used are the carbon-dioxide, YAG, ruby, and argon. These and other laser types are being used in the areas of drilling and welding (metals, ceramics, plastics, diamonds, etc.), material cutting and scribing (plastics, natural and synthetic fabrics, paper, metals, etc.), electronic component controlled fracturing (ceramics, crystals, glass, etc.), and material heating (metals, chemicals, etc.). These systems are most often used in specially equipped locations of R&D or main production facilities where the workers are not necessarily "laser" experts, but are rather, "process" experts.

The survey also identified 18 laser beam-related accidents relating to ocular and skin hazards as well as a general synopsis of current laser safety practices at industrial laser installations.

The laboratory experiments confirmed that hazardous gasses can be produced in carbon-dioxide cutting of plastics. In addition, respirable particulates are released in sufficient quantities in ruby laser drilling of metals to constitute a hazard.

Proper ventilation of laser material processing systems is, therefore, required in these applications.

... .. This segment of the laser industry has experienced a typical growth of 15 percent per year over the last decade, and the projections for future years indicate increased activity for all forms of industrial laser processing activity. This projected growth can only reinforce the original premise of this research program, that significant numbers of employees are now or will soon be involved, on a daily basis, in various material processing activities using laser-type devices.

The principal goal of this study was to examine the potential occupational hazards of the by-products released in laser material processing applications. The hypothesis was that the laser material reaction can release potentially hazardous particulate and/or gaseous matter from the material being irradiated. However, since the temperatures generated by the interaction can be extremely high, the nature of the by-products produced may not, in general, be the same as the by-products released in the more classical material processing methods. In some cases, as will be discussed later, the laser-induced by-products released can be potentially lethal. This should not imply that laser material processing methods should be abandoned and force a return to the more costly and time-consuming material processing methods previously used.

In all cases examined in this study, even though some of the by-products released were potentially hazardous, proven techniques are available to eliminate the hazard from the working environment by standard ventilation and filtration systems. It is hoped that the fact that this study did confirm that the released by-products may be lethal may persuade the casual laser material processing user (who often performs experiments in a nonenclosed environment) to observe the more correct practice of enclosed systems. It should be further emphasized that, prior to this study, there was no quantitative data about the possibly hazardous nature of the by-products released by the laser process.

The principal goals of this study, as delineated in the original proposal, were:

1. To define the scope of the hazards with a survey of existing laser systems used in industry for material processing.
2. To examine the specific hazards in controlled tests which allow for precise measurement and quantitation of the particulate and gaseous by-products produced in the material removal process.
3. To recommend a complete program for laser safety in areas of material processing.

The principal overview of the proposal was to determine the nature and scope of current laser material processing applications via the vehicle of the industrial survey and then, using the results obtained from the survey relating to the specific industrial uses identified in the survey, to conduct laboratory tests to define the nature of the by-products released in the laser radiation, material interaction. Finally, using existing safety standards as a guide, and the results of the laboratory tests and "safety practices" portion of the survey, to recommend a complete program of safety for use by workers in the material processing areas.

One method used to estimate the total number of workers involved was to determine the total number of laser systems which have been sold to industry, as projected by a known and respected source of such marketing data. One such forum for marketing data is the trade journal, Laser Focus. In the January issue each year, this journal provides a market projection in each of the major laser application areas, including material processing. These projections are summarized in Table 1 below for the past eight years.

TABLE I  
EIGHT-YEAR REVIEW OF SALES PROJECTIONS  
FOR INDUSTRIAL LASER APPLICATIONS\*

(In millions of dollars)

CATEGORY	YEAR	1969	1970	1971	1972	1973	1974	1975	1976
Total Sales - For all lasers and associated systems		120	138	161	188	225	266	308	370
Total dollar volume for material processing systems		24.5	30	27	31.5	32	21	27	28.9

\*Laser Focus Magazine, January, 1970-76 inclusive.

One can estimate, using this data, that the total sales during the past eight-year period (which includes most of the total sales in laser material processing) has been 222 million dollars. Using a value of \$50,000 as the average cost of material processing systems over this period (estimate provided by Mr. Jeffrey Hecht, Laser Focus Magazine), this yields a total of 4,400 laser material processing systems which have been installed over the past eight-year period.

This can be used to give a first-order estimate of the total number of workers involved presently in laser material processing applications. The survey conducted as part of this study identified 1,839 workers (full-time and part-time) working with 524 material processing lasers. This yields an average of 3.5 workers per laser system involved in material processing uses. Thus, the total number of full-time and part-time workers involved with material processing systems on a daily basis may be projected as 15,400.

2. The types of applications, especially the types of materials involved.
3. The types and operating characteristics of the lasers used in material processing.
4. An estimate of the usage of the systems.
5. Some projection for increased or decreased use.
6. General laser safety practices.

To achieve some meaningful statistical basis for the survey, two different mailing lists were employed. The first was approximately 2,300 individuals, selected from a list of over 12,000 which is used for the mailings for the "Laser Safety Short Course," held semi-annually at the University of Cincinnati. This list was developed over the past eight years, and is considered as a highly responsive mailing list for those interested in lasers and laser safety. The second list was obtained from Laser Sphere Journal. This list contains over 4,000 names considered by publisher William Bushor as, "The most responsive industrial group" of the more than 19,000 names used by the publication. Neither list specifically addresses itself to a "laser material processing" audience, but rather to a general laser user audience.

Upon return of the questionnaires, the results were coded for an existing statistical analysis computer program used regularly at the Computer Center of the University of Cincinnati Medical Center.

The results which correspond to the six principal goals as previously defined are given below.

Estimate of the Laser Material Processing Universe

As mentioned, a total of 6,300 surveys were sent. A total of 387 were returned (6.1%) which were divided into the three groups as defined below:

<u>Group</u>	<u>Description</u>	<u>No Responses</u>	<u>Percent Of Total Mailing</u>
1	Definite LMP users	87	1.4
2	Non-LMP users, but responded to all other questions	140	2.2
3	Non-LMP users, but did not respond to any questions at all	<u>160</u>	<u>2.5</u>
	TOTALS	387	6.1

Group 3 was excluded from the overall survey statistics because the returns did not provide any meaningful data on any questions asked.

TABLE II  
LASER TYPES IDENTIFIED BY SURVEY

<u>Laser Types</u>	<u>Number</u>
Material processing	524
Low-power alignment	591
Diode	1005
Special	42
Unspecified	<u>305</u>
TOTAL	2467

The analysis in the previous section of the total number of LMP systems (based upon sales volume of U.S. manufacturers) identified approximately 4,400 systems. The 524 lasers identified in the survey represent 11.9% of the total systems in use today as determined by this analysis.

