

STUDY OF THE ORGANIC CONTAMINANTS RELEASED TO THE ENVIRONMENT DURING THE DISPOSAL OF ROCKET MOTORS BY BURNING*

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Summary

The U.S. Navy must constantly dispose of deteriorating and obsolete ordnance, propellants, pyrotechnics, and explosives (PEP). One method of disposal is by open burning. The U.S. Navy wishes this disposal to be carried out in an environmentally sound manner. In this study, rocket motors and sections of rocket motors were burned to sample and analyze the combustion products. The plumes, particulates, and residues from these burns were sampled and analyzed by gas chromatography/mass spectrometry (GC/MS) to identify organic contaminants, particularly polycyclic aromatic hydrocarbons (PAH), released to the environment during the disposal of these motors by open burning. This study determined that the concentrations of organic materials released to the atmosphere were very low and should be of no environmental concern.

Introduction

Every year approximately 25,000 tons of U.S. Navy ordnance, propellants, explosives, and pyrotechnics (PEP) either become obsolete or have deteriorated and must be disposed of. It is the intention of the Navy to conduct this disposal in an environmentally sound manner. As part of this concern, the Navy has been involved in the study of disposal methods that have a minimal deleterious effect on the environment and in the identification of contaminants released to the environment during the disposal of ordnance.

A number of disposal methods are currently available. These include recycling, various types of incineration, detonation, and open burning. Recycling

*This paper is the third in our series describing pollution problems from ordnance. The first two papers are Refs. 1 and 2 of this paper.

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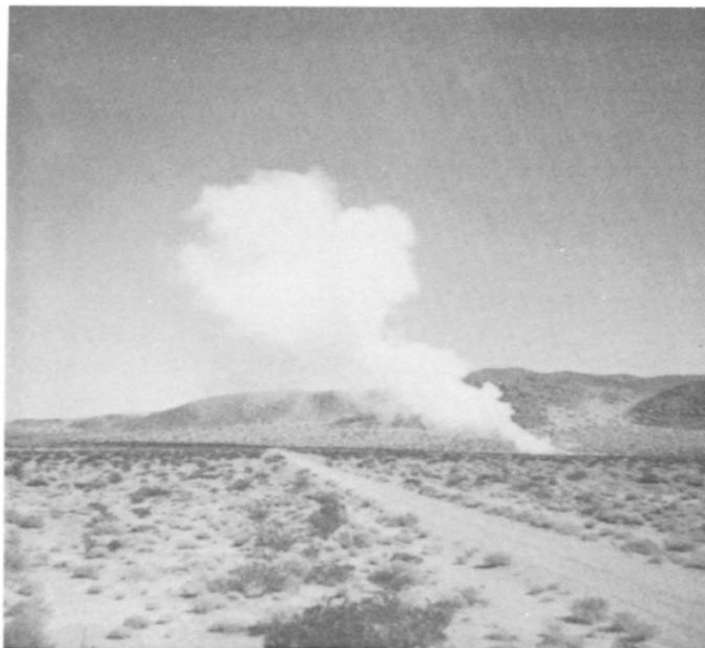


Fig. 1. First stage burn of a rocket motor.

has been deemed impractical because of safety and economic considerations. Incineration methods require a relatively small sample size in order to ensure efficient combustion and to minimize equipment damage in the event of an accidental detonation during the incineration. Items of ordnance that are either too large or too unstable to be disposed of by incineration must be detonated or burned in open spaces away from centers of population.

We have previously reported on the results of the sampling of the post-detonation products of a number of Navy explosives and the analysis of these samples to identify and quantify the organic products [1,2]. Particular attention was paid to the polycyclic aromatic hydrocarbons (PAH) formed during the detonations. In this paper, we will report on the work to identify and quantify the organic contaminants released to the environment during the disposal of large rocket motors by burning. These large rocket motors consist of thousands of kilograms of a solid propellant encapsulated in a rubber liner and a fiberglass case.

