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THERMAL DECOMPOSITION PRODUCTS OF AIRCRAFT INTERIOR MATERIALS

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16. Abstract

Seventy-five typical aircraft interior materials were thermally decomposed using a combustion tube furnace. A 250-milligram sample was exposed to a temperature of 600° C for 5 minutes while maintaining an airflow rate of 2 liters per minute through the combustion tube. The combustion products were collected in liquid-filled fritted bubblers, and the contents were analyzed for hydrogen cyanide, hydrogen sulfide, hydrogen chloride, hydrogen bromide, and formaldehyde by differential pulse polarography; nitrogen dioxide and sulfur dioxide by visible spectrophotometry; and hydrogen fluoride by potentiometric titration. Carbon monoxide was collected in plastic sample bags and measured by nondispersive infrared analysis. The yields of the nine gases have been reported in terms of milligrams per gram of material. Parametric studies were also conducted to characterize the effects of experimental parameters on gas yields. These parameters include sample weight (250 and 750 mg), percent oxygen (0, 10.5, and 21 percent), airflow rate (1 to 3 lpm), and temperature (400°, 600°, and 800° C).

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PREFACE

The studies and data reported herein respond to the results and conclusions of prior in-house work (refer to reference 19). That work indicated that the combustion tube furnace was more suitable than the NBS smoke chamber for the analysis of combustion products. It was also apparent that the method for ranking a material for toxicity would require the use of animal response data. Thus, two concurrent data acquisition projects for 75 typical aircraft interior materials were initiated--a gas analysis effort by the FAA's National Aviation Facilities Experimental Center (NAFEC) and an animal exposure effort by the FAA'S Civil Aeromedical Institute (CAMI). This report documents the portion of the effort conducted by NAFEC. The complementary work conducted by CAMI is being reported separately. The correlation of the results of both tasks will be published as a separate FAA report in the near future.

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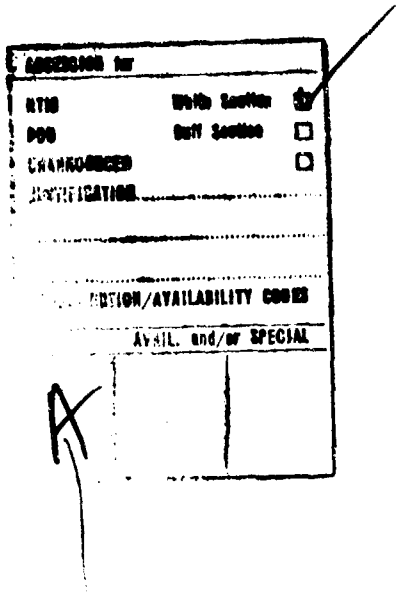

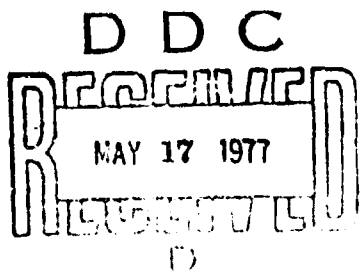

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INTRODUCTION

PURPOSE.

The purpose of this project was to determine the relative amounts of nine toxic combustion gases which are released during the oxidative pyrolysis of typical aircraft interior materials. The objective was to establish a data bank and demonstrate the applicability of a test procedure which could be used to rank aircraft interior materials according to the potential toxicity of their combustion products.

BACKGROUND.

The Federal Aviation Administration (FAA) has been concerned with the combustion products of synthetic and natural materials which are used in aircraft interiors since as early as 1965, when carbon monoxide and hydrogen cyanide were first tentatively implicated in the incapacitation of air-crash victims (reference 1). The National Aviation Facilities Experimental Center (NAFEC) first became involved in combustion-gas analysis in 1968 through work done under contract at the National Bureau of Standards (reference 2). The impetus provided by that effort has resulted in an ever-expanding involvement of the FAA with combustion product analysis and toxicity. The direct involvement of NAFEC in the area of combustion gas analysis greatly accelerated following the two Chicago air carrier accidents in December 1972, involving a B737 and DC9, in which hydrogen cyanide was widely publicized as contributing to the fatalities.

In previous studies, Einhorn has concluded that most fire deaths result from the victim inhaling smoke and/or toxic gases (reference 3). Research conducted by Johns Hopkins University supports this conclusion. It was reported that carbon monoxide contributed to 80 percent of 107 fire deaths that were studied (reference 4). However, carbon monoxide can not be considered as the only important toxic gas present in aircraft cabin fires. A typical wide-body jet contains approximately 6,000 pounds of plastics, in addition to carpeting and upholstery (reference 5). Therefore, other combustion gases may become equally important if the synthetic environment in a wide-body aircraft should become thermally involved. These combustion gases are not only important for their toxic effects, they can also produce a loss of visual acuity in addition to that produced by smoke obscuration. In a study of the smoke emission characteristics of aircraft interior materials using a 2,800 cubic-foot cabin mockup, Lopez (reference 6) found that eye irritation in human test subjects became intolerable prior to a significant loss of visibility due to smoke density.

NAFEC was given the task of measuring the concentrations of selected toxic gases which are present in the combustion products of wide-body aircraft cabin materials. The objective of this task was to demonstrate the applicability of a test procedure which can be used to rank aircraft interior materials according to their potential toxicity hazard in a fire. The

application of such a test method to the rule-making process would allow those materials which pose the greatest hazard to be eliminated from service. The philosophy of this approach is similar to the current FAA flammability regulation, in that the objective is to achieve incremental increases in safety as the state of the art permits.

Materials which are proposed for use in commercial jet aircraft, in addition to being as safe as the state of the art permits, must be cost-effective, functional (durable, easily cleaned, etc.), and aesthetically acceptable. The materials described in this report fulfill these requirements, since they were chosen from more than 140 inservice materials which were supplied by the Aerospace Industries Association and leading seat manufacturers. Furthermore, all 66 materials pass the current "self-extinguishing" flammability requirements (FAR 25.853, May, 1972).

Although the amount of literature available on the combustion products of synthetic materials is extensive, it is often difficult to assess the relative merits of materials; first, because the data have not been obtained under similar experimental conditions (combustion products are influenced both qualitatively and quantitatively by such experimental parameters as (1) sample size, (2) ignition source, (3) heating rate, (4) temperature, and (5) oxygen supply (references 7, 8)); second, the studies are usually limited to a narrow selection of materials, often to a single polymer. Finally, much of the data on combustion gas analysis have been obtained using nonspecific methods of analysis. NAFEC has attempted to address these problems by (1) employing a reproducible method for generating combustion products, (2) measuring the combustion products of a large selection of materials under identical experimental conditions, and (3) utilizing relatively specific methods of analysis for selected combustion gases. In addition, animal toxicity data have been obtained for these materials under similar experimental conditions at the FAA's Civil Aeromedical Institute (CAMI) (reference 9). These data will be available as a separate report, although the CAMI test protocol has already been described (reference 10).

EXPERIMENTAL SECTION

GENERAL APPROACH.

A wide selection of aircraft interior materials was thermally decomposed using a combustion tube furnace. A 250-mg (milligram) sample of material was exposed to a temperature of 600° C (centigrade) for 5 minutes while maintaining an airflow rate of 2 lpm (liters per minute) through the combustion tube. The combustion products were collected in liquid-filled fritted bubblers containing an appropriate collection medium. The contents were analyzed for hydrogen cyanide (HCN), hydrogen sulfide (H_2S), hydrogen chloride (HCl), hydrogen bromide (HBr), formaldehyde (HCHO), nitrogen dioxide (NO_2), sulfur dioxide (SO_2), and hydrogen fluoride (HF). Carbon monoxide (CO) was collected

for later analysis by replacing the liquid-filled bubblers with a plastic sample bag. Three replicate tests were made on each material, and the data contained in this report were an average of the three tests. The CO measurements were made by conducting an additional series of three replicate tests.

INSTRUMENTATION.

Differential pulse polarography (reference 11) can be used for the analysis of HCN (references 12, 13), H_2S (references 14, 15), HCl and HBr (references 16, 17) and HCHO (reference 18). This technique appears to be preferable to the use of ion-selective electrodes (ISE), which were employed in this laboratory for a preliminary study (reference 19), in complex mixtures. The advantages of polarographic techniques include the following: (1) multiple species, such as cyanide, sulfide, and chloride, can be determined simultaneously without prior sample treatment; (2) electroactive cations, anions, and organics can be determined; and (3) the presence of interfering species is readily apparent.

Since the concentrations of H_2S in the initial sample were relatively high (millimolar) and the samples were analyzed immediately following a test, an antioxidant was not required. Hydrogen sulfide concentrations in the fritted bubblers, when spot checked, remained stable for at least 30 minutes after the completion of a test. Although polarography is an acceptable method of analysis for either chloride or bromide (reference 17), combinations of the two interact catalytically at the mercury electrode. Therefore, values of HCl and HBr contained in this report for the 10 materials in which both are present are in error by as much as 50 percent.

The higher concentrations of fluoride have been measured by lanthanum nitrate titration using the fluoride ISE as the endpoint detector, since the titration technique is less prone to electrode effects (adsorption, etc.). However, a calibration curve is required for the determination of low fluoride concentrations. A comparison of the two procedures for the higher fluoride concentrations indicates that there is a correspondence between the results. Fluoride values obtained by titration were approximately 17 percent higher than those obtained using a calibration curve. It should be noted, however, that an all-glass apparatus was employed to decompose fluoride-containing materials. Therefore, the recovery of fluoride is not quantitative. Only 50 percent of the theoretically available fluoride was recovered from a polyvinylfluoride film (material 18) which was 70-percent PVF.

Interfering absorbance peaks were often encountered in the spectrophotometric analyses of NO_2 and SO_2. In addition, the concentrations of these gases were difficult to ascertain for some materials due to the presence of a large background absorbance. These problems are associated with the high concentrations of interferences produced in using the combustion tube approach. When the same materials were tested under flaming conditions in the National Bureau of Standards (NBS) smoke chamber, relatively clean spectral scans resulted for both NO_2 and SO_2.

AIRCRAFT INTERIOR MATERIALS.

The materials utilized in this study were chosen from among those interior materials which are currently used in wide-bodied aircraft. They were obtained through the cooperation of the Aerospace Industries Association of America and leading materials suppliers to the aircraft industry. The 75 test materials include panels (13), fabrics (12), panel components (9), foams (9), thermoplastics (8), flooring (6), cargo liners (5), coated fabrics (4), insulation (4), transparencies (3), and elastomers (2). The chemical and physical characteristics of the materials, including their usage categories, are described in table 1. This table has been reproduced in its entirety from reference 19.

All materials were cut to approximate weights and placed in a humidity chamber at 50-percent relative humidity and 70° Fahrenheit (F) (21.1° C) for at least 24 hours. The materials were then reweighed prior to testing. Sample weights were 250 ±5 mg. However, test materials 27, 66, 115A (insulations), and 143A (foam) were tested using 125-mg sample weights due to their low densities.

GAS SAMPLING AND ANALYSIS.

A Lindberg single-zone tube furnace (model 54031A) was used in conjunction with a temperature control module (model 59344) to thermally decompose the test materials. The materials were exposed to a temperature of 600° C for a period of 5 minutes. An airflow rate of 2 lpm was normally maintained by drawing ambient air through the combustion tube with a laboratory vacuum pump. However, carbon monoxide was measured by collecting the combustion products in a 12-liter Saran® sample bag and analyzing the contents with a nondispersive infrared analyzer. The airflow for CO analysis was therefore maintained with purified air from a gas cylinder.

The tube furnace and associated apparatus are pictured in figure 1. The Vycor® combustion tubes were 76 centimeters (cm) long, with an inside diameter (i.d.) of 1.5 cm. During a test, the combustion tube was positioned such that 13 cm of the tube extended beyond the downstream side of the furnace. As a result, the temperature at the interface between the combustion tube and sampling manifold was maintained at a reasonably constant 120° C, which minimized condensation losses. The temperature profile in the tube furnace was determined by probing the length of the furnace with a chromel-alumel thermocouple. The test samples were manually injected into the central 5-cm "isothermal region" of the tube furnace by placing them in sample boats which were constructed by sawing in half 2.5 to 5-cm lengths of 0.9-cm i.d. Vycor tubing (reference 21).

The combustion gases, upon exiting the furnace, were divided into four streams in the glass sampling manifold so that each of the four liquid-filled bubblers received approximately equal portions of the total gas flow. The portion of the combustion gases passing through each bubbler was controlled by a separate rotameter. All connections upstream of the bubblers were made with heat-shrink polyolefin tubing. A description of the collection medium in each bubbler and the combustion gases that were collected in it is contained in table 2. (Note that HF was only measured for known fluoride-containing panels; otherwise, formaldehyde was collected in the fourth bubbler.)

TABLE 1. DESCRIPTION OF MATERIALS

No.	Chemical Composition	Thickness (in)	Unit Weight (oz/yd^2)	Designation	Cabin Use
1	PVF/Epoxy-Fiberglas/Aramid Honeycomb/Epoxy-Fiberglas	0.388	48.5	Panel	Ceiling panel
2	Epoxy-Fiberglas/Aramid Honeycomb/Epoxy-Fiberglas (No. 1 without PVF finish)	0.375	39.6	Panel	Ceiling panel
6	PVF/Aramid Fiber-Phenolic	0.048	56.4	Panel component	Face for sidewall or window reveal (upper surface)
6a	PVF/Aramid Fiber-Phenolic	0.050	58.4	Panel component	Face for sidewall or window reveal (lower surface)
9	Aluminum/Aramid Honeycomb/Aluminum	0.371	86.3	Flooring	Floor
10	Fiberglas-Polyester	0.039	35.1	Cargo liner	Side cargo liner
12	PVF/Polyester-Chopped Glass/Aramid Honeycomb/Polyester-Chopped Glass	0.525	90.4	Panel	Overhead stowage door assembly
14	PVF/Aramid-Epoxy/Aramid Honeycomb/Epoxy Fiberglas	0.532	49.7	Panel	Acoustic wall panel
15	PVF/Aramid-Epoxy (Acoustic Skin for No. 14)	0.015	9.75	Panel component	Face of acoustic wall panel
18	PVF (Clear Film)	0.001	1.11	Panel component	Panel finish
20	PVF/Epoxy-Fiberglas/Aramid Honeycomb/Epoxy-Fiberglas/PVF	0.958	82.8	Panel	Partition
24	Epoxy-Fiberglas/PVC/Epoxy-Fiberglas	0.410	117	Flooring	Floor
25	PVF/Fiberglas-Epoxy/PVF	0.051	76.7	Cargo liner	Cargo liner
26	Fiberglas-Epoxy	0.013	16.3	Cargo liner	Cargo liner
27	Melamine-Fiberglas	1.19	5.43	Insulation	Fuselage insulation
28	Aluminized PVF/Nylon Scrim	0.007	1.33	Insulation	Cover for insulation batt
32	Polycarbonate	0.054	47.6	Thermoplastic	Molded part
33	Wool Pile/Polyester Backing/Latex Coating	0.265	51.8	Flooring	Carpet
34	Wool Pile/Polyester Backing/Latex Coating/Urethane Pad	0.345	51.3	Flooring	Carpet
37	PVF/Phenolic-Fiberglas Screen/Aramid Honeycomb filled with Phenolic-Fiberglas Batt/Phenolic-Fiberglas	0.517	77.2	Panel	Center ceiling panel
38	Epoxy Coated Phenolic-Fiberglas (Backing for No. 37)	0.017	18.4	Panel component	Backface of ceiling panel
39	Epoxy Coated Phenolic-Fiberglas (Adhesive used in No. 37)	0.018	17.6	Panel component	Adhesived used in ceiling panel

TABLE 1. DESCRIPTION OF MATERIALS (Continued)

