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The Chemical and Physical Characterization of Phosphorus Smokes for Inhalation Exposure and Toxicology Studies

Chemical Characterization and Toxicologic Evaluation of Airborne Mixtures

FINAL REPORT

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

June, 1984

Supported by

U.S. ARMY MEDICAL RESEARCH
AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, MD 21701

Army Project Order Nos. 9600, 0027, and 1807

Project Officer: James C. Eaton

Health Effects Research Division
U.S. ARMY MEDICAL BIOENGINEERING
RESEARCH AND DEVELOPMENT LABORATORY

Fort Detrick, Frederick, MD 21701

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Printed in the United States of America. Available from
National Technical Information Service
U.S. Department of Commerce
5285 Port Royal Road, Springfield, Virginia 22161
NTIS price codes—Printed Copy: A04; Microfiche A01

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Unclassified

SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS BEFORE COMPLETING FORM

1. REPORT NUMBER

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)

The Chemical and Physical Characterization of Phosphorus Smokes for Inhalation Exposure and Toxicology Studies

5. TYPE OF REPORT & PERIOD COVERED

Final Report 1982-1984

6. PERFORMING ORG. REPORT NUMBER

7. AUTHOR(s)

R.S. Brazell-Ramsey
J. H. Moneyhun and
R. W. Holmberg

8. CONTRACT OR GRANT NUMBER(s)

Army Project Orders
No. 9600 and 0027

9. PERFORMING ORGANIZATION NAME AND ADDRESS

Oak Ridge National Laboratory
Oak Ridge, TN 37831

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS

62777 A
3E162777A878

11. CONTROLLING OFFICE NAME AND ADDRESS

U.S. Army Medical Research and Development Command
Fort Detrick, Frederick, MD 21701-5012

12. REPORT DATE

June, 1984

13. NUMBER OF PAGES

60

14. MONITORING AGENCY NAME & ADDRESS (if different from Controlling Office)

U.S. Army Medical Bioengineering Research and Development Laboratory
Fort Detrick, Frederick, MD 21701-5010

15. SECURITY CLASS. (of this report)

Unclassified

15a. DECLASSIFICATION/DOWNGRADING SCHEDULE

16. DISTRIBUTION STATEMENT (of this Report)

Approved for public release; distribution unlimited.

17. DISTRIBUTION STATEMENT (of the abstract entered in Block 20, if different from Report)

18. SUPPLEMENTARY NOTES

19. KEY WORDS (Continue on reverse side if necessary and identify by block number)

Red phosphorus - butyl rubber
White phosphorus - felt
Aerosol
Combustion products
Phosphoric acids

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

The chemical and physical properties of the aerosols produced from the combustion of red phosphorus containing butyl rubber (RPBR) and white phosphorus impregnated in felt (WPF) have been examined. The aerosols were produced at a uniform concentration by extruding softened raw material and burning the emerging filament or by igniting fragments of the formulations in a convective air flow. Aerosol particle sizes were found to be within the respirable range, varying from 0.4 to 1.0 micrometers depending upon generation conditions and aerosol age at collection. Chemical

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WPF aerosols were found to be very similar, composed primarily of water and phosphoric acids. Organic compounds and inorganic gases were detected only at trace levels.

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Chemical Characterization and Toxicologic Evaluation of Airborne Mixtures

THE CHEMICAL AND PHYSICAL CHARACTERIZATION OF PHOSPHORUS SMOKES FOR INHALATION EXPOSURE AND TOXICOLOGY STUDIES

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DATE PUBLISHED: April 1985

Supported by

U.S. ARMY MEDICAL RESEARCH AND DEVELOPMENT COMMAND
Fort Detrick, Frederick, MD 21701-5012
Army Project Order Nos. 9600 and 0027

Project Officer: James C. Eaton
Health Effects Research Division
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Fort Detrick, Frederick, MD 21701-5010

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U.S. DEPARTMENT OF ENERGY
Under Contract No. DE-AC05-84OR21400

EXECUTIVE SUMMARY

This report describes the chemical and physical properties of aerosols and combustion products produced from the burning of two military obscurant sources: red phosphorus containing butyl rubber (RPBR) and white phosphorus impregnated in felt (WPF). Particular emphasis has been placed on those properties of toxicological interest. Aerosols formed under two different generation conditions have been investigated. In one, with RPBR only, the material was softened with hexane, extruded and burned continuously for introduction into chambers at a uniform concentration for inhalation toxicology testing. In the other, where both RPBR and WPF were burned for chemical comparison, fragments of the materials were placed on a surface and burned in a convective air flow. In addition, the RPBR source material has been analyzed for composition and impurities.