Disposal by burning is carried out in remote areas. The nozzles are removed from the motors to prevent any movement of the motors during disposal. The motors are ignited by the detonation of shaped charges that are attached to the fiberglass case of the motor. The detonation of the shaped charges splits the case of the motor and ignites the propellant. Once ignited, the motors burn in

two distinguishable stages. The first stage of the burn (lasting about 15 minutes) is the combustion of the propellant. During this stage, a heavy white plume is created (Fig. 1). The major components of this plume have been identified in previous studies of the combustion of solid propellants as Al_2O_3 , H_2O , CO , CO_2 , N_2 , HCl , NO_x , and carbon particulates [3,4]. The second stage, the burning of the liner, occurs after the propellant has been consumed. The combustion of the liner gives rise to a black plume. The composition of this plume would be expected to consist of organic compounds similar to those formed during the manufacture or disposal of rubber tires [5] and the combustion of polymers [6,7].

Our efforts were directed toward the identification of the organic components in the effluent smoke from these rocket motor burns. Particular emphasis was placed on the identification and quantification of the PAH which are produced during the combustion and pyrolysis of organic matter [8–11]. Many PAH are suspected or known carcinogens or mutagens [12–15].

Experimental

Sampling of the smoke plume of the burning motors was divided into two strategies. The first set of tests was conducted to identify contaminants and the second set of tests was conducted to quantify these contaminants. For the first set of tests, motors weighing between 4,000 and 30,000 kg were burned and sampled in the open; for the second set of tests small sections of motors weighing under 10 kg were burned in test chambers so that the amount of pollutant produced per kilogram of motor burned could be determined.

Sampling of large motors

The sampling of combustion gases from large motors was carried out in essentially the same way as described previously [16]. The rocket motor was placed at the bottom of a canyon several hundred feet wide with walls about 150 feet high (45 m). Sampling equipment included: (1) evacuated 1 L sample flasks for grab samples (2) Tenax-GC traps for collecting high molecular weight organic compounds. (These traps followed the design of Jones et al. [17] and were cleaned and conditioned according to their recommendations.) (3) A high-speed particle collector to collect and determine the size distribution of particulate matter in the smoke plume. All gas sampling devices were radio controlled and were arranged so that samples could be obtained from each of the two stages of the rocket motor burn.

In some of the tests commercial infrared CO and chemiluminescent NO_x monitors were used. In a number of tests glass frits were used to collect particulate matter to supplement the information from the high speed particle collector. Small traps constructed of 3 in. \times 1/4 in. pyrex tubing and packed with cleaned conditioned Tenax-GC were also used to collect samples of high mo-

lecular weight organic compounds. These traps could be directly desorbed in the injection port of the gas chromatograph. The use of these traps was discontinued when it was observed that most of the compounds desorbed from the Tenax-GC could be correlated with the materials from which the Tenax-GC was prepared. We have discussed the problem of artifacts observed when using Tenax-GC for gas sampling in a separate paper [18].

To sample the plume of the rocket burn, a number of configurations were used for the placement of the gas sampling probes. (1) Probes were placed on small hills about 30 m downwind from the burning motor. (2) The sample was conducted 30 m to a barricade and to the sample flasks by 1/2-inch stainless steel probes located 4.5 m above ground level and placed 1.8 m on each side of the motor. (3) To avoid any movement of the motor, the rocket motor was anchored with 2-inch pipe set in concrete and the products of the motor burn were sampled from behind 1/2-inch steel plates placed on each side of the motor. In this sampling procedure, the probes and all electrical lines were run underground to a barricade 30 m from the burning motor. (4) The gas sampling was conducted from a platform that was suspended from a Cable strung between the two walls of the canyon.

Sampling of motor section burns in a test chamber

The samplings of the combustion products of the small motor sections were carried out in a concrete-enclosed steel room $4.42 \times 3.30 \times 2.72$ m (volume = 38.1 m^3 when the volume of a 1.6 m^3 utility box is subtracted). This chamber was equipped with three shock-baffled chimneys in the ceiling and an escape corridor with two sharp turns. Holes in a steel plate 0.8 m above the floor in one wall provided access for sample probes. The pumps, sampling flasks, and polymer traps were in an adjacent room. A portal in another wall led to a second chamber which served as the control room and camera room.

The rocket motor sections were placed on four $5 \times 5 \times 1$ cm steel blocks on a steel platform in the center of the test chamber. The sample probes were positioned about 130 cm above the motor section. The motor sections were ignited with an igniter prepared by wrapping a small piece of propellant with high resistance wire.

The sampling of the motor sections in the test chamber was carried out with the apparatus shown in Fig. 2. This apparatus is designed to collect one set of samples during the burning of the propellant and a second set of samples during the burning of the liner.

