DETERMINATION OF PRODUCTS OF COMBUSTION FROM FIRES INVOLVING SOLVENTS COMMONLY CARRIED BY RAIL

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Summary

The apparatus and protocols used to determine the semi-volatile products of combustion from controlled laboratory-scale fires are presented. Products of combustion were collected in a sampling train consisting of a filter (heated to $160°C$) and Tenax and charcoal sorbent tubes. The Tenax tubes were extracted with cyclohexane and the extracts analyzed. Quantitative measurement of the semi-volatile components was made using gas chromatography/flame ionization detection and identification of the products was performed using gas chromatography/mass spectrometry. The results for sixteen solvents commonly carried by rail are presented.

Introduction

According to the *1984 Emergency Response Guidebook* [1] issued by the U.S. Department of Transportation to personnel responding to rail accidents, the recommended procedure for serious fires is to evacuate personnel in the immediate vicinity and areas downwind and to let the fire burn itself out. The sponsors of this study were interested in determining the products of combustion of solvents carried in railroad tankcars in order to assess the potential toxicity of plumes from rail accidents involving fire. Such information could be used to estimate a safe evacuation distance using a simple dispersion model. The solvents selected for study were the sixteen most-commonly carried hazardous liquids shipped in large quantity by rail. These were: methanol, isopropanol, n-butanol, methyl ethyl ketone, methyl isobutyl ketone, acrylonitrile, benzene, toluene, mixed xylenes, acetone, butyraldehyde, ethyl acetate, butyl acetate, vinyl acetate, hexane, and cyclohexane.

Environmental conditions can vary widely in such accidents, altering the composition of the combustion products [2—4]. A chamber was therefore constructed to permit control of the conditions surrounding combustion of the solvent. The design of the chamber was evaluated by combustion of two sets of model compounds and comparison of the burn data with calorimeter

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studies. The effects of experimental conditions on the rate of solvent consumption (burnrate), and the relative amounts of soot produced as a function of oxygen availability were the subjects of a previous paper [5].

Table 1 summarizes the effects of the three experimental variables on the rate of product consumption, or "burnrate" for the model compounds. Decreasing the oxygen content of the inlet air reduces the burnrate, as does decreasing the inlet air flow rate at constant oxygen concentration. These effects are a result of altering the stoichiometic conditions of the burn. Heating the solvent increases its volatility and results in an increase in burnrate. Based on these observations and in order to simulate typical conditions surrounding a tankcar fire, the combustion of solvents for collection of samples of the products was performed under the "standard" conditions listed in Table 2.

A great deal of work has been performed on the toxicity of the combustion products [6—9] from a variety of samples. Polyaromatic hydrocarbons (PAHs) have been identified in the products of combustion of methane/ oxygen flames [10], wood and straw soot [11], polymer smoke [12, 13], diesel exhaust [14, 15] and in ambient aerosols [16, 17]. Due to the potential mutagenicity and/or toxicity of PAHs [18], the sampling and analysis methods in this study were chosen to optimize for detection of moderate molecular weight, semi-volatile organic species, including, but not limited to, PAHs. Problems associated with sampling for carbon species [19], and errors due to artifact formation [20, 21] have been reported. The potential for reduced efficiency of the sorbent when sampling streams with high moisture

TABLE 1

Effect of experimental conditions on the burnrate of model compounds (mg/cm^2 min)

Compound	Experiment 1 Temp. = 25°C Oxygen = 20.9% Air flow rate, L/min				Experiment 2 Temp. = 25°C Flow = 10.0 L/min Oxygen content %			Experiment 3 Oxygen = 20.9% Flow = 10.0 L/min Temperature, °C	
	5.0	7.5	10	15	10.5	15.7	20.9	25	35
Pentane	62	86	107	146	n	55	107	107	176
Hexane	47	73	90	99	n	32	90	90	113
Heptane	30	38	46	44	n	i	46	46	79
Decane	n	n	n	n	n	n	n	n	26
Methanol	52	60	65	64	n	68	65	65	76
Ethanol	41	48	48	48	n	i	48	48	58
2-Propanol	36	41	49	46	n	i	49	49	57
Butanol	n	n	33	—	n	n	33	33	40

n: did not burn
i: incomplete burn

TABLE 2

Standard conditions for combustion of solvents and collection of combustion products

