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PRODUCTS OBTAINED DURING COMBUSTION OF POLYMERS UNDER SIMULATED INCINERATOR CONDITIONS

III. POLYVINYL CHLORIDE

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SUMMARY

Combustion products from polyvinyl chloride were determined using gas chromatography and gas chromatography-mass spectrometry. Combustion conditions were varied from 800 to 950°C, and an attempt was made to approximate municipal incinerator conditions. Compounds identified consisted of PAHs and alkylbenzenes. Two chlorinated species were identified.

INTRODUCTION

Our interest in the products produced from simulated incineration of polymers has been described in previous papers concerned with polyethylene¹ and polystyrene² combustion products. Because some of the organic species identified in fly ash from municipal incinerators are chlorinated species³⁻⁷, it becomes logical to investigate a chlorinated polymer such as polyvinyl chloride (PVC) as a possible source of these species.

In order to form chlorinated species during combustion, a source of chlorine or chloride is necessary in the fuel. In a municipal incinerator, chloride is found in many refuse components as metallic chlorides such as sodium or calcium chloride. Chlorinated compounds such as PVC and polyvinylidene chloride release their chlorine as HCl, and may be a major source of chlorine during incineration⁸. Unless an incinerator is handling hazardous waste, chlorinated compounds such as polychlorinated biphenyls (known PCDD precursors) would not be present during incineration.

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Polyvinyl chloride and other chlorine-containing polymers such as polychloroprene are known to release HCl upon heating⁹⁻¹¹. Hydrogen chloride generation begins at temperatures as low as 130°C, and continues up to 400°C¹²⁻¹⁶. Up to 99% of the chlorine contained in polyvinyl chloride is lost as HCl, with very little vinyl chloride monomer formed¹².

The loss of HCl occurs via a process known as "unzipping", in which there is an initial loss of chlorine as a chlorine radical, followed by the abstraction of a hydrogen atom, and eventually resulting in a long polyene^{12,16-18}. With further heating, degradation continues with the production of aromatic and alkyl species. The exact products formed depend to a degree upon the degradation conditions. Many of the previous investigations have been performed in an inert atmosphere¹⁸⁻²⁷, although work has been done in oxygen-containing atmospheres²⁷⁻³⁷.

In inert atmospheres, usually nitrogen but sometimes helium, and at temperatures ranging from 160 to 700°C, the degradation products identified have included aliphatic and olefinic hydrocarbons^{18-20,22-24}, benzene, substituted benzenes such as toluene, xylenes, and ethylbenzenes^{18-20,22,24} and naphthalenes, indenes, indanes and methylated species^{18,20-24,26}. In some cases, condensed aromatics such as biphenyl, acenaphthylene, anthracene, and 1,1-diphenylethylene were also identified^{18,20}. In all cases the major products of pyrolysis were hydrogen chloride gas and benzene. In some cases, chlorinated compounds were identified; for example, ethylene chloride at 400°C¹⁹, chlorobenzene, di- and trichlorobenzenes at 500-700°C^{20-22,24}, and vinyl and ethyl chloride at 550°C²⁴.

Although investigation of the pyrolysis products of polyvinyl chloride began in the 1940's, inquiry into the combustion products did not begin until the mid to late 1960's²⁸. A brief review article on the products and reaction mechanisms for combustion of PVC had been published by O'Mara¹³. Combustion of polyvinyl chloride has been studied at temperatures between 400 and 800°C in the laboratory^{28,29,31,34,36,37}, and at 140-790°C using a pilotscale incinerator³³. Samples were subject to oxidative pyrolysis in a fixed volume of air^{28,31} or under air flows varying between 0.1 and 30 l/min, depending upon combustion apparatus and sample size^{29,30,34,36}. Most investigators have looked at very small sample sizes for both pyrolysis and combustion experiments, varying from 0.002 to 2 g for small-scale investigations^{14,15,18-21,25,28} and from 16 g to 225 kg for larger scale combustions^{33,34}. Ahling *et al.*³³ used supplemental fuel in the form of wood chips and LP gas to support combustion of PVC in their pilot plant study.

