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Chemical Characterization and Toxicologic
Evaluation of Airborne Mixtures

The Chemical and Physical Characterization of XM819 Red Phosphorus Formulation and the Aerosol Produced by Its Combustion

FINAL REPORT

R. S. Ramsey
J. H. Moneyhun
R. W. Holmberg

JULY 1985

Supported by
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The red phosphorus-sodium nitrate ($RPNO_3$) incendiary formulation was examined to determine the chemical and physical homogeneity of the product and to identify any constituents of known toxicity which could also influence the toxicity of the aerosol produced from the material. The formulation was found to be uniform in weight, density, and composition of phosphorus, extractables, sodium, nitrate, and silica. The epoxy binder also appeared to be uniformly polymerized, containing no unreacted resin detectable by

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infrared spectroscopy. Only a few trace elements were determined and they were present in low concentration.

The RPNO$_3$ was combusted under the same static burn conditions used to generate smoke from RPBR and WPF (i.e., fragments were burned in a convective air flow). The analyses on the aerosol were also conducted in the same manner as used for these other phosphorus formulations or the other formulations were reanalyzed with methods used for RPNO$_3$ (e.g., total volatile hydrocarbons) to ensure that a side-by-side comparison between the smokes could be made. The particle sizes of all three aerosols as generated were within the respirable ranges, having median diameters slightly less than 1 um. The compositions of all three aerosols were also very similar, being composed primarily of phosphoric acids and water. The organics in the RPNO$_3$ were essentially completely burned as indicated by the low concentration of organic compounds in the particulate and vapor phase. Total organic carbon values were intermediate between those found in RPBR and WPF smokes. A significantly lower concentration of volatile organics was found in the gas phase compared to the other smokes. No attempts were made to determine the individual compounds which combine to give the TOC values. Nitrogen dioxide was slightly above NIOSH toxicity limits (maximum allowable exposure for short term exposure) when RPNO$_3$ aerosol concentrations were about 3 mg/L. The variation in the concentration of this compound as a function of burn conditions was not investigated. Overall, the aerosols from the three different formulations were found to be largely the same.

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Chemical Characterization and Toxicologic Evaluation of Airborne Mixtures

THE CHEMICAL AND PHYSICAL CHARACTERIZATION OF XM819 RED PHOSPHORUS FORMULATION AND THE AEROSOL PRODUCED BY ITS COMBUSTION

FINAL REPORT

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EXECUTIVE SUMMARY

This report describes the chemical and physical properties of the aerosol produced from the combustion of a red-phosphorus-sodium nitrate ($RPNO_3$) formulation used in the XM819 mortar round. The aerosol was generated by burning fragments of the material in a convective air flow. As it was generated, the smoke was delivered to a 0.3 cubic meter exposure chamber from which samples for various analyses were taken. Generation and collection conditions were similar to those used for two other phosphorous obscurant sources, red phosporus-butyl rubber (RPBR) and white phosphorus-felt (WPF), to allow direct comparisons between the aerosols. The $RPNO_3$ material was also analyzed for composition and impurities.

The formulation was found to be uniform in weight, density, and composition of phosphorus, extractables, sodium, nitrate, and silica. An epoxy binder present in the material was uniformly polymerized, containing no unreacted resin detectable by infrared spectroscopy. Elemental impurities were determined to be less than 0.1 percent by weight.

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Aerosol particle sizes measured by cascade impactor techniques, were within the respirable range, having median diameters slightly less than 1 μm. The composition of the aerosol was found to be primarily ortho-phosphoric acid, polymeric phosphoric acids, and water. The highest polymeric phosphate was P_{12}. These results are very similar to those obtained for RPBR and WPF under the same burn conditions. The organics in the $RPNO_3$ were essentially completely burned as indicated by the low concentrations of organic compounds determined in the particulate and vapor phase. Traces of carbon monoxide, nitric oxide, and nitrogen oxide were present in the gas phase. Nitrogen dioxide was slightly above NIOSH toxicity limits (maximum allowable exposure for short term exposure). Overall the smoke generated from $RPNO_3$ was found to be very similar to the aerosols from RPBR and WPF.

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INTRODUCTION

The XM819 Red Phosphorus ($RPNO_3$) is a mortar round using a newly-developed formulation for the production of an obscurant smoke cloud. The fill material consists primarily of red phosphorus, sodium nitrate, and an epoxy binder in approximately an 80:14:6 percent weight ratio. It is manufactured by blending an epoxy resin (Epon 828), curing agent (Versamid 140), and solvent (acetone) with powdered red phosphorus and sodium nitrate. The resulting slurry is partially dried and then granulated with approximately 1 percent colloidal silica (Cab-O-Sil). The material is pressed into wedges and finally cured at an elevated temperature to polymerize the epoxy resin. The final product is a hard cake (4 segments make up a 2.85 in. diameter disk, 1 in. thick). Each mortar charge contains a total of 28 wedges (seven layers of four wedges each). When the charge is detonated the wedges ignite and disperse to burn in the air and on the ground to produce an obscuring cloud.

Section I of this report concerns itself with analyses of the unburned material. These analyses were performed to measure any deviations in the gross composition from the specifications, to determine the homogeneity of the $RPNO_3$ wedges, and to detect trace impurities that might contribute to the toxicity of the combustion aerosol. In Section II, the chemical and physical properties of the aerosol atmosphere formed when $RPNO_3$ is burned under controlled conditions are discussed. Comparisons are made with similar phosphorous aerosols from red phosphorus-butyl rubber (RPBR) used in the L8A1 grenade and white phosphorus-felt (WPF) used in the M825 155 mm artillery round. Each section includes a brief description of sample preparation, collection, and analytical methodology.

I. Characterization of Unburned $RPNO_3$

The $RPNO_3$ used in all experiments was obtained from the U.S. Arm Chemical Research and Development Center (CRDC), Aberdeen Provin Ground, MD. The hazardous component safety data sheet for the RPNO formulation is given in Appendix 1.

Physical Properties of the $RPNO_3$ Wedges

Wedges of $RPNO_3$ with and without Cab-O-Sil were obtained from CRDC. The average weight of the 50 wedges received containing silica was 43.341 ± 0.295 grams while the average weight of the 49 wedges without silica was 43.492 ± 0.343 grams. The material containing Cab-O-Sil was only slightly more dense than that without (1.769 ± 0.00 grams/mL as compared to 1.759 ± 0.004 grams/mL). Density measurements were also made on fragments of wedges within each group. The values which are tabulated below are very similar to those obtained for the whole wedges.

Table I

Density of Wedge Fragments

Containing Cab-O-Sil		Without Cab-O-sil	
Wedge	Fragment Density (grams/mL)	Wedge	Fragment Density (grams/mL)
1	1.768	1	1.738
	1.763		1.747
	1.770		1.752
2	1.759	2	1.763
	1.772		1.748
	1.775		1.751
3	1.772	3	1.749
	1.741		1.756
	1.770		1.749
mean	1.766		1.750
std. dev.	0.010		0.007

Visual examination of fragmented $RPNO_3$ material did not reveal internal voids or other evidence of physical inhomogeneity.

Chemical Analysis of $RPNO_3$

To estimate compositional variability, total phosphorus and sodium nitrate determinations were made on samples randomly selected from the lot. The samples were initially crushed under liquid nitrogen and then ground to particles less than 20 mesh in size. The liquid nitrogen prevented accidental ignition due to the generation of frictional heat in crushing and grinding. A portion of the ground wedge or wedge segment was then taken for analysis.

Phosphorus. Phosphorus was determined gravimetrically using standard analytical procedures. The results are presented in Table II. The mean values are ca. 3% lower than the manufacturing specifications (78.7 and 79.4 percent with and without silica, respectively). We note that, previously, an examination of reagent grade red phosphorus also gave lower than expected results (1). We can suggest two possibilities for the discrepancy: an unexpected negative bias in the analytical method or unaccounted for impurties in the source red phosphorus. Red phosphorus could easily develop a hydrous oxide layer on its surface by partial oxidation at room temperature which would lower its overall phosphorous content. Similarly, if oiled red phosphorus were used in the preparation of the formulation low results would be expected. The method, however, is satisfactory for determining relative differences in composition and the results for the $RPNO_3$ formulation show no major variations for phosphorous content either between wedges or within a given wedge.

