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IDENTIFICATION OF ORGANIC COMPOUNDS PRODUCED DURING COMBUSTION OF A POLYMER MIXTURE

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SUMMARY

A mixture containing polyethylene, polystyrene, and polyvinyl chloride was subjected to oxidative thermal degradation at temperatures of 800–950°C. Breakdown products were collected on glass wool or in cold traps for analysis by capillary gas chromatography and gas chromatography–mass spectrometry. Combustion products included alkyl benzenes, hydrocarbons, alkenes, biphenyls, and polycyclic aromatic hydrocarbons containing from two through six rings.

INTRODUCTION

In recent years a large amount of study has concentrated on the analysis of the complex organic mixtures found in various combustion effluents, and in combustion in general. Fly ash from municipal incinerators has been found to be a source of polycyclic aromatic hydrocarbons (PAHs)[1–3], as have emissions from diesel engines[4], coal combustion[2,5], and burning of forest litter[6]. Chlorinated compounds have also been observed in incinerator emission[7,8] as well as during wood burning and in the effluents from coal-fired electrical generation[9]. Two recent reviews have focused on general organic emissions and on chlorinated compounds from various combustion processes[10,11].

While identification of various organic species on fly ash has proven valuable in assessing the health risks of airborne pollutants from combustion processes, in most cases the sources of these compounds have not been the subject of study. Municipal waste is a complex mixture of combustible and non-combustible components (Table I), providing many precursors for formation of a wide variety of compounds. We have in the past examined the combustion products of individual polymers in an attempt to determine possible sources of organic species identified in combustion effluents[16–18].

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TABLE I

MUNICIPAL WASTE COMPOSITION

Component	*Composition (%)*			
	Ref. 12	*Ref. 13*	*Ref. 14*	*Ref. 15*
Paper	50.6	50	51.7	39.6
Leather and rubber	1.4	3.4	0.7	2.7
Food	—	16.8	4.4	13.3
Fabrics	4.4	2	1.8	—
Plastics	5.3	5.2	5	4.1
Wood	2.5	4.6	2.6	3.6
Miscellaneous*	35.8	17.8	33.7	36.6

* May include non-combustible material.

Although some work has been done on combustion of pure polymers and polymer formulations[19–24], little or no work can be found involving copolymer formulations or mixtures of polymers. During our investigation of pure polymer combustion, we included a mixture containing polyethylene, polystyrene and polyvinyl chloride in order to determine if the products obtained from the mixture would differ significantly from those of the individual components.

EXPERIMENTAL

Polymers

The pure polymers for all combustion experiments were obtained from Aldrich (Milwaukee, WI, U.S.A.). Low density polyethylene was obtained in pellet form, density 0.92, melting temperature 115°C. Polystyrene was obtained in pellet form, density 1.047, glass transition temperature 100°C, melting temperature 237.5°C. Polyvinyl chloride was obtained as a powder, density 1.40. All polymers were used as obtained for combustion experiments. The 1:1:1 (w/w/w) mixture was prepared in 2-g lots prior to use.

Standards

Seven standard solutions were used to evaluate chromatographic performance and to aid in identification of PAH isomers. The solutions consisted of a hydrocarbon standard containing *n*-hydrocarbons from C_{14} through C_{26}, C_{28}, C_{30}, and C_{32} at 100 ng/μl in cyclohexane; a mixed standard containing *n*-hydrocarbons, *n*-alcohols, phthalates and PAHs in cyclohexane; and five PAH standards containing various PAH and methyl-PAH isomers in benzene. All solvents used throughout were distilled-in-glass grade (Burdick and Jackson, Muskegon, MI, U.S.A.). The exact composition of the standards has been reported elsewhere[25].

Combustion apparatus

The combustion apparatus has been described previously[16,25], but a brief description will be given here. The apparatus consisted of a 57 cm × 3 cm O.D. quartz combustion tube, which narrowed to 1.25 cm O.D. at one end was fitted with an outer 34/45 joint at the other end. The quartz tube was equipped with two thermocouple wells for determination of temperatures at the center of the heated zone (directly above the burning polymer) and approximately 18 cm downstream near the exit from the combustion tube.

A pyrex tube, 9 cm × 1.25 cm O.D., loosely packed with pyrex wool was placed at the exit of the combustion tube to trap carbonaceous material and prevent it from entering the cold traps. Two liquid nitrogen cold traps constructed from pyrex glass were placed in series following the glass wool trap, followed by a trap containing activated charcoal. All glassware was joined using 0.5 in. Swagelok unions equipped with Teflon^{TM} ferrules(Arizona Valve and Fitting, Phoenix, AZ, U.S.A.).

After allowing the apparatus to reach the desired combustion temperature, 2 g of the polymer mixture in a nickel sample boat was admitted into the center of the heated zone through the 34/45 opening. Air for combustion was provided through fittings attached to the inner 34/45 joint. After combustion was completed, the apparatus was cooled to room temperature. The pyrex wool filter was washed with 100 ml of methylene chloride and concentrated to *ca.* 500 μl. The cold traps were washed with 40 ml methylene chloride, the washings combined and concentrated to *ca.* 500 μl.