Many of the combustion products of PVC are similar or identical to those found during pyrolysis. Hydrocarbons and alkenes make up the majority of products identified by many researchers^{28,29,31,36,37}. Chlorinated hydrocarbons have been identified at 400, 440, and 800°C^{31,36,37}, with chain lengths of 2 to 6 carbons^{31,36}. Again, benzene was found to be the major organic species produced. Chlorinated aromatics, such as benzyl chloride³¹, di- through hexachlorobenzenes^{33,36} and chlorinated biphenyls³³ were identified. In addition, higher-molecular-weight polycyclic aromatic hydrocarbons ranging from naphthalene to 7,12-dimethylbenzo[*a*]anthracene have been identified in extracts from smoke particulates obtained from PVC combustion³⁴. Gardner³⁸ has investigated the oxidative pyrolysis of several polyvinyl chloride formulations at temperatures of 250-500°C, and identified 54 components. These compounds were largely hydrocarbons and substituted aromatics such as

ethylstyrene, ethyltoluenes, and naphthalenes. Some chlorinated species were identified, but as with other researchers, the majority of compounds identified did not contain chlorine.

EXPERIMENTAL

Polyvinyl chloride was obtained in powder form, density 1.40, from Aldrich (Milwaukee, WI, U.S.A.), and was used as received. Standard solutions containing hydrocarbons, phthalates, alcohols and polycyclic aromatic hydrocarbons (PAHs) have been described in detail elsewhere, along with the combustion apparatus, gas chromatography (GC) and gas chromatography-mass spectrometry (GC-MS) analysis conditions^{1,39}.

RESULTS AND DISCUSSION

Cold traps

Fig. 1 presents the total ion chromatograms (TIC) of the cold trap extracts produced during PVC combustion at temperatures of 800–950°C. Full scale total ion

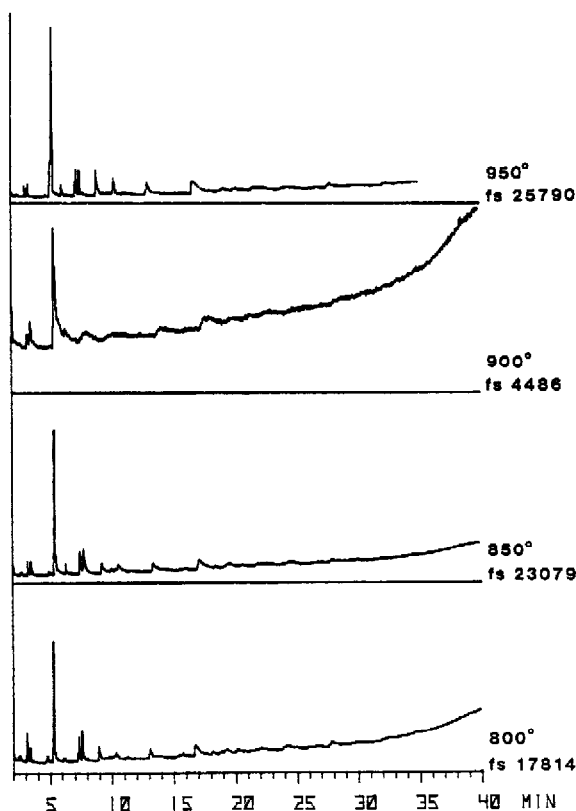


Fig. 1. Total ion chromatograms from polyvinyl chloride combustion cold trap extracts. Full scale values and combustion temperatures are given to the right of each chromatogram.

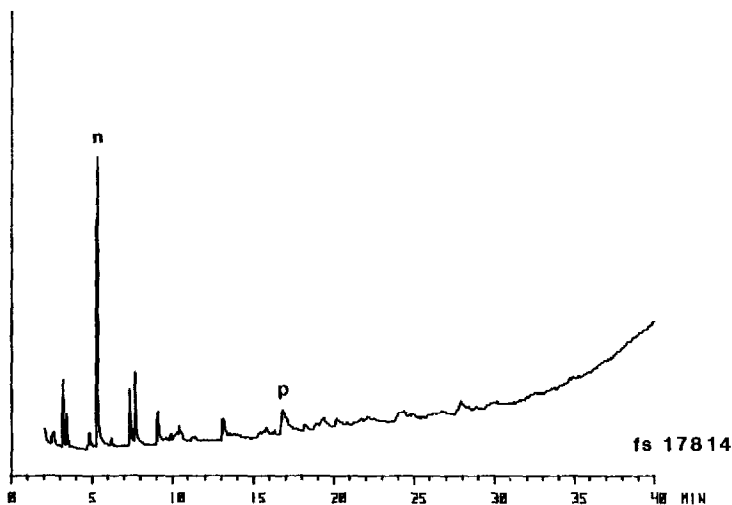


Fig. 2. Total ion chromatogram for PVC, 800°C, cold trap extracts. Peak marked n is naphthalene; p is phenanthrene.