Two probes were used for collecting gas samples; one for collecting samples in the sample flasks and on the large polymer traps, and the other for collecting samples on the small polymer traps.

In this sampling apparatus, combustion products from the burning motor drawn through the first probe passed through quartz wool filters. These filters prevented particulates from entering the gas sampling equipment and made it

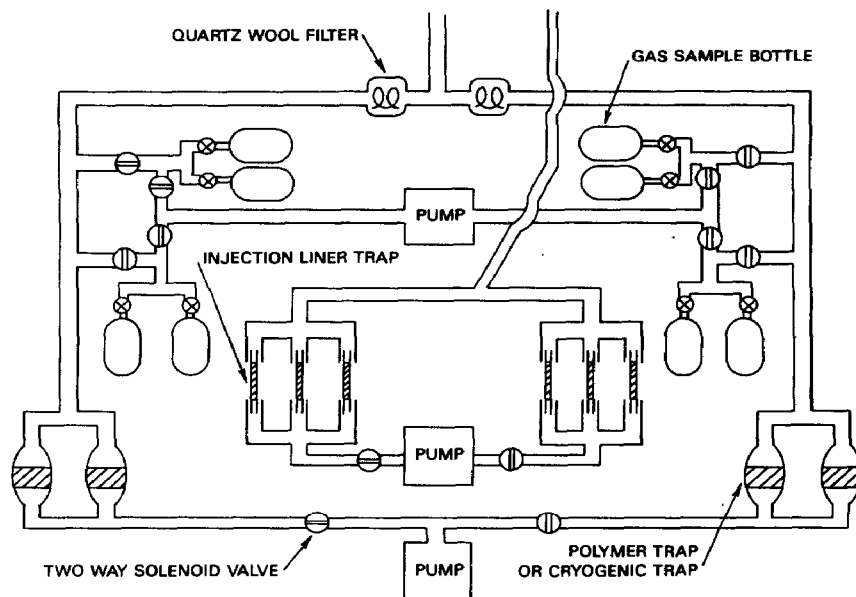


Fig. 2. Apparatus for collecting gas samples from the motor sections.

possible to determine whether organic compounds were in the gaseous state or sorbed on particulate matter. Duplicate gas samples were collected at various times during each stage of the burn. Combustion products from the burning motor drawn through the second probe were collected on gas chromatograph injection liner traps filled with Tenax-GC, Poropak-P, or Spherocarb.

Additional probes were used for samplings with bulk filters of Teflon-coated glass fiber to measure the concentration of particulates above the flame. The observer in the control room switched the sampling between the two stages of the burn.

Measurement of air flow through the chamber

In order to calculate the absolute values of the concentrations of the combustion products, it was necessary to determine the volume of air in which these products were diluted. To calculate this dilution, the volume of air flowing through the chamber must be known. The volume of air flowing through the chamber during the combustion of the rocket motor was determined by sealing the escape corridor with a sheet of plywood in which a 30 cm diameter round hole was cut. A velometer or hot wire anemometer was placed in front of this hole to measure the velocity of air entering the test chamber. Readings from these instruments were obtained with a video camera which was monitored in the control room.

Sample analyses

Indicator tube analysis

The HCl indicator tubes were prepared by coating AgNO_3 on glass beads and operated on the principle that AgCl formed when HCl was drawn over the AgNO_3 coated glass beads. After the HCl tubes were used in a test, they were exposed to UV light which reduced the Ag^+ to Ag forming a purple stain on the glass beads. The length of the stain was a measure of the HCl concentration.

Analysis of low molecular weight gases

The grab samples in the 1-liter flasks were analyzed by gas chromatography. Samples from early tests were analyzed with a Carle 8500 gas chromatograph with a thermal conductivity detector. The operation was isothermal; helium was the carrier gas and the flow rate was 15 cc/min. By means of a manually operated series/bypass valve the flow was switched from a 5\AA molecular sieve column to a $1.8\text{ m} \times 3.2\text{ mm}$ ($6\text{ ft} \times 1/8\text{ inch}$) Poropak N column. In this way, H_2 , O_2 , N_2 , CH_4 , CO , CO_2 , C_2H_4 , and C_2H_6 could be analyzed in one step. Samples from later tests were analyzed with a Perkin-Elmer Sigma 2000 using the same columns. In the final test, a catalyst was used to convert CO and CO_2 to methane so that these compounds could be detected with a flame ionization detector.