Table II

Percent Phosphorus in $RPNO_3$

Wedge	Wedge Segment	Percent Phosphorus by Weight
Material Containing Cab-O-Sil		
1		74.03
2		75.79
3		75.30
4	a	75.60
	b	73.96
	c	75.02
5	a	67.75
	b	69.88
	c	75.94
mean		73.70
std. dev.		2.90
Material Without Cab-O-Sil		
1		75.42
2		76.82
3		74.21
4	a	76.08
	b	75.54
	c	75.27
5	a	75.82
	b	76.13
	c	75.77
mean		75.67
std. dev.		0.72

Sodium Nitrate. Sodium nitrate content was estimated by aqueously extracting the salt from the raw material and weighing the dried filtrate. These values were then corrected for any phosphoric acid found in the extract to eliminate errors in measurement due to acid adsorbed onto the powdered $RPNO_3$. At normal temperatures and humidities, red phosphorus slowly reacts with water vapor and oxygen in air to form a mixture of oxo acids (2). Adsorbed acids and water vapor would increase the weight of the sample and introduce an error into the weight percent value of the residue. The results are presented in Table III.

Table III

Estimated $NaNO_3$ by $RPNO_3$ Extraction*

Wedge	Wedge Fragment	Filtrate Residue	Total Phosphate	Corrected $NaNO_3$
Material Containing Cab-O-Sil				
1		15.00	0.90	14.10
1		14.97	0.91	14.06
2		15.07	0.93	14.14
2		15.14	0.87	14.27
3		15.18	0.80	14.38
3		15.15	0.82	14.33
4		15.32	0.92	14.40
4		15.47	0.87	14.60
5		15.02	0.97	14.03
5		14.98	0.97	14.01
	a	15.30	0.95	14.35
	a	15.30	0.99	14.31
	b	15.20	0.95	14.25
6	b	15.30	0.99	14.33
	c	15.18	1.07	14.13
	c	14.70	1.07	13.63
mean		15.14	0.94	14.21
std. dev.		0.18	0.08	0.22

Table III (Cont'd)

Estimated $NaNO_3$ by $RPNO_3$ Extraction*

Wedge	Wedge Fragment	Filtrate Residue	Total Phosphate	Corrected $NaNO_3$
Material Without Cab-O-Sil				
1		14.70	0.57	14.13
2		14.60	0.54	14.06
2		14.60	0.55	14.05
3		14.40	0.70	13.70
3		14.60	0.67	13.93
4		14.20	0.69	13.51
4		13.90	0.59	13.31
5	a	14.40	0.59	13.80
	b	14.30	0.65	13.70
	c	14.60	0.65	14.00
6	a	13.90	0.84	13.06
	a	14.10	0.86	13.24
	b	14.40	0.71	13.69
	b	14.60	0.71	13.89
	c	14.40	1.00	13.40
mean		14.38	0.69	13.70
std. dev.		0.26	0.13	0.33

---

*Values reported as percent of total weight. Analyses performed in duplicate as indicated.

A more accurate determination for $NaNO_3$ was obtained by analyzing the extract for both sodium and nitrate and then calculating the amount based on the concentration of each. This data is shown in Table IV. The $NaNO_3$ values based on these separate determinations are in close agreement with each other. The average values, however, are slightly lower than indicated in the manufacturing specifications (i.e., 13.89 and 14.02 percent $NaNO_3$ with and without silica, respectively). The values are also lower than the weight of the extracted residues. Since a simple extraction procedure may also remove other impurities, the direct analysis is expected to be more reliable. Either of the methods, however, is adequate for examining compositional variation. The combined data show that the wedges are very similar and uniform in $NaNO_3$ content.

Table IV

$NaNO_3$ Determination in $RPNO_3$*

Wedge	Percent Na	Percent $NaNO_3$ From Na	Percent NO_3	Percent $NaKO_3$ From NO_3
Material Containing Cab-O-Sil				
1	3.51	12.98	8.79	12.05
1	3.58	13.22	8.92	12.23
2	3.31	12.25	8.99	12.32
2	3.54	13.07	9.10	12.48
3	3.46	12.80	9.05	12.40
3	2.98	11.01	8.42	11.54
mean	3.40	12.56	8.88	12.17
std. dev.	0.22	0.83	0.25	0.34
Material Without Cab-O-Sil				
1	3.16	11.68	8.54	11.70
1	3.50	12.92	8.48	11.60
2	3.41	12.60	8.57	11.75
2	3.19	11.77	8.34	11.44
3	2.38	8.80	8.61	11.81
3	3.36	12.44	8.63	11.83
mean	3.17	11.70	8.53	11.69
std. dev.	0.41	1.50	0.11	0.15

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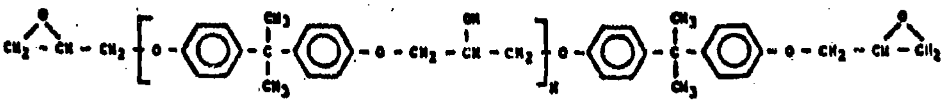
*Duplicate analyses performed as indicated.

Unpolymerized Epoxy Resin. The epoxy binder is formed by reacting the resin with a curing agent. It not only binds the other material, allowing it to be molded into a solid mass, but it also imparts mechanical strength. The resin, Epon 828, is a commercial product of the diglycidyl ether of bisphenol A with the following structure:



2,2-bis-[p-(2,3-epoxypropoxy)phenyl]-propane

It is composed primarily of the dimer (N=1) (85-90 percent) with higher oligomers present as the remainder. Versamid 140, the curing agent, is a fatty polyamide formed by reacting tall oil dimerized fatty acids with diethylenetriamine. A three dimensional polymeric network is formed when the two are mixed and heated at an elevated temperature. The extent of the "cure" or crosslinking is dependent upon the mole fractions of the reactants, temperature, and other reaction conditions. Crosslinking occurs at the highly reactive epoxide sites by coupling with the polyamide and involves opening of the epoxide ring. By monitoring the 3-membered epoxide ring vibration in the mid-infrared region at 914 cm^{-1}, the extent of the cure or the amount of unpolymerized resin can be determined.

Samples for epoxy analysis were prepared by grinding an entire wedge and blending the powder with potassium bromide in a 5 to 50 percent (w/w) mixture. Diffuse reflectance fourier transform infrared spectra were recorded on a Digilab FTS-20C spectrometer. A sample of Epon 828 was received from Shell Chemical Company, Houston, TX, and Versamide 140 was obtained from Henkel Corporation, Charlotte, NC.

Spectra of uncured Epon 828 and a 1:1 (w/w) mixture of Versamid 140 and Epon 828 hardened overnight at 115°C are shown in Figures 1 and 2, respectively. The absorption band at 1508 cm^{-1} due to benzene ring vibrations is not affected by polymerization while the band at 914 cm^{-1} decreases as the resin is cured. The spectrum obtained from powdered $RPNO_3$ is shown in Figure 3. There is no discrete peak at 914 cm^{-1} although there is some background absorbance. Extraction of $NaNO_3$ from the raw material does not reduce the background in this region. By adding varying amounts of Epon 828 to $RPNO_3$ and recording the spectra (Figure 4) an increase in the absorption at 914 cm^{-1} can be observed. When the absorbance at 1508 cm^{-1} has increased by 10 to 20 percent due to the additions of Epon 828, the band at 914 cm^{-1} due to the epoxide ring becomes apparent. The minimum quantity of Epon or the amount of unreacted resin which can be detected in the $RPNO_3$ material corresponds