Parameter	Condition
Solvent	
Volume	7.0 ml
Surface area	7.1 cm^2
Initial temperature	25°C
Air supply	
Oxygen concentration	20.9% (v/v)
Inlet flow rate	10.0 L/min
Relative humidity	0.0%
Sample Collection	
Aspiration rate	325 mL/min
Time	duration of burn
Filter temperature	160°C

content has yet to be examined thoroughly. In general, however, sampling for such species involves use of a filter to remove particulate material and one or more sorbent tubes to collect the vapors or gases. For the study of combustion products described here, the sampling train consisted of a glass-fiber filter in series with a Tenax tube to collect the semi-volatile vapors and a charcoal tube to remove volatile gases. To minimize condensation of vapors on the filter during sampling, the filter was maintained at 160°C during sampling, as was the inlet and the top of the chamber. Various sorbents have been used to collect polyaromatic species including XAD-2, XAD-4, Florisil, and Tenax-GC. The latter was selected for this work since it has a high efficiency for "neutral" (nonpolar) organics of moderate molecular weight and volatility such as the PAHs [22, 23].

The sorbent tubes can be either thermally desorbed [23] or extracted with a suitable solvent. A variety of solvents have been used to study various organic fractions of combustion products. The neutral fraction contains the majority of the PAHs of interest. Benzene [16, 24], chloroform/methanol mixtures [24], acetone [21], dichloromethane [15, 25] and cyclohexane [24, 26] have been used to extract the neutral organic fraction. The aromaticity of benzene would indicate that it would be a somewhat better solvent for the polyaromatic hydrocarbons. For this study, however, cyclohexane was used since it is less toxic than benzene. As was indicated elsewhere [19], a definition for "extractable organic" content must, in any case, be an operational and method-dependent one. It should be kept in mind, therefore, that only the cyclohexane-extractable organic fraction was investigated in this study.

A wide choice of modern analytical techniques is available for studying

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such extracts including: conventional and capillary gas chromatography (GC); GC/mass spectrometry (GC/MS) and MS/MS [14]; high performance liquid chromatography [27—29] using various detectors; and synchronous luminescence and room temperature phosphorescence [30]. For this study, the cyclohexane extracts were analyzed by GC/FID to quantitate the species present, and GC/MS was used for identification of the species found, when possible. Results of the analyses of combustion products from sixteen commonly shipped solvents burned under controlled conditions are reported.

Experimental

Reagents

All gases were obtained from Linde Corporation (Union Carbide, Linde Division, Danbury, CT). Solvents were obtained from Fisher Scientific (Atlanta, GA) and were spectranalyzed grade except for the "xylenes", which was a commercial solvent-grade mixture of the type shipped by rail. The cyclohexane used for extraction was HPLC grade.
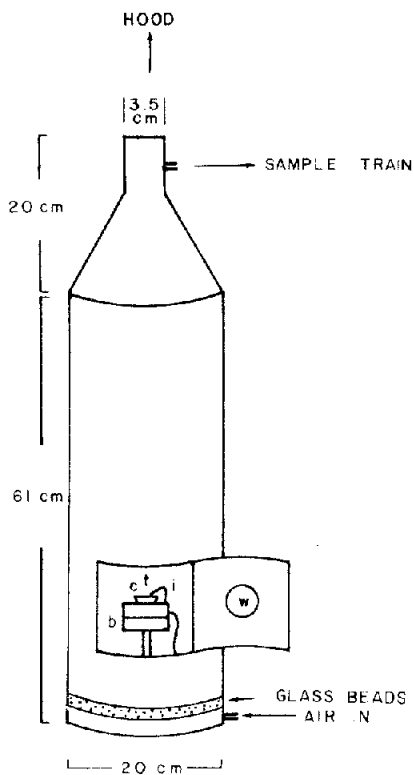
Fig. 1. Schematic diagram of combustion chamber used to generate samples. The sample block (b), crucible (c), igniter wire (i), thermocouple (t) and windowed door (w) are shown.