abundance values and combustion temperatures are given at the right of each plot. From initial inspection of the figure, it appears that there is no significant change in the number of components produced in changing combustion temperatures. With the exception of the 900°C sample, there appear to be approximately 11–12 readily observable peaks in the TIC. Although not easily seen in the total ion chromatogram plots, the number of components identified by GC-MS decreases from 25 to 800°C to 18 at 950°C. An examination of the results of analyses of combustion products at 800 and 950°C will be used to describe the compounds produced in greater detail.

The TIC of the combustion of a 2-g sample of PVC at 800°C is shown in Fig.

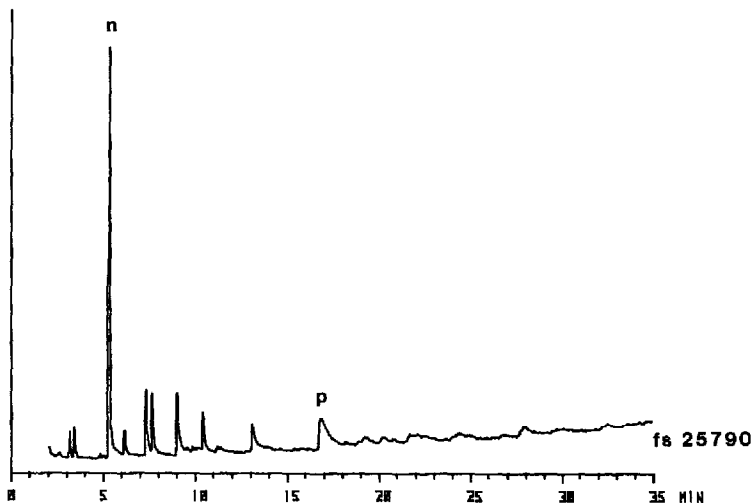


Fig. 3. Total ion chromatogram for PVC, 950°C, cold trap extracts. Peak marked n is naphthalene; p is phenanthrene.

2. The large component at a retention time of 5.5 min is naphthalene. Compounds which eluted before naphthalene were identified as two $C_{10}H_{10}$ isomers, indene, a chlorinated C_2H_5 benzene isomer, and phenol. There are several compounds with molecular formula $C_{10}H_{10}$ whose mass spectra matched the observed spectra obtained from the PVC combustion samples. Final compound assignment, though ambiguous in some cases, was based on both mass spectral and boiling point information.

In the region between naphthalene and phenanthrene [retention indices (RI), of 200 and 300, retention times of 5.5 and 16.9 min, respectively] the compounds identified are a chlorinated C_3H_5 benzene compound, the methylnaphthalenes (2-methyl and 1-methyl), biphenyl, two dimethylnaphthalene isomers (1,3- and possibly 2,3-), acenaphthylene, 4-methylbiphenyl, fluorene, and 2-methylfluorene. In the region after phenanthrene, the compounds identified are 3- and 9-methylphenanthrene, dihydronaphthacene, and chrysene at retention time of 27.9 min and an RI of 400.

The TIC for PVC at 950°C is presented in Fig. 3; 12 sharp peaks are easily discernable, and may be identified from mass spectra. Compounds identified in order of increasing retention time are indene, a chlorinated C_2 -benzene isomer, azulene, and naphthalene to 5.5 min. Between naphthalene and phenanthrene (16.9 min), compounds identified are 3-chloropropylbenzene, 2- and 1-methylnaphthalene, biphenyl, acenaphthylene, 4-methylbiphenyl and fluorene. Following phenanthrene, compounds detected were 9-methylphenanthrene, 2-phenylnaphthalene, fluoranthene, benzo[*a*]fluorene, benzo[*a*]anthracene, chrysene, a methylbenzo[*a*]anthracene and a benzofluoranthene isomer. Once again, ion monitoring at m/z 252 detects two major components, a benzofluoranthene isomer at approximately 32 min, and a benzopyrene isomer at 34 min. However, in this instance the benzofluoranthene isomer was present in sufficient quantities to obtain a mass spectrum.