Aerosol particles produced from burning phosphorus are present as concentrated solutions of phosphoric acid in water. In humid air, the phosphorus burns to form phosphorus pentoxide and hydrates to form the phosphoric acid which then absorbs more water vapor to form the aqueous aerosol particles. The acid concentration in the particles varies with humidity. At the lowest humidity studied, 14 percent, the aerosol composition was 83 percent phosphoric acid; at 84 percent relative humdity, a concentration of 31 percent phosphoric acid was found.

The phosphoric acid exists in the aerosol particles in polymeric form. Linear polyphosphate chains with as many as 18 phosphorus atoms have been resolved by anion exchange chromatography. In addition, more complex polymeric forms contribute to the anion exchange profile. Only minor changes were observed in these polymer profiles with changes in burn conditions in the continuously generated aerosol from RPBR. In the free burn experiments with both RPBR and WPF, the higher polymers were not evident. No pronounced differences were seen when comparing the smokes from RPBR and WPF. The polymeric character of the aerosol apparently depends more on the conditions under which it was burned than on whether it was red or white phosphorus.

Aerosol particle size was measured by cascade impactor techniques. In all experiments, mass median diameters found were within the respirable limit, varying from 0.4 to 1.0 micrometers diameter depending on generation conditions, age, and humidity. Continuously generated aerosols were nearer the smaller size listed above while those produced from free burns were near the upper limit. The residence time of the aerosol in the exposure chamber had a larger influence on particle size than did humidity in the range studied.

The aerosols and exposure atmospheres were examined for organic compounds and other trace impurities of possible toxicological interest. Phosphine was not detected, and elemental phosphorus was seen only with sensitive detection, but at non-significant levels. Traces of hexane were detected in softened RPBR; methylene chloride was not. Total organic carbon analyses were performed to establish an upper limit to organic impurities that might arise from the source materials. Results indicated no more than 0.04 percent organic contribution to the aerosol. Traces of carbon monoxide and nitrogen oxides were determined, but again these were below established toxicity limits.

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INTRODUCTION

The combustion products of two phosphorus-containing obscurants that are in the military inventory -- red phosphorus-butyl rubber (RPBR) and white phosphorus impregnated in felt (WPF) -- have been chemically and physically characterized in support of the toxicology program of the U. S. Army Medical Bioengineering Research and Development Laboratory, Fort Detrick, Frederick, MD. Additionally, since the RPBR formulation is still developmental, the particular batch of material that is being used in the ongoing toxicological studies at the Illinois Institute of Technology Research Institute, Chicago, IL, has been analyzed.

In Army field use, these two obscurant systems are deployed explosively from grenades or howitzer shells. Fragments of the phosphorus formulations ignite and produce a dense and obscuring white cloud. Both formulations are primarily phosphorus in one of its elemental forms, but contain organic binders (felt or butyl rubber) added for pyrotechnological reasons. These organic constituents and their transformation products may also be present in what is primarily an inorganic smoke matrix, and are potential contributors to the toxicity of the smoke. The analytical work presented here also addresses these impurities as well as other impurities of toxicological interest.

To put the analytical results in perspective, we shall briefly and simply review the primary chemical processes that underlie the formation of the aerosol. Elemental phosphorus, in either of its allotropic forms, burns in air to form phosphorus pentoxide:

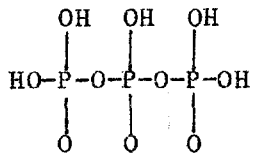
$$4\ P + 5\ O_2 \longrightarrow P_4O_{10} \qquad (1)$$

Incomplete oxidation to lower valent phosphorus oxides is also possible, but these would not be expected in major amounts in the strongly oxidizing conditions that occur in obscurant deployment. In even slightly humid air, there is sufficient water vapor so that the phosphorus pentoxide reacts to form phosphoric acid:

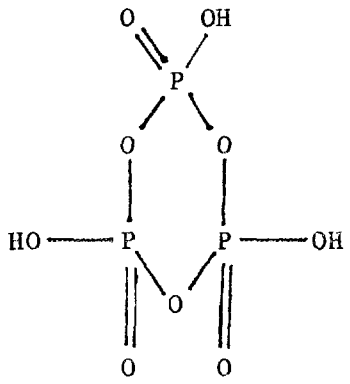
$$P_4O_{10} + 6\ H_2O \longrightarrow 4\ H_3PO_4 \qquad (2)$$

and then further hydrates to form liquid aerosol particles that may be regarded as a concentrated solution of phosphoric acid in water. The acid concentration of this solution depends on the water vapor concentration in the aerosol atmosphere.