On this basis, one can project the total number of workers involved in LMP as follows:

Total Number Of Full-Time LMP Users: 7,756  
 Total Number of Part-Time LMP Users: 7,697  
 Total Part-Time/Full-Time: 15,453

Identification of Applications and Materials

Applications. The principal uses of lasers in material processing applications were divided into four major categories:

1. Hole drilling
2. Scribing
3. Cutting
4. Other

5. Micro-alloying
6. Edge sealing
7. Nuclear fusion

Materials. In total, 9 different material categories were identified which included 74 different materials. These materials were then cross-tabulated with respect to the four use categories. The results were then expressed as a percent of the total respondents (in the LMP group) who identified that process and that material together. The highest percentage materials by process are given in Table III.

#### Identification of Laser Types

Detailed analysis of the different laser types which were identified by the survey is given in Table IV. Those which are considered as "material processing lasers" (vis: actually used for material removal) were distributed between the laser material processing and non-laser material processing groups as given in Table V.

TABLE III

## MOST POPULAR MATERIALS IN LMP GROUPS

Process	Metals	Plastics	Rubber	Cloth	Glass	Semi-Conductor	Ceramics
Hole Drilling	Stainless Steel 28.6%	(NS)* 20.4%	(NS) 8.2%	(NS) 8.2%	(NS) 14.3%	(NS) 22.4%	Alumina 24.5%
Scribing	Silicon 25.5%	-	-	-	(NS) 10.6%	(NS) 27.7%	(NS) 29.8% Alumina 40.4%
Cutting	Stainless Steel 25.6% Precious 20.5%	(NS) 25.6%	(NS) 7.7%	(NS) 20.5%	(NS) 2.6%	-	(NS) & Alumina 5.1%
Other	(NS) 16.7% Precious 16.7%	-	-	-	(NS) 8.3%	(NS) 16.7%	-

\*(NS) - Non-Specific

Percentages given represent the percentage of all respondents in the LMP group who indicated both material shown. Values given represent the highest values for each cross-tabulation of material and

1) Ruby	25	3	4	43
2) Nd-YAG	31	37	57	24
3) Nd-Glass	4	1	1	15
4) Nd-YALO	x	4	x	1
5) Argon	3	1	3	93
6) Krypton	x	x	x	2
7) Xenon	x	5	x	28
8) CO <sub>2</sub>	35	46	55	59

Non-LMP Systems

1) HeNe	1	x	12	521
2) GaAs (diode)	x	x	x	1004
3) HF	x	x	x	2
4) Ni	1	x	1	4
5) Dye	x	x	x	5
6) HeCd	x	x	x	23
7) CO	x	x	x	2
8) uv Argon	x	x	x	1
9) HeSe	x	x	x	2
10) uv - Not Spec.	x	x	x	1
11) Others	5	2	4	560

Ruby	40	27	67
Neodymium-YAG	133	10	143
Neodymium-Glass	12	9	21
Neodymium-YALO	4	0	4
Argon	113	64	177
Krypton	0	3	3
Xenon	7	0	7
Carbon Dioxide	<u>87</u>	<u>15</u>	<u>102</u>
TOTALS	396	128	524

Clearly, the Ruby, Neodymium-YAG, Argon, and Carbon-Dioxide are the most common lasers used in material processing. These devices emit at the wavelengths given in Table VI.

TABLE VI  
WAVELENGTHS OF MOST COMMON

<u>Type</u>	<u>Wavelength (nm)</u>	<u>Details</u>
Argon	488-514	Visible blue-green
Ruby	694.3	Visible red
Nd-YAG	1060	Invisible near-infrared
Carbon Dioxide	10,600	Invisible far-infrared

As a consequence, completely different ocular safety controls would be required for each laser type.

1) Laser Safety Officer	62	38	44.5	55.5	50.9	49.1
2) Use Enclosed Systems	49.4	50.6	23.2	76.8	32.6	67.4
3) Goggles Available	87.5	12.5	67.2	32.8	74.8	25.2
4) Goggles Used	65.8	34.2	38.9	61.1	49.0	51.0
5) Separate Ventilation	47.4	52.6	23.4	76.6	32.7	67.3
6) Breathing Complaints	1.3	98.7	0.9	99.1	1.1	98.9
7) Electrical Shocks	20	80	5.3	94.7	10.8	89.2
8) Lamp Explosions	3.9	96.1	3.8	96.2	3.9	96.1
9) Educational Programs	65.4	34.6	46.2	53.8	53.4	46.6
10) Standards Used	55.2	44.8	37.8	62.2	44.1	55.9
11) Eye Exams	61.7	38.3	35.9	64.1	45.8	54.2
12) Accidents	16.5	83.5	3.7	96.4	8.3	91.7
13) Separate Facilities	65.4	34.6	40	60	49.8	50.2
14) Main Production Areas	35.1	64.9	21.6	78.4	27.5	72.5
15) Special Control Measures	78.5	21.5	53.3	46.7	63.3	36.7

followed better safety practices than did the non-LMP group. For example, the LMP group was more apt to:

1. Have a Laser Safety Officer (62% vs. 44.5%)
2. Use completely enclosed systems (49% vs. 23.2%)
3. Both have and use safety goggles (87.5% vs. 67.2%) and (65.8% vs. 38.9%)
4. Have separate ventilation for the laser area (47.4% vs. 23.4%)
5. Have Educational Programs (65.4% vs. 46.2%)
6. Use laser safety standards (55.2% vs. 37.8%)
7. Have regular eye exams (61.7% vs. 35.9%)
8. Have the laser work in separate facilities (65.4% vs. 40%)
9. Have special control measures (78.5% vs. 53.3%)

B. In contradiction of the previous conclusion, however, is the fact that the LMP group reported nearly 3 times as many accidents with lasers, as reviewed in Table VIII.

TABLE VIII  
LASER ACCIDENTS REPORTED

<u>Accident Type</u>	<u>LMP Group</u>	<u>Non-LMP Group</u>	<u>Total</u>
Skin	8	2	10
Ocular	3	3	6
Non-Specified	<u>2</u>	<u>0</u>	<u>2</u>
	13	5	18

The comments on these accidents recorded by the respondents included one statement that the accident was caused because the user "intentionally looked into a 12mw/cm<sup>2</sup> helium-neon laser to see how bright it was."

C. One revealing cross-correlation of the two questions on laser safety goggles gave the interesting results shown in Table IX. This result indicates that the LMP group is 30% more prone to use available safety goggles than the non-LMP group.

Identify Usage of Systems. Information on system usage was derived from two parts of the survey. First, the statistical analysis yielded a median number of 11.5 individuals involved in all uses (for each respondent) and also that there was a median of 3.5 part-time and 3.6 full-time people involved in Laser Material Processing applications at each site.