No.	Chemical Composition	Thickness (in)	Unit Weight (oz/yd^2)	Designation	Cabin Use
40	Aramid Honeycomb filled with Phenolic-Fiberglas Batt (Core for No. 37)	0.451	10.8	Panel component	Ceiling panel core
41	Epoxy Coated Phenolic Fiberglas (Screen used in No. 37)	0.038	15.3	Panel component	Screen used in ceiling panel
42	PVF (Acoustic Skin for No. 37)	0.015	12.7	Panel component	Ceiling panel finish
43	PVF/Phenolic-Fiberglas Screen/ Aramid Honeycomb/Aramid Honeycomb filled with Phenolic-Fiberglas Batt/Phenolic-Fiberglas	0.732	85.8	Panel	Drop ceiling panel
46	PVF/PVC/Phenolic-Fiberglas/ Aramid Honeycomb/Epoxy-Fiberglas	0.500	79.2	Panel	Upper sidewall panel
50	Wool Carpet/Phenolic-Fiberglas/ Aramid Honeycomb/Epoxy-Fiberglas	0.445	95.0	Panel	Lower sidewall panel
52	Wool Carpet/Epoxy Adhesive/Aluminum/ Balsa Wood/Epoxy Adhesive/Aluminum	0.690	198	Flooring	Floor panel
56	PVC/Stainless Steel/Epoxy Adhesive/ Aramid-Phenolic Honeycomb/Epoxy Adhesive/Stainless Steel	0.490	168	Flooring	Floor panel
60	Epoxy-Fiberglas	0.018	22.9	Cargo liner	Cargo liner
61	PVF/PVC/Phenolic-Fiberglas/Epoxy Adhesive/Aramid Honeycomb/Epoxy Adhesive/Phenolic-Fiberglas	0.500	69.1	Panel	Overhead stowage panel
66	Silicone-Treated Phenolic-Fiberglas	1.38	6.09	Insulation	Fuselage insulation
67	PVC/Phenolic-Fiberglas/Aramid Honeycomb/Epoxy-Fiberglas	0.273	68.1	Panel	Door liner
69	PVF/PVC/Phenolic-Fiberglas/Aramid Honeycomb/Epoxy-Fiberglac	0.531	93.0	Panel	Door assembly
70	FR Wool (90 percent)/Nylon (10 percent)	0.037	11.3	Fabric	Upholstery
73	FR Urethane	0.500	17.4	Foam	Seat pad
74	FR Urethane	0.500	12.4	Foam	Seat pad
78	Aramid	0.046	12.1	Fabric	Upholstery
79	FR Polyether Urethane	0.500	13.7	Foam	Seat cushion
80	FR Urethane	0.500	11.3	Foam	Seat cushion
81	PVC (untreated)	0.096	25.3	Fabric	Upholstery
82	FR Wool (76 percent)/PVC (24 percent)	0.039	12.6	Fabric	Upholstery

TABLE 1. DESCRIPTION OF MATERIALS (Continued)

No.	Chemical Composition	Thickness (in)	Unit Weight (oz/yd^2)	Designation	Cabin Use
84	PVC/Cotton (untreated)	0.058	26.9	Coated fabric	Arm rest cover
85	ABS-PVC (untreated)	0.060	56.4	Thermoplastic	Seat side panels and trays
86	PVC (untreated)	0.500	28.8	Foam	Flotation cushion and padding for seat back and arm rest
88	FR Wool	0.055	17.2	Fabric	Upholstery
89	FR PVC/Nylon	0.059	26.3	Coated fabric	Seat arm cap
92	Aramid	0.036	11.8	Fabric	Upholstery
93	FR Cotton	0.012	3.06	Fabric	Upholstery
95	FR Rayon	0.041	15.4	Fabric	Upholstery
96	Wool (49 percent)/PVC (51 percent)	0.044	13.8	Fabric	Upholstery
97	FR PVC-Polyester	0.018	11.4	Coated fabric	Seat bottom diaphragm
99	FR PVC-Polymethyl Methacrylate	0.044	39.6	Thermoplastic	Seat shroud
100	FR PVC/ABS	0.092	86.9	Thermoplastic	Seat shroud
102	FR Polyethylene (rigid)	0.500	13.7	Foam	Flotation cushion
104	FR Polyester Urethane	0.500	40.1	Foam	Seat cushion
107	ABS-PVC	0.127	122	Thermoplastic	Molded part
108	FR Polymethyl Methacrylate	0.054	46.6	Transparency	Scratch shield
109	Polymethyl Methacrylate	0.260	228	Transparency	Window pane
111	Polycarbonate	0.052	46.2	Transparency	Windscreen
112	Silicone	0.094	86.3	Elastomer	Door seals
113	PVF/Polycarbonate/PVF	0.431	151	Thermoplastic	
115a	Phenolic-Fiberglas	1.09	6.40	Insulation	Fuselage insulation
116	Polycarbonate	0.043	36.8	Thermoplastic	Passenger service units and luminaires
117	Polyphenylene Oxide	0.041	31.4	Thermoplastic	Flight station and lavatory parts
118a	Fiberglas-Epoxy/Asbestos	0.020	28.9	Cargo liner	Cargo liner
123	Silicone	0.124	116	Elastomer	Door seals
127	Modacrylic	0.032	8.63	Fabric	Drapery
130	Cotton/Rayon	0.040	15.0	Fabric	Upholstery
136	PVC/Cotton	0.057	28.3	Coated fabric	Upholstery
142	FR Wool (90 percent)/Nylon (10 percent)	0.035	10.3	Fabric	Upholstery

TABLE 1. DESCRIPTION OF MATERIALS (Continued)

No.	Chemical Composition	Thickness (in)	Unit Weight (oz/yd^2)	Designation	Cabin Use
143a	FR Polyether Urethane	0.500	13.9	Foam	Seat cushion
143c	FR Polyester Urethane	0.500	38.8	Foam	Seat cushion
144	PVF/Epoxy-Fiberglas/Aramid Honeycomb/Epoxy-Fiberglas	0.276	43.3	Panel	Wall panel

ABBREVIATIONS

ABS - Acrylonitrile/Butadiene/Styrene
FR - Flame-retardant treated
PVC - Polyvinyl chloride
PVF - Polyvinyl fluoride

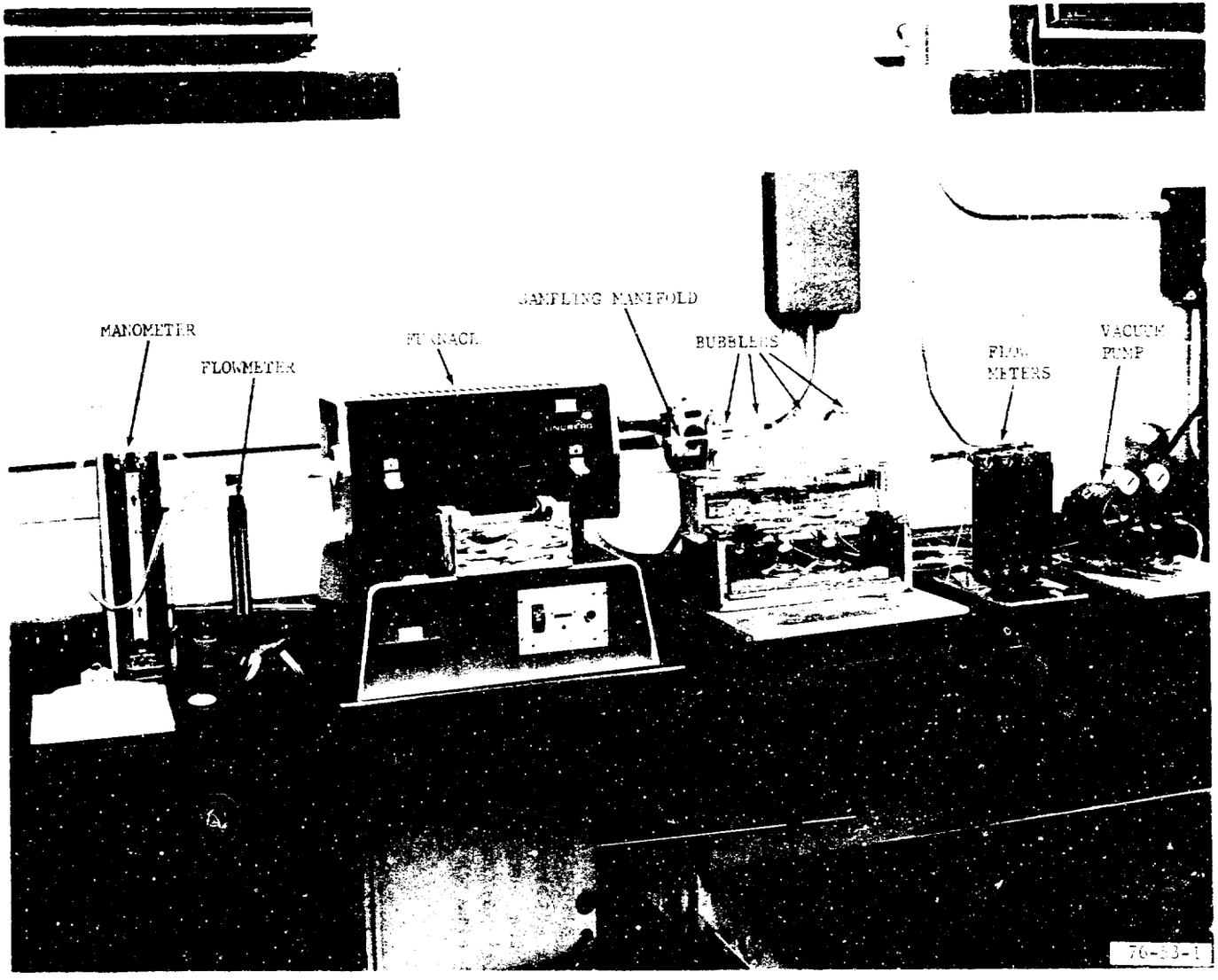


FIGURE 1. COMBUSTION TUBE FURNACE AND GAS SAMPLING SYSTEM

TABLE 2. GAS SAMPLING PROCEDURES

Bubbler	Collection Medium	Gases Collected
1	25 ml of modified Griess-Saltzman reagent (reference 22)	NO_2
2	100 ml of 0.05 M NaOH	HCN, H_2S, HCl, HBr
3	100 ml of 0.04 M tetrachloromercurate (reference 22)	SO_2
4	(a) 10 ml of 1 percent $NaHSO_3$ (b) 10 ml of 0.05 M NaOH (fluoride-containing materials)	HCHO HF

The method of analysis employed for each of the nine gases is summarized in table 3. All the methods except polarographic analysis are standardized procedures and are simply referenced. A Princeton Applied Research (PAR) model 174A polarographic analyzer equipped with a model 172A drop timer and a model 315 automated electroanalysis controller was used for the determination of HCN, H_2S, HCl, HBr, and HCHO concentrations. The polarograph was operated in the differential pulse mode using a three-electrode configuration, including a dropping-mercury working electrode, a platinum-wire counter electrode, and a saturated calomel reference electrode (SCE). The SCE was isolated from the sample solution by a 1 M (molar) sodium nitrate salt bridge. Instrumental parameters included a scan rate of 1 millivolt per second (mV/s), a drop time of 1 second, and a pulse amplitude of 10 mV.

DISCUSSION OF RESULTS

REPRODUCIBILITY.

The average yields of the nine gases have been reported in terms of milligrams per gram of material. These data are contained in table 4. Data on the average percent weight-loss of each material and the number of times the material ignited are also included in table 4. Variations in both of these parameters influenced the precision of the results to some degree. Significant variations in sample weight-loss (20 percent) often occurred among the three replicate tests. This could have been caused by either slight changes in the experimental procedure (sample positioning, furnace temperature, sample conditioning), material characteristics (unhomogeneous construction), or the combustion process.

Ignition of the sample during a test was normally accompanied by a visible (and generally audible) flash, and the combustion train would become covered with carbonaceous particles. However, some ignitions could only be detected

by observing a sharp increase in pressure on the manometer. An ignition often resulted in higher yields of HCl and, less frequently, higher yields of HCN and SO_2, although this behavior depended upon the composition of the particular test material. Sample ignition did not affect the yields of the other gases to a noticeable degree.

TABLE 3. ANALYTICAL PROCEDURES

Instrumentation	Toxic Gas	Analytical Procedure
PAR Model 174A Polarographic Analyzer (differential pulse mode)	HCN, H_2S	Add 1 ml of sample to 9 ml of deaerated 0.05 M NaOH; scan from -0.90 V to -0.15 V VS SCE
	HCl, HBr	Add 1 ml of sample to 9 ml of deaerated 0.05 M NaOH; acidify with 0.10 ml of 10 M HNO_3; scan from 0 V to +0.40 V VS SCE
	HCHO	Add 1 ml of sample to 9 ml of deaerated 0.05 M NaOH; scan from -1.40 V to -1.80 V VS SCE
Coleman Model 124 Scanning UV/VIS Spectrophotometer	SO_2	Modified West - Gaeke Procedure (reference 22)
	NO_2	Griess - Saltzman Procedure (reference 22)
Orion Model 801 pH/Millivolt Meter with Solid State Fluoride Electrode	HF	(a) Calibration curve for concentration less than $5x10^{-4}$ M, in acetate buffer (pH=5) (b) $La(NO_3)_3$ titration in mixed alcohol/acetate buffer (reference 23)
Beckman Model 864 Nondispersive Infrared Analyzer	CO	(a) Bag Sampling Prior to Analysis (b) Continuous for concentration-time profiles

The precision which is attainable for the routine analysis of combustion products appears to be limited primarily by the reproducibility of the combustion process. Boettner (reference 8) reported that the random nature of the combustion process provided the greatest source of variation in the analysis of combustion products; he found that reproducibilities were typically $\pm$25 percent.

TABLE 4. AVERAGE GAS YIELDS FOR THREE REPLICATE TESTS

Material Number	Number of Ignitions	Weight Loss (%)	TOXIC GAS YIELDS (mg/g)*								
			CO	HCN	H_2S	HCl	HBr	NO_2	SO_2	HCHO	HF
1	0	61.4	96	4.7	0	33.0	5.0	0.08	0	-	8.3
2	1	55.0	101	7.5	0	T	7.1	0.43	0	-	0.2
6	0	29.7	159	0	0	4.6	1.7	0.04	0	-	14.0
6A	0	34.8	162	0	0	22.0	0	0.04	0	-	11.6
9	0	47.2	94	6.7	0	0	0	0.32	0	T	-
10	2	95.2	90	8.6	0	88.0	0	0.59	0	0.8	-
12	0	61.3	90	2.3	0	34.4	T	0.09	1.2	-	7.1
14	0	75.2	174	7.5	0	0	5.0	1.07	0	-	0.3
15	0	96.7	153	2.9	0	0	6.6	0.15	0	-	36.0
18	3	97.9	88	0	0	0	0	0.02	0	-	152
20	0	68.7	164	6.4	0	T	T	0.26	0	-	7.0
24	0	52.0	41	2.4	0	82.0	0	T	0	0.5	-
25	0	25.6	31	0	0	4.3	8.5	0.01	0	-	8.8
26	3	46.6	66	0	0	105	0	T	0	0.9	-
27	0	20.6	0	15.0	0	0	0	0.34	0	0.8	-
28	0	97.1	37	3.1	0	27.7	0	0.01	0	-	63.1
32	0	97.0	398	0	0	0	21.0	T	0	0.6	-
33	0	90.9	55	14.9	5.3	21.9	0	0	2.2	T	-
34	0	91.3	46	13.5	6.1	24.9	0	0	2.5	1.0	-
37	0	56.1	156	4.7	0	12.0	2.6	0.39	0	-	4.5
38	0	24.8	161	0.6	0	0	0	0.62	0	-	T
39	0	46.1	124	1.5	0	0	T	0.85	0	0.7	T
40	0	77.3	159	16.4	0	0	5.3	2.0	0	T	-
41	0	38.5	89	0.7	0	T	5.3	0.29	0	2.1	-
42	3	77.7	106	3.2	0	45.2	15.6	0.08	0	-	48.8
43	1	57.8	147	5.2	0	11.3	T	0.37	0	-	8.5
46	0	53.1	124	3.2	0	23.3	0	0.20	0	T	4.4
50	0	60.0	101	8.9	0.9	5.4	8.0	0.63	T	0.4	-
52	1	62.8	52	4.1	0.7	19.0	0	0.01	1.4	3.7	-
56	0	69.8	77	3.1	0	158	0	0.04	T	1.5	-
60	3	44.3	62	0	0	61.0	0	0.01	0	2.6	-
61	0	62.9	142	6.8	0	27.6	0	0.25	0	-	5.5

TABLE 4. AVERAGE GAS YIELDS FOR THREE REPLICATE TESTS (Continued)