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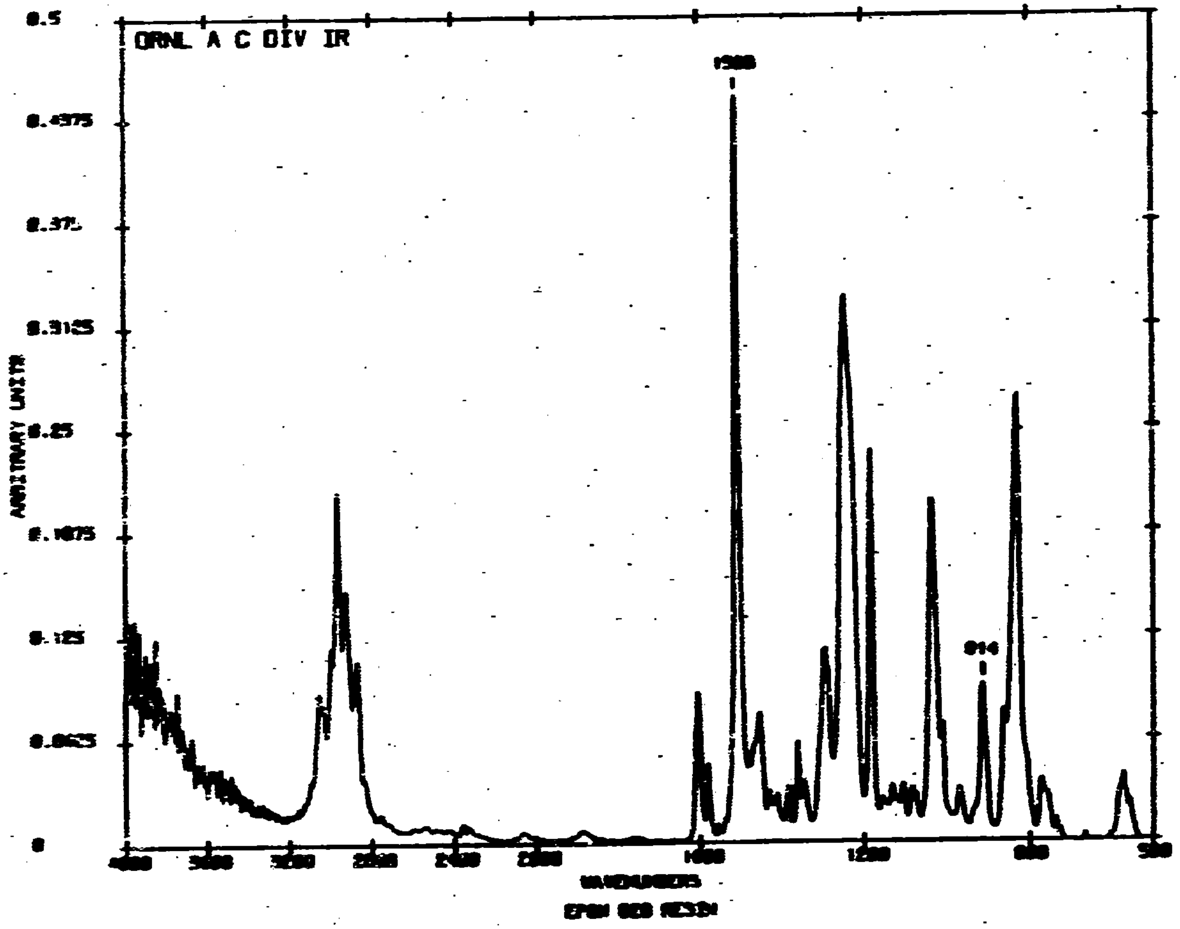

Figure 1. Infrared Spectrum of Unhardened Epon 828

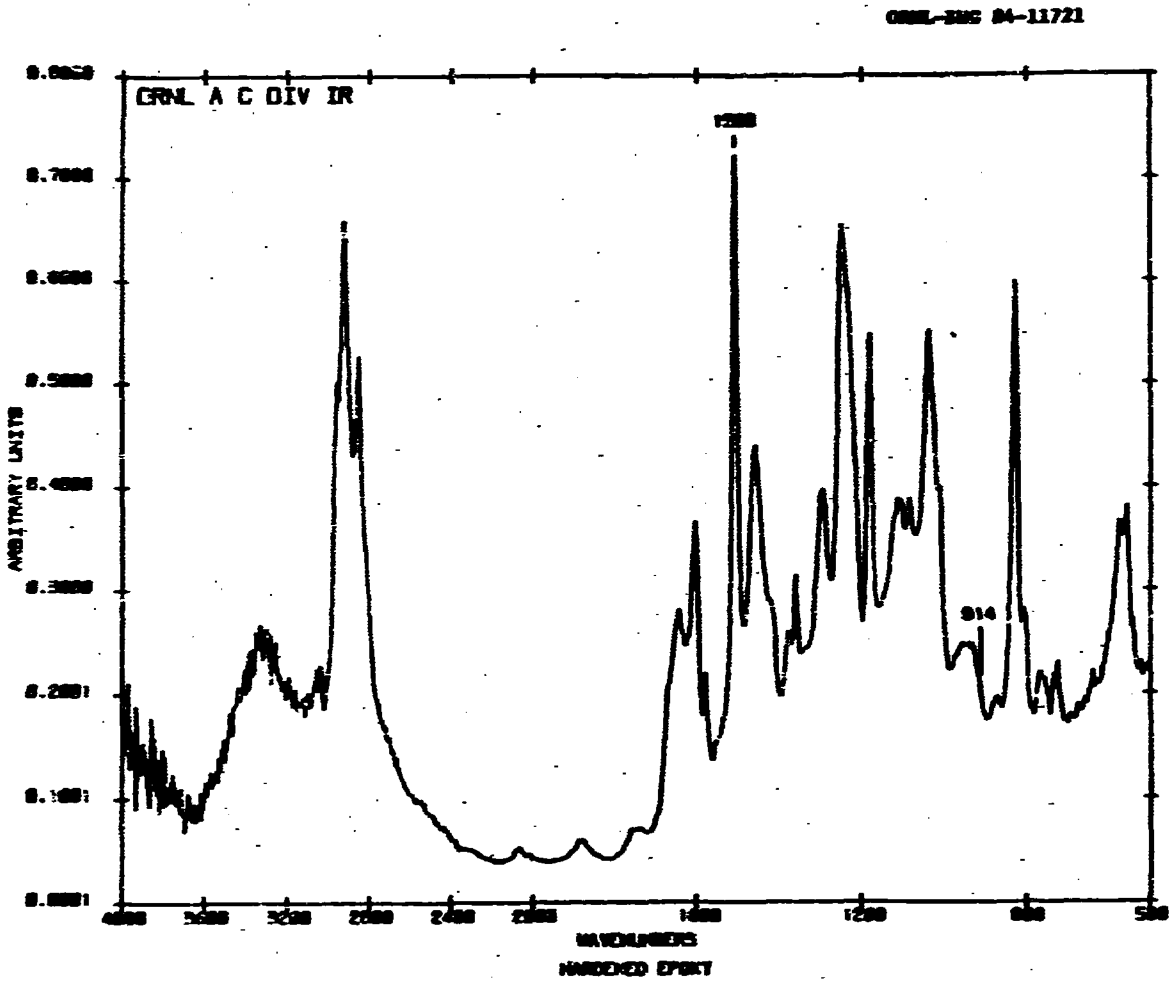

Figure 2. Infrared Spectrum of Epon 828 Hardened with Versamid 140

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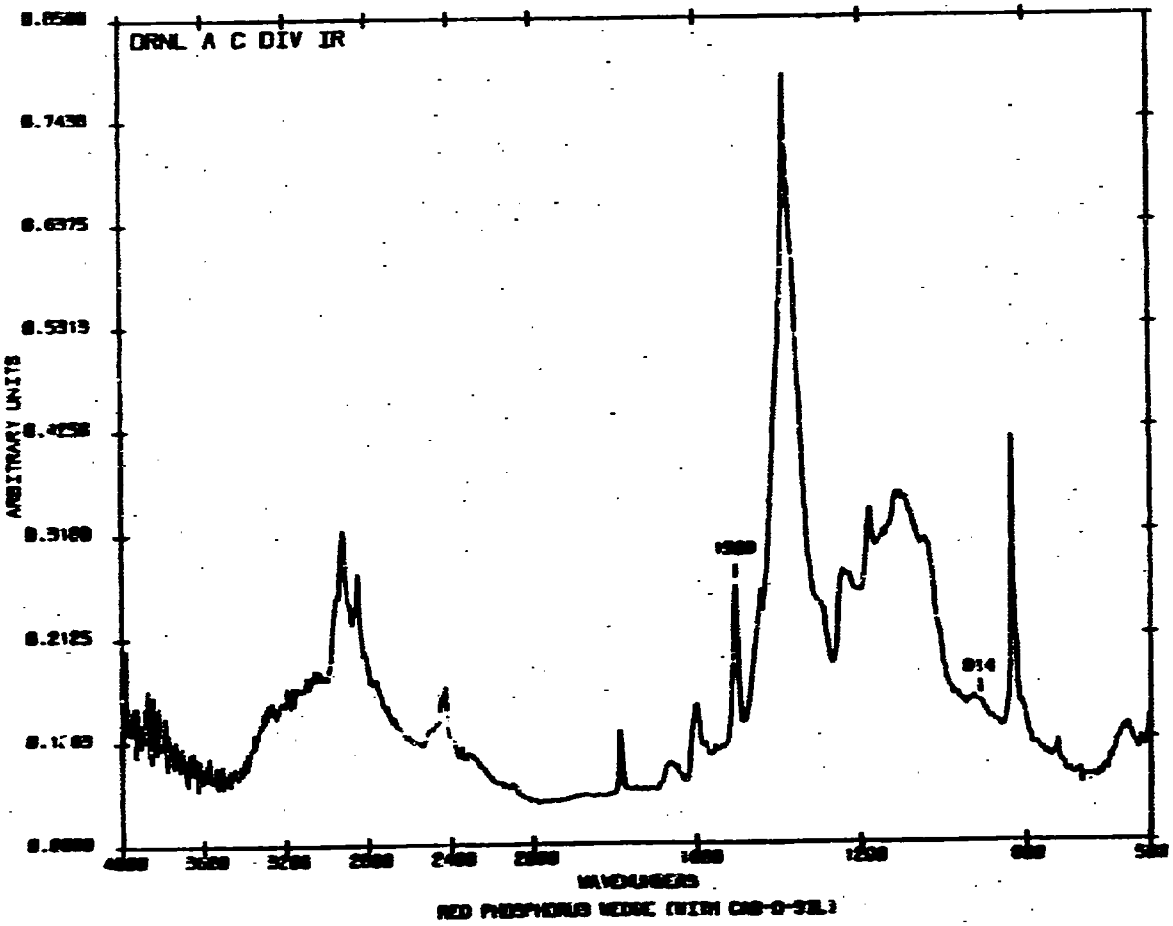