Polymer traps

The Tenax-GC traps were extracted for 24 h with 200 ml of Burdick and Jackson "Distilled in Glass" pentane using the modified Soxhlet apparatus described by Jones et al. [17]. Pentane was used as the extraction solvent because it was found by Jones et al. to be the most efficient solvent for the extraction of PAH from Tenax-GC.

After the extraction, either 2.0 ml of a solution of a known amount of anthracene- d_{10} in isooctane or 2.0 ml of a solution of a known amount of naphthalene- d_8 , anthracene- d_{10} , and pyrene- d_{10} in isooctane was added to the extract. The deuterated PAH served as internal standards and the isooctane served to reduce the volatility of the concentrated extract. The extracts were reduced in volume to about 0.5 ml by rotary evaporation.

XAD-2 traps were treated in the same way as Tenax-GC traps except that methylene chloride was used as the solvent. Probes were rinsed with pentane and this wash solution was reduced in volume by rotary evaporation. Bulk filters, liner residues, and Al_2O_3 residues were Soxhlet extracted using either pentane or methylene chloride as the solvent. Two hundred milliliters of methylene chloride were added to the cryogenic traps, the traps were placed in an ultrasonic cleaner for 15 minutes, then the samples were poured into 1-liter flasks, the internal standard dissolved in isooctane was added, and the solutions were concentrated by rotary evaporation.

Extracts were analyzed using a Hewlett-Packard 5985 GC/MS equipped with a 50–60 m fused silica capillary column. During the course of this work, a number of silicone columns were used; these included OV-1, SE-30, SE-52, SE-54 and DB-5. Temperature programming from 50°C to between 275 and 300°C at 5°C/min was used. Both splitless injection and on-column injections were used at different stages of this work. When the mass spectrometer was operated in the electron impact mode, operating parameters were determined by the data system's AUTOTUNE program. When the mass spectrometer was used in the chemical ionization mode, methane was used as the chemical ionization gas and operating parameters were determined by manual tuning.

Identification of the components in the samples was made by comparing the mass spectra with standard tables of mass spectra [19–21]. Identification of isomers was performed by calculating retention indexes with the aid of a C₁₀ to C₃₀ normal alkane standard [22] and comparing these indexes with those of the published values of known compounds. Quantification was performed by comparison of the chromatographic peak areas with the peak areas of the internal standards.

Particulate composition

The glass wool particle filters were used to identify the type of carbon produced during the rocket motor burning. Before and after the filter was used, it was heated to 100°C in a vacuum oven, dried in a desiccator and weighed. This measurement determined the total mass of the particulates collected. The filter was then heated to about 500°C with a stream of dry nitrogen or helium passing through the filter. The weight loss in this step was assumed to be due to the volatilization of organic compounds. The filter was then heated to 500°C in air. The weight loss from this step was due to the oxidation of elemental carbon. The mass of the residue on the filter was due to metal oxides (most probably, aluminum oxide from the propellant).

Thermal desorption

Thermal desorption was used in an attempt to measure the volatile compounds which are usually lost during Soxhlet extraction. Sample tubes containing the polymer sorbet (Tenax-GC, Poropak-N) or SpheroCarb were placed in the heated injection port of the gas chromatograph, the column was cooled to –50°C and the carrier gas was temporarily diverted through the sample tube. Samples desorbed from the desorption tube collected at the head of the chromatographic column. When desorption was complete, the flow path of the carrier gas was returned to its normal mode and temperature programming was initiated. A complete description of the experimental procedure has been reported elsewhere [23].

Calculation of the masses of the products per unit mass of rocket motor section

In order to determine the amount of contaminant produced per unit mass of motor section, it was necessary to determine the total volume of air in which the combustion products were dispersed. To calculate this value, it was necessary to determine the volume of air that entered the chamber during the combustion of the motor section. The velocity, v , of air flowing through the 30 cm diameter hole cut in the plywood sheet that blocked the entrance to the chamber was measured as described under Experimental. The volume of air flowing through the chamber during combustion, V_d , was the product of the cross-sectional area of the hole, the velocity, v , and the sampling time, t ;

$$V_d = (\pi)r^2vt = (\pi)(0.023 \text{ m}^2)vt \quad (1)$$

and the total volume, V_t , of air into which the combustion products were diluted is the sum of the volume of the chamber, V_c , plus this volume of air that flowed through the chamber.