Analysis by gas chromatography (GC) and GC–mass spectrometry (GC–MS)

A Hewlett-Packard 5830A gas chromatograph equipped with a flame ionization detector and packed columns was used for preliminary analyses. A Hewlett-Packard 5880 gas chromatograph equipped with a flame ionization detector and capillary column (30 m × 0.32 mm I.D., DB-5 column) was used for quantitative analyses. GC–MS analyses were performed on a Hewlett-Packard 5992 quadrupole system equipped with a 30 m × 0.32 mm I.D. DB-5 capillary column and cool on-column injection. Analyses conditions have been described in detail elsewhere[16,25].

High-performance liquid chromatographic (HPLC) separation

A single sample was selected for HPLC fractionation, followed by capillary column GC and GC–MS analyses. The sample extract was diluted 1:50 (v:v) with benzene before HPLC injection. A Spectra-Physics SP-8000 HPLC apparatus equipped with an SP-8400 UV–VIS detector and SP-4100 integrator was used for the HPLC separation. The monitoring wavelength was 254 nm. A 10-μm semi-preparative Spherisorb silica column (250 × 10 mm I.D.) was used (Tetrochem, Toronto, Canada) with a 140-μl sample loop. A gradient elution program developed at the University of Waterloo[26] was used for sample fractionation. The gradient program is as follows: 100% *n*-hexane for 20 min; programmed to 100% methylene chloride for 20 min; programmed change to 100% acetonitrile over 10 min; 100% acetonitrile for 1 min; programmed change to 100% methylene chloride over 5 min; programmed change to 100% *n*-hexane over 5 min. The flow-rate was held constant at 5 ml/min.

Five fractions were collected over the 91-min period. The first fraction was collected from 0 to 3 min and contained *n*-hydrocarbons and alkenes; fraction 2 was collected from 3 to 20 min and contained PAHs and dioxins; fraction 3, collected from 20 to 50 min, containing oxy-PAHs; fraction 4 collected from 50 to 70 min, containing phthalates; and fraction 5, 70 to 91 min, containing miscellaneous compounds. Fractions were collected in 300-ml roundbottom flasks and concentrated to *ca.* 10 ml by rotary evaporation at approximately 50°C using a hot water bath, quantitatively transferred into 25-ml pear-shaped flasks and further concentrated by rotary evaporation to 300 μl. Samples were then transferred to 1-ml reacti-vials and concentrated to 50 μl under a stream of high-purity nitrogen, followed by capillary column GC and GC–MS analysis.

RESULTS AND DISCUSSION

Fig. 1 presents the total ion current (TIC) chromatograms of the cold trap extracts from combustion at 800–950°C. Upon examination of the TIC chromatograms one notes that at lower temperatures (800–850°C) there appears to be a greater number of components than at 900–950°C, and that a large number of these elute in the first 6 min of the chromatogram. These compounds decrease with increasing

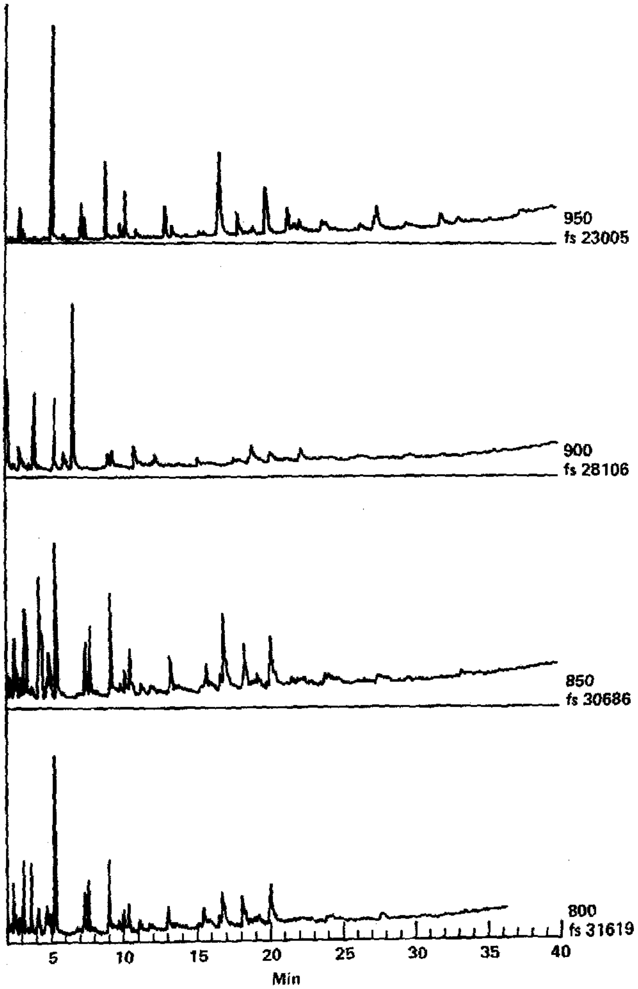

Fig. 1. TIC chromatograms from combustion of polymer mixture at 800 to 950°C, cold trap extracts. Combustion temperature (in °C) and full scale values are given to the right of each chromatogram.