	(Percent)	(Percent)	(Percent)
<u>Have and regularly use laser safety goggles</u>	73.9	57.0	64.5
<u>Have but do not use laser safety goggles</u>	26.1	43.0	35.5

Detailed information obtained in the "system use" section of the survey is reviewed in Table X. This information reveals that regular usage of laser systems occurred at 58.7% of the LMP sites as opposed to 38.3% of the non-LMP sites.

Over 70% of both the LMP and non-LMP groups reported that from one to three workers were involved in the use of all lasers at their company on a daily basis.

TABLE X  
SYSTEM USE

	<u>LMP - Only</u>	<u>Non-LMP - Only</u>	Total
Less than 1 hr/day	11.2	32.0	24.0
1 day/week	16.2	7.8	11.1
1 week/month	0	3.9	2.4
1 month/year	2.5	3.9	3.4
Regularly	58.7	38.3	46.2
Other	11.2	14.1	13.0

Projections for Future Use. Results of the final survey question relating to future use is given below in Table XI.

TABLE XI  
PROJECTIONS OF EXPANDED USE IN THE MATERIAL PROCESSING FIELD

Response	LMP	Non-LMP	Total
Yes	66.7	10.5	30
No	33.3	89.5	70

87

The purpose of this study was to decompose various polymers with radiation from a carbon dioxide laser (10,600 nm.) under conditions that would simulate those conditions present in industrial facilities where carbon dioxide lasers are used for cutting plastics.

## (2) Experimental Method

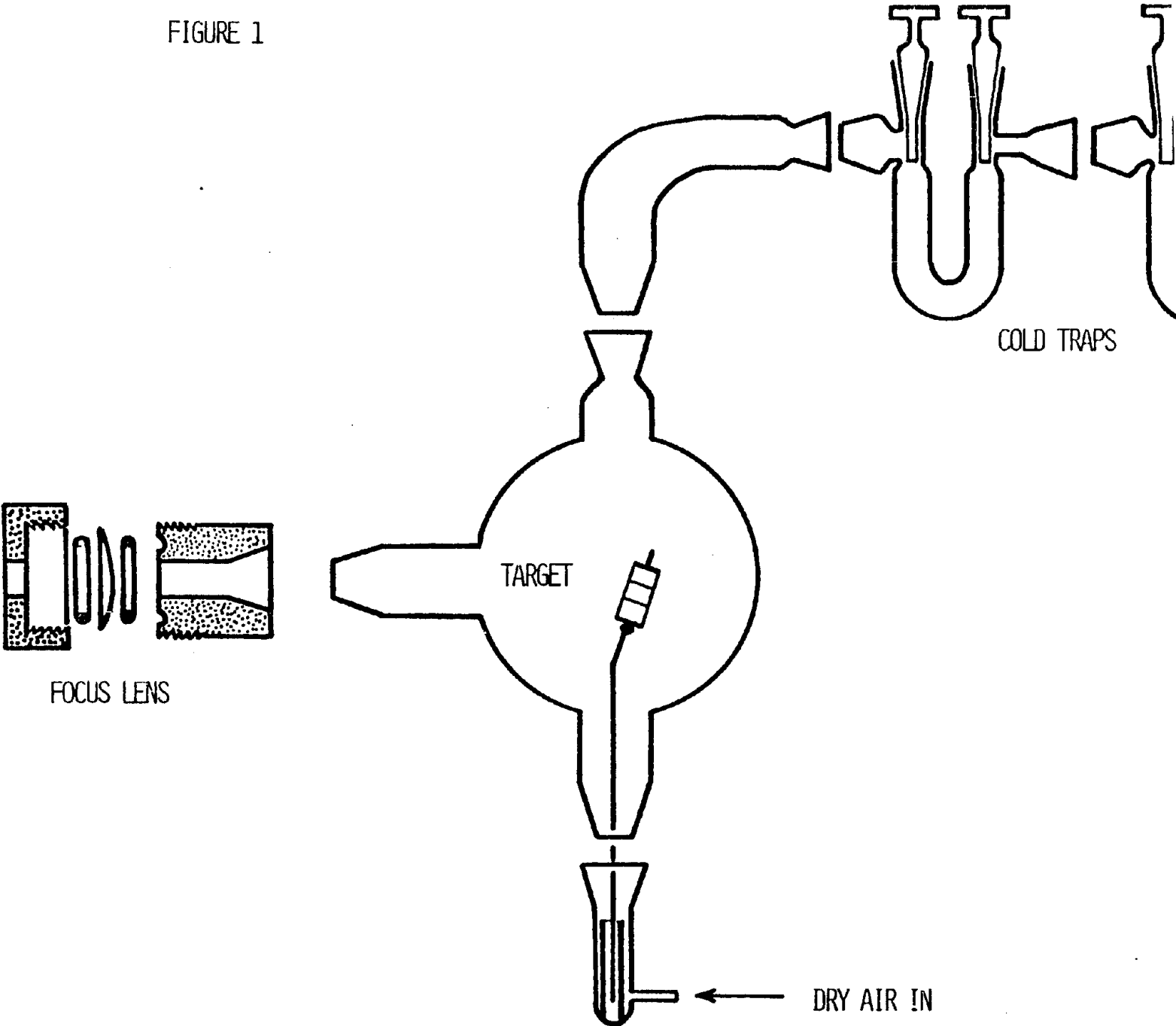
In order to do this, a target of the plastic sample material was fashioned and mounted in a reaction chamber as illustrated in Figure (1). A stream of air was introduced at the target mount, swept through the reaction chamber and cold traps before being vented to the atmosphere. Both cold traps were filled with glass beads and cooled to  $-78^{\circ}\text{C}$  in dry ice-acetone baths. Most of the vapor which was formed when the target was irradiated was condensed in the first of these two traps. The laser beam was adjusted in a range from 15 to 25 watts and focused upon the target by means of Irtran lens. Long bursts of CW radiation filled the chamber with clouds of vapor and particulate matter. The laser beam was periodically shuttered in order to allow the vapors to be swept out of the reaction chamber and into the cold traps.

The accumulation of sample in the traps is a function of the polymer being examined. Some polymers simply melt and emit very little volatile material. These materials require many more laser bursts (such as 50-60 bursts) in order to accumulate a manageable quantity of sample. Furthermore, certain plastics emit particulate matter rather than decomposing into well-defined molecular fragments, other plastic materials have a tendency to ignite rather than undergo simple thermal decomposition. Polyformaldehyde resins and Mylar do not form large amounts of volatile materials and that which is formed is mostly particulate matter. On the other hand, it is very difficult to irradiate butyl rubber without ignition which is accompanied by the formation of large quantities of particulate matter in the form of carbon black. Materials that fell into these categories were not investigated further since the volatiles produced were amenable to our mass spectral analysis scheme.