$$V_t = V_c + V_d = 31.1 + V_d(\text{m}^3) \quad (2)$$

Quantification of the combustion products was accomplished using eqn. (3)

$$C_u = \frac{C_s V_s A_u V_t}{A_s [(f_i + f_f)/2] t W} \quad (3)$$

Where C_u the product concentration in $\mu\text{g/g}$ motor,

C_s the concentration (in the original standard solution) to which the product is compared, g/l

V_s volume of the standard solution, ml

A_u area of the peak of the combustion product

V_t total volume of air (m^3) into which the combustion products are diluted, as calculated using eqn. (2)

A_s area of the peak of the internal standard

f_i, f_f the initial and final flow rates at which the sample was collected, m^3/s

t sampling time,

W mass of the rocket motor section, g

Results and discussion

HCl tubes

The HCl tubes were calibrated with the vapor from a bottle of saturated hydrochloric acid and the indicator reaction worked as expected. When we sampled the combustion plumes from the rocket motor burns, no HCl was ever detected in spite of the large quantities of HCl formed during the combustion of these propellants. Our results are at variance with others who have used this method of measurement [3,9]. We ascribe this disagreement to the fact that

in our application, the HCl in the very hot exhaust gases did not react with the AgNO_3 .

Low molecular weight gases

The analysis of a typical grab sample is listed in Table 1.

The only product identified in the grab samples was carbon dioxide. Carbon monoxide was not detected. The limit of detection of carbon monoxide in the analytical method used was 0.5 parts per million. This shows that combustion of the carbonaceous material of the motor is complete. Other investigators [3] have reported that carbon monoxide is a combustion product found during the disposal of propellants. The results of our 10 tests (based on sensitive calibrated equipment) do not support these observations.

No C_2 or C_3 hydrocarbons were observed among the low molecular weight gases. These compounds have been postulated as the precursors of PAH and soot. Since both PAH and soot were detected in the plumes the steady state concentration of these intermediates, if present, must have been below the 0.5 ppm level in the sampling region above the flame.

High molecular weight gases

Our work with detonations of TNT and other Navy explosives in this test chamber [1,2] showed that high molecular weight compounds and aerosols diffuse from the chamber at a much slower rate than CO_2 . Since we observed that CO_2 is retained in the chamber for about 3 minutes and that particulates are suspended in the chamber for more than 20 minutes, we judged the sampling of the high molecular weight combustion products for 109 minutes after the initiation of combustion to be an adequate sampling time. The analysis of high molecular weight combustion products is given in Tables 6 and 7. Since there is evidence that the Poropak and Tenax-GC underwent decomposition during the sampling procedure (see below), the compounds collected in the cryogenic traps are reported as well as the analysis of the probe washings and extracts from the quartz wool filters, the Pallflex filters (Teflon coated glass fiber filters manufactured by Pallflex Inc., Kennedy Drive, Putnam CT 06260),

TABLE 1

Analysis* of grab sample from test 15 (6.8 kg section of first-stage Polaris)

Time after initiation (s)	Percent CO_2
21	0.54
45	4.82
111	2.67
160	1.52

*Components of air not included.

the charred liners, and the aluminum oxide residues to show that the same products are common to all the samples taken.

Particulate analysis

Particulate samples were collected both on quartz wool and Pallflex filters. Pallflex filters were selected since it has been observed that there is no loss of PAH due to irreversible absorption or chemical reaction on their inert surface [24,25].

The quartz wool filters from tests 9 to 15 were analyzed to identify the particulate matter. The following types of samples were taken. (1) "Early smoke" samples were taken at the beginning of the burn when the propellant was burning. The sampling time for "early smoke" varied between 30 and 90 s. (2) "Late smoke" samples were taken when only the liner was burning. The sampling time for "late smoke" varied between 4 and 10 min. (3) "Chamber smoke" samples were collected inside the test chamber and represented both "early" and "late" smoke. The results of the measurements on the glass wool filters for test 10 are given in Table 2.

The actual values for the other tests differ in detail but all show that: (1) the total mass of particulates is greater in "early" smoke than in "late" smoke, (2) the percentage of carbon in both "early" smoke and "late" smoke is about equally divided between organic and elemental carbon, and (3) carbon makes up less than 20% of the particulates. The "other particulates" consist primarily of aluminum and aluminum oxide.