Material Number	Number of Ignitions	Weight Loss (%)	TOXIC GAS YIELDS (mg/g)*								
			CO	HCN	H_2S	HCl	HBr	NO_2	SO_2	HCHO	HF
66	0	23.2	21	7.3	0	0	0	0.38	0	1.5	-
67	0	60.7	104	3.4	0	80.0	0	0.15	0.4	2.2	-
69	0	54.3	142	4.6	0	19.4	4.1	0.19	0	-	4.5
70	0	80.3	78	33.8	13.9	0	0	0	0	0.8	-
73	1	97.8	129	6.0	0	4.2	0	0.02	0.7	10.6	-
74	1	98.9	108	7.8	0	7.3	0	0.04	0	3.8	-
78	0	90.7	96	7.0	0	43.1	0	0.53	11.2	1.2	-
79	1	98.9	105	5.8	0	0	0	0.03	0	3.5	-
80	1	94.4	68	5.5	0	27.3	0	0.01	0.9	2.7	-
81	0	95.9	92	0	0.3	536	0	0.01	3.0	3.7	-
82	0	97.0	112	19.5	10.7	88.0	0	0.03	4.8	0.8	-
84	0	93.2	103	0	0	221	0	T	0	1.9	-
85	1	92.0	55	4.1	0	162	0	0.02	2.9	6.6	-
86	1	80.6	28	9.1	0.4	56.2	0	T	2.2	3.3	-
88	0	82.8	89	41.7	13.4	0	0	0	0.3	T	-
89	2	91.9	70	0	0	259	0	0.02	1.4	2.3	-
92	0	80.1	63	14.9	0	0	9.6	1.6	8.5	T	-
93	1	82.2	255	1.9	0	0	0	0.57	0	1.3	-
95	2	84.6	144	3.8	0	14.5	5.1	0.39	0.9	1.3	-
96	0	94.8	70	11.2	6.2	205	0	0.04	4.9	3.8	-
97	2	91.8	114	0	0	114	0	T	0	1.2	-
99	0	93.9	148	0	0.2	387	0	0.01	1.9	8.9	-
100	0	90.4	54	2.2	0	197	0	T	2.6	5.9	-
102	3	97.6	149	0	0	8.6	0	T	0	4.3	-
104	1	97.3	83	5.0	0	0	0	0.02	0	3.4	-
107	0	93.3	55	1.7	T	321	0	T	1.1	8.7	-
108	3	98.6	86	0	0	0	47.1	T	0	4.6	-
109	1	99.3	21	0	0	0	0	T	0	63.4	-
111	0	97.9	345	0	0	0	15.5	0.01	0	0.4	-
112	0	25.7	45	0	0	0	0	0.01	0	25.6	-
113	2	98.0	342	0	0	23.0	10.3	0.04	0	-	4.8
115A	0	18.2	31	2.7	0	0	0	0.22	0	2.2	-

TABLE 4. AVERAGE GAS YIELDS FOR THREE REPLICATE TESTS (Continued)

Material Number	Number of Ignitions	Weight Loss (%)	TOXIC GAS YIELDS (mg/g)*								
			CO	HCN	H_2S	HCl	HBr	NO_2	SO_2	HCHO	HF
116	0	97.6	406	0	0	0	47.0	T	0	T	-
117	0	96.5	196	0	0	0	0	T	0	2.7	-
118A	3	27.1	23	0	0	0	17.0	0.02	0	3.3	-
123	0	28.3	9	0	0	0	0	0.01	0	26.7	-
127	0	97.6	88	62.4	0	182	0	0.52	2.1	0.5	-
130	2	92.7	348	1.9	0	28.0	7.1	1.0	1.8	0.4	-
136	3	87.0	56	0	0	220	0	0.01	0.9	2.2	-
142	0	92.1	112	37.2	14.2	0	20.5	0	1.5	0	-
143A	3	95.6	120	11.6	0	23.0	0	0.02	0	2.2	-
143C	0	89.3	28	2.4	2.0	137	0	T	16.6	3.2	-
144	0	59.0	143	8.2	T	0	5.5	0.33	0	-	4.1

*T = Trace Amount
- = No Data

Gordon (reference 24) also observed that the duplicate analyses of combustion gases released by materials exposed to a hydrogen diffusion flame (in a combustion tube) generally agreed to within ±20 percent, although the analyses for some materials varied as much as ±50 percent.

Table 5 contains data on the average relative standard deviations (ARSD) for each of the nine gases measured in this study. The values in table 5 are the averages of the 75 relative standard deviations for each gas. Although the ARSD is a nonsignificant parameter, it does provide a simple comparison of the relative precision obtained for each gas. Carbon monoxide yields are the most reproducible of the nine gases, with a relatively low ARDS of 9 percent. However, the ARDS's for HCN, H_2S, HCl, HBr, and HF are approximately 20 to 25 percent, which are comparable to the reproducibilities reported by Boettner and Gordon. The ARSD's for these gases would probably have been substantially reduced if the combustion tube and sampling manifold had been rinsed and the condensate analyzed (reference 19). The yields of NO_2, SO_2, and HCHO may be influenced to a greater degree by the combustion process and its random nature. Relative standard deviations for individual materials ranged as high as 180 percent for these gases. The utility of measuring NO_2, SO_2, and HCHO for the purpose of ranking interior materials is questionable due to the wide variation in results for replicate tests, particularly with respect to the experimental procedures employed in this study.

TABLE 5. AVERAGE RELATIVE STANDARD DEVIATIONS OF THE TOXIC GASES

Toxic Gas	CO	HCN	H_2S	HCl	HBr	HF	NO_2	SO_2	HCHO
ARSD (%)	9	23	21	18	26	19	60	58	53
Min. RSD (%)	0.3	1.6	7.2	3.8	1.4	1.5	3.5	12	6.0
Max. RSD (%)	32	51	70	55	87	68	167	177	166

RSD = (standard deviation/mean) x 100%

TOXIC GAS YIELDS.

The objective of this materials ranking program is to compare those materials which can be included within the same usage category. Therefore, rather than discuss toxic gas yields in reference to table 4, the materials have been classified according to usage category (reference 20) as shown in figure 2.

PANELS. Panels are difficult to compare using the combustion tube approach for two reasons. First, they are composite materials. In an actual cabin fire, only the front face of the panel would be exposed, while in the combustion tube, the sample is totally immersed in radiant heat. This leads to the decomposition of the core and back face, which results in increased gas yields. An additional effort is required to develop an appropriate test method for all interior materials, including composites; one which incorporates front-face exposure of the sample with acceptable reproducibility for toxic gas analysis.

A second problem arises from using an all-glass system to compare fluoride-containing materials, since HF is reactive towards glass. The transfer efficiency for HF was investigated by testing various weights of polyvinyl-fluoride (PVF) polymer (Aldrich Chemicals) and calculating percent theoretical yields for HF. As indicated in figure 3, the average percent theoretical yield was 45 percent for a sample weight of 250 mg. However, the transfer efficiency for HF appears to be inversely proportional to the absolute quantity of HF in the combustion tube, as might be expected for the formation of the more stable silicon tetrafluoride (SiF_4). Since the hydrolysis of SiF_4 is not complete (equation 1),

$$2\ SiF_4 + 2\ H_2O \rightarrow SiO_2 + 4\ H^+ + SiF_6^{=} + 2F^- \qquad (1)$$

the percent theoretical yields in figure 3 are probably too low.

The combustion tube does provide some discrimination in HF yields between the Tedlar®-covered panels. Panel 144, which was covered with 3 mils of Tedlar, yielded 4.1 mg/g of HF, while panel 20 was covered with a total thickness of 6 mils and yielded 7.0 mg/g of HF. Except for panel 14, for which only a trace of HF was detected, HF yields were in a narrow range between 4 and 9 mg/g. However, HF yields calculated on the basis of unit surface area rather than unit mass varied by more than a factor of 4, as indicated in table 6, with a range between 0.6 and 2.5 mg/cm^2. The relative ranking in table 6 is a more realistic appraisal of HF yields, since the total exposed surface area is the critical factor in an aircraft cabin fire. Panels 43, a drop ceiling, and 12, an overhead stowage door, yielded substantially more HF on the basis of surface area compared to the other panels. Due to their location at the ceiling, both panels would probably receive a maximum thermal exposure in the event of a fire.

TABLE 6. HYDROGEN FLUORIDE YIELDS AS A FUNCTION OF PANEL SURFACE AREA

Panel Number	Density (oz/yd^2)	HF Yield (mg/g)	HF Yield (mg/cm^2)
43	85.8	8.5	2.47
12	90.4	7.1	2.18
69	93.0	4.5	1.42
1	48.5	8.3	1.37
61	69.1	5.5	1.29
46	79.2	4.4	1.19
37	77.2	4.5	1.18
20	82.8	7.0	0.99
144	43.3	4.1	0.60

All the panels produced CO, HCN, and NO_2, and the majority released HCl and HBr. Panel 50, which was covered with wool carpet, produced the highest yield of HCN and the second highest yield of NO_2. Formaldehyde was only measured for two of the panels, since the majority of the panels contained fluoride.

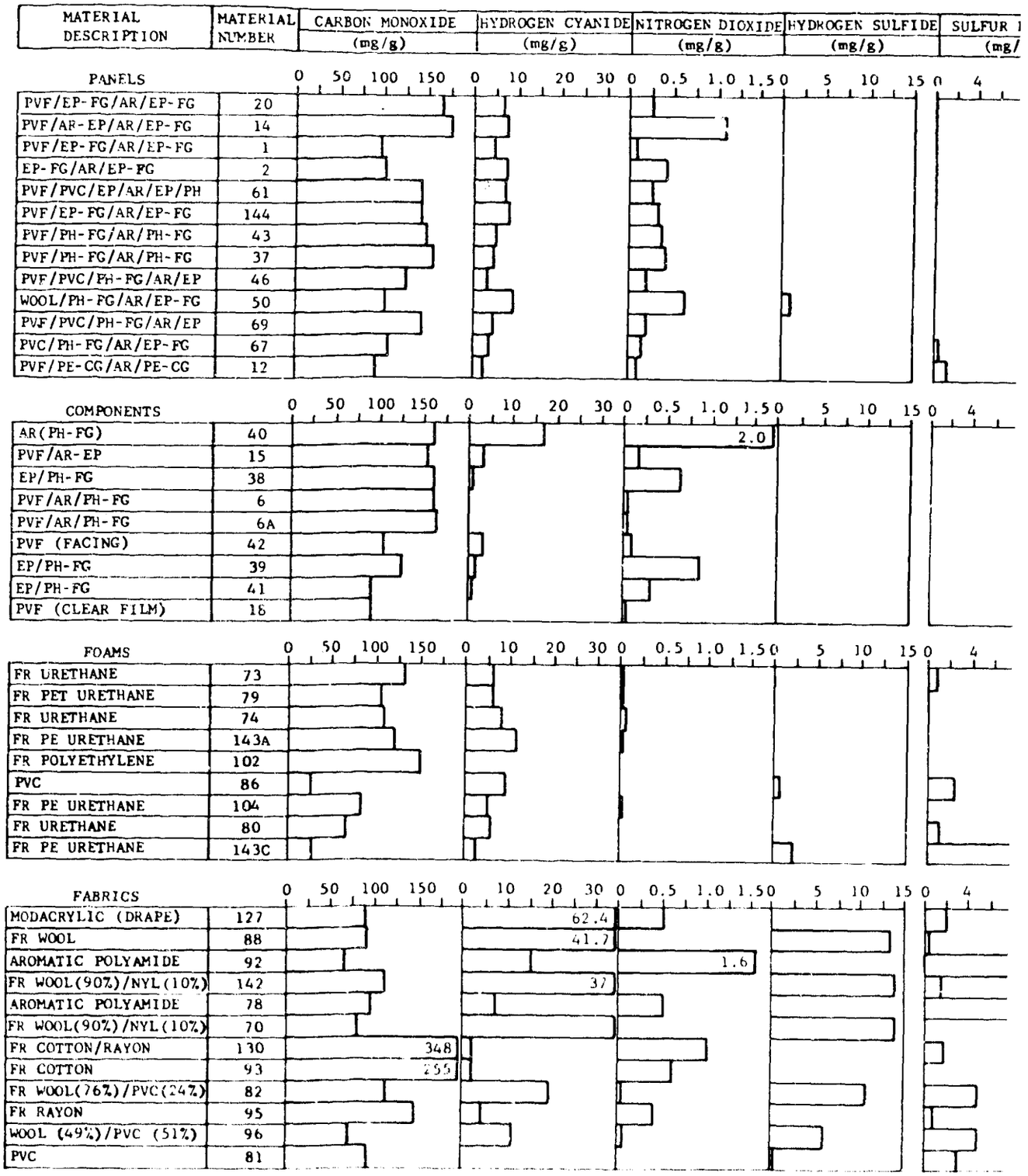
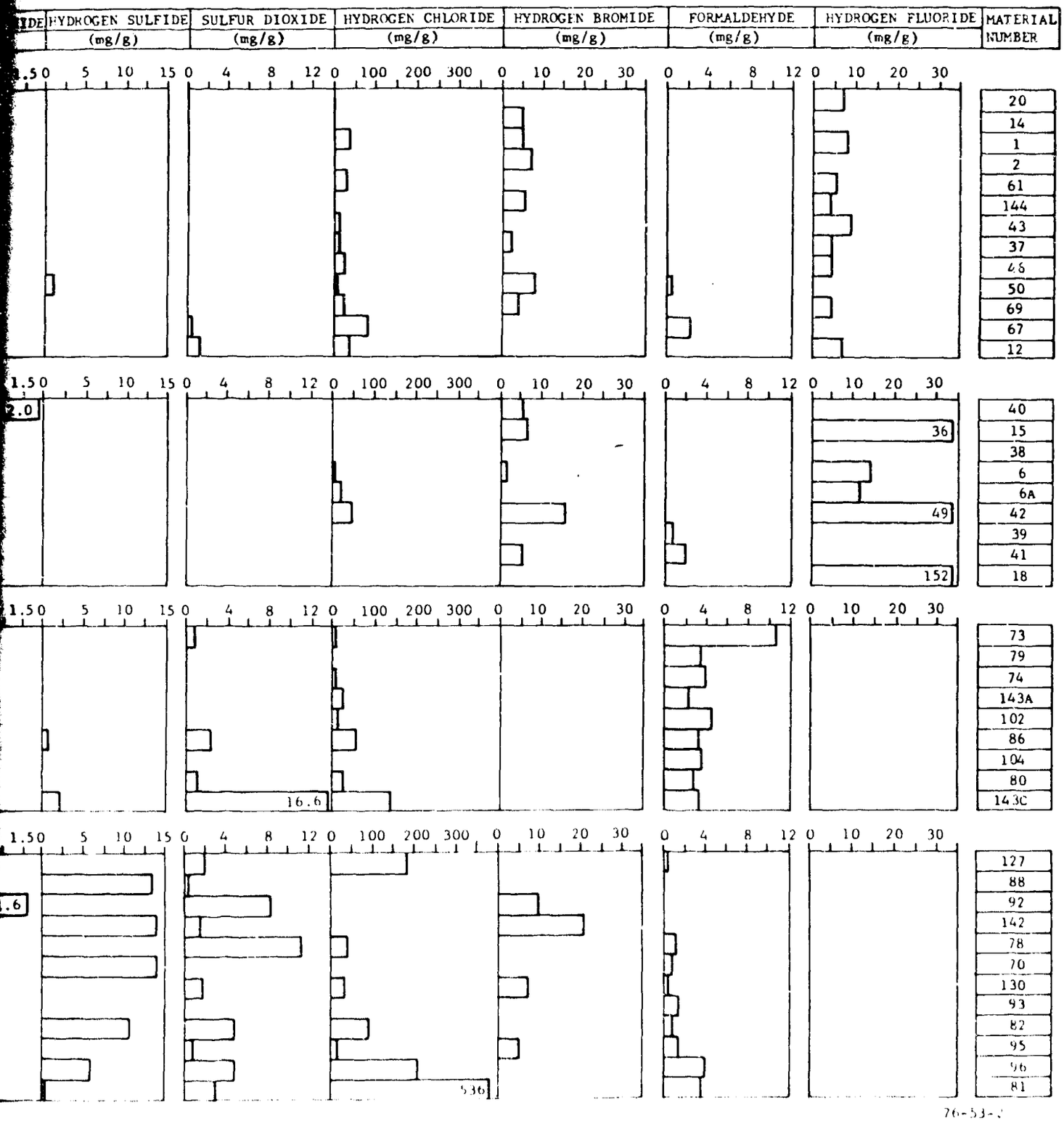