temperature, until at 950°C there are only about 7 peaks eluting before 6 min, as compared with 12–15 components in the lower temperature runs. This large number of lower molecular weight, more volatile compounds is better illustrated by close examination of the TIC chromatogram for the 800°C sample. In the early portion of the chromatogram there are several peaks which appear as doublets and triplets. For example, there is a triplet at 4 min and a quartet of peaks just prior to 5 min. The triplet at 4.2–4.3 min consists of two $C_{10}H_{10}$ isomers (methylindenes or divinylbenzenes) and a chlorinated propylbenzene or other $C_9H_{11}Cl$ isomer. This chlorinated species was not previously identified in polyvinyl chloride combustion products[18] and appears to be unique to the polymer mixture combustion. The quartet of peaks at approximately 5 min contains two more $C_{10}H_{10}$ isomers, a dimethylindene isomer ($C_{11}H_{12}$), and azulene. Altogether, the region of the chromatogram before naphthalene at 5.5 min contains 17 different compounds, including propyl- and propenylbenzene, *p*- and *o*-methylstyrene, indane, indene, and a C_{11} diene and alkene.

Following naphthalene at 5.5 min are several small peaks, three of which have been identified as methyldihydronaphthalenes. Dihydronaphthalene exists in two isomeric forms; 1,2- and 1,4-dihydronaphthalene, with a total of 12 mono-methyl isomers possible. In addition to the three methyldihydronaphthalene isomers, a C_{13} diene and a chlorinated propenylbenzene isomer or chloroindane (C_9H_9Cl) are present before the methylnaphthalene doublet at 7.6–7.9 min. The next major peak is biphenyl at 9 min. Compounds identified in the region between biphenyl and phenanthrene (17 min) include vinylnaphthalenes, methylbiphenyls, diphenylethylenes, alkenes and dienes. Diphenyl methane is one of the compounds found in this region, and is derived from the polystyrene portion of the mixture. The alkenes and dienes detected arise from the polyethylene present in the polymer mixture.

After phenanthrene there are only two major components, 1- and 2-phenylnaphthalene. Several other compounds are identifiable from mass spectra and retention indices, although from examination of the TIC chromatograms there are no sharp peaks observed. These additional compounds consist largely of unsubstituted PAHs such as fluoranthene and benzo[*a*]anthracene. The only hydrocarbon species observed in this region is a C_{26} alkene eluting at about 28 min.

As the temperature increases to 950°C, the number of more volatile components and the compounds present at low levels decreases. This change is easily seen if one compares the TIC chromatograms of the 800°C and 950°C cold trap extracts. Instead of 18 compounds identified in the first 5 min, there are now only five. The chlorinated species are still present (chloroxylene at 3.4 min, $C_9H_{11}Cl$ at 4.3 min, and C_9H_9Cl at 6.2 min), but all of the substituted benzenes and $C_{10}H_{10}$ isomers are no longer present. In addition, the methyldihydronaphthalenes found between 5 and 9 min have vanished, as have many of the aromatics found in the region between naphthalene (5.5 min) and phenanthrene (17 min). Diphenylmethane and 1,3-dimethylnaphthalene are no longer observed, as are 1-methylacenaphthylene, 9,10-dihydronaphthalene and phenanthrene.

There is a difference in the chromatograms after phenanthrene, although here the difference is not just the disappearance of certain species. There are additional compounds formed which were not identified in the extracts obtained at lower temperatures. For example, 4,5-methylene phenanthrene is observed at 950°C and is not identified before that temperature. Benzo[*ghi*]fluoranthene also appears in this region.

A triplet of compounds with molecular weight 202 (fluoranthene, diphenyldiacetylene and pyrene) which occurs in the region 21.5–23 min is larger at the higher temperature. In addition, there appears to be more of the very high molecular weight nonvolatile species such as the benzofluoranthenes and benzopyrene isomers present in the 950°C cold trap sample.

Glass wool traps

The glass wool samples obtained during combustion of the polymer mixture contained compounds ranging from naphthalene to dibenzo[*def,mno*]chrysene (retention time 5.5 and 50 min; mol. wt. 128–278). Most of the compounds produced were not unique to the polymer mixture, but were compounds which had been identified as combustion products of the individual polymers[16–18].