The major differences between the more volatile trap condensates at 800 and 950°C is the decrease, in compounds eluting prior to naphthalene, and the formation of fewer methyl-substituted aromatics at 950°C. At 800°C several methylated and di-methylated species are formed, while at 950°C only four methylated compounds are identified. In the higher-molecular-weight region, there are no significant differences in compounds formed, as few high-molecular-weight species (MW > 178, RI > 300) are detected.

Glass wool traps

Fig. 4 presents the TIC of the glass wool trap extracts at the various combustion temperatures for PVC. The 800°C sample has the greatest number of components, with slightly fewer compounds produced at 850°C, and the fewest at 900 or 950°C. The compounds identified are, in general, higher-molecular-weight PAHs and methylated PAHs. There are a larger number of compounds in the glass wool extracts than in the cold trap extracts; at 800°C, 24 compounds in the cold traps vs. 53 in the glass wool trap, and at 950°C, 16 vs. 28. The TIC of the 800°C glass wool trap sample is given in Fig. 5. Indene, naphthalene, and the methylnaphthalenes are present, along with three isomers of molecular weight 154, eluting at 9.1, 9.7 and 10.1 min (retention indices of 232.7, 237.9 and 241.4, respectively). The first of these corresponds to biphenyl, but the other two are not readily identified from mass spectra, and their retention indices do not correspond to known compounds. From exam-

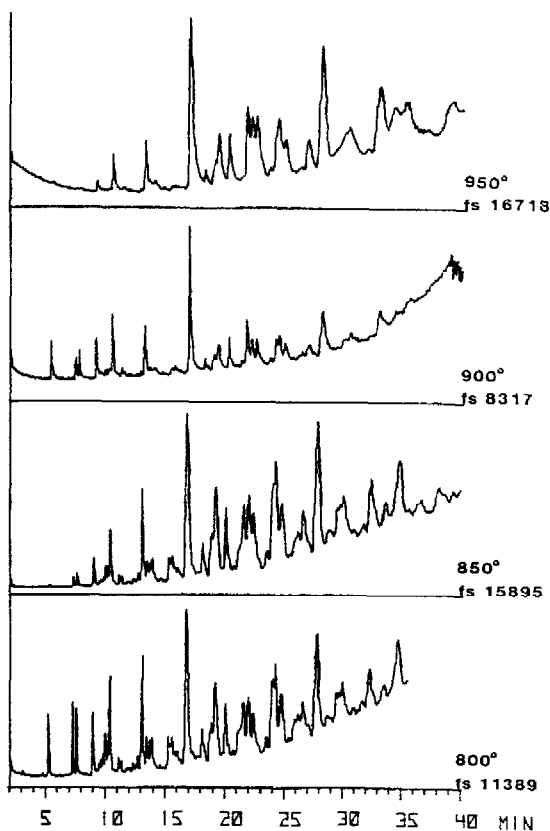


Fig. 4. Total ion chromatograms for glass wool extracts from PVC combustion.

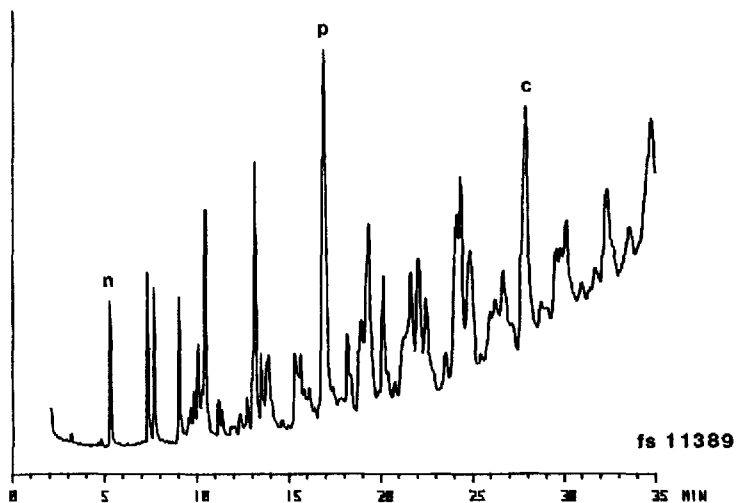


Fig. 5. Total ion chromatogram from 800°C glass wool sample, PVC combustion. Peak marked n is naphthalene; p is phenanthrene; c is chrysene.