FIGURE 2. COMPARISON OF GAS YI



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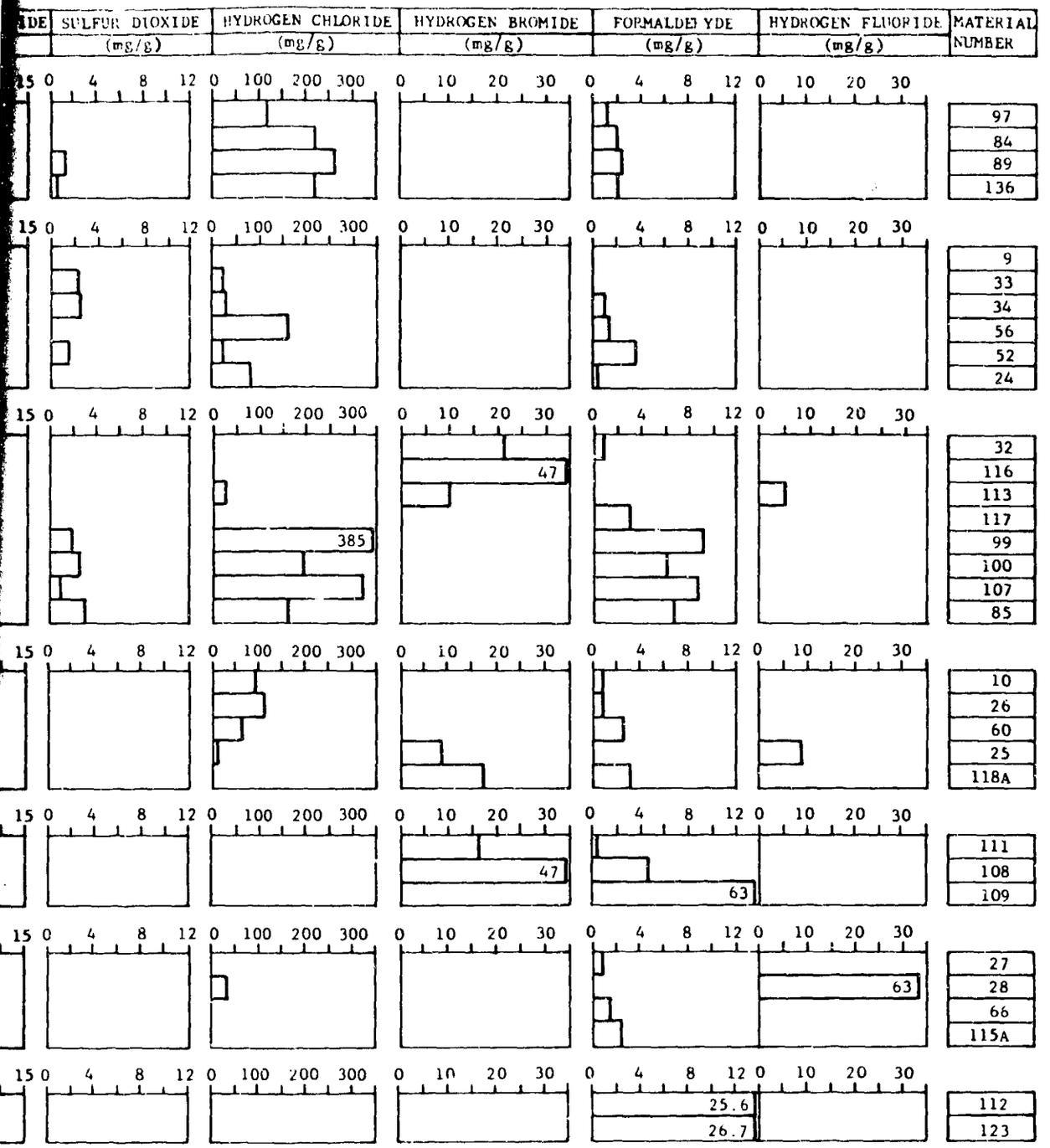
2. COMPARISON OF GAS YIELDS ACCORDING TO MATERIAL USAGE CATEGORY (Sheet 1 of 2)

MATERIAL DESCRIPTION	MATERIAL NUMBER	CARBON MONOXIDE (mg/g)	HYDROGEN CYANIDE (mg/g)	NITROGEN DIOXIDE (mg/g)	HYDROGEN SULFIDE (mg/g)	SULFUR DIOXIDE (mg/g)	HYL
COATED FABRICS		0 50 100 150	0 10 20 30	0 0.5 1.0 1.5	0 5 10 15	0 4 8 12	0
FR PVC-PE	97						
PVC/COTTON	84						
FR PVC/NYL	89						
PVC/COTTON	136						
FLOORING		0 50 100 150	0 10 20 30	0 0.5 1.0 1.5	0 5 10 15	0 4 8 12	0
AL/AR/AL	9						
WOOL/PE/LATEX	33						
WOOL/PE/LATEX/UR	34						
PVC/SS/AR/SS	56						
WOOL/AL/BALSA/AL	52						
EP-FG/PVC/EP-FG	24						
THERMOPLASTICS		0 50 100 150	0 10 20 30	0 0.5 1.0 1.5	0 5 10 15	0 4 8 12	0
PC	32	398					
PC	116	406					
PVF/PC/PVF	113	342					
PPO	117						
FR PVC-PMMA	99						
FR PVC/ABS	100						
ABS-PVC	107						
ABS-PVC	85						
CARGO LINERS		0 50 100 150	0 10 20 30	0 0.5 1.0 1.5	0 5 10 15	0 4 8 12	0
FG-PE	10						
FG-EP	26						
FG-EP	60						
PVF/FG-EP/PVF	25						
FG-EP/ASBESTOS	118A						
TRANSPARENCIES		0 50 100 150	0 10 20 30	0 0.5 1.0 1.5	0 5 10 15	0 4 8 12	0
PC	111	345					
FR PMMA	108						
PMMA	109						
INSULATION		0 50 100 150	0 10 20 30	0 0.5 1.0 1.5	0 5 10 15	0 4 8 12	0
MEL-FG	27						
AL/PVF-NYL	28						
SI-PH-FG	66						
PH-FG	115A						
ELASTOMERS		0 50 100 150	0 10 20 30	0 0.5 1.0 1.5	0 5 10 15	0 4 8 12	0
SILICONE	112						
SILICONE	123						

ABS	ACRYLONITRILE/BUTADIENE/STYRENE	FR	FLAME-RETARDANT	PH	PHENOLIC
AL	ALUMINUM	MEL	MELAMINE	PMMA	POLYMETH
AR	AROMATIC POLYAMIDE	NYL	NYLON	PPO	POLYPHEN
CG	CHOPPED GLASS	PC	POLYCARBONATE	PVC	POLYVINY
EP	EPOXY	PE	POLYESTER	PVF	POLYVINY
FG	FIBERGLASS	PET	POLYETHER	SI	SILICON

FIGURE 2. COMPARISON OF GAS YIELD



PH	PHENOLIC
PMMA	POLYMETHYLMETHACRYLATE
PPO	POLYPHENYLENE OXIDE
PVC	POLYVINYLCHLORIDE
PVF	POLYVINYLFLUORIDE
SI	SILICONE
SS	STAINLESS STEEL
UR	URETHANE

76-53-2

ARISON OF GAS YIELDS ACCORDING TO MATERIAL USAGE CATEGORY (Sheet 2 of 2)

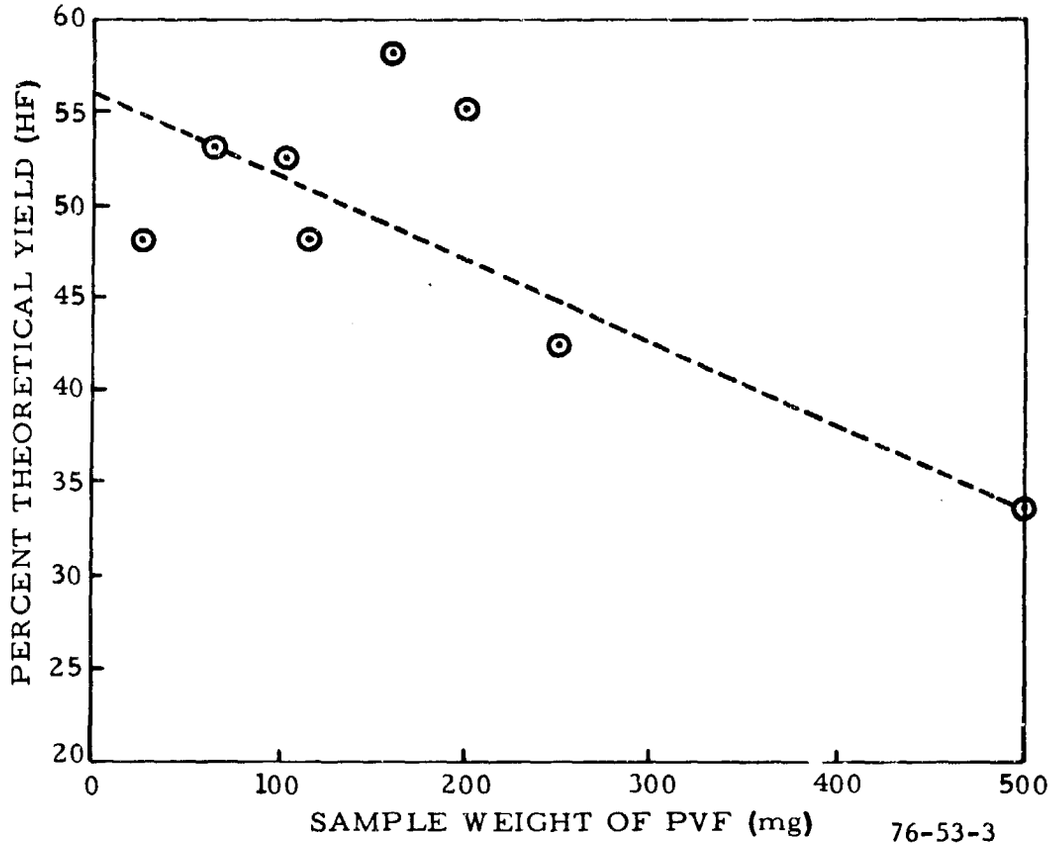


FIGURE 3. RECOVERY OF HYDROGEN FLUORIDE IN AN ALL-GLASS SYSTEM

PANEL COMPONENTS. The highest yields of HF were obtained for those materials used for the front face of the panel, materials 15, 42, and 18. Material 15, which is the acoustic skin for panel 14, yielded 1.20 mg/cm^2 of HF compared to only trace amounts for the panel assembly. Similar results were obtained for material 42, the acoustic skin for panel 37. Material 42 yielded 2.2 mg/cm^2 of HF versus 1.2 mg/cm^2 for panel 37. In general, the yield of HF on a unit area basis was much less for the entire panel assembly as compared to just the front face. For example, the heavier materials 6 and 6A produced relatively low HF yields of 14.0 and 11.6 mg/g, respectively.

Material 40, which is the core for panel 37, produced more than 5 times the yield of HCN than any of the other panel components, and more than twice the amount of NO_2. Formaldehyde was only measured for two of the panel components due to the expected presence of HF in the others, and was only detected in relatively small amounts.

FOAMS. All the urethane foams produced CO, HCN, and HCHO. In addition, material 143C produced the highest apparent yield of SO_2 of any of the materials, and twice as much HCl as the PVC foam (86). However, the CO yields of both 143C and 86 were low. Material 73 produced more than twice the HCHO yield than any of the other foams. The foams produced very little NO_2 or H_2S, and no HBr.

FABRICS. The highest CO yield was obtained from material 130, a cotton/rayon blend, while the second and third highest CO yields were produced by cotton (93) and rayon (95), respectively. Material 130 also produced a comparatively high yield of NO_2.

The modacrylic drape (127) produced the highest yield of HCN (62.4 mg/g) in addition to a high yield of HCl. The wool (88) and the wool/nylon blends (142, 70) also produced high yields of HCN. These materials did not produce any NO_2 or HCl; although material 142 did produce a high yield of HBr. The wools (including 82 and 96) were the only materials which produced H_2S in significant amounts, although the SO_2 yields were low except for the wool/PVC blends. The wool/PVC blends (82, 96) produced more than 10 times the SO_2 produced by material 88 (wool) and substantially more SO_2 than material 81 (PVC).

The aromatic polyamide fabrics (92 and 78) differed in their yields of HCN and NO_2, although both materials produced high yields of SO_2. Both materials, which were received by NAFEC in 1972, contain several tenths of a percent sulfur, which is a sufficient quantity to account for the observed SO_2 yields (reference 25). Material 92, which produced HBr as opposed to the HCl from material 78, produced twice the yield of HCN and three times the NO_2 yield.

COATED FABRICS. The coated fabrics produced only CO, HCl, and HCHO in significant amounts, although the HCHO yields were not noteworthy in comparison to the yields from the other material categories. The CO yields, in general, were inversely related to the HCl yields of the materials.

FLOORING. Materials 9 and 56 produced more CO than the other flooring materials and were the only ones which produced NO_2. The yields of HCN were greatest

for the wool carpets (33, 34) and the wool-covered material 52. Wools were the only materials to produce H_2S and SO_2. As previously mentioned, composites such as flooring materials were subjected to a greater total thermal exposure in the combustion tube than would be encountered in a test method such as the NBS smoke chamber.

THERMOPLASTICS. The thermoplastics can be divided into two basic groups based upon chemical composition, the polycarbonates and the ABS/PVC materials. The polyphenylene oxide (117) and polymethylmethacrylate (99) are approximately intermediate in behavior to the two groups. The polycarbonate materials (32, 116, 113) produced the highest yields of CO of any of the materials and significant yields of HBr. The ABS/PVC materials (100, 107, 85) produced much lower CO yields. However, these materials produced high yields of HCl in addition to HCN, SO_2, and HCHO.

CARGO LINERS. The CO yields of the cargo liners varied from moderate to low, with only material 10 (polyester) producing HCN or NO_2. All the cargo liners produced either HCl or HBr in moderate amounts.

TRANSPARENCIES. The only gases produced by the transparencies are CO, HBr, and HCHO. The polycarbonate (111) again produced the highest CO yield. Although the polymethylmethacrylates produced much lower CO yields, the fire-retarded material (108) produced more than four times as much CO as the untreated material (109). However, the untreated material produced an exceptionally high yield of HCHO (63 mg/g).

INSULATION. The behavior of material 27 was unique in that it was the only material tested which did not produce a detectable amount of CO. However, this material did produce a moderate yield of HCN. Although, in general, the yields of the other gases were not significant, the HF yield from material 28 was the second highest measured.

ELASTOMERS. The elastomers produced low yields of CO and all the other gases except HCHO. Aldehyde yields were exceptionally high compared to the materials in the other usage categories.

PARAMETRIC STUDIES.

A basic dilemma is encountered when one attempts to rank interior materials according to their potential "analytical toxicity" in a fire. The commonly available laboratory test methods either (1) lack sufficient reproducibility for gas analysis, and/or (2) do not simulate the conditions of a real fire. In addition, the results of a test are influenced by the experimental parameters, which are usually somewhat arbitrary in nature. Since the 75 materials were thermally decomposed under artificial conditions which were not intended to simulate a full-scale fire, the results and conclusions herein only pertain to the test conditions as outlined in this report. However, the behaviors of 12 randomly chosen materials were investigated while varying such experimental parameters as sample weight, oxygen availability, airflow rate, and temperature. These parametric studies were performed in order to gain some insight

as to what effect these variables might have on the relative rankings of the 75 materials. However, it should be emphasized that the discussions in this section are based on the results of a single test and not the averaged results of three tests.

CONCENTRATION-TIME PROFILES. The sample materials were exposed to a temperature of 600° C for a period of 5 minutes. This exposure time resulted in some discrimination among materials in percent weight loss values, while an exposure time of 10 minutes resulted in essentially complete weight losses for the materials. It was therefore assumed that a 5-minute exposure period would benefit those materials which are more thermally stable. Nomex (78), for example, exhibits a weight loss of 77 percent at 5 minutes and 95 percent at 10 minutes. However, concentration-time profiles for selected gases have been obtained for several materials in order to determine whether or not the majority of the toxic gases are released within the first 5 minutes.

Figures 4 through 8 indicate the CO concentration-time profiles for wool (88), urethane (73), PVC (81), Nomex (78), and polycarbonate (32), respectively. These curves indicate the diverse behavior exhibited by the 12 materials that were investigated. The majority of the curves approximated the behavior of material 88 (wool), for which the evolution of CO was a two-part process. The weight loss observed for these materials in the first minute was approximately 85 percent of the total weight loss that occurred within the 5-minute exposure period. The second CO peak in figure 4 was apparently due to the further decomposition of the char. The urethane foams, as illustrated by material 73 in figure 5, underwent an almost complete weight loss within the first minute, and therefore a secondary CO peak was not observed. The evolution of CO occurred very rapidly with a resultant high peak CO concentration.

Figures 6 (PVC, 81), 7 (Nomex, 78), and 8 (polycarbonate,32) have been presented in order to indicate the complexity of the decomposition patterns that can be encountered. In addition, figures 7 and 8 illustrate the fact that the combustion gases were emitted within the 5-minute exposure period by most of the materials, although this was not the case for some of the more thermally stable materials.