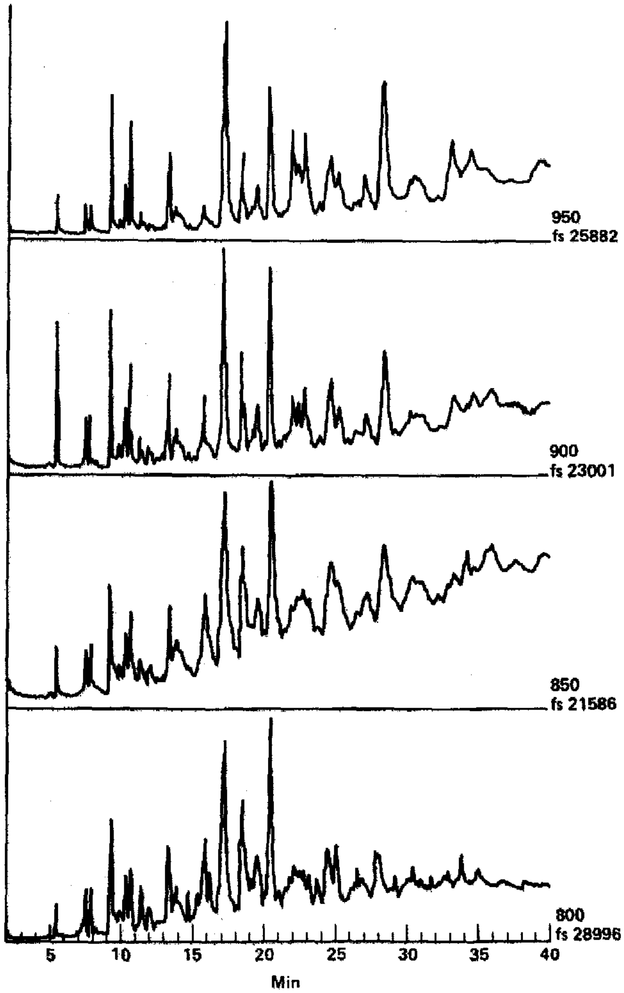

Fig. 2. TIC chromatograms from polymer mixture combustion at various temperatures, glass wool extracts. Full scale values and combustion temperatures (in °C) are at right of each chromatogram.

The TIC chromatograms of the glass wool trap extracts at each combustion temperature are shown in Fig. 2. In this instance, the decrease in the number of compounds formed as temperature increases is not quite as obvious as in the cold trap extracts. Most major differences occur in the early portion of the chromatograms, where many of the very small peaks observed at 800°C are no longer present at 950°C. Except in the 800°C sample, the region of the TIC chromatograms after *ca.* 17 min are very similar, although there is an increase in peak height for chrysene (28 min) with increasing temperature. The raised baseline and broad peak shapes for many of the later-eluting components suggests a high background of unresolved components, although some of the increased baseline is due to column bleed. All of the combustion samples were darkly colored, and the glass wool extracts were especially viscous samples which seemed to rapidly degrade column performance. This degradation was partially due to the presence of very fine particulate matter in the glass wool trap samples, in addition to the complex nature of the samples.

The large number of component peaks in the 800°C glass wool trap sample is more easily seen in Fig. 3. The TIC chromatogram is presented at the bottom of the figure, with selected ions plotted above it. The anomolous peak shape at 21 min was caused by analyzer shut-down due to excessive ion current (> 32000 counts). The species eluting at that point is 2-phenylnaphthalene. As determined by GC analysis with flame ionization detection (FID), the amount of 2-phenylnaphthalene present in that sample injection was determined at 800 ng. The total amounts of selected PAHs identified in the glass wool extracts from the polymer mixture are given in Table II.

In the early part of the chromatogram there are few peaks, which is typical of the glass wool trap extracts. The first major component is naphthalene, although it is preceded by azulene and a $C_{10}H_{10}$ isomer at low levels. An interesting feature of the glass wool trap extracts is that they contained the alkene and diene fragments produced from polyethylene. Except for the very volatile hydrocarbons (less than C_{13}), all the alkenes identified in the 800°C sample were found in the glass wool extracts. In many cases the hydrocarbons were not completely resolved from coeluting PAHs; however, mass spectra remained easily interpretable and both compounds could be identified.

Combustion products from the mixture resembled largely the products of pure polystyrene combustion in both appearance of chromatograms and compounds identified. In the glass wool traps were several compounds of molecular weight 192, 194, 204, 206 and 218 which could not be unambiguously identified from mass spectra and retention indicies. These compounds have been found in pure polystyrene effluents[17]. 1,1′-Binaphthyl was the only compound identified in the polymer mixture which was not previously found in individual polymer combustion products[16–18]. Many PAHs, including fluorene, methylfluorenes, phenanthrene, phenylnaphthalenes, fluoranthene, pyrene, and the benzofluorenes were found in the 800°C sample.