TABLE I
COMPOUNDS IDENTIFIED BY GC-MS IN PVC COMBUSTION

× means detected in that sample. T = Liquid nitrogen cold traps; GW = Pyrex glass wool trap.

Compound	800°C		850°C		900°C		950°C	
	T	GW	T	GW	T	GW	T	GW
Phenol	×							
Propylbenzene	×							
C ₃ H ₅ -Benzene			×					
Indene	×	×	×		×		×	
Chloroxylyene	×		×		×		×	
C ₁₀ H ₁₀ , isomer No. 5	×							
C ₁₀ H ₁₀ , isomer No. 6	×							
Azulene			×					
Naphthalene	×	×	×	×	×	×	×	
3-Chloropropenylbenzene	×		×				×	
2-Methylnaphthalene	×	×	×	×		×		
1-Methylnaphthalene	×	×	×	×	×	×		
Biphenyl	×	×	×	×		×	×	×
2,6-Dimethylnaphthalene		×						
1-Ethylnaphthalene				×				
1-Vinylnaphthalene		×		×				
1,3-Dimethylnaphthalene	×	×	×	×		×		
2-Vinylnaphthalene		×		×	×	×		
2,3-Dimethylnaphthalene	×	×						
1,4-Dimethylnaphthalene			×					
Acenaphthylene	×	×	×	×		×	×	×
4-Methylbiphenyl	×	×		×		×	×	×
3-Methylbiphenyl		×	×	×				
Unknown 168		×	×	×				
1-Methylacenaphthylene		×		×		×		×
Unknown, MW 166				×				
Fluorene	×	×	×	×		×	×	×
1-H Phenalene		×	×	×				
4-Methylacenaphthylene		×		×	×			×
3-Methylacenaphthylene		×		×				
Diphenylacetylene				×				
Dihydrophenanthrene		×		×		×	×	
2-Methylfluorene	×							
1-Methylfluorene		×		×		×		
Unknown, MW 192		×		×				
(<i>p</i> -Methylphenyl)phenylacetylene		×		×				
Phenanthrene	×	×	×	×		×	×	×
Anthracene			×					
1-Phenylnaphthalene		×		×		×		×
4,5-Methylenephenanthrene		×			×			

(Continued on p. 218)

TABLE I (continued)

Compound	800°C		850°C		900°C		950°C	
	T	GW	T	GW	T	GW	T	GW
2-Methylanthracene		x	x					
9-Methylphenanthrene	x			x			x	x
2-Phenyl-naphthalene	x	x		x		x	x	x
Unknown, MW 218		x		x				
2,7-Dimethylphenanthrene		x		x		x		
Unknown 204		x						
Fluoranthene	x	x	x	x			x	x
Diphenyl-diacytylene		x		x		x		x
Pyrene		x		x		x		x
Unknown, MW 228		x						
p-Terphenyl	x			x				x
Benzo[a]fluorene	x	x	x	x		x	x	x
Benzo[b]fluorene		x		x		x		x
1-Methylpyrene		x				x		
Unknown, MW 228		x	x					x
Dihydronaphthacene	x	x		x		x		x
1-Ethylpyrene		x		x				
Benzo[ghi]fluoranthene							x	x
Benzo[c]phenanthrene		x		x		x		x
Benzo[a]anthracene						x		
Chrysene	x	x	x	x		x	x	x
11-Methylbenzo[a]anthracene		x		x				
1-Methyltriphenylene		x						
1-Methylbenzo[a]anthracene								x
8-Methylbenzo[a]anthracene			x				x	
3-Methylchrysene					x			
1-Phenylphenanthrene		x		x				x
6-Methylchrysene		x						
2,2'-Binaphthyl				x		x		
Benzo[fluoranthene] isomer		x		x				x
Benzo[e]pyrene		x				x		
Benzo[a]pyrene		x		x				
Perylene				x				x
3-Methylcholanthrene		x						x
Unknown, MW 280		x		x				
Pentacene				x				
Picene		x		x		x		
Benzo[ghi]perylene								x
Diphenylacenaphthene				x				

ination of boiling points and mass spectral data, it was felt that the best identification of the two components corresponded to the isomeric vinyl-substituted naphthalenes. This same use of isomer boiling points served to identify isomers of molecular weight 166 eluting in the region of retention time 12.8–14 min, where there were a total of six compounds with molecular weight 166 and similar mass spectra. From RI data, fluorene and 1-methylacenaphthylene could be identified, leaving 3-, 4-, and 5-methylacenaphthylene and 1-H phenalene as possibilities for the other compounds. The compound eluting at a retention time of 13 min (RI 266.3) could not be identified based on boiling point or mass spectra, and has been assigned as unknown 166.