Syringe sampling (reference 18) was used to establish the concentration-time profiles for HCN, HCl, HBr, and H_2S in addition to CO concentration-time profiles for the relevant gases illustrated in figures 9 (wool, 88) and 10 (wool/PVC, 96). In general, H_2S and HBr were two of the first gases to be evolved, normally occurring as single peaks within the first minute. Cyanide tended to parallel the evolution of CO, so that there were often two HCN peaks observed. This was especially noticeable for the wool/PVC blend in figure 10.

SAMPLE WEIGHT. The experimental procedure employed by CAMI for the animal toxicity tests involved exposing a 750-mg sample of material to 600° C for 10 minutes, with an airflow rate of 4 lpm. Therefore, several materials were tested at both 250 mg/2 lpm and 750 mg/4 lpm in order to compare the evolution of CO at the two experimental conditions. Figures 11 (urethane, 73) and 12 (wool, 88) are typical of the materials that were compared. The two curves in each figure are similar except for the thermal lag which is present for

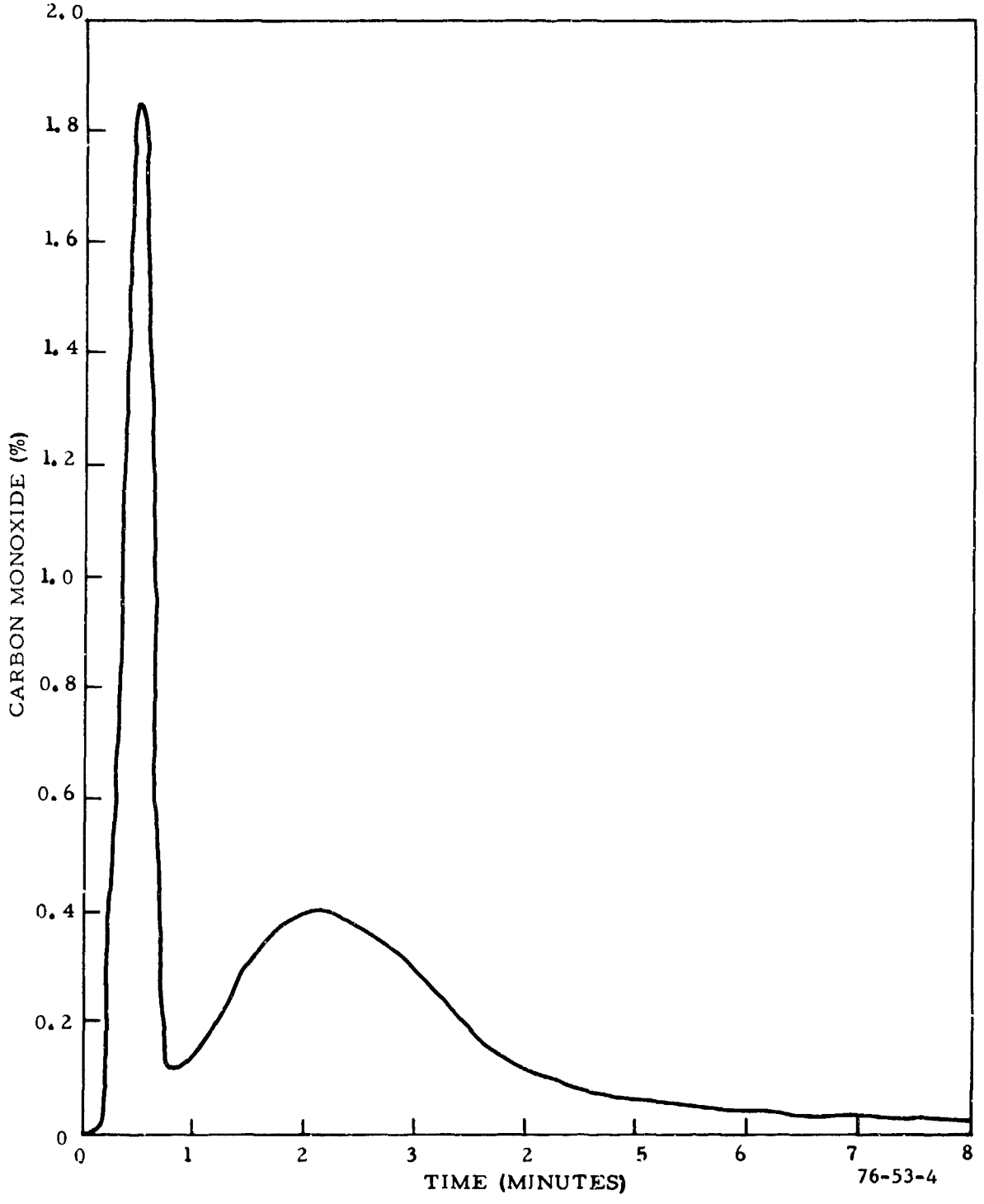


FIGURE 4. CONCENTRATION-TIME PROFILE OF CARBON MONOXIDE FOR WOOL (88)

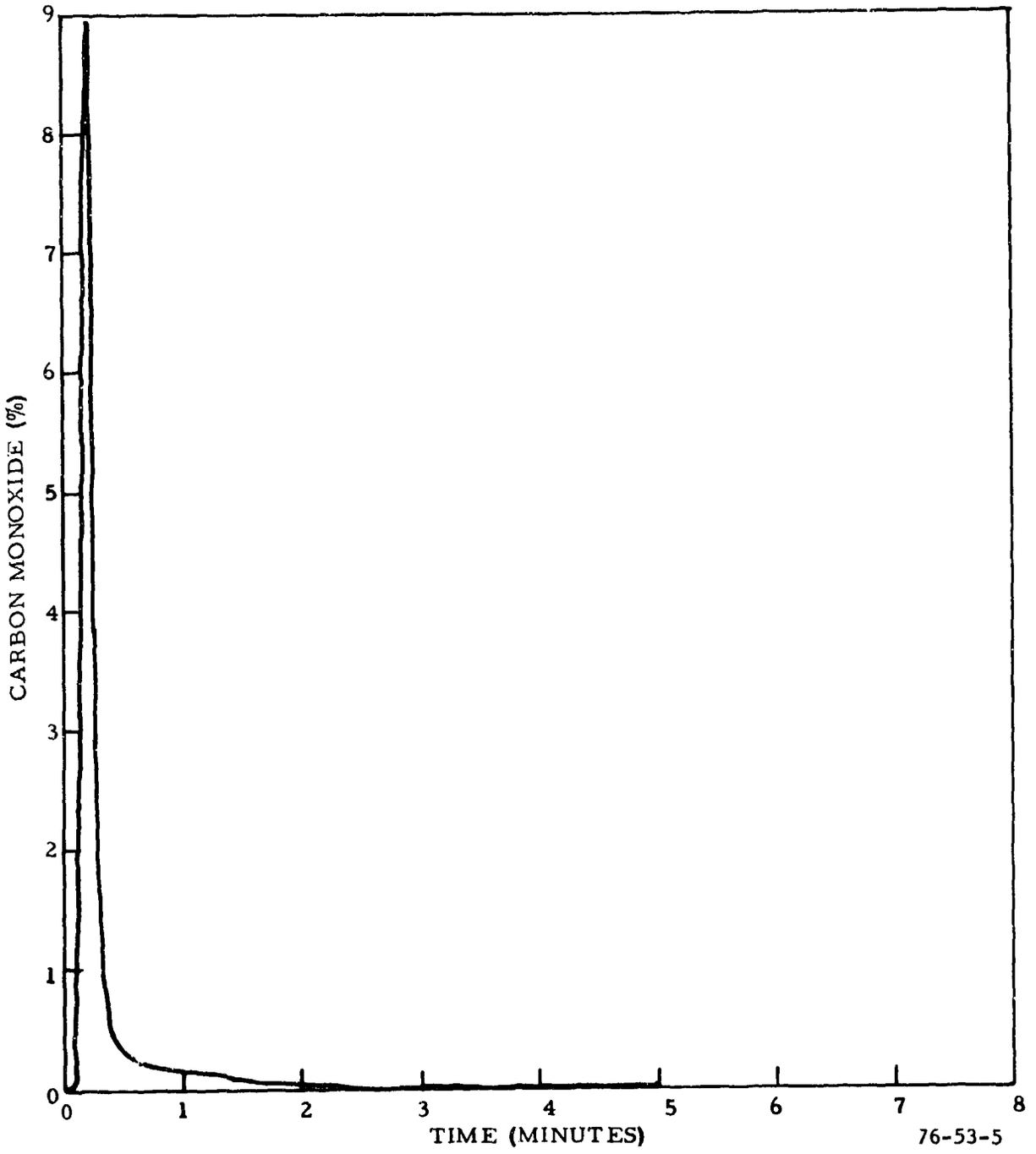


FIGURE 5. CONCENTRATION-TIME PROFILE OF CARBON MONOXIDE FOR URETHANE FOAM (73)

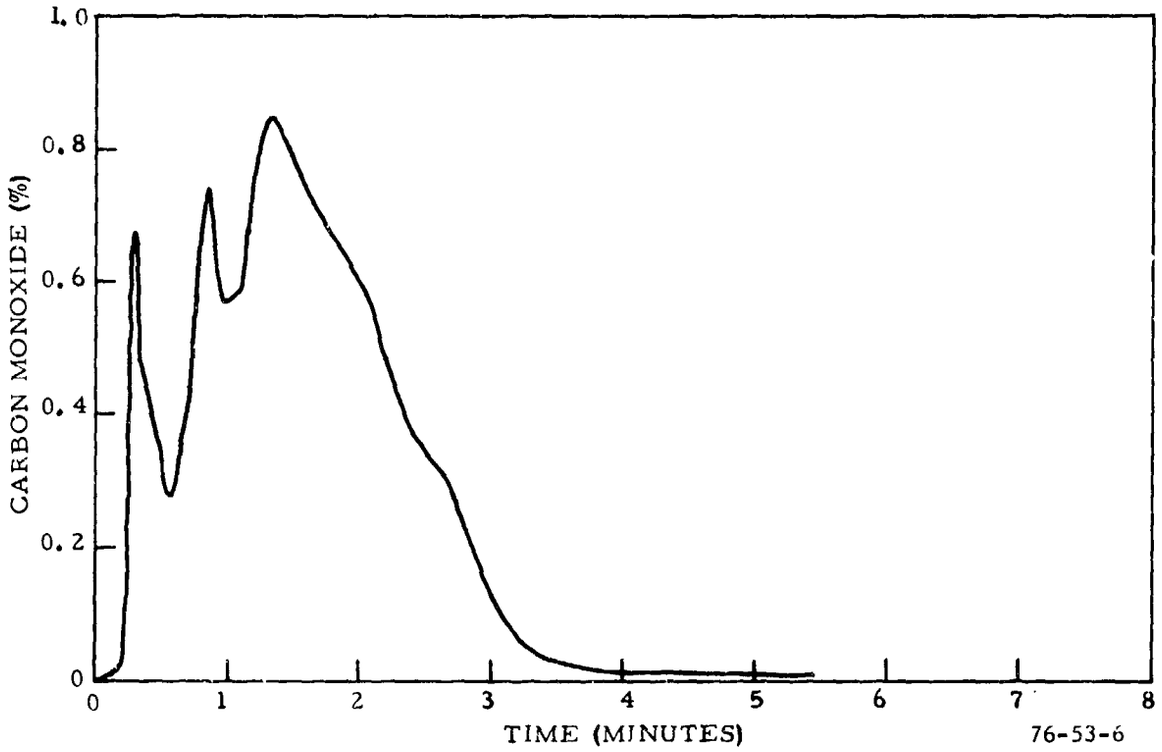


FIGURE 6. CONCENTRATION-TIME PROFILE OF CARBON MONOXIDE FOR PVC FABRIC (81)

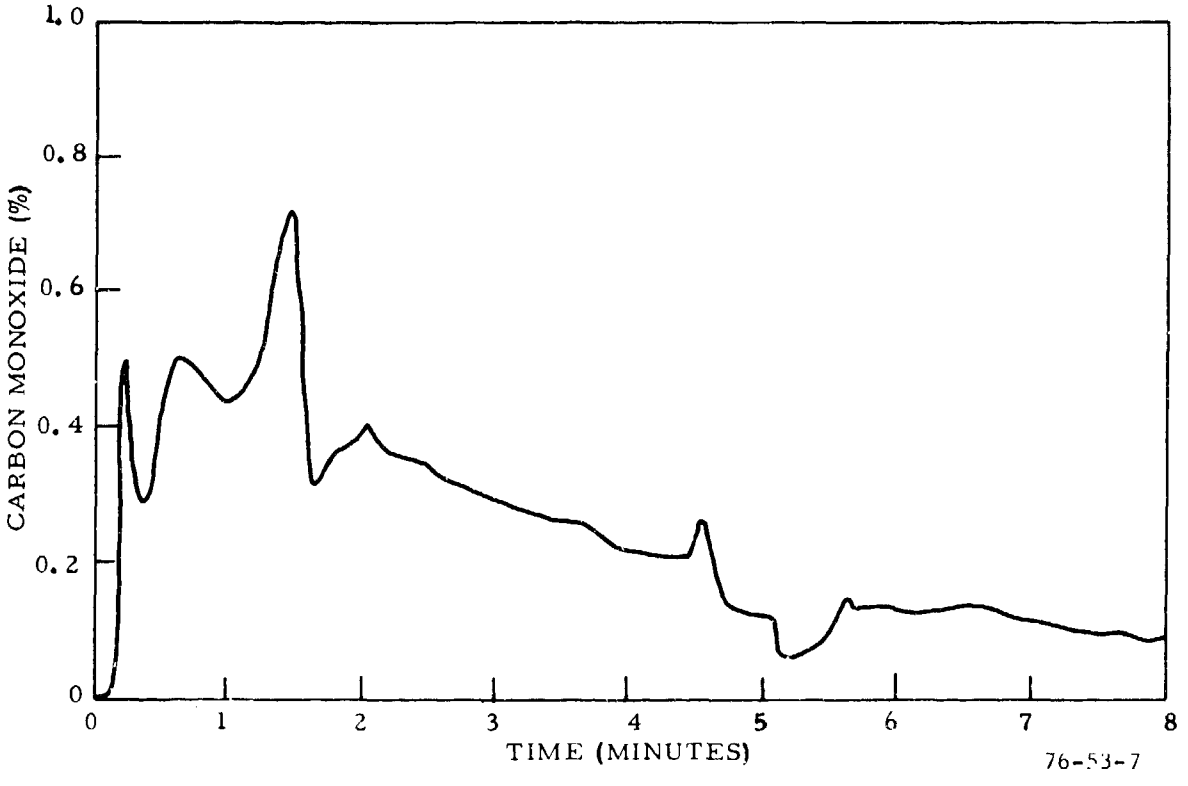


FIGURE 7. CONCENTRATION-TIME PROFILE OF CARBON MONOXIDE FOR NOMEX (78)

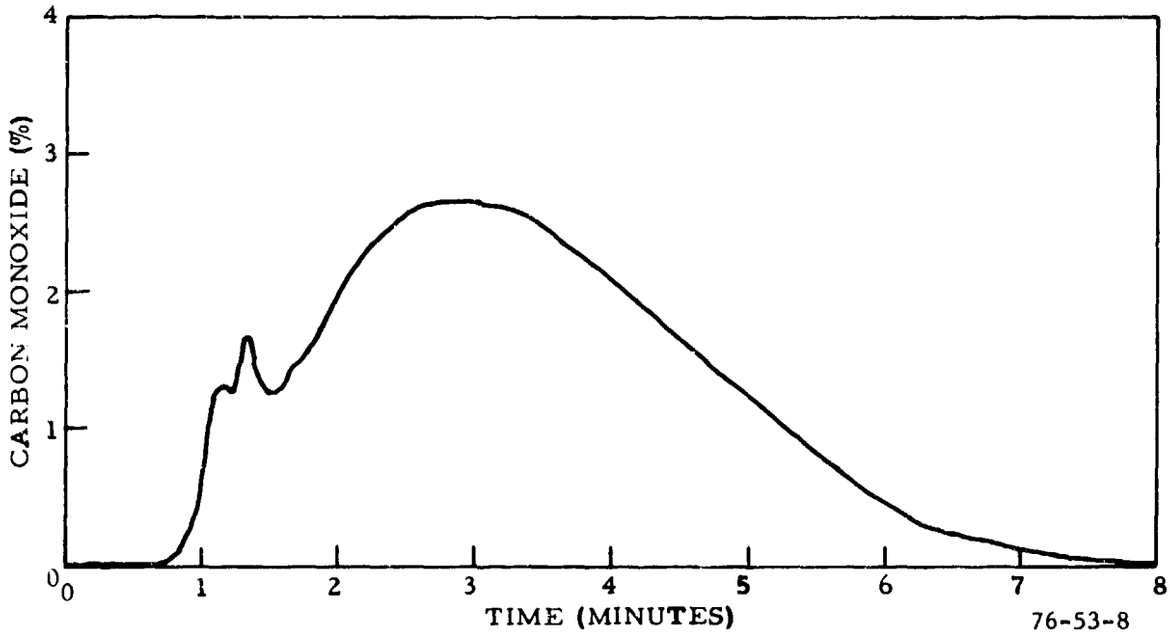


FIGURE 8. CONCENTRATION-TIME PROFILE OF CARBON MONOXIDE FOR POLYCARBONATE (32)