By 950°C, hydrocarbons were no longer produced during combustion of the polymer mixture. In fact, hydrocarbon species were detected only at 800°C. GC–MS analysis identified 48 different compounds at 950°C, as compared with 71 at the lowest combustion temperature. Many of the species present in smaller amounts at 800°C were not detected in analysis at 950°C. Most of these species were the unknowns of various molecular weights (192–206), although in general any minor spe-

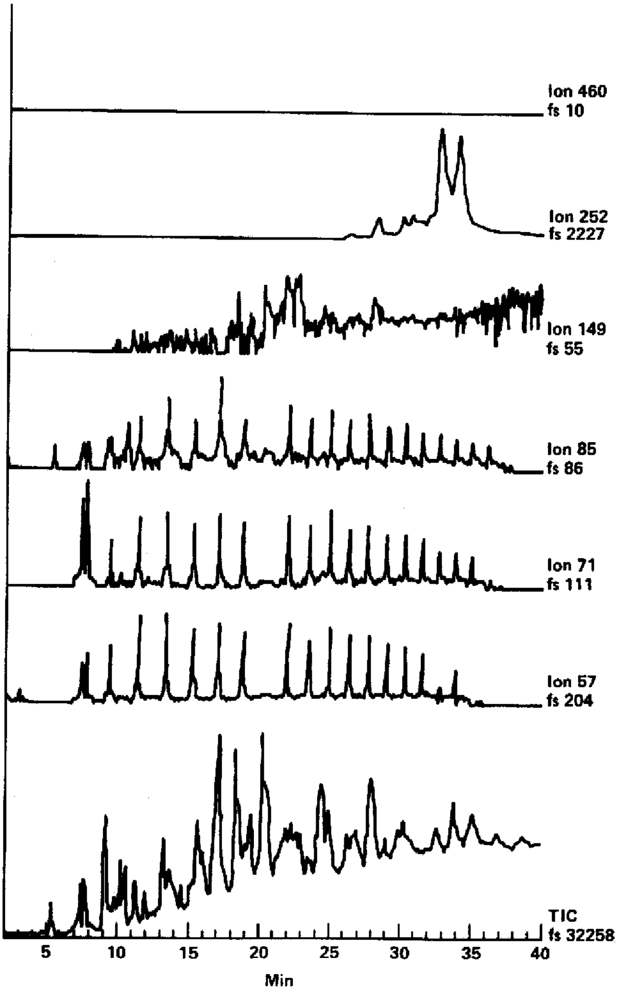

Fig. 3. TIC chromatograms and six monitored ions from polymer mixture, 800°C glass wool extract. Full scale values are at right of each ion trace,

cies found at 800°C was absent at 950°C. The major components in the glass wool trap from the 950°C combustion were phenanthrene (17 min), 2-phenylnaphthalene (20.4 min), benzo[*c*]phenanthrene (27 min), biphenyl (9 min), and acenaphthylene (10.6 min).

HPLC separation and analysis

As a check of compound identification, and in an attempt to determine if cleanup before GC–MS analysis was feasible, an HPLC separation was carried out on the 800°C cold trap sample. The HPLC procedure separates the sample into five fractions, containing hydrocarbons, PAHs and dioxins, oxy- and nitro-PAH, phthalates, and miscellaneous compounds (in that order), and has been described in detail

TABLE II

TOTAL AMOUNTS OF SELECTED COMPOUNDS IDENTIFIED IN GLASS WOOL EXTRACTS FROM COMBUSTION OF A POLYMER MIXTURE

Compound	*Total amount identified (mg)*			
	800°C	*850°C*	*900°C*	*950°C*
Napthalene	0.19	0.42	1.2	0.60
2-Methylnaphthalene	0.29	0.40	0.47	0.49
1-Methylnaphthalene	0.27	0.39	0.41	0.39
Biphenyl	0.59	0.97	1.3	2.0
Acenaphthylene	0.34	0.70	1.0	2.2
4-Methylbiphenyl	0.20	0.22	0.11	0.12
Fluorene	0.46	0.87	1.1	1.5
9-Methylfluorene	0.20	0.27	0.24	0.26
Dihydronaphthalene	0.065	0.017	0	0.015
(*p*-Methylphenyl)phenylacetylene	0.23	0.32	0	0
Phenanthrene	0.98	2.1	3.3	5.7
1-Phenylnaphthalene	0.48	0.82	0.85	0.77
o-Terphenyl	0.063	0.23	0.21	0.21
2-Methylanthracene	0	0.077	0	0.42
9-Methylphenanthrene	0.32	0	0	0
Tetrahydropyrene	0.15	0.21	0	0
2-Phenylnaphthalene	1.1	1.9	2.0	2.0
Fluoranthene	0.22	0.51	0.72	1.7
Pyrene	0.19	0.49	0.72	1.7
m-Terphenyl	0.074	0.17	0.17	0.15
Benzo[*a*]fluorene	0.32	0.72	0.82	0.46
Benzo[*c*]phenanthrene	0.12	0.21	0.41	0.17
Chrysene	0.23	0.66	0.96	1.7
1-Phenylphenanthrene	0.053	0.43	0.54	0.069

elsewhere[26]. The 800°C sample was chosen because at the time of analysis it was felt to be the most complex sample.