## (3) Results

The three plastics that were examined decomposed to form significant quantities of well-defined molecular fragments; they were polymethyl methacrylate, polyvinyl chloride, and Nylon. The condensate from

FIGURE 1



... cases use gas chromatography column used for analysis was an 8 foot (-1/8 inch diameter) stainless steel column packed with 5% SE-30 on silanized chromosorb W. The analysis was conducted with a helium flow rate of about 10 ml/min. and temperature programming rate of 6°/mm.

(1) Polymethyl Methacrylate (Lucite)

Samples of Lucite decomposed cleanly to produce monomeric methyl methacrylate in nearly quantitative yield. Since methyl methacrylate is considered very toxic, it is clear that all cutting operations involving Lucite should be conducted only in well ventilated chambers.

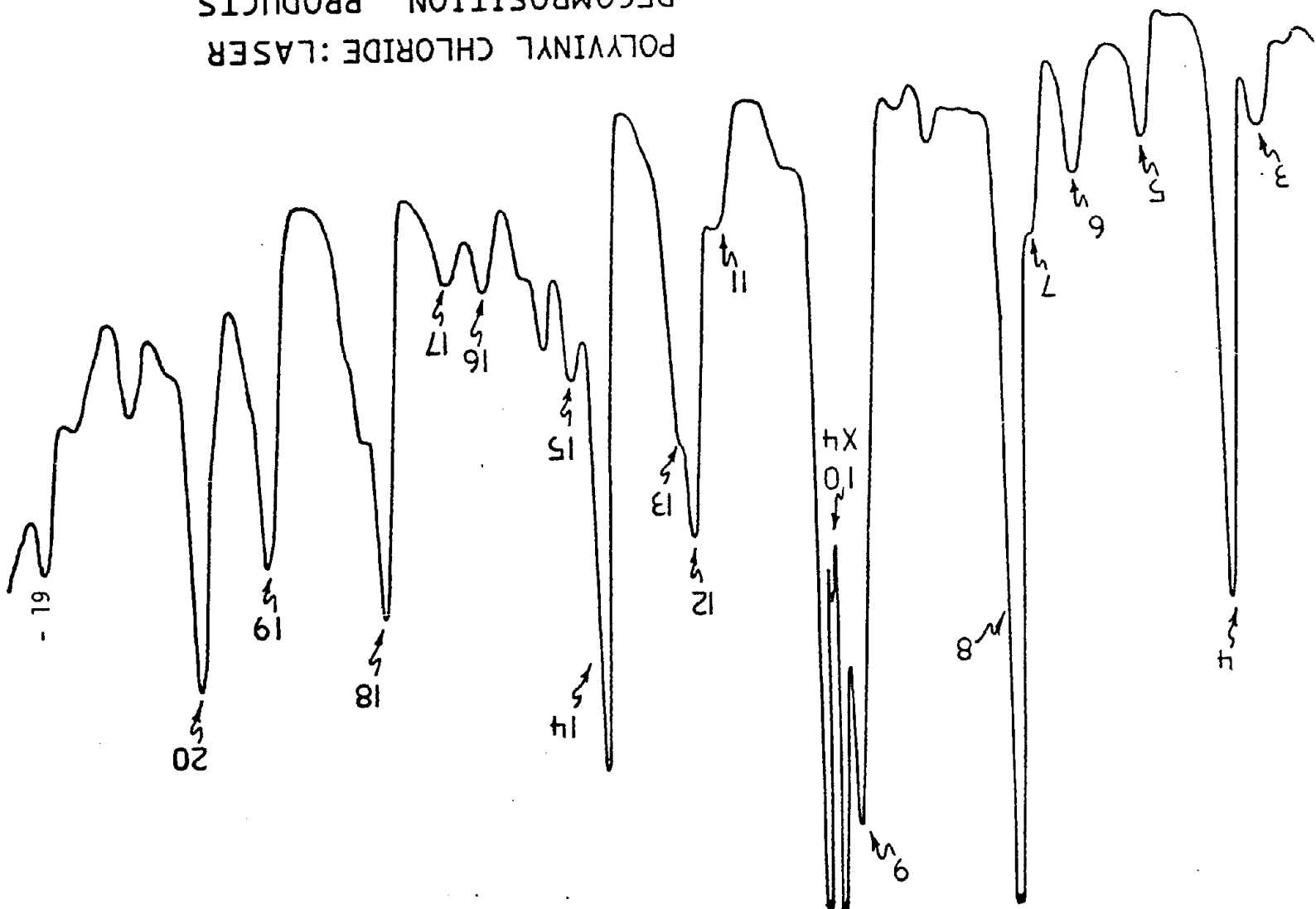
(2) Polyvinyl chloride (PVC)

Several samples of PVC were examined. With soft varieties of PVC such as Tygon tubing the major volatile material was the plastisizer, di-n-octyl phthalate. This substance was present in such large quantities that it completely masked any other constituents that might have been present.

Hard samples of PVC which did not contain plastisizers afford a highly complex mixture of substances. Figure 2 is a drawing of the gas chromatograph trace obtained from this mixture. The mass spectra associated with each of these gas chromatograph peaks leads to the following structure assignments.

- Peak No. 1: Molecular ion 78. Assignment - C<sub>6</sub>H<sub>6</sub> (benzene)
- Peak No. 2: Molecular ion - 92, base peak 91  
Assignment - C<sub>7</sub>H<sub>8</sub> (toluene)
- Peak No. 3: Molecular ion - 106 Assignment - C<sub>7</sub>H<sub>6</sub>O  
(benzaldehyde)
- Peak No. 4: Molecular ion - 104 Assignment - C<sub>8</sub>H<sub>8</sub>(styrene)
- Peak No. 5: Molecular ion - 118, also 106 and 103  
Assignment - C<sub>9</sub>H<sub>10</sub> PhCh = CHCH<sub>3</sub>, C<sub>8</sub>H<sub>10</sub>  
(ethylbenzene)
- Peak No. 6: Molecular ion - 118, base peak 91  
Assignment - C<sub>9</sub>H<sub>10</sub> (PhCH<sub>2</sub>CH = CH<sub>2</sub>)
- Peak No. 7: Assignment - uncertain
- Peak No. 8: Molecular ion - 116, base peak 91  
Assignment - C<sub>9</sub>H<sub>8</sub> (PhCH<sub>2</sub>C = CH or indene)
- Peak No. 9: Molecular ion - 130, also 129 and 128.  
Assignment - C<sub>10</sub>H<sub>10</sub> (probably dihydronaphthalene)
- Peak No. 10: Molecular ion - 128. Assignment - C<sub>10</sub>H<sub>8</sub> (naphthalene)

POLYVINYL CHLORIDE: LASER  
DECOMPOSITION PRODUCTS



MOLECULAR IONS - 134 and 174, 176, and 178.