In eq. (2) we have written the stoichiometric formula for orthophosphoric acid. The formal composition of the aerosol particles may always be expressed in these terms; e.g., percent phosphoric acid. Chemically, the phosphoric acid may exist as polymers. Both linear polymeric chains, e.g., ortho-tripolyphosphoric acid:



and cyclic forms; e.g.,as trimetaphosphoric acid:



are known to exist. More complicated forms such as branched chains and mixed cyclic-linear forms are undoubtedly possible. All of the forms can be considered to be formed from o-phosphoric acid by dehydration-polymerization reactions of the type:

$$3\ H_3PO_4 \rightarrow H_5P_3O_{10} + 2\ H_2O \qquad \text{(tripolyphosphoric acid)}$$

$$3\ H_3PO_4 \rightarrow H_3P_3O_9 + 3\ H_2O \qquad \text{(trimetaphosphoric acid)}$$

R. F. Jameson[1] has shown that polymeric phosphoric acids exist at equilibrium only in exceedingly concentrated solutions, when the composition of the solution exceeds 73 percent when expressed as weight percent phosphorus pentoxide (100 percent expressed as weight percent H_3PO_4). Liquid solutions of this concentration, and higher, can be formed by addition of phosphorus pentoxide to ortho phosphoric acid or by dehydration of phosphoric acid solutions. As the concentration increases, longer chains and the more complicated forms are produced and exist at equilibrium. In the data we shall present, aerosol compositions were always less than 84 percent phosphoric acid (61 percent expressed as phosphorus pentoxide), yet a wide variety of polymers was found. These are evidently not in thermodynamic equilibrium, but exist because of the slow rates of depolymerization. One can envision their formation in the following manner. Water is progressively absorbed by the nascent phosphorus pentoxide. For a short time, the ratio of phosphorus pentoxide to water is very high. Under these conditions, very high polymers can form rapidly. As more water is absorbed to dilute the acid, the equilibrium conditions are reversed, but because of the slowness of the depolymerization reaction, the higher polymers exist more or less stably throughout the lifetime of the aerosol.

MATERIALS AND METHODS

RAW MATERIALS

RPBR. The RPBR used in these experiments was an engineering development batch (105 Kg) obtained from the U.S. Army Chemical Research and

Development Center (CRDC), Aberdeen Proving Ground, MD. The formulation had been prepared by mixing oiled red phosphorus with butyl rubber in the presence of methylene chloride which serves as a softening/swelling agent for the rubber. The butyl rubber is added at a nominal five percent of the phosphorus. After thorough mixing, the material was mechanically extruded through one-quarter inch dies and chopped into small pellets. It was then dusted lightly with talc to prevent cohesion of the individual pellets, and oven dried at low temperatures to remove the methylene chloride.

For much of the work reported here, the RPBR has been further processed to allow extrusion in the ORNL extrusion-combustion generator.[2] The material is softened by the absorption of hexane vapors to 7 to 8 percent. The details of this softening procedure are given elsewhere.[3]

WPF. A phosphorus containing cylinder from a 155-mm artillery shell was received from the Army via the Illinois Institute of Technology Research Institute, Chicago, IL. This stainless steel casing was cut open under water and the white phosphorus-felt wedges were separated from the internal spacers and phosphorus scrap. In all, 108 wedges were harvested. Each was shaped as a 90 degree sector of a 12.7 cm diameter circle and was 2.2 cm thick. The average weight per wedge was 65 g and consisted nominally of 80 percent α-white phosphorus impregnated in a wool felt matrix material. They were stored under water prior to use.

ANALYTICAL METHODS FOR THE RPBR FORMULATION

Characterization of the raw material is required to ensure a uniform product for smoke generation for the inhalation toxicology and to identify any constituents which may have toxicological consequence in the exposure experiments. Parameters which were measured on a routine basis for quality assurance of RPBR are total phosphorus, organic extractables, and hexane softening agent. Other constituents that have been measured are elemental impurities, and residual methylene chloride.

Total Phosphorus. Phosphorus is determined gravimetrically as magnesium pyrophosphate following dissolution of the RPBR in nitric acid and bromine.[4]

Organic Extractables. Organic constituents are extracted with hexane and consist primarily of butyl rubber and mineral oil. Approximately 5 g of RPBR is weighed and placed in a tared centrifuge tube to which 5 mL of hexane are added. The mixture is shaken vigorously to break up the sample. The tube is then centrifuged for 10 min and the solvent decanted into a weighed bottle. This procedure is repeated twice, adding the solvent to the same bottle. The bottle is dried to remove hexane, and the weight loss is taken as the amount of organic extractables. Three separate determinations are made and the average is reported as the percent extracted.

An alternate procedure in which the collected hexane solvent is slowly evaporated in a stream of dry nitrogen and the residue weighed was also investigated. Generally this alternate procedure yielded results which were slightly lower (ca. 0.25 percent). This may reflect the presence of slightly volatile organic components.