Open burn systems

The furnace design had to allow for direct measurement or control of three key variables: oxygen concentration, air flow rate, and sample temperature. The combustion chamber, designed from the above considerations, is illustrated in Fig. 1. It consisted of a 0.64 cm stainless steel cylinder, 20 cm ID and 61 cm in height. A demountable stainless steel funnel which terminated in a 3.5 cm ID tube was affixed to the top. Pressurized laboratory air (20.9% oxygen) was passed through a tube containing Drierite and 4A molecular sieve before entering a gas-dilution manifold which consisted of a set of flowmeters and precision metering valves. The air entered at the base of the cylinder through a coiled, perforated copper tube below a 0.65 cm thick bed of glass beads. A windowed door located approximately 15 cm from the base allowed observation of, and access to, the sample. A 7.00 (± 0.05) ml aliquot of the solvent to be burned was transferred volumetrically to a platinum crucible. The crucible rested in a 7.5 x 10 x 5 cm aluminum block fitted with a resistive heater to control the sample temperature prior to ignition. The block was maintained at 25°C. A nichrome igniter wire was positioned above the sample well. Iron-constantan thermocouple wires were placed in the sample block, above the sample, on the funnel and in the filter holder. The thermocouples were connected through a selector switch to a Fisher Series 500 strip-chart recorder. The burn was initiated using a Variac to increase the igniter wire voltage until the sample ignited, as indicated by the thermocouple above the sample, which was monitored during the burn.

Standard conditions

Several assumptions were required concerning the accident situation to be simulated. The commodities used as samples represented solvents carried in large quantity by rail. The sample was assumed to be liquid at room temperature (25°C), and on fire. Conditions surrounding ignition of the sample were not considered. The tankcar was assumed to have a single breach in the shell through which air entered and combustion gases exited. Because of the air flow pattern, it was assumed that a dynamic equilibrium was reached between influent air flow, product volatilization rate, total heat released during combustion, and exhaust gassing. Additionally, the following environmental assumptions were made: (a) all burns would occur in normal air (20.9% oxygen); (b) the ambient pressure would be one atmosphere; (c) the relative humidity would be constant during the burn; and (d) burning conditions could range from a minimum of air required for combustion to a condition of unlimited supply.

Table 2 lists the conditions selected for combustion of the solvent and collection of samples for analysis. Since the air flow into the system was constant, the stoichiometry of combustion changed with the burnrate of the solvent. For the fastest burning normal alkane, pentane, twice the stoichiometrically required oxygen was supplied to the chamber. For some slow-burning materials, the amount of oxygen supplied was in ten-fold excess.

Such conditions realistically simulate conditions which occur in open burning of solvents where inflow and composition of the air is relatively constant.

Sample collection

The products of combustion were sampled under the conditions listed in Table 2 through a port at the top of the open-burn chamber. The sampling train is shown in detail in Fig. 2. The components of the sampling train were connected with Teflon swage-type fittings. The inlet is a downward-facing Teflon-coated stainless steel tube. The tube was attached to a stainless steel filter holder containing a 37 mm diameter glass fiber filter (GFF/A Gelman Sciences Inc., Ann Arbor, MI) supported by a stainless steel screen. The funnel, sampling probe and filter holder were maintained at 160°C to minimize condensation of semi-volatile components on the filter.
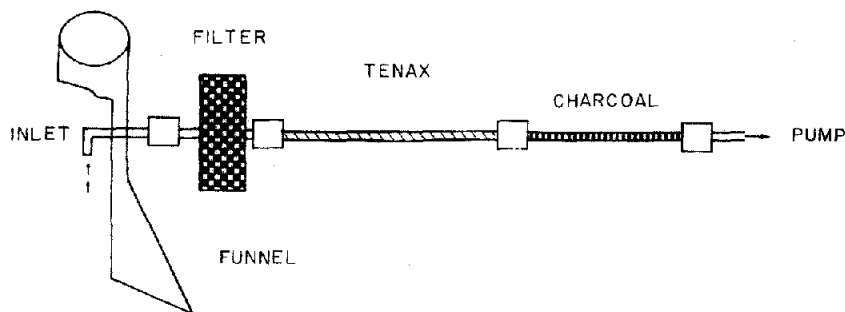
Fig. 2. Diagram of sampling train used to collect combustion products during combustion of solvents in the chamber shown in Fig. 1.