Figure 3. Infrared Spectrum of Powdered XM-819 Wedge

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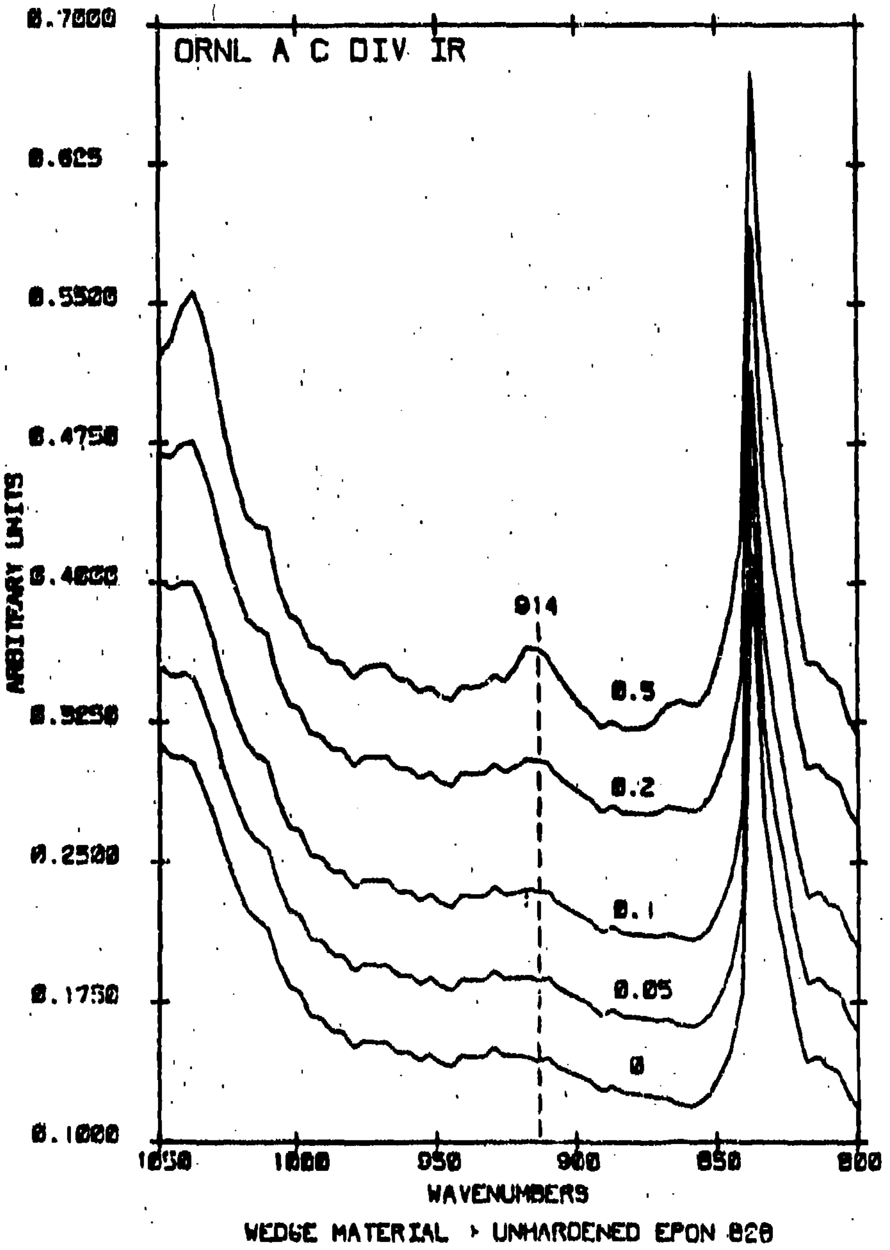

Figure 4. Composite Infrared Spectra of XM-819 Wedge Plus Unhardened Epon 828

to the concentration represented by this increase at 1508 cm^{-1}. Since Epon comprises 3.2 percent of the wedge material by weight, the detection limit is 0.15 x 0.032 per gram of wedge material, or 0.5 percent of unpolymerized resin in the wedge. The concentration of unreacted resin in $RPNO_3$ was estimated to be less than 0.5 percent, since it was not detected by this method.

Trace Elements. A semiquantitative measure of trace elements in the wedge material was obtained by emission spectroscopy and a more accurate measure of selected elements of known toxic potential was obtained by atomic absorption. The data are presented in Table V. The total concentration of all the elemental impurities was less than 0.1 percent of the weight of the material. Elements which are not listed were not detected. Arsenic, an impurity often found in phosphorus, was present at a concentration lower than that found in the RPBR formulation (i.e., 44 vs 210 µg/g of raw material). Overall, the low concentrations indicate that the elements are unlikely to contribute to the toxicity of the combustion products of the $RPNO_3$ material.

Table V

Trace Elements in $RPNO_3$

	Concentration*	
Element	Emission	Atomic Absorption
Ag	3	
As		44
Ba	5	
Be		< 0.05
Ca	150	
Cd		< 1.0
Cu	20	
Fe	400	
K	20	
Mn	50	
Pb		< 3.0
Ti	15	
V	3	

*part per million by weight

Silica. Silica was determined by a gravimetric procedure which involves filtering the insoluble SiO_2 residue remaining in an acid digest of $RPNO_3$. The SiO_2 was volatilized by the addition of hydrofluoric acid and the weight loss of the residue was determined. Three different wedges containing Cab-O-Sil were analyzed and gave the following results: 1.05, 1.19, and 1.38 percent SiO_2 by weight. The values are within the expected range for the amount of colloidal silica added to the raw material.

II. Chemical and Physical Characterization of $RPNO_3$ Combustion Aerosol

The $RPNO_3$ was burned in a manner similar to that used for the free burns of the RPBR and WPF formulations (1) to allow direct comparisons of the combustion products of all the different formulations. The smoke generator basically consists of a platform upon which fragments of the material are burned, enclosed by a container which is connected to the delivery system of a 0.3 cubic meter exposure chamber. All materials are metal, glass and teflon to minimize artifactual contamination of the smoke products. The container has openings whereby air flow is regulated. Dilution air is added via a tee in the transfer line to the exposure chamber to maintain a total flow of 250 mL/min. Air flow through the burn chamber was regulated at approximately 100 L/min. All burns were conducted at ambient humidity. The aerosol concentration was continuously monitored by backscattering particle sensors placed within the exposure chamber (3). The concentration was controlled manually adding fragments of $RPNO_3$ to maintain a reasonably uniform monitor response. A diagram of the generator system is shown in Figure 5.

Samples were collected directly from the exposure chamber for analysis of the combustion products, gravimetric determination of aerosol mass concentration (to confirm the online particle sensor results), and determination of the weight of phosphoric acid per unit volume.

Particle Size Analysis

A Mercer type seven stage cascade impactor was used to determine particle size distribution. Details of the sampling and analytical procedure have been previously described (1). The mass median diameters and geometric standard deviations which were determined are given in Table VI. The particle diameter at the lowest humidity was found to be significantly less than at the higher humidity and may well reflect the differing water content of the aerosol particles. We note, however, that generation conditions and growth of particles with time by coagulation at these high aerosol concentrations may easily obscure humidity-dependent size growth. A plot of the aerosol particle size distribution obtained at 24 percent relative humidity and 2.9 mg/L aerosol concentration is shown in Figure 6. Two different cascade impactors (A and B in Figure 6) were used to sample the aerosol. The results are similar to those found for RPBR and WPF in that the mean diameters were less than 1 μm.