Particulate collection on the Pallflex filters confirmed that the density of particulates in the smoke was greater in the "early" smoke than in the "late" smoke. This is the result of aluminum and aluminum oxide in the smoke when the propellant is burning.

TABLE 2

Particulate composition as determined from the glass wool filters in test No. 10

	Early smoke	Late smoke	Chamber smoke
Total particulates	77.3 mg 3.7 mg/l	20.6 mg 0.14 mg/l	48.2 mg 1.1 mg/l*
Organic carbon	2.9 mg 3.6%	0.6 mg 2.9%	1.8 mg 3.7%
Elemental carbon	2.2 mg 2.9%	0.9 mg 4.4%	2.0 mg 4.2%
Other particulates	72.2 mg 93.0%	19.1 mg 93.0%	44.4 mg 92.0%

*This value was obtained by dividing the total particulate mass collected by the volume of air passed through filter.

TABLE 3

PAH's found in the extracts of the Pallflex filters used in test 12 (2.5 kg section of second-stage Poseidon)

Molecular weight g/mol	Identification	Early smoke $\mu\text{g}/\text{g}$ particulates	Late smoke $\mu\text{g}/\text{g}$ particulates
128	Naphthalene	<0.03	0.36
166	$\text{C}_{13}\text{H}_{10}$	<0.03	3.5
168	$\text{C}_{13}\text{H}_{12}$	<0.03	1.3
169	Diphenylamine	<0.03	1.2
178	Phenanthrene	<0.03	4.5
192	$\text{C}_{15}\text{H}_{12}$	<0.03	0.89
202	$\text{C}_{16}\text{H}_{10}$	<0.03	7.8
204	$\text{C}_{16}\text{H}_{12}$	<0.03	0.71
228	$\text{C}_{18}\text{H}_{12}$	<0.03	1.5
252	Benzo(a)pyrene	<0.03	0.64

TABLE 4

PAH's found in the extracts of the Pallflex filters used in test 13 (6.6 kg section of first-stage Polaris)

Molecular weight	Identification	Early smoke $\mu\text{g}/\text{g}$ particulates	Late smoke $\mu\text{g}/\text{g}$ particulates
128	Naphthalene	0.17	0.20
142	Methylnaphthalene	<0.02	0.04
178	Phenanthrene	0.15	0.64
178	Anthracene	0.02	<0.04
192	$\text{C}_{15}\text{H}_{12}$	0.04	<0.04
202	$\text{C}_{16}\text{H}_{10}$	0.63	1.8

TABLE 5

PAH's found in the extracts of the Pallflex filters used in test 15 (6.8 kg section of first-stage Polaris)

Molecular weight	Identification	Early smoke $\mu\text{g}/\text{g}$ particulates	Late smoke $\mu\text{g}/\text{g}$ particulates
128	Naphthalene	<0.1	5.1
142	Methylnaphthalene	<0.1	0.74
152	Acenaphthylene	<0.1	0.95
154	Acenaphthene	<0.1	1.5
178	Phenanthrene	<0.1	1.7
202	$\text{C}_{16}\text{H}_{10}$	<0.1	1.5
202	Pyrene	1.4	2.6
228	$\text{C}_{18}\text{H}_{12}$	<0.03	1.5
252	Benzo(a)pyrene	<0.03	0.64

TABLE 6

Analysis of samples collected from the burn of a section of a first-stage Poseidon motor used in test 11