Vapors were collected in sorbent tubes attached in series between the filter and sampling pump. Moderate molecular weight species not deposited on the filter were collected in a tube containing Tenax-GC, 60—80 mesh (Supelco, Inc., Bellefonte, PA). This sorbent is recommended for collection of species with moderate volatility [22, 23]. The Tenax was extracted in a Soxhlet apparatus for twenty-four hours with cyclohexane and dried prior to packing. Glass wool used to plug the tubes was similarly treated. The Tenax (155 ± 5 mg) was packed in a 0.63 cm OD x 20 cm long glass tube. After packing, the tubes were conditioned by outgassing at 260°C for 30 min at low helium flow, then cooled, capped and stored. Sorbent tubes were stored at all times at 4°C to minimize contamination or volatilization losses. Commercially available (SKC Inc., Appomatox, VA) charcoal tubes were used to remove the more volatile components of the sample. The charcoal tubes were not analyzed.

A carbon-vane pump, regulated with a precision metering valve, was used to draw the sample through the train. In order to avoid biases in sampling due to the momentum of the particulate matter, the flow rate of the sample was adjusted so that its face velocity matched that of the stream exiting the

chamber. Under such conditions, the system was iso-kinetic with respect to to particle size and was free from bias. Given the diameters of the exit tube and sample probe and the flow rate of the air stream supplied to the chamber, a sample rate of 325 mL/min was required. The flow was set prior to sampling by adjustment of a metering valve while measuring the flow at the probe inlet with a rotameter. The flow was remeasured after sampling and corrected for any decrease. In most cases, the flow did not change during sampling. Sampling was begun once the flame temperature stabilized and was stopped when the flame temperature became erratic, indicating the flame was about to extinguish. Sampling time was measured by marking the start and stop time on the strip chart recording the burn duration. The total volume sampled was calculated from the flow rate and time.

Extraction procedure

The Tenax and glass wool were emptied into a cellulose micro-thimble and extracted with HPLC-grade cyclohexane for eight (8) hours using a micro-Soxhlet extractor. The extract was then reduced to a volume of 0.50 mL in a graduated Kuderna—Danish evaporative concentrator. The concentrated extract was transferred with three 0.5 ml rinses to a volumetrically calibrated septum-capped vial and stored at 4°C. Blank Tenax tubes were similarly extracted. Immediately prior to analysis, the volume was reduced to 0.2 mL by mild heating.

GC/FID analysis of extracts

Table 3 shows the chromatographic conditions used to separate the components of the Tenax extracts for both GC/MS and GC/FID. In order to minimize differences in retention characteristics, identical columns were obtained for the two instruments. A Perkin-Elmer Model Sigma 3B gas chromatograph linked to a Model Sigma 15 data station was used for quantitative analysis. Standard solutions were prepared by dilution of pure normal hydrocarbons (Kit No. 21C, Alltech Assoc., Deerfield, IL) with cyclohexane. Mixtures containing 1/1000 (v/v) dilutions of C_6 through C_{15} and C_{16} through C_{20} normal hydrocarbons were prepared as working solutions and portions were injected into the GC/FID. Calibration curves of response versus mass for pure hydrocarbon were plotted.