Based upon the UV monitoring of the HPLC eluent for the fractionation procedure, the majority of UV absorbing species (254 nm; aromatic species) were found almost exclusively in fraction 2. Although all five fractions were analyzed by GC–MS, only fractions 1 and 2 contained compounds derived from the sample.

The TIC chromatograms for the HPLC sample before fractionation and fractions 1 and 2 are given in Fig. 4. The total sample and fraction 2 have almost identical TIC traces, with some smoothing of the background observed in fraction 2. From peak heights it appears that there is some loss of earlier eluting components during fractionation, no doubt due to the additional sample concentration necessary.

The major components in fraction 1, collected during the first three minutes, were alkenes and dienes. From ion monitoring during GC–MS analysis, it appeared that alkanes were also present, although the ions monitored for alkenes (*m*/*e* 57, 71 and 85) also appear in alkene spectra. GC–FID chromatograms did contain the triplets of peaks typical of polyethylene combustion[13,27] with the alkene components dominant over the dienes and alkanes. Alkenes from C_{11} through C_{30} and dienes from C_{19} through C_{21} were detected in GC–MS analysis. GC–FID analysis found

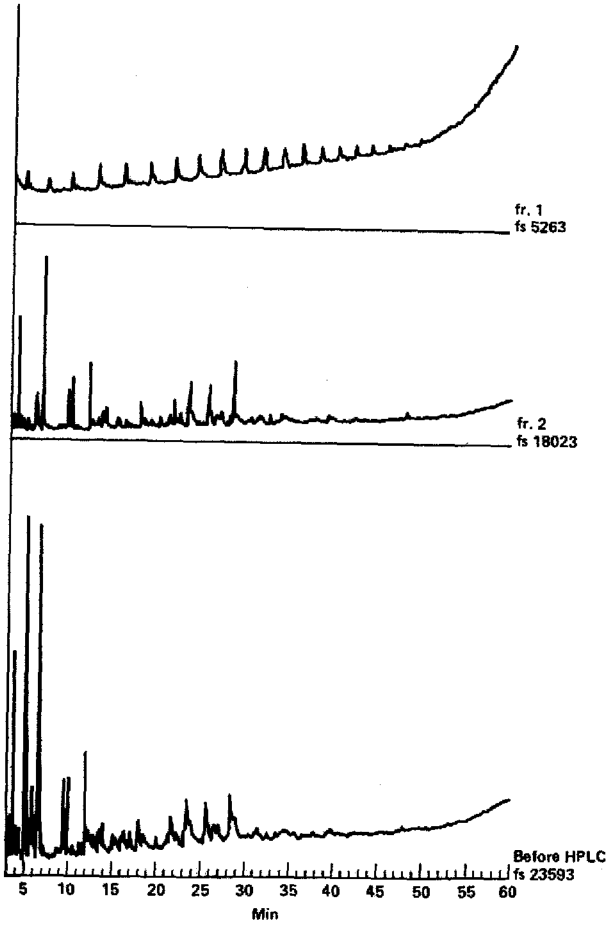

Fig. 4. TIC chromatograms of HPLC sample before fractionation (bottom), Fraction two (middle) and fraction one (top).

alkenes from C_9 through C_{29} and dienes from C_{19} through C_{25}, with other components below the integration threshold (0.4 ng).

Fraction 2 from the HPLC separation contained the PAHs found in the unfractionated sample. As a check of the GC–MS analysis of the unfractionated sample, the sample was analyzed by GC–MS under the same conditions as were used for capillary GC–FID analysis. The major difference in conditions is a slower temperature ramp rate used for the HPLC samples (4°/min *vs.* 6°/min). Even with the lower ramp rate used, only about 30 compounds were detected in the various HPLC samples which had not been previously identified during regular GC–MS analysis. Over 20 of these were alkenes and dienes, which may have been hidden in the high background in the normal combustion analysis. Although a slower temperature ramp rate resulted in "prettier" chromatography, it was not felt to result in significantly better or easier compound separation and identification. While the HPLC procedure did increase the number of compounds identified, losses of the more volatile species did occur. In addition, use of the HPLC clean-up procedure substantially increased the time necessary for sample throughout without an appreciable increase in information, and so was not applied to other samples.

CONCLUSIONS

Although over one hundred different organic species were identified in combustion effluents from the polymer mixture, few of the compounds arise solely from the mixture itself. Table III lists the compounds identified in alphabetical order at

TABLE III

COMPOUNDS IDENTIFIED IN COMBUSTION OF A POLYMER MIXTURE

Abbreviations and symbols: T = liquid nitrogen cold trap; GW = pyrex glass wool trap; × = present in that sample; b = multiple isomers detected.