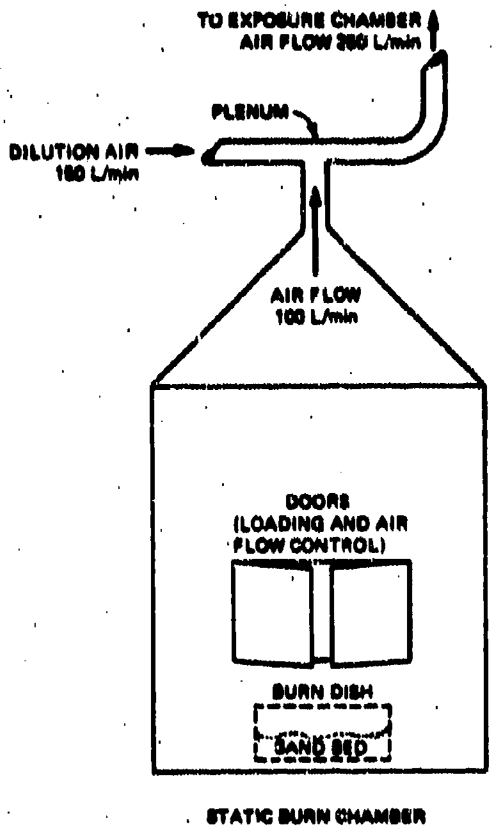

Figure 5. Static Burn Chamber

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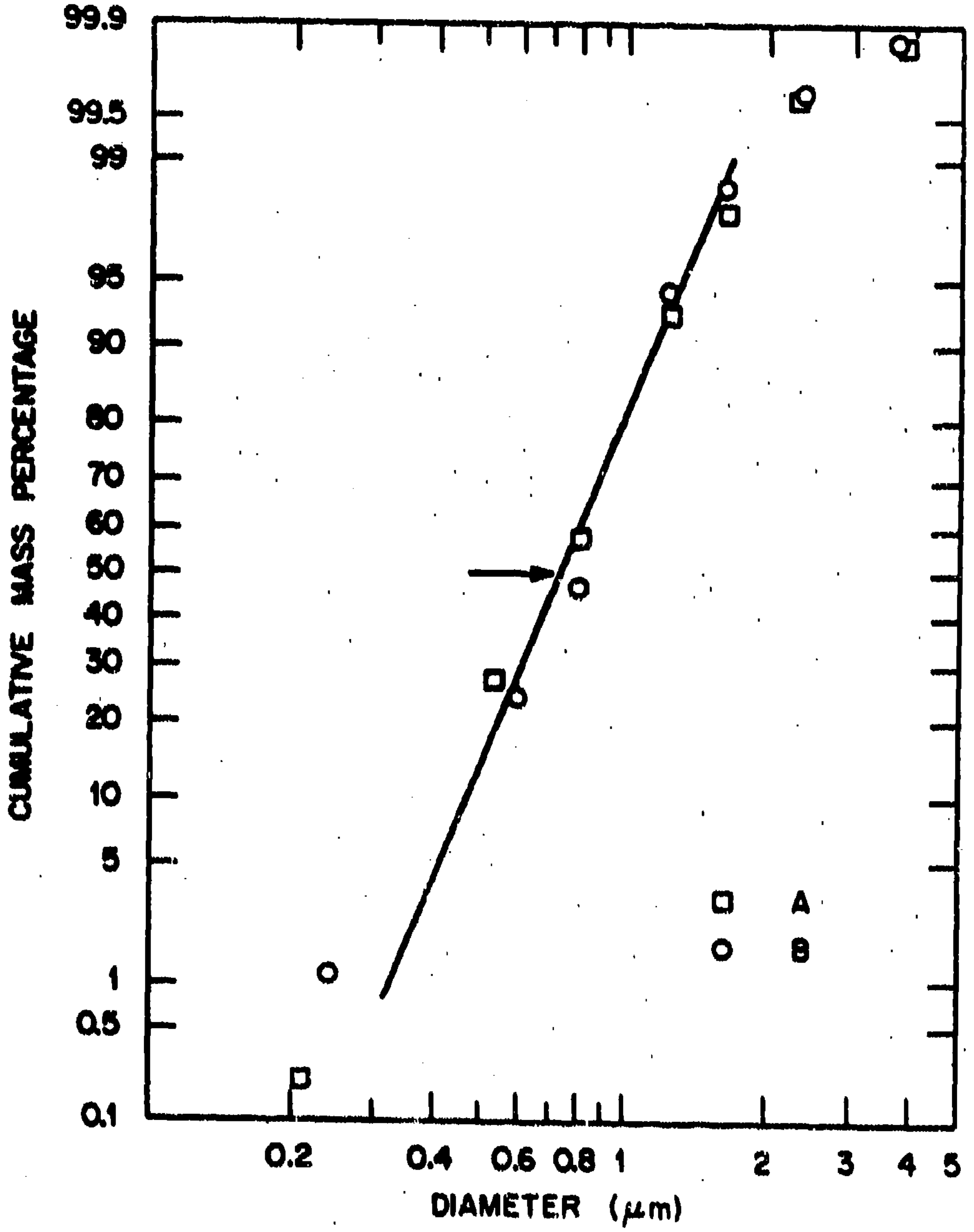

Figure 6. Aerosol Particle Size Distribution
(□, ○ impactors used for sampling)

Table VI

Particle Size for $RPNO_3$

Relative Humidity	Aerosol Concentration mg/L	H_3PO_4 Percent	Particle Size µM	Geometric Std. Dev.
61	4.14	66	0.96	2.2
60	3.71	58	0.96	2.0
24	2.9	89	0.73	1.5

Chemical Analysis of the Aerosol Particulate and Gas Phases

Total Phosphate and Phosphoric Acid Speciation. The aerosol produced from the $RPNO_3$ formulation was found to be composed primarily of orthophosphoric and polymeric phosphoric acids. Samples of the aerosol collected on glass fiber filters were analyzed by the high performance liquid chromatographic method developed for the examination of the RPBR aerosol. This method has been previously described in detail (4). Essentially it allows visualization of phosphoric acid species ranging from ortho-phosphoric acid up to the P_{13} polymer, produced by the condensation of ortho-phosphoric acid. Certain cyclic phosphoric acids (i.e., trimeta- and tetrametaphosphoric acids) are also resolved and can be quantitated by the method. A typical profile for the $RPNO_3$ aerosol is shown in Figure 7. As indicated, the first peak corresponds to ortho-phosphoric acid and the following peaks to polymers of increasing order. The highest polymeric phosphate found was P_{12} and here there was no evidence of cyclic compounds. The sample was collected at an aerosol concentration of 3.96 mg/L or 2.13 mg (as H_3PO_4/L), 58 percent relative humidity, and 24 °C chamber temperature. The results are very similar to those obtained for RPBR and WPF under similar combustion conditions. Figure 8 shows profiles of these other formulations for comparative purposes.

The total phosphate concentration of the aerosol varied depending upon the humidity. At relatively high humidities, phosphate comprised a lower percentage of the weight of the aerosol due to the increased water content, whereas, at lower humidities, phosphate accounted for a greater percentage of the aerosol (see Table VI). The analysis for total phosphate was performed with a colorimetric procedure also previously described (4).