The concentrations of the unknowns were obtained from these plots using the Hydrocarbon Equivalent Method. This procedure is used when the analytes are unknown and present in large number. In such cases, the preparation of standards of exact composition is not possible. In order to use the Hydrocarbon Equivalent Method, one assumption is made which may result in significant errors. It is assumed that each species will have the same FID response factor as the hydrocarbon standard nearest it in retention time. If the response factor is different, the error is proportional to the difference. In most cases, an error, if any, will tend to underestimate the concentration since the response of the FID is generally higher for normal hydrocarbons. In

TABLE 3

Chromatographic conditions for GC/FID and GC/MS analysis of cyclohexane extracts of Tenax tubes

Parameter	Condition
Extraction volume	0.20 mL
Injection volume	0.1—0.5 μL
Column	glass, 0.63 cm OD $\times$ 2 m
Support	100—120 mesh Supelcoport
Stationary phase	5% SP-2250 DB
Carrier gas	30 mL/min helium
Temperature program:	
Injector temperature	270°C
Detector temperature	270°C
Initial temperature	40°C
Initial time	5.0 min
Ramp rate	10°C/min
Final temperature	250°C
Final time	10 min

practice, the amount of analyte is determined by dividing the area of the unknown peak by the slope of the calibration curve for the nearest hydrocarbon standard. The detection limit of the FID (8 pg) was calculated from the amount of hydrocarbon standard which produced a peak area twice that of the minimum detectable (background) signal for a pure standard solution. For a burn of typical length, this is equivalent to a minimum detectable concentration of 0.2 μg of analyte per cubic meter of air sampled. For the sorbent tube extracts, however, the background signal was higher, and concentrations below approximately 0.05 mg/m^3 have high uncertainties due to the difficulty in resolving the small peaks from the background signal. Since the Tenax was extracted prior to packing in the tubes, no species were found in blank tubes extracted with cyclohexane other than those from the background, primarily column and septum bleed. In some cases traces of C$_6$ species were observed (e.g. 3-methylpentane, 3-methylcyclopentane), which were assumed to be contaminants in the cyclohexane. Direct injection of the cyclohexane did not show these species; however, the extracts were concentrated approximately 200- to 500-fold prior to analysis.

GC/MS analysis of extracts

Identification of the components was made with a Hewlett-Packard Model 5985 GC/mass spectrometer. The mass fragmentation patterns of constituents were compared to the mass spectrum of each of over 35,000 compounds using a Model 5840 data processor and a prioritized "best fit" list was produced. Some caution must be used in interpreting the results of the mass spectrometric data presented in the tables to follow. Due primarily to column

and septum bleed, it was difficult to decide whether small peaks were due to the background. At low concentrations, the mass spectrometer had difficulty in identifying most species. In addition, the accuracy with which a peak can be assigned is greater for species with higher molecular weights due to the less ambiguous fragmentation patterns produced. Further, some subjectivity is required in making peak assignments since the computer lists the eight best matches, assigning a "quality index" to each. In cases where more than one species gave equally high quality indices, the possibilities are listed.

Results and discussion

The amounts of each species generated during combustion of the solvent could be reported in several ways, including the percent of original mass of solvent represented by the species or the amount of species generated per unit time, given the burn rate and sample mass. For this study, the mass of species present in the extract was divided by the total sample volume and the amounts presented as the concentration in the actual air stream sampled. The values in the tables are therefore reasonable estimates of the concentration in a plume from a fire involving the solvent. These concentration data can be used to approximate the source strength term in a model to calculate safe evacuation distances. The sixteen solvents most commonly carried by rail were burned. These were: methanol, isopropanol, n-butanol, methyl ethyl ketone, methyl isobutyl ketone, acrylonitrile, benzene, toluene, mixed xylenes, acetone, butyraldehyde, ethyl acetate, butyl acetate, vinyl acetate, hexane and cyclohexane. These compounds represent a number of chemical classes; however, they can be separated into two distinct categories — those which contain oxygen and those which do not. The presence of intramolecular oxygen results in a much cleaner (more complete) combustion. As a result, some species were produced at concentrations below the detection limit of one or both of the instruments. For all solvents the detection limit of the GC/FID was sufficiently low to record the presence of combustion products in Tenax tube extracts. In many cases, however, the concentrations were below the detection limit of the mass spectrometer. This was particularly true for oxygen-containing solvents.