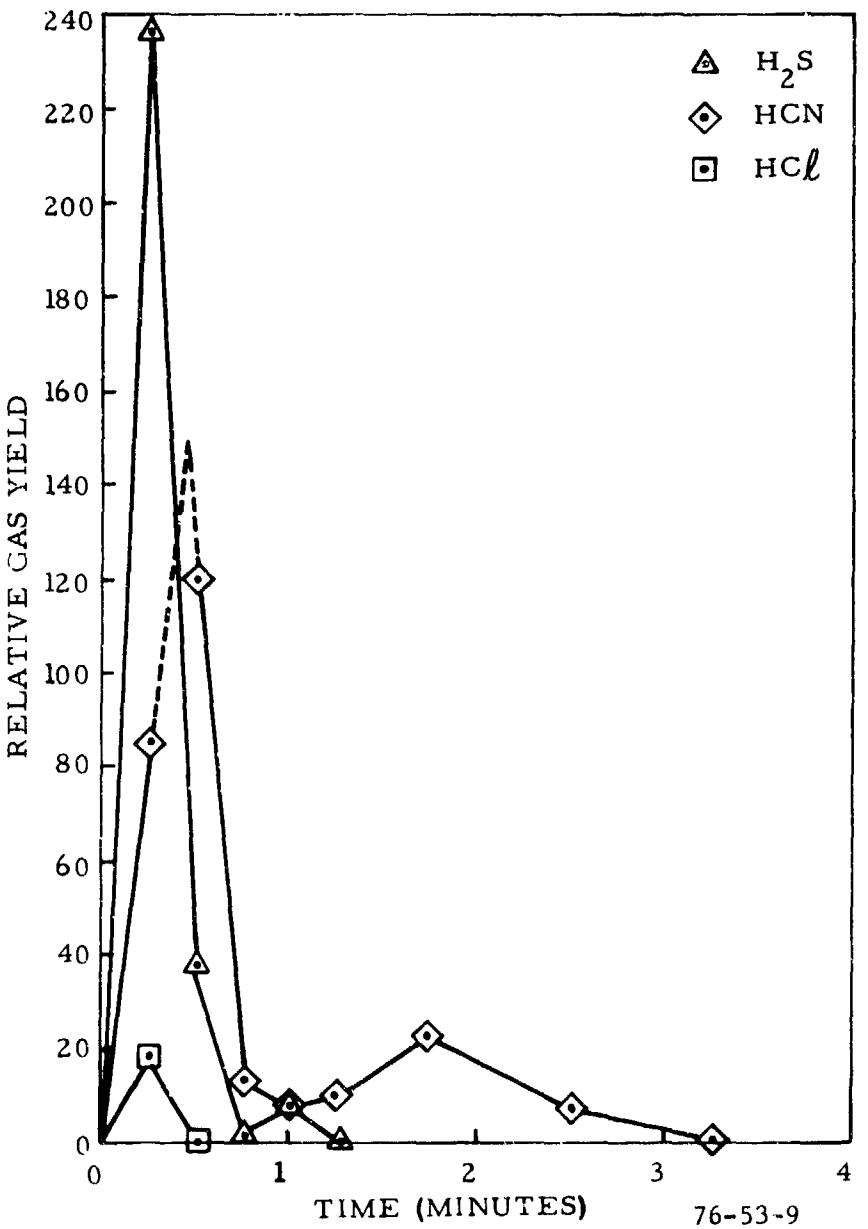


FIGURE 9. CONCENTRATION-TIME PROFILES OF TOXIC GASES FOR WOOL (88)

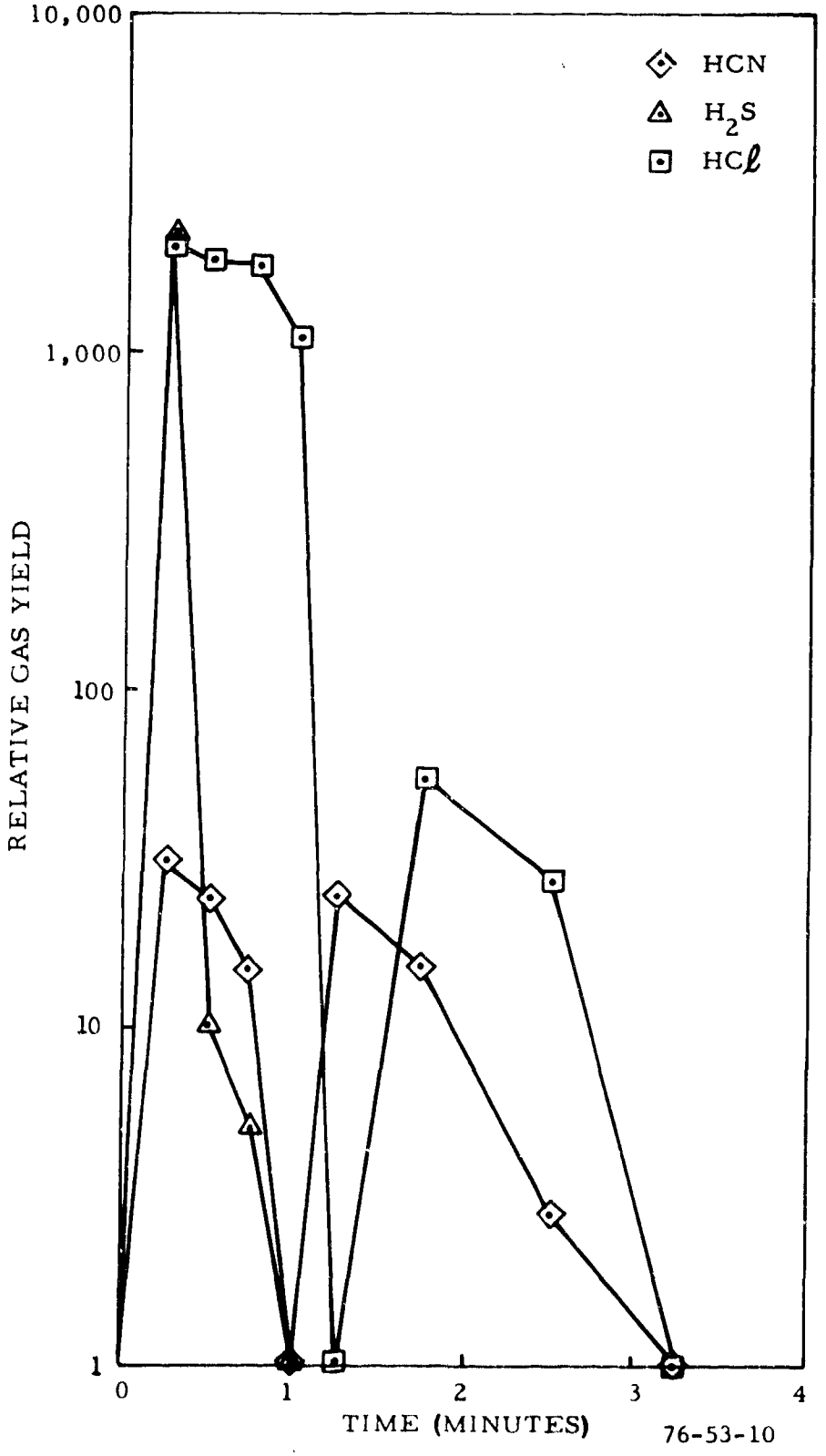


FIGURE 10. CONCENTRATION-TIME PROFILES OF TOXIC GASES FOR A WOOL/PVC BLEND (96)

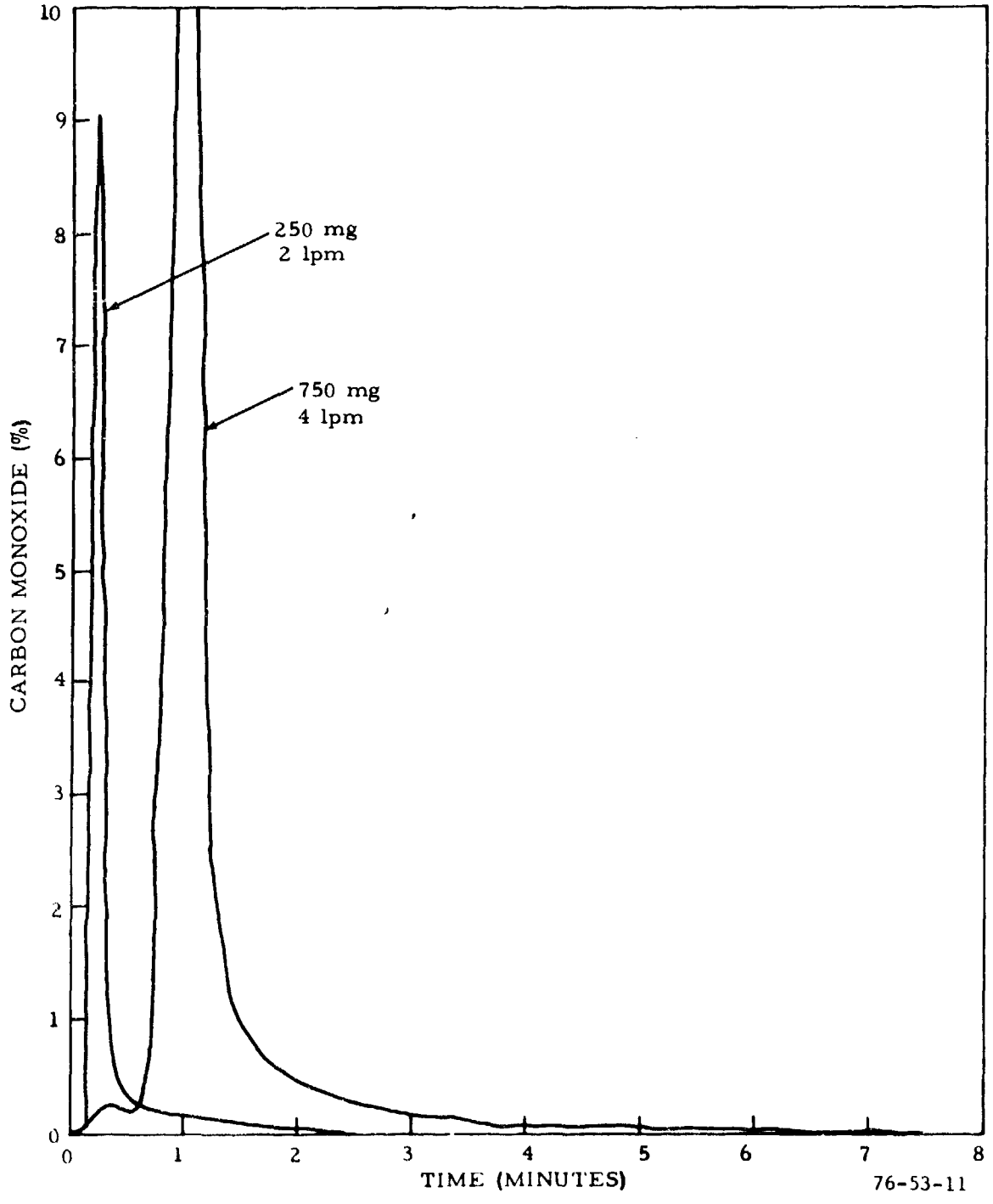


FIGURE 11. CONCENTRATION-TIME PROFILES OF CARBON MONOXIDE AS A FUNCTION OF SAMPLE WEIGHT AND AIRFLOW RATE FOR URETHANE FOAM (73)

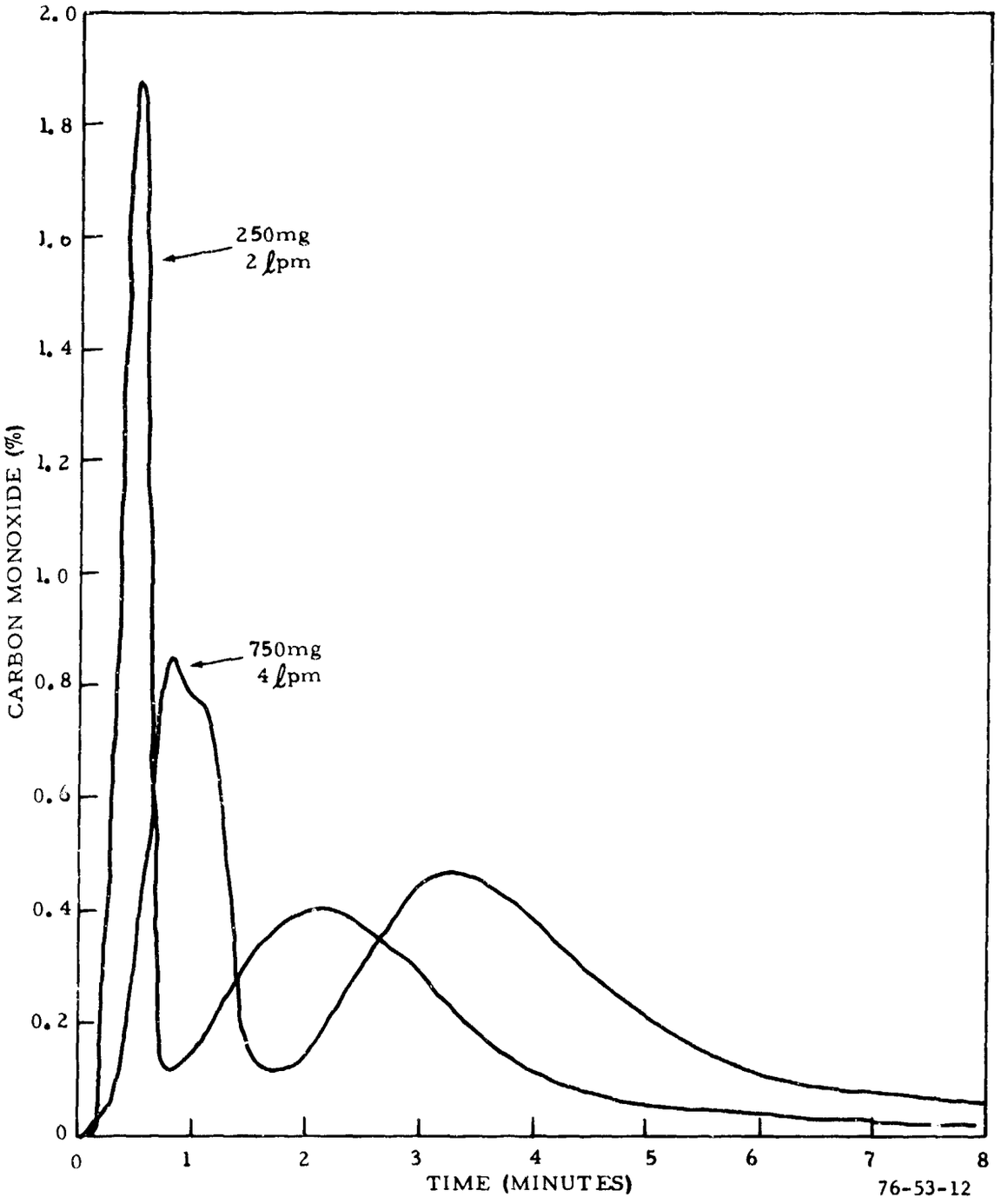


FIGURE 12. CONCENTRATION-TIME PROFILES OF CARBON MONOXIDE AS A FUNCTION OF SAMPLE WEIGHT AND AIRFLOW RATE FOR WOOL (88)

the 750-mg sample. However, figure 13 (wool/nylon, 70) illustrates the fact that a few of the materials exhibit a difference in behavior at the two test conditions.