Compound	*800°C*		*850°C*		*900°C*		*950°C*	
	T	*GW*	*T*	*GW*	*T*	*GW*	*T*	*GW*
Acenaphthylene	×	×	×	×	×	×	×	×
Anthracene		×	×		×		×	
Azulene	×	×	×	×	×	×	×	
Benzo[*a*]anthracene	×	×	×					×
Benzo[*a*]fluorene	×		×	×	×	×	×	
Benzo[*b*]fluorene		×	×	×	×	×	×	×
Benzo[*c*]phenanthrene		×	×	×	×	×		×
Benzo[*ghi*]fluoranthene							×	
Benzo[*ghi*]perylene				×				
Benzofluoranthenes		×	×	×	×	×	×	
Benzopyrenes				×		×	×	b
Benzylnaphthalene			×	×		×		
1-Benzylnaphthalene		×						
1,1'-Binaphthyl		×						
1,2'-Binaphthyl				×		×		
2,2'-Binaphthyl								×
Biphenyl	×	×	×	×	×	×	×	×
$C_{10}H_{10}$, isomer No. 1			×					
$C_{10}H_{10}$, isomer No. 2			×					
$C_{10}H_{10}$, isomer No. 3	×				×	×		
$C_{10}H_{10}$, isomer No. 5	×	×						
$C_{10}H_{10}$, isomer No. 6			×					
$C_{10}H_{10}$, isomer No. 7	×				×			
$C_{10}H_{10}$, isomer No. 8			×		×			
$C_{10}H_{10}$, isomer No. 9	×				×			
$C_{11}H_{20}$	×							
$C_{11}H_{22}$	×							
$C_{13}H_{24}$	×	×						
$C_{14}H_{26}$		×						
$C_{14}H_{28}$		×						
$C_{15}H_{28}$		×						
$C_{15}H_{30}$		×						
$C_{16}H_{32}$		×						
$C_{17}H_{32}$		×						
$C_{17}H_{34}$		×						

(Continued on p. 218)

TABLE III (*continued*)

Compound	*800°C*		*850°C*		*900°C*		*950°C*	
	T	*GW*	*T*	*GW*	*T*	*GW*	*T*	*GW*
$C_{19}H_{38}$		×						
$C_{21}H_{40}$		×						
$C_{21}H_{42}$		×						
$C_{22}H_{42}$		×						
$C_{22}H_{44}$		×						
$C_{23}H_{46}$		×						
$C_{24}H_{48}$		×						
$C_{25}H_{50}$		×						
$C_{26}H_{52}$	×	×						
$C_{27}H_{54}$		×						
$C_9H_{11}Cl$	×		×		×		×	
C_9H_9Cl							×	
Chloroxylene	×		×		×		×	
Chrysene	×	×	×	×	×	×	×	
Cumene			×					
Dibenz[*a,c*]anthracene	b	×						
Dibenzo[*def,mno*]chrysene								×
Dihydroanthracene	×	×	×	×	×	×		×
Dihydronaphthacene	×	×	×	×		×		×
Dihydrophenanthrene	×	×	×			×		×
Dimethylindene (?)	×							
1,3-Dimethylnaphthalene	×	×	×		×			
Diphenylacetylene						×	×	×
1,1-Diphenylethene	×	×	×	×	×	×	×	×
1,2-Diphenylethene	×		×	×		×		
Diphenylmethane	×	×	×	×				×
1,3-Diphenylpropane	×	×	×	×				
1,8-Di-*n*-propylnaphthalene (204)		×						×
1-Ethylnaphthalene			×			×		
2-Ethylnaphthalene	×	×		×				
Fluoranthene	×	×	×	×	×	×	×	×
Fluorene	×		×	×	×	×	×	×
Indane	×		×		×			
Indene	×		×		×		×	
1-Methylacenaphthylene		×	×	×	×	×		×
3-Methylacenaphthylene			×	×		×	×	×
1-Methylanthracene		×	×	×		×		
1-Methylbenzo[*a*]anthracene				×				×
3-Methyl benzo[*a*]anthracene						×		
11-Methyl benzo[*a*]anthracene				×		×		
2-Methylbiphenyl			×	×				
3-Methylbiphenyl	×		×	×		×	×	×
4-Methylbiphenyl	×	×	×	×	×	×	×	×
3-Methylcholanthrene		×		×		×		×
4-Methylchrysene								×
Methyldihydronaphthalenes	b	b	b					
Methylethylbenzene			×					
4,5-Methylenephenanthrene							×	×
1-Methylfluorene	×			×	×			

TABLE III (*continued*)