Oxygen-containing solvents

The filters used to remove particulate matter prior to collection of the vapors on the Tenax tubes were generally white, reflecting the relatively clean-burning nature of these solvents. Extracts of the filters were free from any detectable species for the oxygen-containing solvents. The effects of intramolecular oxygen on soot formation and rate of product combustion have been reported previously to be a decrease in soot and an increase in burnrate relative to hydrocarbons of similar molecular weight or boiling point [5]. The results of the product analysis also show a significant difference between oxygenated and oxygen-free solvents. The following species

were tentatively identified in extracts of the solvents noted: phenanthrene from methyl ethyl ketone; cyclohexanone from ethyl acetate; and 1-naphthalene carbonitrile from acrylonitrile. While the identification of the latter was unambiguous, its presence is not, since it was not observed in all runs. It may be an artifact due to reaction of HCN formed during combustion with the Tenax or some other reaction product. It is also possible that "cyanonaphthalene" is formed during the combustion of acrylonitrile ($H_2C=CH-CN$). The remainder of the combustion products were unidentifiable. Nevertheless, some information can be obtained from the number of peaks produced. The number of peaks generally increases with increasing complexity of the structure of the solvent burned (or molecular weight in an homologous series), as did the amount of soot formed [5]. The oxygen-containing solvents burned and the number of unidentified peaks are: methanol, 4; isopropanol, 6; n-butanol, 18; acetone, 3; methyl ethyl ketone, 4; methyl isobutyl ketone, 5; butyraldehyde, 5; ethyl acetate, 13; butyl acetate, 9; vinyl acetate, 8; and acrylonitrile, 12. In order to identify the species observed, a longer sampling time would be required, necessitating a volume of solvent in excess of the capacity of the crucible used.

Hydrocarbons

As was previously reported [5], aromatic solvents produce large amounts of soot. Similarly, many semi-volatile components were present in identifiable concentrations. Table 4 lists the combustion products identified (and the number of unidentifiable peaks) in cyclohexane extracts of the Tenax tubes. In some cases, the identity could not be unambiguously assigned due to similarities in the mass spectra of two or more compounds. In those cases, all species are reported. The combustion products are listed in the approximate order of elution from the chromatograph, and molecular weights and boiling points are included for reference. It should be recalled that the filter was maintained at 160°C during sample collection. The species range in boiling point from approximately 100 to 340°C. The maximum temperature of the chromatographic analysis is limited by the stationary phase. As a result, species with low volatility at 250°C will not be detected. Separation of poly-aromatic species containing more than two or three rings would require liquid chromatography. In addition, condensation on the filter of the less volatile species may have occurred even at 160°C.

Hexane and cyclohexane, which are not themselves aromatic, produced few aromatic combustion products. The aromatic solvents, however, produced several species in relatively high concentrations. The concentration values in Table 4 were calculated from the mass observed and the volume sampled. Concentrations were observed to be in the mg/m^3 range. This is approximately six orders of magnitude higher than ambient concentration of other PAHs. These concentration data can be used to estimate emission rates of the identified species from rail accidents where a particular solvent is on fire. Such source strength data are required in dispersion models. Combined with

TABLE 4

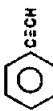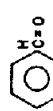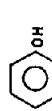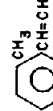The concentrations of combustion products from solvent fires
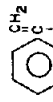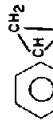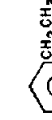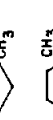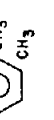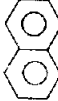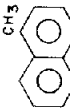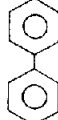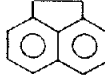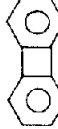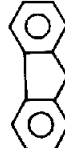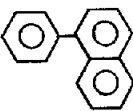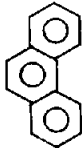
Compound	MW	BP, °C	Structure	Concentration, mg/m³				
				Benzene	Toluene	Xylene	Cyclohexane	Hexane
Phenylacetylene	102	143	C≡CH	2.7	1.1	0.4	0.09	—
Benzaldehyde	106	178	CH=O	0.54	0.21	0.17	—	—
Phenol	94	182	OH	2.7	—	—	—	—
Tolylacetylene (isomers)	118		CH₃, CH₂CH₂					
2-Phenylpropene	118		CH₂=C−CH₃	a	a	a	—	
Cyclopropylbenzene	118		CH, CH₂, CH₂					
Ethylmethylbenzene (isomers)	120	176	CH₂CH₃, CH₃					
Trimethylbenzene (isomers)	120	176	CH₃, CH₃, CH₃	—	0.12	0.87	—	—
1,2-Propadienylbenzene	116		CH=C=CH₂	—	—	—	0.65	—
1-Phenyl-1-propyne	116		C≡CCH₃					