Differences in speciation as a function of chamber humidity, aerosol concentration, or other generation conditions were not investigated. In our previous investigations on RPBR aerosol generated with the extrusion system the concentrations varied only slightly with humidity, air velocity, or aerosol concentration. The most pronounced changes were observed as the aerosol was allowed to age (1). There were also significant differences in the acid profiles of the RPBR

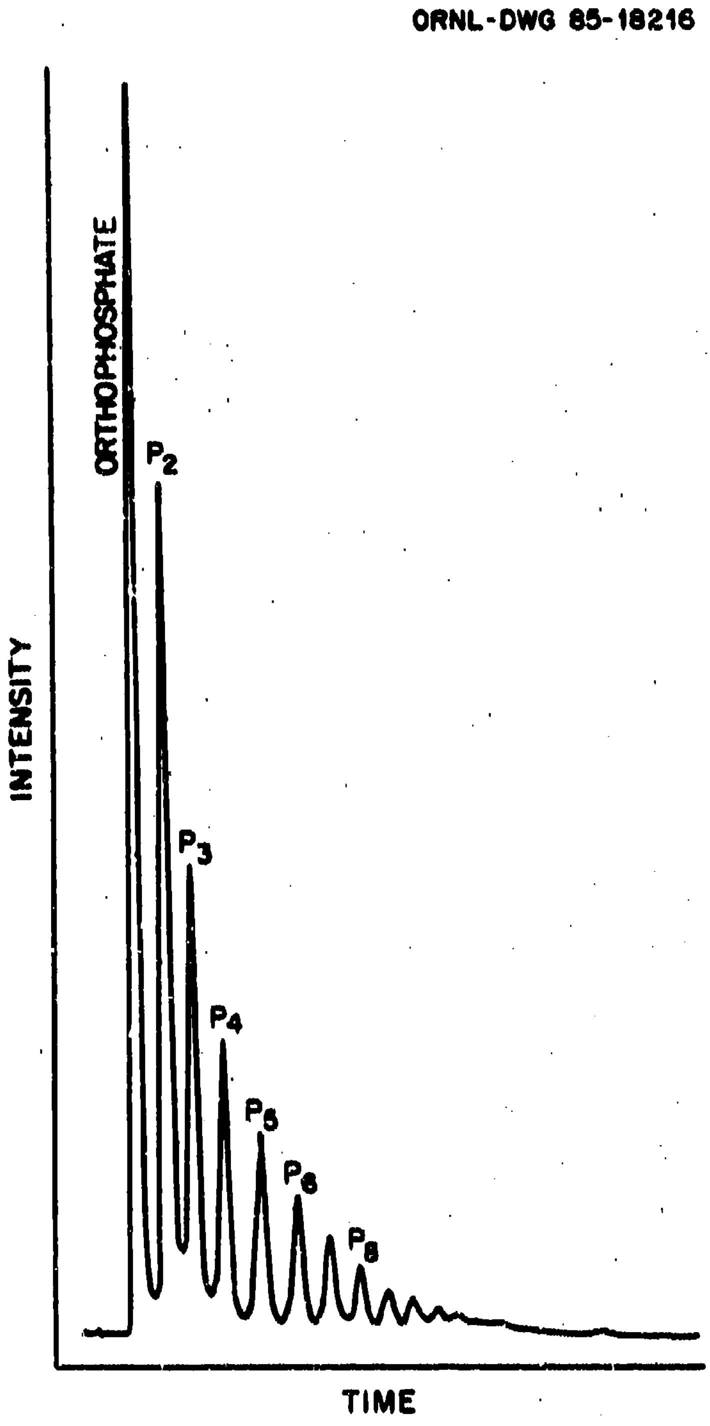

Figure 7. Phosphoric Acids in $RPNO_3$ Aerosol

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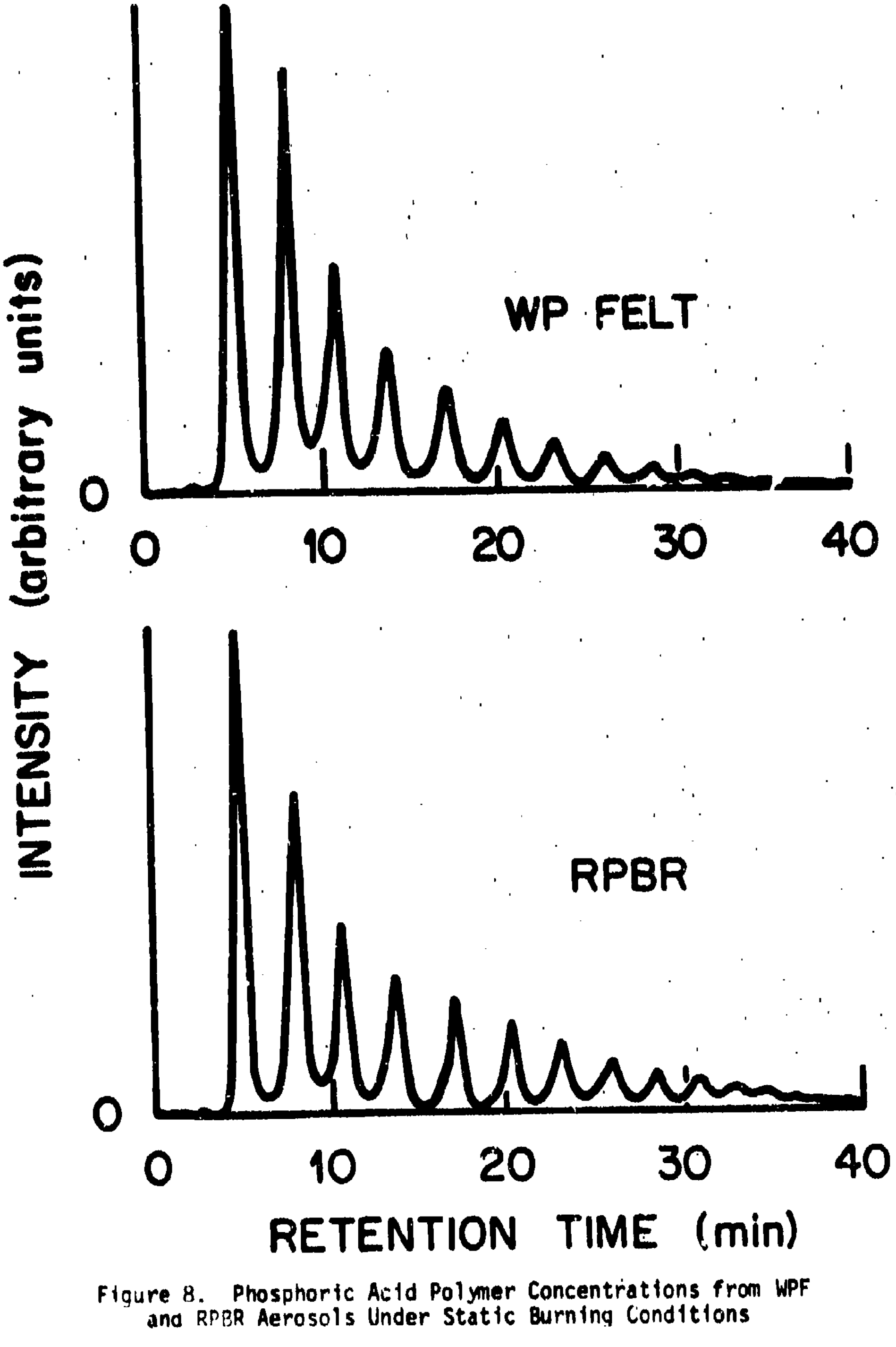

Figure 8. Phosphoric Acid Polymer Concentrations from WPF and RPBR Aerosols Under Static Burning Conditions

aerosols produced using an extrusion generator rather than by burning under the less controlled conditions used in the experiments reported here. All of the analyses on the $RPNO_3$ smoke were conducted on fresh aerosol collected as it continuously swept through the exposure chamber.

<u>Sodium and Total Nitrate</u>. The sodium content of the particulate phase was determined by atomic absorption analysis, and total nitrate was determined by a standard colorimetric procedure. Samples were collected by impingement. The collection efficiency of the sampling method was examined and found to be approximately 97 percent. For aerosol concentrations ranging from 2.4 to 3.1 mg H_3PO_4/L, an average concentration of 42 µg Na/g H_3PO_4 was obtained. The average nitrate concentration was less than 106 µg/g H_3PO_4.

<u>Organic Compounds</u>. Organics in the vapor and particulate phase derive from the pyrolysis of the epoxy binder in the $RPNO_3$ formulation. The combustion of the polymer may yield water, carbon monoxide, carbon dioxide, hydrogen, methane, ethane and other compounds depending upon the extent of the dagradation. The exact products formed are dependent upon reaction conditions and temperature, as is the case in all pyrolysis. To establish the organic content in the particle phase of the aerosol, total organic carbon analysis (TOC) was performed. An average of 140 µg TOC/g of H_3PO_4 was obtained for aerosol concentrations ranging from 2.4 to 3.1 mg of H_3PO_4/L. This value compares to approximately 30 µg TOC/g H_3PO_4 for smokes produced from RPBR at an aerosol concentration of 2.9 mg H_3PO_4/L and approximately 400 µg TOC/g H_3PO_4 for WPF smokes at a concentration of 4.2 mg H_3PO_4/L. The highest TOC concentration found in the $RPNO_3$ aerosol was 242 µg/g H_3PO_4 at 2.4 mg H_3PO_4/L. The values are intermediate between those from the RPBR and WPF aerosols, and are likely a reflection of the organic content of the uncombusted formulations.