- Assignments -  $C_{12}H_{10}$  (vinyl naphthalate) and  $C_5H_5Cl_3$  (trichloropentadiene)
- Peak No. 15: Molecular ions - 168 and 156, base peak 141. Assignments -  $C_{18}H_{12}$  (allylnaphthalene),  $C_{12}H_{12}$  (ethylnaphthalene)
- Peak No. 16: Molecular ions - 186, 184, and 182 and 168. Assignments -  $C_6H_5Cl_3$  (trichlorohexatriene)  $C_{13}H_{12}$  (allylnaphthalene)
- Peak No. 17: Molecular ion - 180. Assignment -  $C_{14}H_{12}$  (butadienyl naphthalene or isomer)
- Peak No. 18: Lower field side of peak no. 18 - Molecular ions - 182 and 166. Assignment  $C_{14}H_{14}$  (butylnaphthalene) and  $C_{13}H_{10}$  (benzoidene or isomer)
- High field side of peak no. 18 - Molecular ions - 198, 196, 194, and 184, 182, 180, 178. Assignments - major  $C_4H_6Cl_4$  (tetrachlorobutane) and  $C_3H_2Cl_4$  (trichloropropene)
- Peak No. 19: Molecular ions 0 212, 210, 208, 206 and 196, 194, 192, and 180 (also 179 and 178) Assignments -  $C_5H_6Cl_4$  (tetrachloropentene) and  $C_4H_4Cl_4$  (tetrachlorobutene) and  $C_{10}H_1$  (dihydroanthracene or dihydrophenanthrene)
- Peak No. 20: Molecular ion - 178. Assignment -  $C_{14}H_{10}$  (anthracene or phenanthrene)

The general pattern observed in this decomposition was the formation of polycyclic aromatic hydrocarbons and alkylated polycyclic aromatic hydrocarbons. We detected members of this class of compounds ranging from benzene to anthracene or phenanthrene. Higher homologs were undoubtedly present, but above column temperatures of 245°C the column bleed becomes so severe that it tended to confuse and obscure the mass spectra of the decomposition products. Beginning at about peak 11 in the gas chromatograph trace a series of polychlorinated alkanes and alkenes began to appear. The net result was that above peak 11 the assignment of structure must be regarded as tentative, since several substances were present in many of the peaks and since a rather large number of isomeric possibilities exists for many of the chlorocarbons that were observed. Above peak no. 20 a continuum of products was observed and it was no longer possible to make any rational assignment of structure.



are proposed. (see Figure 3)

Peak No. 1:  $m/e = 74, 73, \text{ and } 71$ ; the assignment of these peaks was not unequivocal, since we are not certain of the exact structure of the nylon sample, and since the signal intensity was so low that only the most intense peaks in the spectrum of the sample were observed. However, several possible structures might be proposed:

$m/e = 71$   $\text{CH}_2=\text{CHCONH}$   
 $m/e = 73$   $\text{CH}_3\text{CH}_2\text{CONH}_2$  or  $\text{CH}_3\text{CONHCH}_3$

The first structure would seem more likely on the basis of its close relationship to the structure assigned to the  $m/e=71$  peak.

$m/e = 74$

$\text{CH}_3\text{CH}_2\text{CO}_2\text{H}$  or  $\text{H}_2\text{NCH}_2\text{CH}_2\text{NH}_2$   
Here it would be most useful to know the structure of this nylon sample. Since propylene diamine is not normally a constituent of nylon, the former structure is considered more likely.

These data indicate that chromatogram peak number 1 was not completely resolved into its separate chemical constituents.

Peak No. 2:  $m/e =$  (major fragments) 87, 85, 83; (minor fragments) 120, 118; here again, the fragment assignments are not unequivocal and the chromatogram peak may not be completely resolved into its separate chemical constituents. However, several possible structures for the major fragments might be the following:

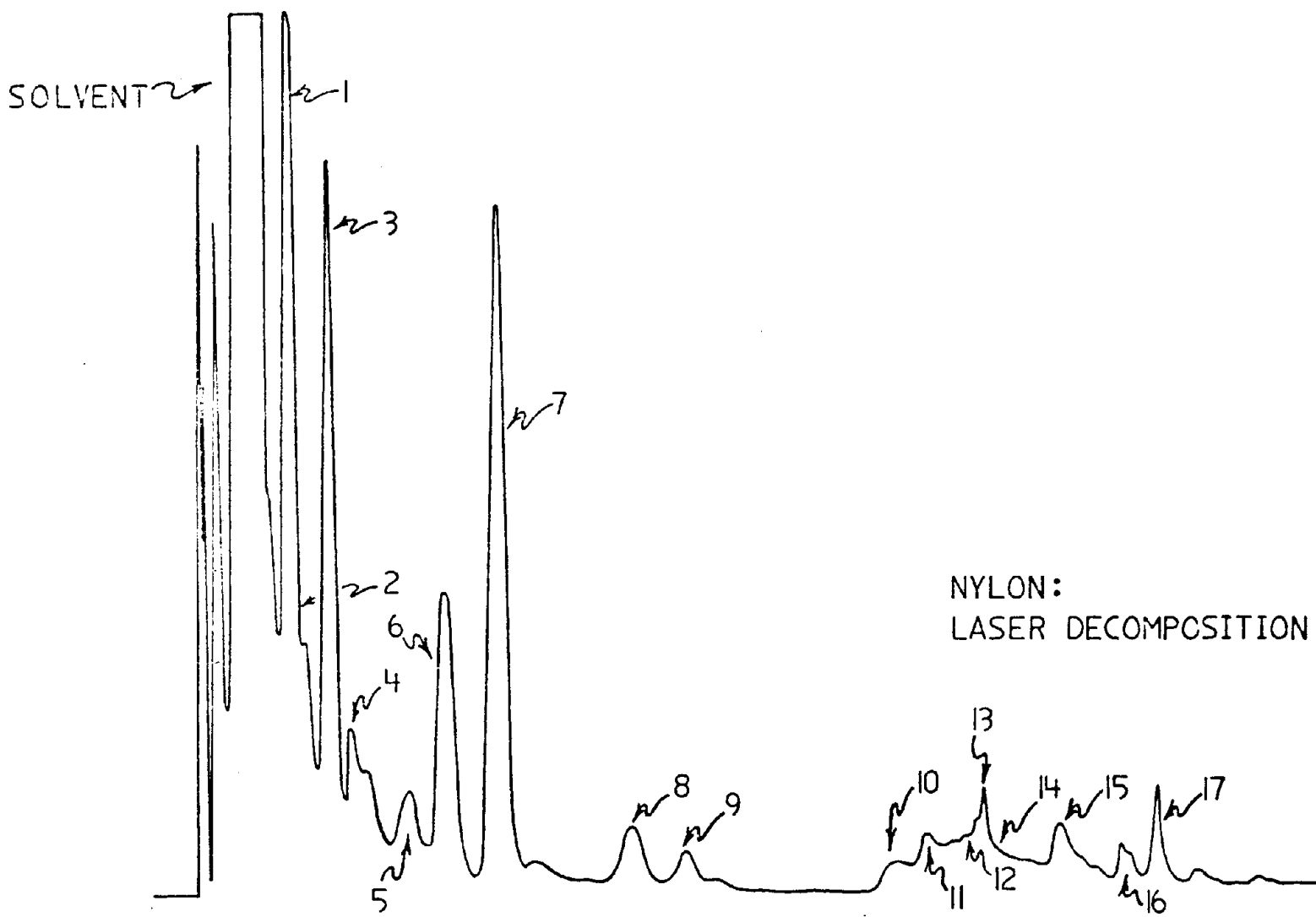
$m/e = 87$   $\text{CH}_3\text{CH}_2\text{CH}_2\text{CONH}_2$   
 $m/e = 85$   $\text{CH}_3\text{CH} = \text{CHCONH}_2$   
 $m/e = 83$   $\text{CH}_2 = \text{C} = \text{CHCONH}_2$