TABLE 4 (continued)

Compound	MW	BP, °C	Structure	Concentration, mg/m³				
				Benzene	Toluene	Xylene	Cyclohexane	Hexane
Tolualdehyde	120	200		—	—	0.81	—	—
Indene	116	183		—	—	0.68	—	—
Azulene	128	270		1.0	0.15	0.55	2.3	—
Naphthalene	128	218		6.8	3.5	6.6	a	0.23
2-Methylnaphthalene	142	241		1.2	0.23	1.0	—	—
1-Methylnaphthalene	142	244		3.1	0.29	a	—	—
Biphenyl	154	255		14	0.31	2.0	a	—
Acenaphthalene	154	279		3.9	0.50	4.2	2.1	—
Biphenylene	152			6.5	a	—	—	—

Compound							
Dibenzofuran	168	287		7.4	1.1	3.8	—	—
Fluorene	166	294		7.4	1.9	5.0	—	—
1-Phenylnapthalene	204	334		a	0.78	3.6	—	—
Phenanthrene	178	340		—	a	11.1	—	—
Number of unidentified peaks				3	15	5	14	—

a Not quantitative

toxicity data, the results can be used to calculate minimum safe evacuation distances. Such work is in its initial stages and will be the subject of a future report.

References

1 1984 Emergency Response Guidebook—Guidebook for Hazardous Materials Incidents, Materials Transportation Bureau, Research and Special Programs Administration, U.S. Department of Transportation, DOT-P-5800-3 1984.
2 W.J. Wilson, Large scale test fires, J. Fire Flammability, 7 (1976) 112—124.
3 C.J. Hildado, The correlation of laboratory test results with behavior in real fires, J. Fire Flammability, 8 (1977) 202—209.
4 H.S. Homan, The dependence of soot yield on flame conditions — A unifying picture, Combust. Sci. Technol., 33 (1983) 1—15.
5 R.D. Delumyea, K.P. Moore, G.I. Miller, S.A. Dukes and M.A. Morgan, Determination of the rates of product consumption and soot formation during combustion of solvents commonly carried by rail, J. Hazardous Materials, 13 (1986) 169—185.
6 C.J. Hildado and H.J. Cummings, The effect of test conditions on the relative toxicity of the pyrolysis products from some plastics, Fire Technol., 13 (1977) 325—328.
7 D.G. Sauers, The effects of forced air flow and oxygen concentration on flammability, smoke density and pyrolytic toxicity, J. Fire Flammability, 7 (1976) 181—199.
8 R.M. Harrington and B.A. Story, The release rate of heat, smoke and primary toxicants from burning materials, J. Fire Flammability, 9 (1978) 284—307.
9 C.J. Hildado and C.J. Casey, Pyrolysis of polymeric materials: I. Effect of chemical structure, temperature, heating rate, and air flow on char yield and toxicity, J. Fire Flammability, 10 (1979) 140—168.
10 A. DiLorenzo, S. Masi and N. Colandra, New sampling-collection apparatus for the study of polyaromatic hydrocarbon formation in flames, Combust. Sci. Technol., 30 (1983) 303—309.
11 R.V. Petrella, The mass burning rate of polymers, wood and organic liquids, J. Fire Flammability, 11 (1980) 3—21.
12 C.J. Hildado and C.J. Casey, Pyrolysis of polymeric materials: II. Effect of chemical structure and temperature on char yield and flammability, J. Fire Flammability, 10 (1979) 227—239.
13 M. Pasternak, B.T. Zinn and R.F. Browner, The role of polycyclic aromatic hydrocarbons (PAH) in the formation of smoke particulates during the combustion of polymer materials, Proceedings Eighteenth Symposium on Combustion, The Combustion Institute, 1981, p. 91.