The concentration of organics in the gas phase was determined with a total hydrocarbon monitor. The particulates were filtered and removed, and the vapor phase drawn through a Bendix Model 8401 Total Hydrocarbon Analyzer which utilizes a flame ionization detector for establishing ambient organic levels. The instrument was calibrated with n-hexane. By measuring the weight loss of hexane in a diffusion cell placed within the exposure chamber at a given flow rate, an exact concentration can be determined. Results are presented in Figure 9. The chamber was simultaneously monitored for both total hydrocarbon and for particle concentrations. Response curves for RPBR and WPF are also shown. The analyses were conducted over a 20 minute time interval during which the aerosol from the different formulations would fill the chamber and then empty at the end of a burn. The $RPNO_3$ smoke was found to contain essentially no organics when burned. WPF and RPBR softened with hexane produced or released some volatile organics. The concentrations, however, were low (i.e., less than 10 ppm at an average aerosol concentartion of 5 to 6 mg/L).

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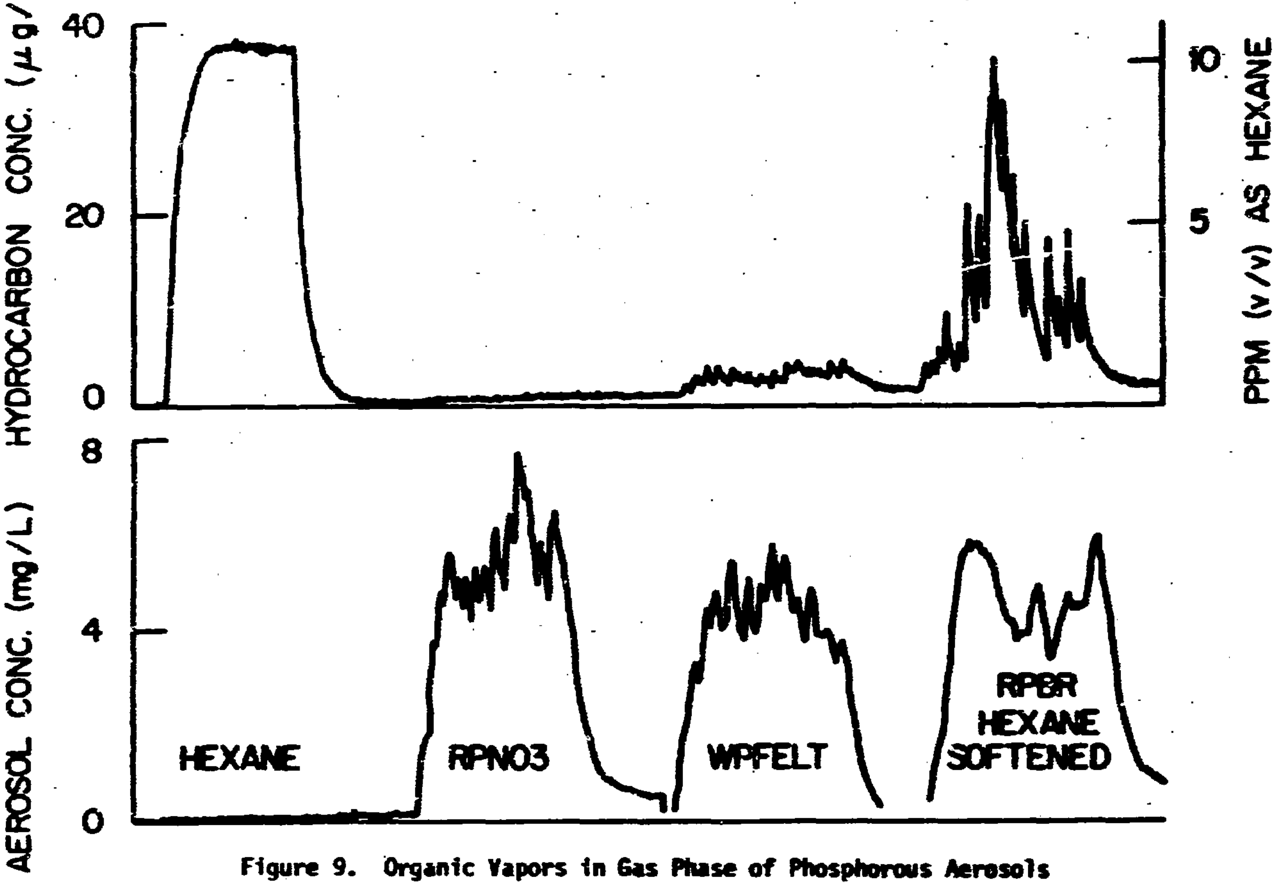

Figure 9. Organic Vapors in Gas Phase of Phosphorous Aerosols
Upper Curves: Response of Total Hydrocarbon Detector
Lower Curves: Response of Aerosol Particle Monitor

The vapor phase was also analyzed chromatographically. The vapor phase was concentrated by passing approximately 1 L of the filtered aerosol through Tenax adsorbent cartridges. The trapped volatiles were then thermally desorbed and analyzed by GC/FID on a 30 m x 0.25 mm fused silica capillary column coated with a nonpolar stationary phase. A chromatogram is shown in Figure 10 along with a blank obtained by collecting and analyzing 1 L of chamber air which did not contain any phosphorous aerosol. The profiles show that there are no high molecular weight organics present (i.e., peaks are observed only in the first portion of the chromatogram). Peaks that were detected were not significantly higher in concentration than the blank values.

Overall, the organic content in the gas and particle phase of the $RPNO_3$ aerosol was very low. This result is similar to that found for RPBR and WPF.

Gaseous Constituents. The gas phase of the aerosol was analyzed for carbon monoxide, carbon dioxide, and oxides of nitrogen. Carbon monoxide was determined on an Ecolyzer 2000 series continuous CO monitor (Energetics Science, Elmsford, NJ) which quantitatively converts CO to CO_2 and measures the current produced by the reaction. Carbon dioxide was analyzed on a Carle 111 GC with a thermal conductivity detector. It was separated from other constituents on a concentric packed column containing molecular sieve of nitrogen were determined with a Beckman Model 951A NO/NO_x Analyzer. In this instrument, nitric oxide (NO) reacts with ozone to produce nitrogen dioxide (NO_2). A certain population of the NO_2 molecules produced are in an excited state and when they decay to ground level, emit light which is detected by a photomultiplier. The sum of NO and NO_2 (NO_x) is detected in the same manner, although NO_2 in the original samples is initially reduced to NO. All samples for gas analysis were collected in Tedlar bags (SKC, Inc., Eighty Four, PA) and were analyzed immediately following collection.

The average values obtained for these constituents in the $RPNO_3$ smoke are given in Table VII along with the values previously obtained for RPBR and WPF aerosols produced under similar burn conditions (1). The CO_2 concentrations reported are the levels above ambient air. Oxides of nitrogen were not determined in RPBR or WPF. The current OSHA standard for carbon monoxide is 50 ppm in air averaged over an 8 hr (TWA) exposure period (5). The standard for NO is 25 ppm and a 5 ppm ceiling (not to be exceeded) has been set for NO_2.

Residue

A black carbonaceous residue remained from the combustion of the $RPNO_3$ material. It was hard and brittle immediately following the burn but became soft and pliable upon standing. Phosphoric acids were adsorbed upon the surface. It also appeared to be very hygroscopic. The weight of the residue was approximately 50 percent of the weight of the uncombusted raw material. A similar type of residue was obtained from the combustion of RPBR and WPF.