Compound	*800°C*		*850°C*		*900°C*		*950°C*	
	T	*GW*	*T*	*GW*	*T*	*GW*	*T*	*GW*
2-Methylfluorene					×	×	×	
9-Methylfluorene	×	×	×	×	×	×	×	×
1-Methylnaphthalene	×	×	×	×	×	×	×	×
2-Methylnaphthalene	×	×	×	×	×	×	×	×
3-Methylphenanthrene	×		×	×	×	×	×	×
9-Methylphenanthrene		×	×	×		×		
(*p*-Methylphenyl)-phenylacetylene	×		×	×	×	×	×	×
1-Methylpyrene		×		×				
m-Methylstyrene			×					
o-Methylstyrene	×		×					
p-Methylstyrene	×				×		×	
1-Methyltriphenylene		×		×				
Naphthacene								×
Naphthalene	×	×	×	×	×	×	×	×
Pentacene								×
1-H-Phenalene	×		×	×	×	×		×
Phenanthrene	×	×	×	×	×	×	×	×
1-Phenylnaphthalene	×	×	×	×	×	×	×	×
2-Phenylnaphthalene	×		×	×	×	×	×	×
1-Phenylphenanthrene		×	×	×	×	×	×	
3-Phenylpropene	×		×		×			
Picene		×						
1-Propenylbenzene	×		×		×			
2-Propenyl-1-naphthalene		×	×	×		×		×
n-Propylbenzene	×		×					
Pyrene		×	×	×	×	×	×	×
Quaterphenyl	×		×		×	×		
Styrene			×					
m-Terphenyl	×	×	×	×	×	×		
o-Terphenyl	×	×	×	×	×	×		
p-Terphenyl		×		×		×		×
Tetrahydropyrene	×	×	×	×		×		
Triphenylene					×			
1-Vinylnaphthalene	×	×	×	×	×	×	×	×
2-Vinylnaphthalene	×	×	×	×	×	×	×	×

the various combustion temperatures. Except for two compounds ($C_9H_{11}Cl$ and 1,1′-binaphthyl), all organics present have been identified in effluents from combustion of pure polyethylene, polystyrene, or PVC[16–18].

As can be seen by close examination of Table III, the lighter, more volatile, combustion products were trapped largely in the cold traps, while the heavier compounds were trapped on the glass wool. The glass wool traps were present to prevent soot from entering the cold traps. Most of the higher molecular compounds trapped on the glass wool were polynuclear aromatics, while compounds found almost exclusively in the cold traps were substituted benzene and naphthalene species. Soot from various sources has been found to contain polyaromatics such as benzopyrenes, anthracene, phenanthrene, chrysene, methylphenanthrenes and anthacenes, benzofluorenes, and other PAHs[21,22,28,29]. It is therefore not surprising that the glass wool extracts, which were essentially soot extracts, had higher levels of PAHs than the cold trap extracts. The cold traps appear to be more efficient at trapping smaller molecules which would not necessarily be associated with soot particles. The absence of compounds lighter than styrene (boiling point 145°C) or undecene (boiling point *ca.* 192°C) in the cold trap extracts suggests that very volatile species, if formed, were not adequately trapped in the system as designed, and their possible formation during combustion cannot be ruled out.

Sample clean-up using HPLC fractionation resultd in losses of more volatile components without significantly improving the ability to identify species produced. While some peak overlap did occur in unfractionated samples, the use of GC–MS permitted the identities of compounds which co-eluted to be determined in many of these occurances. The hydrocarbon species which were found only in the HPLC fractions were present at very low levels (0.4 ng). HPLC fractionation has been used for separation of PAHs from complex mixtures in the presence of large amounts of interfering compounds such as hydrocarbons, phenols, bases, etc.[26,30,31]. Except for the hydrocarbon species present as low levels, these types of interfering compounds were not detected in the combustion effluents. Because the combustion samples contained relatively few interferances, the minor increase in sensitivity resulting from the HPLC clean-up was not felt to outweigh the loss of more volatile components and the increased time required for sample preparation.

It should be noted that only three chlorinated species were identified, and that all three compounds were alkyl benzenes containing chlorine attached to a side chain of the aromatic portion of the molecule. Because it has been postulated that chlorinated dibenzo-*p*-dioxins are formed in all combustion processes[32], we had expected to detect chlorodioxins or dioxin precursors such as polychlorinated biphenyls. Ion monitoring at 460 a.m.u. (octachlorodibenzo-*p*-dioxin) for all combustion analyses and selected-ion monitoring analysis of the 800°C polymer mixture samples did not detect Cl_3 through Cl_8 dioxins (instrument detection limit *ca.* 0.1 ng/μl). While polyvinyl chloride has been postulated as a dioxin precursor in incineration, work done by Karasek *et al.*[33] has failed to find increased dioxin production upon the addition of polyvinyl chloride to a municipal incinerator. Because of the complex nature of the samples, the apparent absence of chlorodioxins in effluents from polymer mixture combustion should not be considered as proof that polyvinyl chloride and other plastics are not dioxin precursors. Components in plastic formulations such as dyes, flame retardants or plasticizers undoubtedly contribute to emissions during combustion, while refuse components such as food wastes and paper products may also be sources of chlorinated species. Further work is necessary to identify the sources of all organic species produced during combustion processes.

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