Of course alternative structures would be the isomeric N-alkylated amides.

Peak No. 4, 5, and 6: These chromatogram peaks did not yield sufficient sample quantities to provide any meaningful mass spectral data.

Peak No. 7:  $m/e = 101, 57, \text{ and } 56$ : the composition of this chromatogram peak seems to be unequivocal on the basis of the following fragmentation pattern and molecular ion assignments:

FIGURE 3



Peak No. 8-16: These chromatogram peaks did not yield sufficient sample quantities to provide any meaningful mass spectral data.

Peak No. 17:  $m/e = 132$  (weak), 119, 117, 115 (all strong), and 93, 91, 89 (all strong): No unequivocal assignment can be made for these peaks.

In summary, then, it would seem that nylon is thermally decomposing to form a complex series of volatile amides. Further work is necessary to verify the structures of these decomposition products, since on the runs examined to date low signal intensities were obtained and there is some question as to whether the apparently well resolved peaks are due to a single substance or a mixture of substances.

#### (4) Conclusions and Summary

The principal results from the analysis of the gaseous by-products produced by carbon dioxide laser radiation confirm the release of hazardous materials in some cases. Materials examined included: Delrin (linear polyoxymethylene), Lucite (polymethyl methacrylate), PVC (polyvinyl chloride), polyformaldehyde resins, mylar, butyl rubber, and nylon.

In the case of Lucite, the sample was thermally decomposed by the carbon dioxide laser into methyl methacrylate - a highly toxic substance. The amount of methyl methacrylate that was volatilized is undoubtedly greater than 33%, as the trap efficiency is certainly low under the conditions employed. The high concentration of methyl methacrylate is cause for some concern. The Merck Index states that the parent acid to which methyl methacrylate is closely related and can be readily converted as the following toxicity: "Inhalation of vapors produced nasal and conjunctival irritation, retching, narcosis, and death from pulmonary irritation. Exposure to 1% vapor for 2½ hours or to 5% vapor for ½ hour is lethal."

PVC decomposed into a material which displayed at least 20 mass spectral peaks. General patterns of the peaks indicated the formation of polycyclic aromatic hydrocarbons and alkylated polycyclic aromatic hydrocarbons. Vinyl chlorid itself was not detected, however, this may have been a result of its loss during the extraction process, due to its high volatility. Nylon appeared to decompose into a series of volatile anides.

contains, in addition to ionized matter, a particulate "Doll off" plume. The question of concern in regard to these particulates is whether they constitute a respirable hazard and, if so, how much of the total material which has been removed in the laser interaction is released as respirable-sized particles (10 microns or less).

## 2. Experimental Methods

### A. Particulate Collection System

To form a sample collection system as shown in Figure 4, the system begins with an absolute filter, which served to clean up the air which feeds into the laser chamber. A flow meter was located just before the laser chamber. Out of the chamber the released sample is pulled through a short length of tube past an iso-kinetic sampling port. The port was used to collect samples for Andersen Impactor Analysis. The particulates pass next into a respirable sampling cyclone (400 l/min. air correction). The cyclone was used to separate the larger particles from the respirable-size particles. Using centrifugal force and a known flow rate of air through the device, large particles are "spun-out" and collected in a jar beneath the cyclone. The cyclone is calibrated such that a flow rate of 15 CFM provides a certain probability that the particles collected will be of a known size (or mass). In all cases in the experiments done, virtually no material was collected in the cyclone.

The main filter was located next in the path. This was an 8" X 10" standard glass fiber filter which captures respirable sized particles.

Finally, the system passed into an absolute safety filter (same type as the pre-filter) for the remote possibility that the 8" X 10" glass fiber filter must rupture. The entire system was pulled by a Lobe blower (Sutorbilt Inc.), high volume, high-vacuum pump. Differential pressure gauges were placed across all sampling equipment to monitor for filter breakage, (i.e., the cyclone sampler, the 8" X 10" filter and the safety filter).

### B. Andersen Impactor Analysis

A special probe was constructed and inserted in the side of the section of quartz glass tubing through which the main volume of air flows. This probe was designed to sample the volume of air flowing past with as little selectivity to the size of the airborne particulates as possible. This was achieved by cutting the end of a