Compound	$\mu\text{g/g}$ Motor	Compound	$\mu\text{g/g}$ Motor
<i>A. Early smoke collected in a cryogenic trap</i>			
Butylbutyrate	1.1	$\text{C}_{24}\text{H}_{50}$	0.39
$\text{C}_{15}\text{H}_{32}$	0.26	$\text{C}_{25}\text{H}_{52}$ + Phthalate ester	0.78
Phthalate ester	0.51	$\text{C}_{26}\text{H}_{54}$	0.23
Phthalate ester	0.10		
<i>B. Late smoke collected in a cryogenic trap</i>			
Benzaldehyde	0.11	Hydroxynitrotoluene	0.19
$\text{C}_7\text{H}_5\text{N}$	0.18	$\text{C}_{10}\text{H}_{14}$ (PAH M_w 134)	0.20
Phenol	0.07	Butylbutyrate	0.27
$\text{C}_7\text{H}_6\text{O}_2$	0.04	$\text{C}_{10}\text{H}_{13}\text{NO}_2$	0.51
Hydroxybenzaldehyde	0.10	$\text{C}_{15}\text{H}_{32}$	0.10
$\text{C}_{10}\text{H}_{20}$	0.05	$\text{C}_{10}\text{H}_{19}\text{NO}_2$	0.08
$\text{C}_{10}\text{H}_{22}$	0.05	Phthalate ester	0.14
Acetophenone + $\text{C}_8\text{H}_7\text{N}$	0.05	Phthalate ester	0.10
Nitrophenol	3.4	$\text{C}_{22}\text{H}_{46}$	0.02
Naphthalene	0.11	$\text{C}_{23}\text{H}_{48}$	0.04
Hydroxynitrotoluene	0.76	Phthalate ester	0.14
<i>C. Extract of liner residue</i>			
$\text{C}_5\text{H}_{12}\text{O}_3$	0.79	$\text{C}_{14}\text{H}_3\text{O}$	0.49
Phenol	0.22	Dimethylphthalate	0.39
Cresol	2.1	$\text{C}_{15}\text{H}_{32}$	0.27
Cresol	0.45	Phthalate ester	0.54
$\text{C}_8\text{H}_{10}\text{O}$	0.99	NI*	0.54
Methoxybenzaldehyde	0.20	$\text{C}_{16}\text{H}_{34}$	0.24
NI*	0.50	$\text{C}_{17}\text{H}_{36}$	0.35
$\text{C}_8\text{H}_{10}\text{O}$	1.17	Fluorenone	0.15
NI*	0.66	Phenanthrene	0.10
$\text{C}_9\text{H}_{12}\text{O}$	0.66	$\text{C}_{18}\text{H}_{38}$	0.32
Methylnaphthalene	0.20	$\text{C}_{19}\text{H}_4\text{O}$	0.11
$\text{C}_{13}\text{H}_{28}$	0.36	Phthalate ester	7.20
Butylbutyrate	0.52	Phthalate ester	0.65
Butylbutyrate	2.6	Phthalate ester	0.18
<i>D. Residue on table after burn</i>			
Naphthalene	0.020	Phthalate ester	0.023
Phthalate ester	0.18	Phthalate ester	3.6
NI*	0.020	Phthalate ester	0.34
Phenanthrene	0.001	Phthalate ester	0.18
<i>E. Residue in chamber below table after burn</i>			
Alkane	0.019	Acenaphthalene	0.19
Alkene	0.021	Methylacenaphthalene	0.015
Alkene	0.013	NI*	0.026
Naphthalene	0.19	Phthalate ester	0.060
Methylnaphthalene	0.063	Alkene	0.021
Methylnaphthalene	0.052	Alkene	0.060
Acenaphthene	0.039	Phenanthrene	0.064
Dimethylnaphthalene	0.039	Phthalate ester	0.043
Dimethylnaphthalene	0.026	Phthalate ester	6.4
Biphenyl	0.018	Phthalate ester	0.056
Phthalate ester	0.33		

*Not identified.

TABLE 7

Analysis of samples collected from the burn of a section of a second-stage Poseidon motor used in test 8