In addition, these materials were tested at a sample weight of 250 mg and an airflow rate of 2 lpm in order to look at the effect of sample weight. The variations in the yields of HCN, HCl, H_2S, and HCHO as a function of sample weight are described for urethane (73) (figure 14), Nomex (78) (figure 15), and wool/nylon (70) (figure 16). The yields of HCN, HCl, and HCHO all decrease with an increase in sample weight for material 73, while HCN and HCl yields increase for material 78. The behavior of material 70 is more complex, in that the yield of HCN decreases with sample weight, while the H_2S yield increases. These data suggest that it would be difficult to generalize about the effect of sample weight on gas yields without a more detailed study.

PERCENT OXYGEN. The oxygen (O_2) content of the airflow was varied by mixing the airstream with nitrogen to produce either a 0, 10.5, or 21-percent concentration. The other experimental parameters remained constant (250 mg, 2 lpm, 600° C). Figure 17 indicates the yields of CO from three materials as the oxygen level is varied. The CO yield increased monotonically with oxygen availability for wool/nylon (70) and Nomex (78), although this was not true for the urethane foam. The CO yield from urethane (73) was significantly higher at 10.5 percent than it was at 21-percent oxygen.

Figure 18 shows the effect of oxygen concentration on the HCN yields of four materials. In general, the HCN yield increased quite rapidly between zero and 10-percent oxygen, but increased at a more moderate rate from 10 to 21-percent oxygen. The behavior of Nomex (78) was an exception, however, in that the HCN yield was much higher at 10-percent oxygen (33 mg/g) than at 21-percent oxygen (7 mg/g).

The behavior of the H_2S yield from material 70 was contrary to the general behavior of cyanide. The H_2S yield decreased almost linearly from 49 mg/g at zero-percent oxygen to 14 mg/g at 21-percent oxygen.

Gordon (reference 24) found that HCN yields increase as oxygen availability is reduced, and that CO is not greatly affected. However, the results of this study suggest that the HCN yield tends to reach a maximum under oxidative conditions. Although it is difficult to extrapolate results obtained under different experimental conditions, it should also be noted that analytical procedures can affect the conclusions of a study. Wagner (reference 7) states that the cyanide concentration from a polyimide was found to be independent of combustion conditions when determined by ion selective electrode, but varied by a factor of 5 to 10 when the HCN was determined by gas chromatography.

FLOW RATE. An airflow rate of 2 lpm was chosen in view of the experimental constraints imposed by the test procedure. The use of an airflow rate greater than 2 lpm caused excessive frothing of the collection media in the fritted bubblers, which resulted in a loss of sample for many of the materials. Therefore, this represents the most oxidative condition that could be maintained on a routine basis.

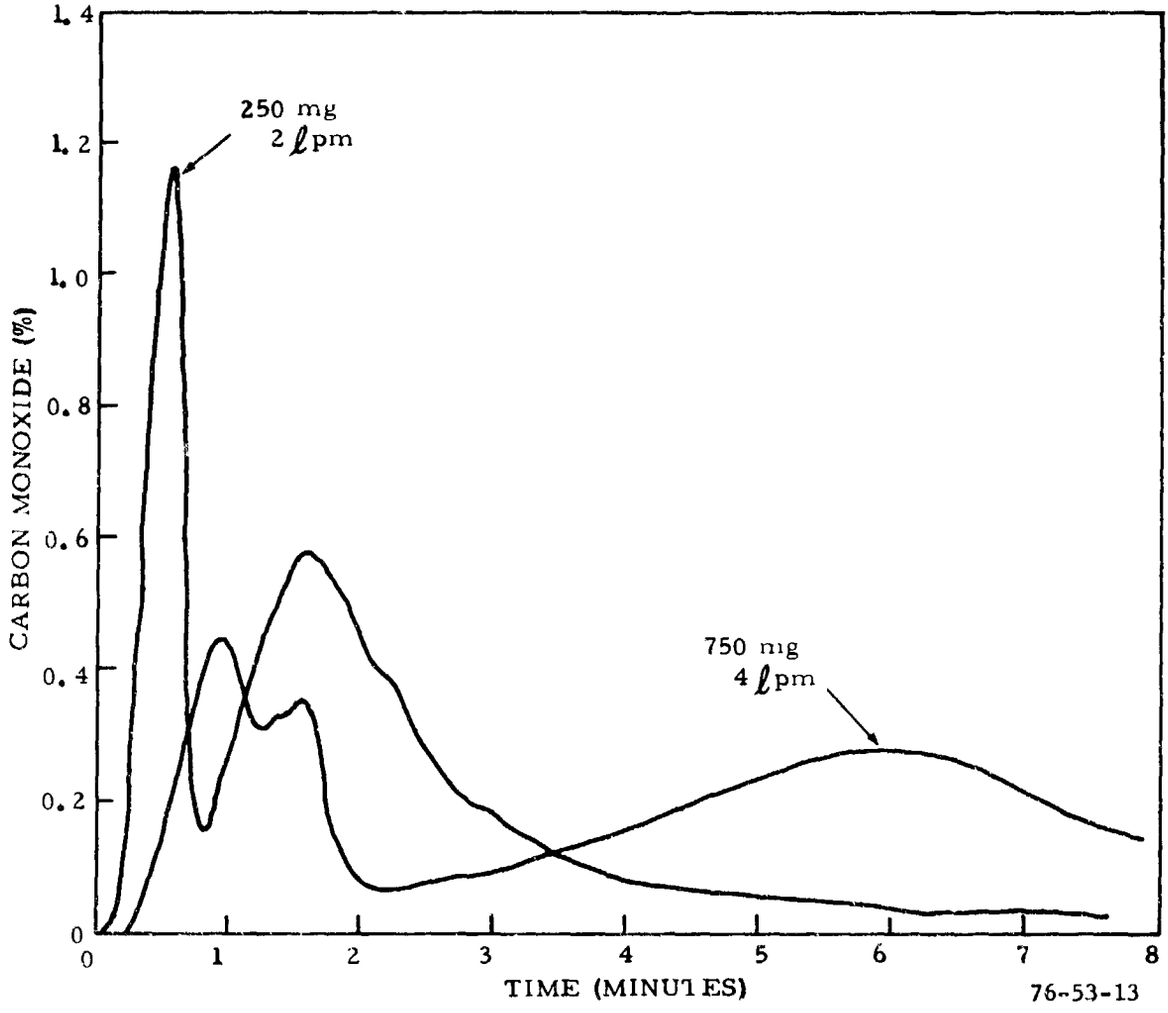


FIGURE 13. CONCENTRATION-TIME PROFILES OF CARBON MONOXIDE AS A FUNCTION OF SAMPLE WEIGHT AND AIRFLOW RATE FOR A WOOL/NYLON BLEND (70)