In the region between phenanthrene and chrysene (retention times 17 to 28 min) the compounds identified included methylphenanthrenes, fluoranthene, pyrene, benzofluorenes, substituted pyrenes, and benzo[*c*]phenanthrene. There were also present several compounds whose identities could not be determined based on mass spectra and retention index. The compounds of molecular weight 204 were believed to be benzoacenaphthylene isomers or dibenzoheptafulvenes from mass spectral data; however, without standards, positive identification could not be made.

Compounds eluting after chrysene were higher-molecular-weight aromatics, including methylbenzo[*a*]anthracenes, 1-phenylphenanthrene, benzo[*j*]fluoranthene, benzo[*a*]- and benzo[*e*]pyrene and larger 5- and 6-ring condensed aromatics. The chlorinated species identified in the cold trap extracts were not present in the glass wool traps, although compounds which eluted before and after them were identified.

GC-MS analysis of the glass wool extract from the 950°C combustion of PVC indicated the presence of fewer compounds than at the lower temperature. The earliest eluting compound identified was biphenyl, and in general the combustion products were less complex. Very few methylated or substituted PAHs were identified: generally, the compounds formed were PAHs skeletons such as acenaphthylene, fluorene, phenanthrene, benzofluorene and chrysene. A summary of all compounds identified in the PVC samples is given in Table I.

Single ions were monitored to aid in compound identification; among the single ions was ion 460 which is the most abundant ion of the eight chlorine isotope clusters at the molecular weight of octachlorodibenzo-*p*-dioxin. This ion was not observed in any sample.

CONCLUSIONS

Polyvinyl chloride produced the fewest number of different compounds of any of the different polymers studied to date^{1,2}. The species produced consisted largely of simple polycyclics, such as naphthalene, acenaphthylene, fluorene, phenanthrene and phenyl naphthalenes. Some methylated species were found, although in general the compounds produced were unsubstituted PAH nuclei. Two chlorinated species were identified; both were chlorinated alkylbenzenes and both appeared to contain the chlorine attached to an alkyl side group and not to the aromatic nucleus. No chlorinated aromatics containing chlorine attached to an aromatic ring were identified.

The small numbers and amounts of PAHs produced during PVC combustion is demonstrated in Table II. The compounds listed have also been identified in combustion products of polyethylene or polystyrene^{1,2} although in some cases at much

TABLE II

TOTAL AMOUNTS (mg) OF SELECTED COMPOUNDS IDENTIFIED IN COLD TRAP EXTRACTS

Compound	Temperature (°C)			
	800	850	900	950
Indene	0.771	0.868	0.411	0.786
Naphthalene	1.91	9.505	4.716	15.03
2-Methylnaphthalene	0	2.054	0.452	2.098
1-Methylnaphthalene	0	1.893	0.380	1.667
Biphenyl	0	1.406	0.511	2.162
Acenaphthylene	0	0.843	0	1.564
Fluorene	0.0891	0.129	0	0.152
9-Methylfluorene	0	1.341	0	1.646
Dihydroanthracene	0	0.082	0	0
Phenanthrene	0.506	1.773	0	2.708
C ₁₉ H ₃₈	1.46	0.172	0	0.095
2-Phenylnaphthalene	0	0.227	0	0.197
Fluoranthene	0.0749	0.371	0	0.242
Pyrene	0	0.251	0	0.637
Benzo[<i>c</i>]phenanthrene	0	0.177	0	0.231
Chrysene	0.0419	0.275	0	0.184
C ₂₆ H ₅₂	0.932	0.214	0	0.455
Total*	24.135	21.581	6.47	29.854
Approx. total PAHs**	35.59	32.07	9.71	37.71

* Total amounts of listed compounds.

** Total PAHs in sample.

higher levels. It is interesting to note that the total amounts of PAHs produced are greatest at 950°C, which appears to be due in large part to the high amounts of naphthalene produced. It is unclear why there should be as noticeable a decrease at 900°C as is observed; a possible explanation is that this temperature produces the most complete combustion of PVC, although further work is necessary to verify this conjecture.

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