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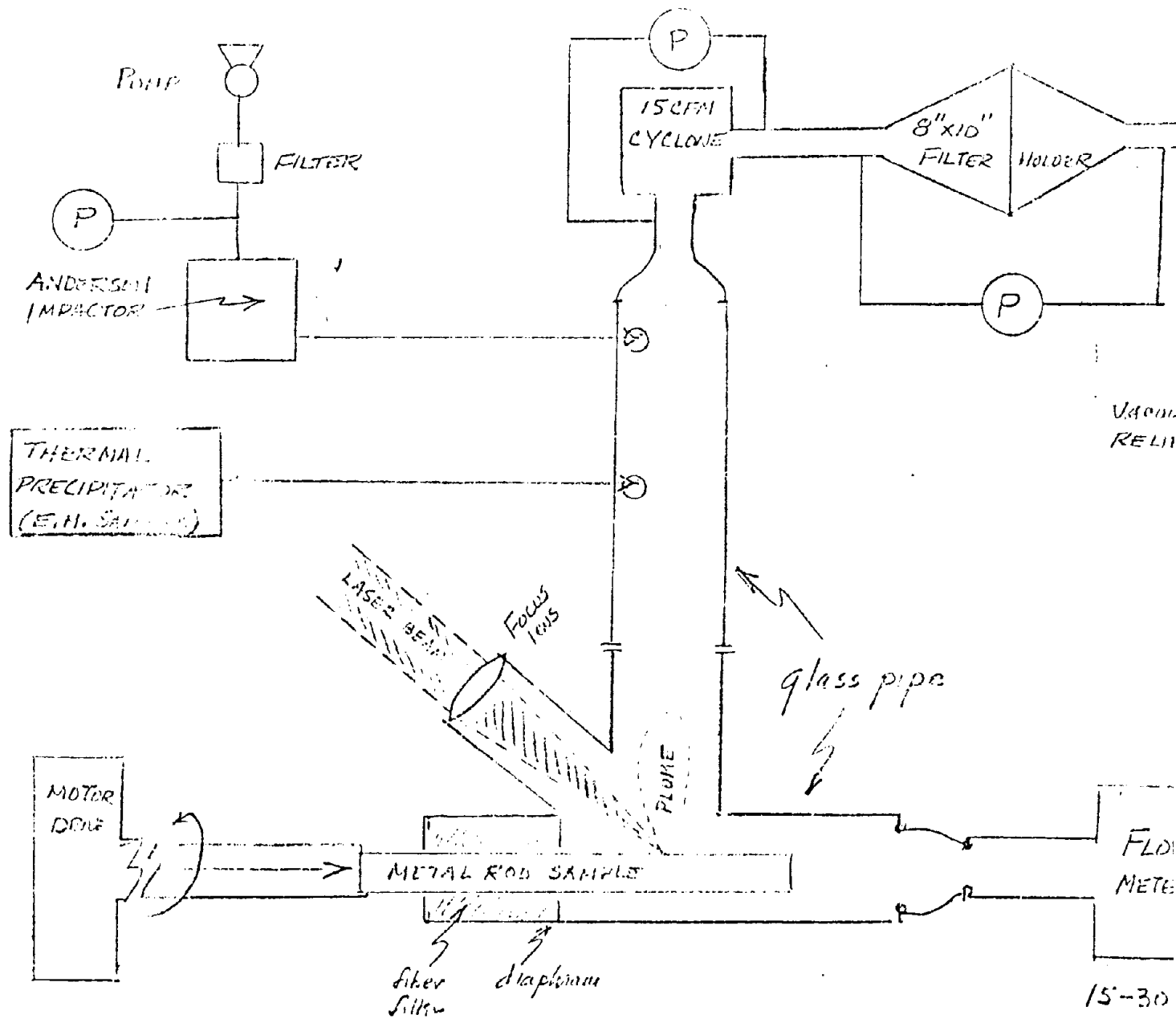


FIGURE 4

at any given moment. An air flow meter and manometer were used to monitor the two flow rates so that they may be kept constant throughout the sample run.

The Andersen sampler is a type of cascade impactor. Cascade impactors separate particles by aerodynamic size. They operate by drawing the air stream through a jet against a plate set at right angles, then through a smaller jet at higher velocity, continuing this process up to seven stages. The largest particles are impacted on the first stage from the largest jet, and successively smaller particles are impacted on the succeeding stages. Particles too small to be impacted on the final stage are collected on a 47 mm circular glass fiber filter following the last stage. As in the other section of the system, this final filter is used as a safety precaution before the air is pulled into the pump and exhausted into the atmosphere.

For a given model cascade impactor, there will be an effective cutoff diameter (ECD) for each stage. This is the aerodynamic diameter for which 50% of the particles are impacted on the given stage. In using the cascade impactor, it is assumed that all particles collected on the stage are larger than the ECD.

ECD's for the Andersen Sampler operated, in our study at an airflow of 28 liters per minute, are as follows:

<u>STAGE NO.</u>	<u>EFFECTIVE CUTOFF DIAMETER</u>
1	(Approx. 7.0 microns)
2	5.35
3	2.95
4	1.53
5	0.95
6	0.54
7	~ 0.24

of the ruby crystal at the other foci of the ellipses in such a way that the light generated by the flashlamps is focused along the central axis of the ruby rod providing for high pumping efficiency.

**COOLING SYSTEM:** Both the flashlamps and the ruby rod are cooled by triply distilled, de-ionized water via quartz glass collimating jackets which are coaxial with the rod and lamps. The double elliptical cavity also has a cooling jacket. Ordinary tap water passed through a heat exchanger is used to carry excessive heat away from the cavity itself. A refrigeration system consisting of a compressor and a series of cooling coils creates an ice bank in the reservoir of the cooling system. Water temperature remains between 40-50° F. provided the laser is not operated at a pulse repetition rate of more than 20 pulses per minute. Dry nitrogen gas is used to purge the laser cavity and to prevent moisture condensation on the rod faces. Firing the laser with moisture on the rod ends can result in severe damage of the coatings.

**POWER SUPPLY:** The power supply for the laser head is contained in a single cabinet and consists of charging, firing, and timing circuitry, inductive pulse forming networks, and capacitor energy storage banks. High-current high-voltage cables carry the stored energy from the capacitors to the flashlamps in the laser head. The laser is calibrated so that a given charge voltage on the capacitor bank produces a known output of laser energy (expressed in joules). The pulsed laser output is of the normal mode with a pulse length of 2 msec.. Pulse repetition rate may be varied by adjusting the clock triggering frequency in the power supply. An audible warning device built into the power supply indicates when the capacitor bank is charged and the system is capable of being fired.

#### D. Test Procedure

The surface of the metal sample was cleaned with acetone and methanol to remove loose dirt and oil. The sample was secured in the sample holder and the shaft of the sample holder is passed through the rubber grommet to facilitate an air-tight seal. This assembly is then inserted into the glass envelope which confined and contained any particles or vapors given off by the sample during the laser pulses. The shaft of the sample holder was connected to a mechanism driven by dual variable speed motors which slowly rotated and inserted the sample so as to continually expose a new surface for each laser dose. A simple positive lens mounted in a rack and pinion arrangement focuses the laser beam onto the surface of the sample. The angle of incidence

become imbedded on the surface of the lens when the incident beam is normal to the surface of the material being impacted.

After the sample is in place, clean filter papers were numbered, pre-weighed, and inserted in the appropriate filter holders. The filter papers in the seven stages of the Andersen sampler do not actually filter the air, that is, the volume of air containing the vapors and particulates does not pass through the filters, but instead, they provide a light-weight, clean, and removable surface for the deposition of particles in each of the seven stages.

When the sample and all filter papers are in place, the laser cooling systems were activated and the dry nitrogen purge was turned on. The laser was fired manually a few times to insure that the beam was focused correctly on the surface of the sample. The pumps were turned on and the two air flow rates adjusted to their proper levels by observing the calibrated flow meter and manometer. The variable speed rotation-insertion mechanism was activated and adjusted so that the doses on the sample surface would be closely spaced but not overlapping. The result is a continuous spiral of impacts inscribed around the sample.