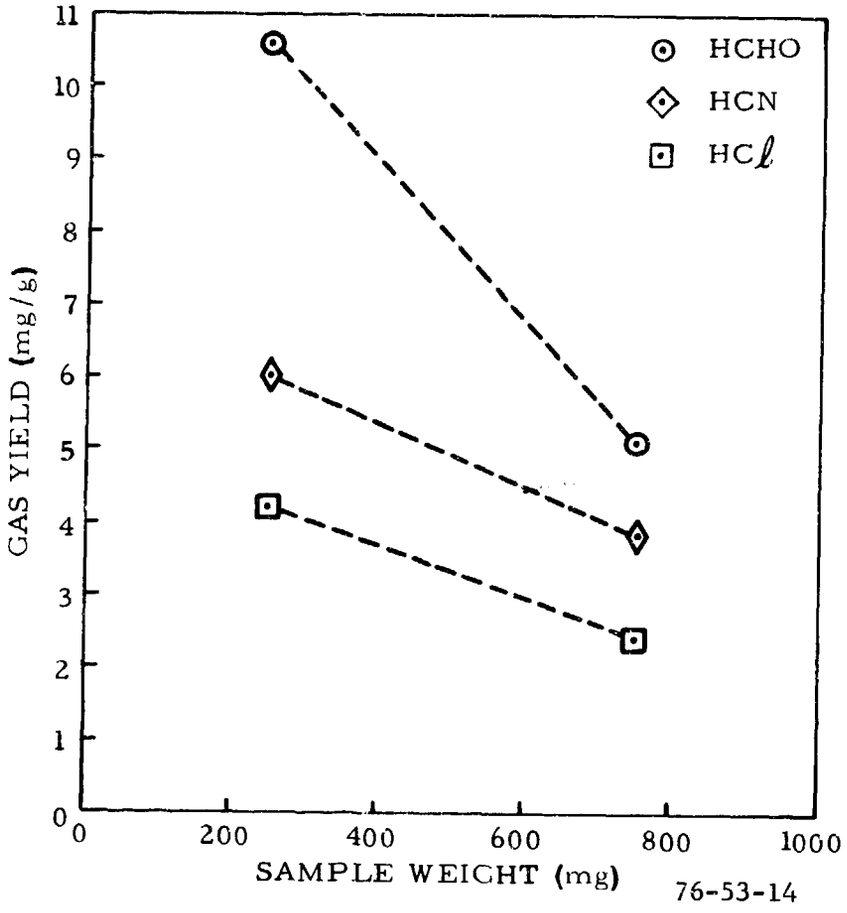


FIGURE 14. EVOLUTION OF TOXIC GASES FROM URETHANE FOAM (73) AS A FUNCTION OF SAMPLE WEIGHT

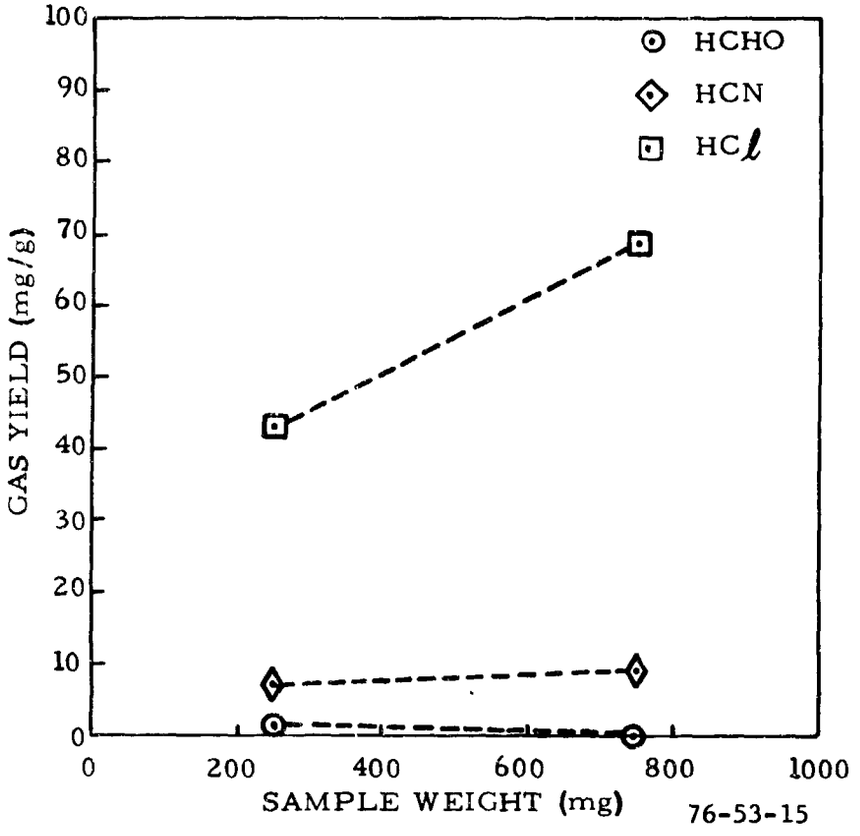


FIGURE 15. EVOLUTION OF TOXIC GASES FROM NOMEX (78) AS A FUNCTION OF SAMPLE WEIGHT

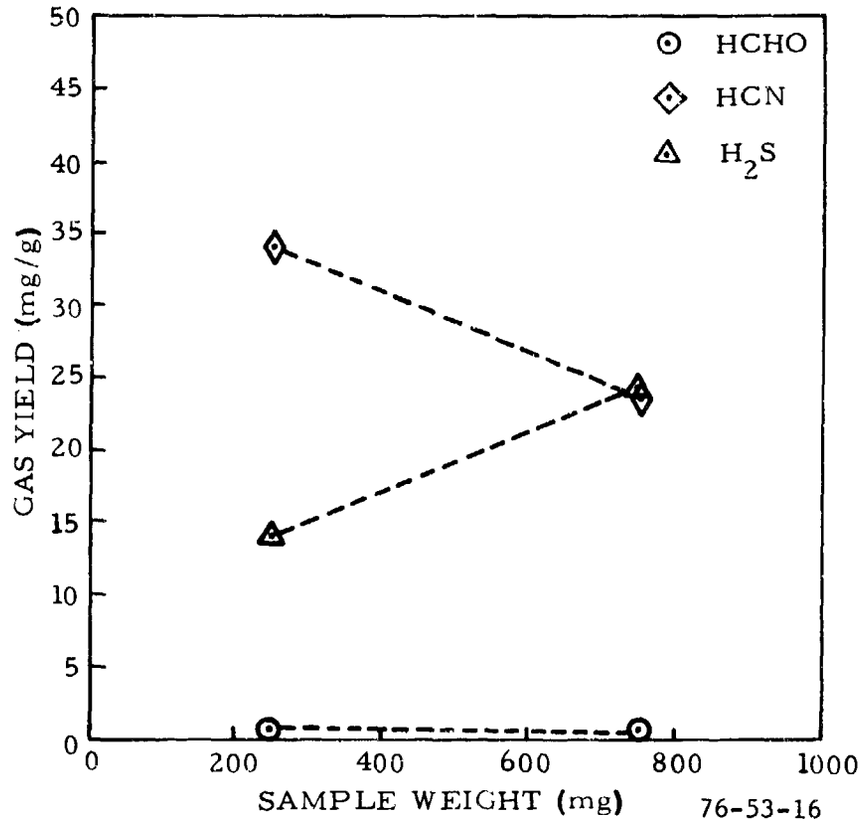


FIGURE 16. EVOLUTION OF TOXIC GASES FROM WOOL/NYLON (70) AS A FUNCTION OF SAMPLE WEIGHT

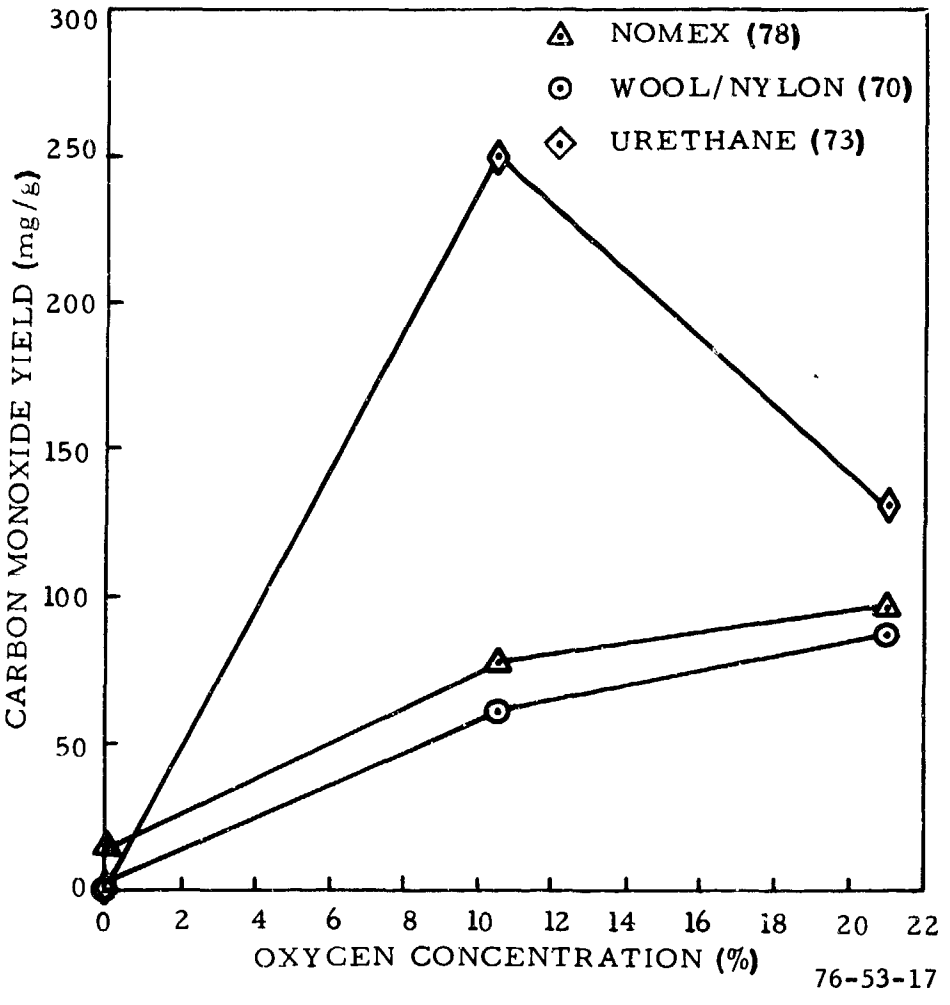


FIGURE 17. CARBON MONOXIDE YIELDS AS A FUNCTION OF OXYGEN AVAILABILITY

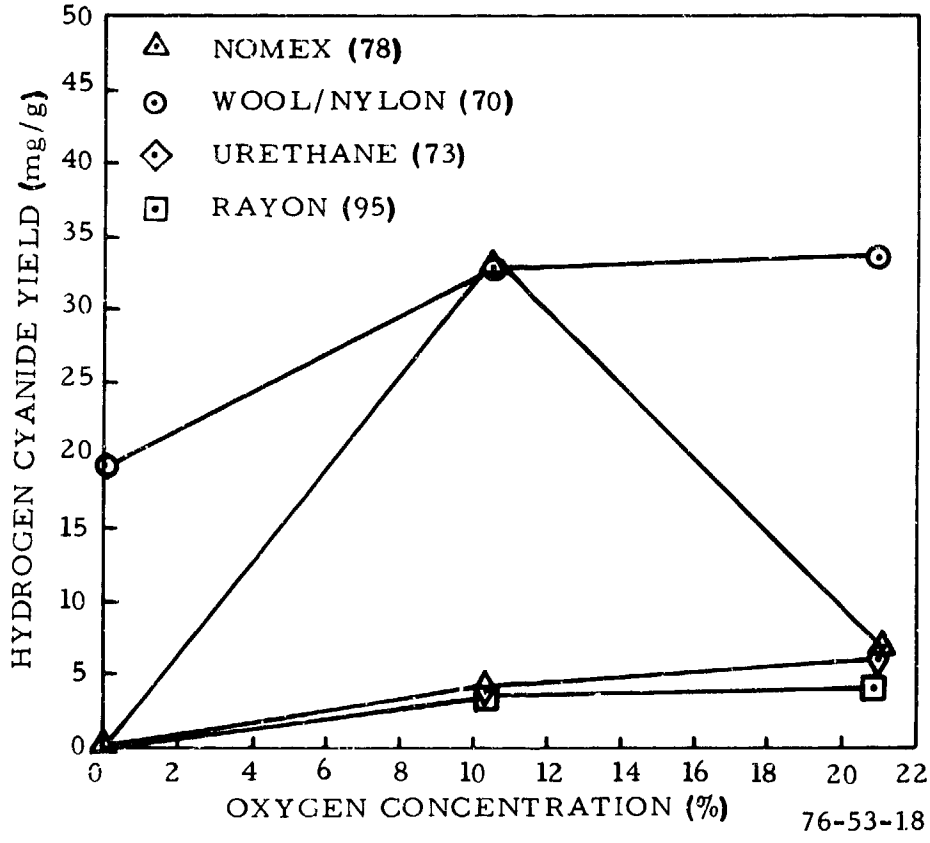


FIGURE 18. HYDROGEN CYANIDE YIELDS AS A FUNCTION OF OXYGEN AVAILABILITY

The CO yields, as a function of flow rate, are indicated in figure 19 for rayon (95) and wool/nylon (70). Both CO yields tend to decrease with an increase in airflow. These results could have been influenced by the fact that the furnace temperature was adjusted to 600° C at 2 lpm and it was not varied with flow rate. Therefore, heat transfer to the sample was somewhat of a variable. This was consistent with the observation that cyanide and sulfide also generally decreased with increased airflow. Gordon (reference 24) and Boettner (reference 8) also found that CO, HCN, and H_2S decrease with airflow rate.

TEMPERATURE. The effect of combustion temperature on the yield of CO for various materials is indicated in figures 20 and 21. Figure 20 illustrates the behavior of rayon (95) and a cotton/rayon blend (130). Both materials have a peak CO yield at 600° C. This is in contrast to figure 21, which contains data for materials containing wool. The wool (88) and wool/PVC blend (96) showed a significant increase in CO yield between 400° C and 600° C, with a tendency to level off at 800° C. Material 70 (wool/nylon), however, showed a significant increase in CO yield between 600° C and 800° C. In addition, it varied from the lowest value at 400° C to the highest at 800° C, while the other materials maintained their relative position.

The yield of HCN tended to increase linearly with temperature between 400° C and 800° C. The yield for wool/nylon (70) varied from 13 mg/g at 400° C to 49 mg/g at 800° C, while for urethane (73) the HCN yields were zero and 12.8 mg/g, respectively. However, the H_2S yield decreased with temperature for material 70, from 41 mg/g at 400° C to less than 5 mg/g at 800° C. Herpol (reference 26) has reported that HCN disappears at higher temperatures due to further oxidation, but this was not generally observed in this study. Only one of four materials, rayon (95), behaved in this manner in the temperature range from 400° C to 800° C.

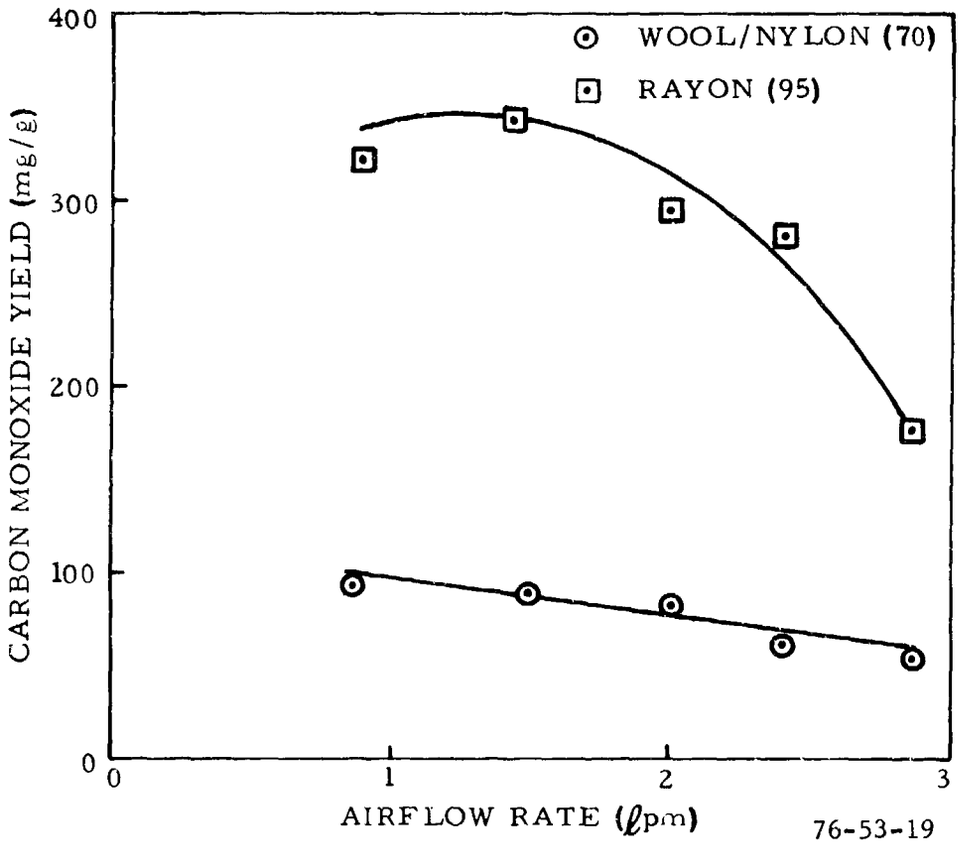


FIGURE 19. CARBON MONOXIDE YIELDS AS A FUNCTION OF AIRFLOW RATE

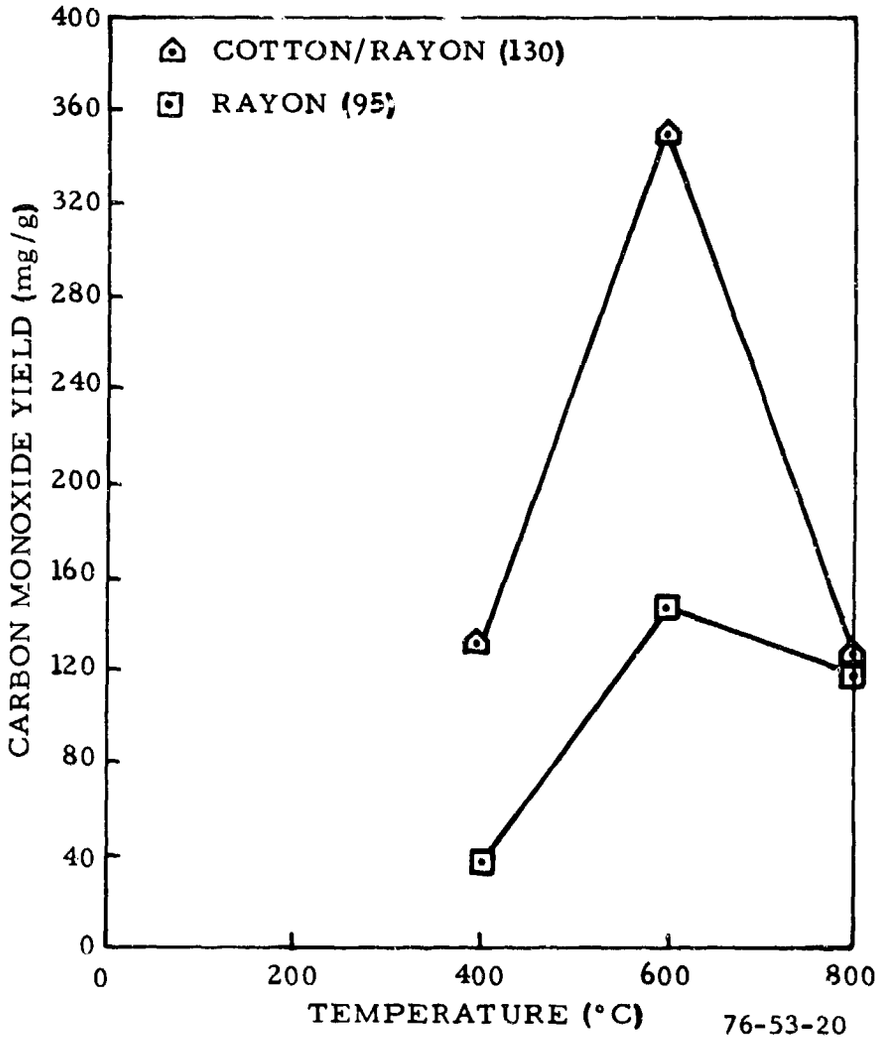


FIGURE 20. EFFECT OF TEMPERATURE ON THE YIELDS OF CARBON MONOXIDE

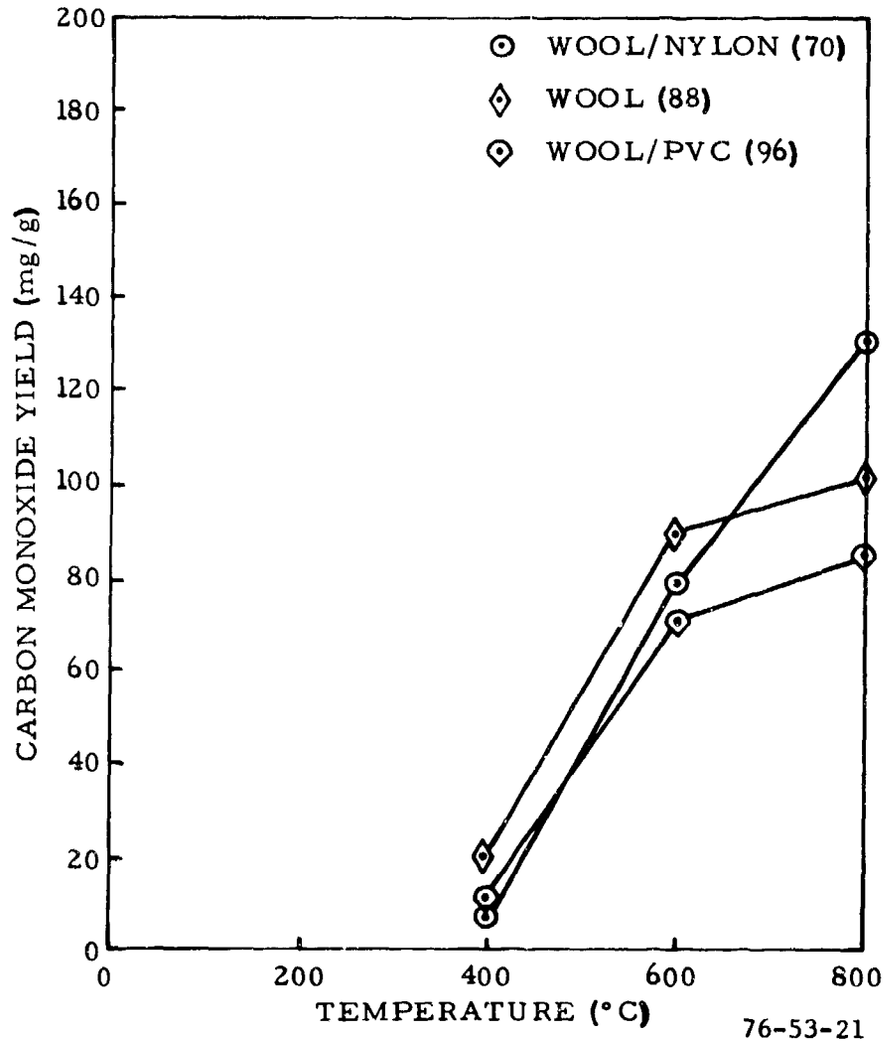


FIGURE 21. EFFECT OF TEMPERATURE ON THE YIELDS OF CARBON MONOXIDE

SUMMARY OF RESULTS

1. The average relative standard deviation (ARSD) for CO was 9 percent, while it was approximately 21 percent for HCN, H_2S, HCl, HBr, and HF. The ARSD was roughly 57 percent for NO_2, SO_2, and HCHO.

2. A cotton/rayon blend (130) produced the highest CO yield of any of the fabrics, while modacrylic (127) produced the highest HCN yield of any material.

3. Wools were the only materials which produced H_2S in significant amounts.

4. Wool/PVC blends (82, 96) produced more than 10 times as much SO_2 as the wool (88).

5. The coated fabrics only produced CO and HCl in significant amounts, and CO yields were generally inversely related to the HCl yields.

6. The polycarbonate thermoplastics produced the highest CO yields of any of the 75 materials.

7. The fire-retarded polymethylmethacrylate (108) produced more than four times as much CO as the untreated material (109).

8. Formaldehyde yields from the elastomers were high compared to the HCHO yields of the other material categories.

9. The sample weight loss observed in the first minute was approximately 85 percent of the total weight loss that occurred within the 5-minute exposure period.

10. Hydrogen sulfide was evolved within the first minute, while the evolution of HCN tended to parallel the evolution of CO.

11. Except for Nomex, the HCN yield tended to reach a maximum under oxidative conditions for oxygen concentrations between zero and 21 percent.

12. The yields of CO, HCN, and H_2S decreased with an increase in airflow rate between 1 and 3 lpm.

13. The yield of HCN increased linearly with temperature between 400° C and 800° C for 3 of the 4 materials tested.

CONCLUSIONS

From the results of this study it is concluded that:

1. The precision of combustion gas analysis is greatly influenced by the random nature of the combustion process.

2. The analysis of NO_2, SO_2, and HCHO may be of limited utility for the purpose of ranking materials due to the large RSD's for these gases.

3. The combustion tube furnace exhibits acceptable reproducibility for generating most of the combustion gases discussed in this report, including CO, HCN, H_2S, HCl, HBr, and HF.

4. Isothermal conditions do not differentiate between the different thermal stabilities of most materials.

5. Broad generalizations about the variations in the yields of combustion gases as a function of experimental conditions may be inappropriate, since the observed effects seem to be dependent upon the composition of the test material.

RECOMMENDATIONS

From the conclusions, it is recommended to:

1. Continue to investigate various analytical procedures as to their applicability to the analysis of complex combustion mixtures.

2. Conduct intermediate and full-scale tests with the objective of ranking materials for relative toxicity, then use this information to develop and parameterize a laboratory test.

3. Develop a standard toxicity test procedure which (1) is valid for composite materials, (2) is acceptable for gas analysis, and (3) simulates the behavior of a material in a fire.

4. Investigate the desirability of using temperature programming in place of the isothermal conditions employed in this study.

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