Compound	$\mu\text{g/g}$ Motor	Compound	$\mu\text{g/g}$ Motor
<i>A. Early smoke collected on a quartz wool filter</i>			
Alkane	0.028	Phthalate ester	0.019
Butylbutyrate	0.13	Phthalate ester	12
Alkane	0.082	Phthalate ester	0.077
<i>B. Late smoke collected on a quartz wool filter</i>			
Oxygenate	0.65	C ₁₆ H ₁₀ (PAH)	0.006
Oxygenate	0.013	C ₁₆ H ₁₀ (PAH)	0.010
Butylbutyrate	0.023	Alkane	<0.082
Butylbutyrate	0.038	Oxygenate	0.050
Oxygenate	0.035	Alkane	<0.082
Phthalate ester	0.051	Alkane	0.082
Phthalate ester	0.51	Alkane	0.082
C ₁₆ H ₁₀ (PAH)	0.017	Phthalate ester	0.077
Alkane	0.003	Alkane	0.008
<i>C. Late smoke collected on Tenax-GC</i>			
Xylene	0.017	Oxygenate	0.053
Xylene	0.033	Naphthalene	0.64
Phenylacetylene	0.024	Oxygenate	1.1
Styrene	0.051	Benzothiazol	0.029
Benzaldehyde	0.096	C ₁₂ H ₁₆ (PAH)	0.025
Phenol	0.59	Methylnaphthalene	0.018
Benzonitrile	0.16	Methylnaphthalene	0.018
Methylstyrene	0.16	Butylbutyrate	0.31
C ₁₀ H ₁₄	0.063	Butylbutyrate	0.55
Methylphenylacetylene	0.17	C ₁₂ H ₁₀ (PAH)	<0.004
Cresol	0.54	C ₁₃ H ₁₉ (PAH)	<0.004
Cresol	0.10	C ₁₂ H ₈	0.060
C ₁₀ H ₁₂	0.028	C ₁₃ H ₁₀	0.004
Methylbenzofuran	0.043	Phthalate ester	0.001
Ethylphenol	0.074	Phthalate ester	0.006
Methylindene	0.031	Phthalate ester	0.19
Methylindene	0.012	Phthalate ester	0.091
<i>D. Probe rinsing after sampling</i>			
Alkene	0.0033	Phthalate ester	0.017
Alkene	0.0088	Dibenzofuran	0.0087
Oxygenate	0.030	Alkane	0.0052
Butylbutyrate	0.0089	Phenanthroline	0.028
Naphthalene	0.0095	Phenanthrene	0.064
Naphthonitrile	0.022	Anthracene	0.0078
Naphthonitrile	0.0071	C ₁₅ H ₁₀ (PAH)	<0.001
C ₁₃ H ₁₀	0.0068	C ₁₆ H ₁₀ (PAH)	<0.001

Organic combustion products extracted from the Pallflex filters were analyzed by GC/MS to determine the presence and concentration of PAH in the particulate matter. Reconstructed mass chromatograms were used to locate and quantify the PAH peaks and the mass spectra of these peaks were compared with library standards to verify the identification. Quantitation of the PAH was done by comparison of the peak areas of the sample with the peak areas of the internal standards. The analyses of the extracts from the smoke from three tests are given in Tables 3–5. Where the peaks have been identified by standards or retention times the names are given, otherwise the molecular formulas are listed.

Thermal desorption analyses

The results of the thermal desorption of the traps packed with Tenax-GC, Poropak-N and Spherocarb are not reported. It was noted in the section “Sampling of large motors”, that artifacts are observed when Tenax-GC is used to sample trace quantities of organic compounds in air; the same problem was also observed with Poropak-N. It was not possible to desorb any compounds from Spherocarb at a level that could be detected by GC/MS.

Recaption and conclusions

The organic compounds identified in the smoke from the combustion of the sections of the rocket motors burned included traces of alkanes, alkenes, polyaromatic hydrocarbons, alkyl substituted aromatic and polyaromatic hydrocarbons, phthalate esters and other oxygenated species, nitroaliphatics, nitroaromatics, phenols, and chlorinated phenols (found in some samples not reported in this paper). Examination of the compounds found in the “early” and “late” smoke samples shows that most of these compounds are the products of the incomplete combustion of the liner. The nitro- and chloro-compounds are probably the products of secondary reactions of NO_x and HCl with the liner and propellant combustion products. Polycyclic aromatic hydrocarbons (which were of particular interest in this study) were identified. The heaviest PAH that was identified (only in the filter extracts) was one with a molecular weight of 252 g/mol (benzo(a)pyrene or one of its isomers).

The combustion residues consist of the charred liner and casing as well as solidified pools of aluminum metal and clumps of aluminum oxide. As would be expected, the metal and metal oxide residues contained no organic matter and the liner residue contained all the compounds listed above that were found in the smoke samplings.

In all cases the quantities of organic compounds found are small, generally less than one microgram of each compound per gram of rocket motor. For the largest motor (a first-stage Poseidon), this amounts to less than 30 grams of organic pollutants dispersed throughout the entire smoke plume. This value is

an upper limit since the samples we burned in our tests are motor sections with a higher liner to propellant mass ratio than that found in a whole motor and the liner produced a proportionately higher percentage of organic pollutants.

This study has shown that the total quantities of pollutants released into the environment by the disposal of Polaris and Poseidon motors by open burning is minimal. The problem of the organic pollutants on the residues can be handled by a second incineration in an incinerator.

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