When all other systems were operating correctly, the laser power supply was placed in the automatic clock triggered mode and adjusted for a pulse repetition rate of approximately twenty pulses per minute (20 ppm). The correct charge voltage was set on the capacitor bank and the trigger switch was turned on so that the laser would fire and recharge automatically. All systems are functioning automatically at this point. The operator must constantly monitor the air flow rates, water temperature of the cooling systems, operation of the power supply, and sample drive mechanism operation throughout the test run.

Protective eyewear designed to filter out the characteristic wavelength of light emitted from the ruby laser (6943 Å) as well as appropriate ear protection to attenuate the excessive noise levels produced by the air pumps were worn by the operator of the system as well as any observers present in the room. Doors were locked and entry into the laboratory was restricted while the laser was operating.

After the desired number of impacts were made on the sample, all systems were shut down and the sample and filter papers were removed for post-weighing and analysis.

below.

TABLE I  
LASER-INDUCED RESPIRABLE PARTICLES

<u>SAMPLE</u>	<u>(FOCUSED) OUTPUT ENERGY (J)</u>	<u>NUMBER LASER DOSES</u>	<u>WEIGHT (GRAMS) 8" X 10" GF FILTER PRE WT.</u>	<u>COLLECTED WEIGHT (DIFF.)</u>
ALUMINUM	35	500	3.5460	14.5
MONEL	30	200	3.5190	52.4
COPPER	30	200	3.5350	9.0
BRASS	30	200	3.5335	32.9
NICKEL	30	200	3.5212	17.0
STAINLESS STEEL	30	600	3.5437	34.9
ICONEL	30	200	3.5608	13.8

In all cases, respirable particles were collected in the 8" X 10" glass filter. Since, due to technical reasons, the number of laser pulses per sample was varied, it is more meaningful, for comparative purposes, to express the weight of captured respirable material as weight per laser pulse. These values are given in Table II.

TABLE II  
WEIGHT OF CAPTURED RESPIRABLE MATERIAL PER LASER PULSE

<u>Sample</u>	<u>Weight Per Dose (Micrograms/Pulse)</u>
Monel	262
Brass	165
Nickel	90
Inconel	69
Stainless Steel	58
Copper	45
Aluminum	29

... cumulated weights of the collected particles should not exceed - in theory - about one-fifteenth - the total weight collected on the 8" X 10" filter. This is clearly not the case. The cause for this apparent error is unknown.

The weights of material collected on the Andersen Back-up filters do have a variance (as given in Table 4). That is not consistent with the amount of material collected on the large 8" X 10" respirable filter. As a result, discussion of size distributions in a quantitative manner is not possible, other than to say that a sizable percentage of the captured material is respirable.

#### F. Conclusions

Pulsed laser drilling of common metals releases a sizable fraction of the removed metal in the form of respirable sized particles. The amount of material released per laser dose was different for each metal examined, the data indicated that alloys (with generally higher melting points) released more respirable matter per laser dose. The notable exception was Nickel (not an alloy - but it does have a rather high melting point at 1455°C). Efforts to quantitate the particle sizing was apparently not successful due to measurement problems.

1	Approx. 7.0	2.5	2.3	1.8	2.5	2.4	2.4	2.9
2	5.35	2.9	2.2	2.1	2.0	1.6	2.9	2.6
3	2.95	2.6	2.0	2.7	2.5	2.5	2.6	3.2
4	1.53	2.9	2.5	2.1	2.2	2.2	2.6	3.1
5	0.95	2.6	2.2	2.5	2.5	2.4	2.6	3.4
6	0.54	2.7	2.3	2.3	2.6	2.2	2.6	2.4
7	Approx. 0.24	2.5	2.7	3.5	2.3	2.4	2.7	2.6

MATERIAL	NO. LASER SHOTS	WEIGHT (mg.)
Aluminum	500	1.6
Monel	200	0.8
Copper	200	0.3
Brass	200	0.2
Nickel	200	0.2
Stainless steel	600	0.6
Inconel	200	0.7

equipped with indirect viewing devices (such as a closed circuit TV monitor or viewing ports made of special high optical density materials), thus, direct eye hazards are usually minimal. This should not imply, however, that all industrial laser devices being used in industry are enclosed systems. Indeed, especially in prototype laboratories where these processes are initially studied, such systems are often open "optical bench" arrangements.

The singular most hazardous part of the type of laser devices used in material processing applications is the high-voltage power supply used to drive the laser. As of this writing, three known deaths have occurred, (a scientist, a student, and a laser company technician) to individuals working with such high energy systems.

The basic hazard areas which can be associated with laser material processing can be thus listed as:

- (1) Eye and skin hazards from the reflection of laser energy from the material surface and vaporization plume.
- (2) Eye and skin hazards from the re-radiation emission of the laser induced gaseous plume.
- (3) Eye and skin hazards from the airborne dissemination of molten fragments produced by the reaction.
- (4) Eye, skin, and respiratory hazards associated with the airborne dissemination of particulate fragments in the reaction plasma.
- (5) Eye, skin, and respiratory hazards associated with possible toxic gases produced in the reaction plasma itself or by recombination with the air or other gases used in the material removal processes.

In addition, the following non-laser beam related hazards must also be considered:

- (1) Electrical hazards associated with the high voltage systems which are used in laser metalworking.
- (2) Hazards associated with gases and chemicals which are sometimes ancillary to the laser metalworking process.

- (1) The circuitry associated with charging the high voltage capacitors shall be interlocked so that the capacitors are fully discharged (less than 1% of rated voltage) before they can be recharged.
- (2) An audible alarm shall be supplied that will sound when the voltage on the capacitors is being discharged into the "dump" resistors until the capacitors are fully discharged.
- (3) The laser enclosure shall be sealed from the lower enclosure by a catch pan designed to hold water in the event of a leak occurring in any of the water cooled laser components. A sensor shall be interlocked to shut down power upon sensing a leak.
- (4) Access door handles are to be interlocked to discharge the laser and cause a shutter block to drop, closing the lens port before door latches are completely disengaged. The shutter shall be controllable manually by means of a key switch. All doors and door openings shall provide a light-tight seal when the doors are closed and shall include key locks.
- (5) All doors are to be redundantly interlocked to completely discharge the capacitors and deactivate the power supply when doors are opened. Redundant interlocking is to be interpreted as two separate systems (or circuits) that will independently control the laser system so that the failure of one system (or circuit) will leave the other system (or circuit) operative.
- (6) The positioning table enclosure for the part to be machined shall have an exhaust duct of sufficient size to remove all metal vapor and airborne dust. The enclosure shall be equipped with a side mounted sight port, of an approved filter material for the laser beam wavelength, located to view the laser drilling process.

From Lasers of the World Health Organization held in Dublin, Ireland,  
October 21-24, 1974.

2. R. James Rockwell, Jr. Respirable Hazards in Laser Material Processing Applications, Electro-Optical Systems Design Journal, In Press.