14 T.R. Henderson, J.D. Sun, A.P. Li, R.L. Hanson, W.E. Bechtold, T.M. Harvey, J. Shabanowitz and D.F. Hunt, GC/MS and MS/MS studies of diesel exhaust mutagenicity and emissions from chemically-defined fuels, Environ. Sci. Technol., 18 (1984) 428—434.

15 M.C. Paputa-Peck, M.S. Marano, D. Schuetzle, T.L. Riley, C.V. Hampton, T.J. Prater, L.M. Skewes, P.H. Ruehle, L.C. Bosch and W.P. Duncan, Determination of nitrated polyaromatic hydrocarbons in particulate extracts by capillary GC with nitrogen selective detection, Anal. Chem., 55 (1983) 1946—1954.

16 D.R. Choudhury and B. Bush, Chromatographic—spectrometric identification of airborne polynuclear aromatic hydrocarbons, Anal. Chem., 53 (1981) 1351—1356.

17 J.R. Cretney, H.K. Lee, G.J. Wright, W.H. Swallow and M.C. Taylor, Analysis of polyaromatic hydrocarbons in air particulate matter from a lightly industrialized area, Environ. Sci. Technol., 19 (1985) 397—404.

18 R. Fruedenthal and P.W. Jones (Eds.), Polynuclear Aromatic Hydrocarbons: Chemistry, Metabolism and Carcinogenesis, Raven Press, New York, NY, 1976.

19 S.H. Cadle, P.J. Groblicki and P.A. Mulawa, Problems in the sampling and analysis of carbon particulate, Atmos. Environ., 17 (1983) 593—600.

20 D.R. Fitz, D.M. Lokensgard and G.J. Doyle, Investigations of filtration artifacts when sampling ambient particulate matter for mutagenicity assay, Atmos. Environ., 18 (1984) 205—213.

21 E. Brorstrom, P. Grennfelt and A. Lindskog, The effect of nitrogen dioxide and ozone on the decomposition of particle-associated polyaromatic hydrocarbons during sampling from the atmosphere, Atmos. Environ., 17 (1983) 601—605.

22 K.J. Krost, E.D. Pellizzari, S.G. Walburn and S.A. Hubbard, Collection and analysis of hazardous organic emissions, Anal. Chem., 54 (1982) 810—817.

23 J.F. Pankow, L.M. Isabelle and T.J. Kristensen, Tenax GC cartridge for interfacing capillary column gas chromatography with adsorption/desorption for determination of trace organics, anal. Chem., 54 (1982) 1815—1819.

24 L.A. Gundel and T. Novakov, Characterization of particles from several sources and three urban areas by solvent extraction, Atmos. Environ., 18 (1984) 273—276.

25 T. Ramdahl and G. Becker, Characterization of polyaromatic hydrocarbon derivatives in emmisions from wood and cereal straw combustion, Anal. Chim. Acta, 144 (1982) 83—91.

26 M.J. Avery, J.J. Richard and G.A. Junk, Simplified determination of polyaromatic hydrocarbons, Talanta, 31 (1984) 49—53.

27 R. Miller, Hydrocarbon class fractionation with bonded-phase liquid chromatography, Anal. Chem., 54 (1982) 1742—1746.

28 W.J. Sonnefeld, W.H. Zoller, W.E. May and S.A. Wise, On-line multidimensional liquid chromatographic determination of polyaromatic hydrocarbons in complex samples, Anal. Chem., 54 (1982) 723—727.

29 A. Matsunaga, Separation of aromatic and polar compounds in fossil fuel liquids, Anal. Chem., 55 (1983) 1375—1379.

30 T. Vo Dinh, T.J. Bruewer, G.C. Colovos, T.J. Wagner and R.H. Jungers, Field evaluation of a cost-effective screening procedure for polyaromatic pollutants in ambient air samples, Environ. Sci. Technol., 18 (1984) 477—482.