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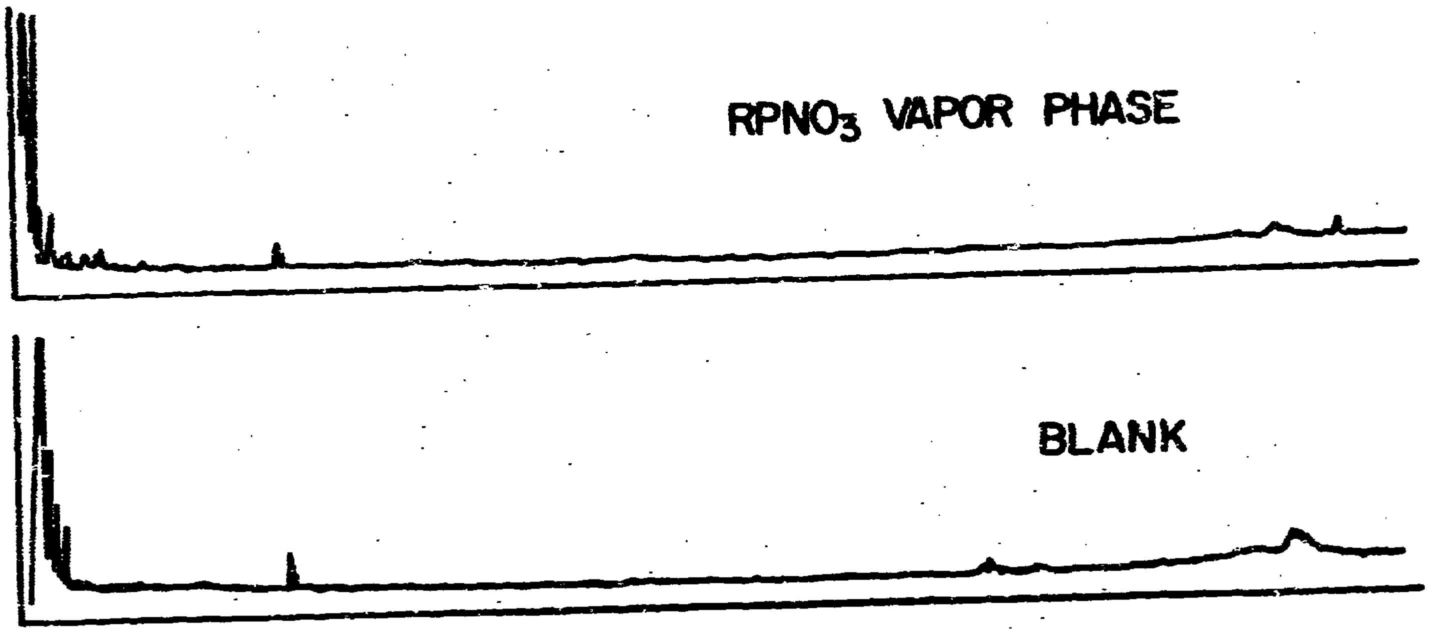


Figure 10. Gas Chromatographic/FID Trace of Organics in the Vapor Phase of RPNO$_3$ Aerosol

Table VII

Gaseous Constituents in Phosphorous Smokes

		ppm (v/v)			
Formulation	Aerosol Concentration (mg/L)	CO_2	CO	NO	NO_2
$RPNO_3$	3.08	100	89	19	21
RPBR	3.20	120	6	--	--
WPF	3.50	250	26	--	--

APPENDIX I

HAZARDOUS COMPONENT SAFETY DATA SHEET

(ARRADCOM Suppl 1 to DARCOM-R 385-17)

Date: 28 OCT 82

Number: 1704

Revision: A

Material/Component/Assembly: COMPOSITION, SMOKE, SW-333 (RED PHOSPHOROUS/$NaNO_3$/EPOXY RESIN)

Applicable ASPR Safety Clause 7-104.79
DAR

SENSITIVITY

Friction Test (Apparatus & Comparison Values): PA STEEL & FIBER - COMPLETE BURNING

Impact Test (Apparatus & Comparison Values): SEE ATTACHED SHEET

Electrostatic Discharge Test (Apparatus & Comparison Values): 20/20 NO FIRES AT 0.25 JOULES

HAZARDS

Fire: MODERATE

Auto Ignition Temp: 258°C (496°F)

Flash Point: -18°C (0°F)

Decomposition Products: TOXIC, AVOID INHALATION AND INGESTION

Flammable Limits: NA

Lower Percent:

Upper Percent:

Explosion: LOW

Explosive Temp (5 sec): 401°C (754°F)

Dusts: UNKNOWN

Toxicity: SLIGHTLY TOXIC BY INHALATION AND INGESTION. MILDLY IRRITATING TO SKIN.

In-Process Hazards Classification: CLASS 1.3

Special Requirements (Continuation Sheets Authorized)

REF - DWG: 9327876
THERE ARE NO APPROVED PACKAGING DRAWINGS. CLASSIFICATION LISTED ARE INTERIM AND ARE FOR INTRA-PLANT STORAGE ONLY TO MEET IN-PROCESS REQUIREMENTS.*

HANDLING AND STORAGE OF THIS MATERIAL SHOULD COMPLY WITH OSHA AND NFPA CODES AND STANDARDS.

* SHIPPING/STORAGE CLASSIFICATION OF ITEM WHEN PACKED IN ACCORDANCE WITH APPROVED PACKING DRAWINGS

DOD Hazard Class: 1.3

DOD Compatibility Group: G

DOT Hazard Class: NOT NORMALLY SHIPPED

DOT Container Marking: NOT NORMALLY SHIPPED

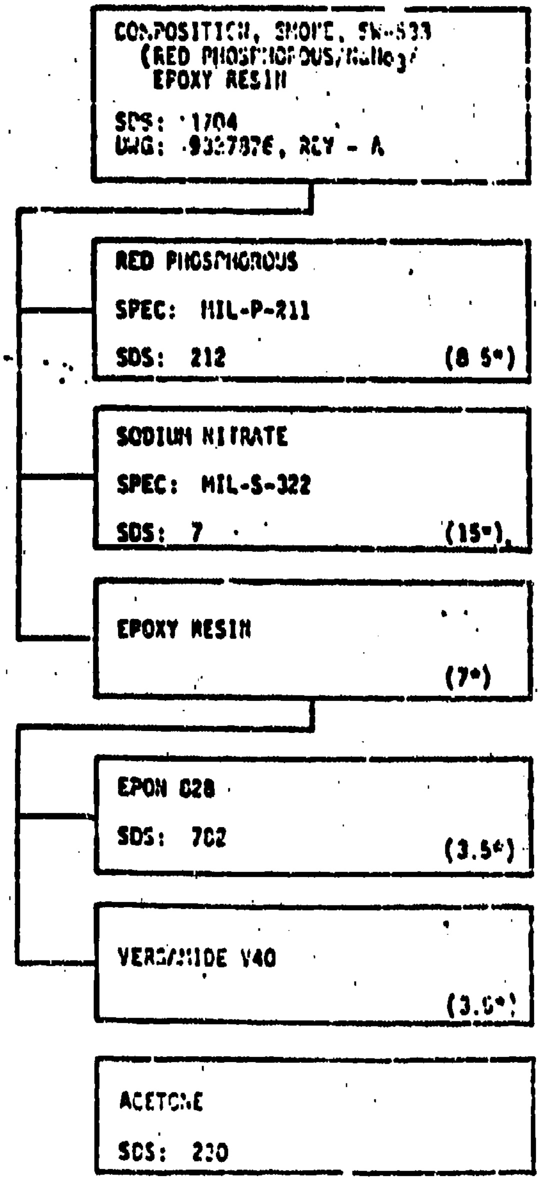
Prepared by: R. BATSON

Checked: E. DEMBERG

Safety Office: S. A. VALTE

[illegible]

SHEET 1 of 1



* F BY WEIGHT

SHEET 2 of 3

1. The Smoke Comp (Designated SW-533) is sensitive to impact, friction, heat, or flame and electrostatic discharge. It should be protected for accidental exposure to these stimuli.

2. CAUTION: EXPLOSIVES MUST BE TESTED FOR COMPATIBILITY WITH ANY MATERIAL NOT SPECIFIED IN THE PRODUCTION/PROCUREMENT PACKAGE WITH WHICH THEY MAY COME IN CONTACT. MATERIALS INCLUDE OTHER EXPLOSIVES, SOLVENTS, ADHESIVES, METALS, PLASTICS, PAINTS, CLEANING COMPOUNDS, FLOOR AND TABLE COVERINGS, PACKING MATERIALS AND OTHER SIMILAR MATERIALS, SITUATIONS AND EQUIPMENT. EXPLOSIVES INCLUDE PROPELLANTS AND PYROTECHNICS.

3. Hazard Classification TEsts (TB 700-2)

a. Detonation Test - No explosion, samples burned.

b. Ignition and Unconfined Burning Test - No explosion. Samples burned Average burning time 565 seconds.

c. Thermal Stability Test - No explosion, ignition or change in configuration.

d. Card Gap Test - No explosion at 0 cards.

4. Additional Sensitivity Data

Impact ERL Apparatus, Type 12 Tools

Material	50% Point, cm
SW-533	72
RDX	35-40
TNT	65-75

5. Sensitivity (Comparison Values)

Electrostatic Discharge, Bureau of Mines Apparatus

Explosive	Joules
Lead Azide	0.007
TNT	Confined 4.4/Unconfined 0.06
RDX	> 11.03
Black Powder	Confined 0.8/Unconfined >12.5

SHEET 3 of 3

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The following personnel received support from the U. S. Army Medical Research and Development Command under Army Project Order No. 82PP2802 in performance of the work described in this report:

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