Hexane. The quantity of hexane added to soften the RPBR for extrusion in the generators is determined gravimetrically.

Mineral Oil. Size exclusion liquid chromatography was used to determine the oil content. The organics are first extracted from the raw material with hexane and the solvent slowly evaporated with a stream of nitrogen. This is then treated twice with 5 mL portions of methylene chloride which extracts the oil. The methylene chloride is evaporated under dry nitrogen and the residue taken up in tetrahydrofuran (THF). An aliquot of the THF sample is chromatographed on two size exclusion columns connected in series: PL gel 100 Å, (5 μm), and PL gel 50 Å (5 μm). Both columns are 30 cm x 7.7 mm I.D. and were purchased from Applied Science, State College, PA. The samples are analyzed isocratically using THF as the mobile phase at 0.7 mL/min, delivered by a Laboratory Data Control (LDC) LC System Support Unit 1 pump. The oil peak elutes in about 25 min and is detected by a Model 1109 LDC Refractomonitor II differential refractometer. The peak height is proportional to the concentration injected. Standards for comparisons are prepared from pure mineral oil dissolved in THF.

Elemental Impurities. RPBR was analyzed for trace metals by optical emission spectroscopy and by inductively coupled plasma spectroscopy (ICP) which provide semiquantitative and quantitative data, respectively. Standard procedures were used for the determinations.

Methylene Chloride. RPBR was also examined for residual methylene chloride because of the use of that solvent in the manufacture of the material and because of the potential toxicity of chlorinated hydrocarbons. One gram samples were extracted with isopropanol, allowing at least 30 min of contact time with the solvent. The isopropanol solution was then analyzed both by GC/FID and GC/MS with chromatographic separations made on a 1.8 m x 3 mm O.D. glass column packed with 1 percent SP 1000 on Carbopack B (60/80 mesh). The column was operated isothermally at 90°C with a helium carrier gas flow rate of 30 mL/min. GC/FID analyses were conducted on a Perkin Elmer 3920 B gas chromatograph equipped with an on-column injector. The identity was confirmed by MS determinations made on a Hewlett-Packard 5935 A instrument with the electron impact source at 70 eV.

COMBUSTION PROCESS

Most of the results reported here refer to phosphorus smoke from the combustion of RPBR produced at known and uniform concentrations using the ORNL extrusion combustion generator. The design and operation of this sytem has been described.[2] Briefly, RPBR softened by the inclusion of hexane was extruded through an orifice and the

emerging filament continuously burned in a stream of air. At constant extrusion rate and airflow, an aerosol of uniform concentration was produced for biological or chemical studies. The aerosol was carried to exposure chambers through flexible stainless steel tubing. To minimize the interference from artifactual organics, an all glass and metal apparatus has been used. At the outset of this work, it was recognized that the air velocity across the burning phosphorus filament may influence the aerosol chemistry. Most of the work was performed here with sampling from a small, 425 L chamber with air throughputs of 250 L/min, while the toxicology at Illinois Institute of Technology Research Institute was carried out in approximately 1400 L chambers at 500 L/min. To maintain an air velocity equivalent to the IITRI burn conditions, a restrictor was placed before the burn site to control the air velocity. Aerosol concentrations were controlled by adjusting the extrusion rate and were monitored on-line with a backscattering particle sensor. Moisture levels of the incoming air were controlled in the range from 20 to 85 percent. Details on the manner in which specific generator conditions were varied to study their effects on aerosol composition are described in corresponding sections of this report.

In addition to the production of aerosol using the generator, both RPBR and WPF were "statically burned". Simply, fragments of the material were burned in air and the smoke carried to the chambers for sampling as described above. A more or less continuous generation of aerosol was achieved by manually adding another fragment of the phosphorus as the flame from previous ones began to subside. Again the aerosol concentration was monitored using on-line particle sensors. The capability of observing this instantaneous concentration aided the operator in maintaining a more uniform chamber concentration as samples were being taken for analysis. The phosphorus formulations were burned on the surface of a bed of clean sand. The rationale for the static burn experiments was two-fold. First, it was desired to compare the smoke from the two formulations under similar burn conditions, and the technology for extruding the WPF was not available. Secondly, the static burn more closely mimics the production of smoke in the second phase of the field usage, i.e., particles burning on the ground with only convective air flow across the burn.

No direct comparisons of field generated smoke and our laboratory simulations have been made. It is therefore appropriate to discuss the type of burning conditions that exist when an obscurant charge is deployed. We consider here primarily different air flow conditions; this flow controls the rapidity, the temperature, and completeness of the oxidation process and might be important not only for the phosphorus chemistry, but also for that of the organic binders. Two extremes of conditions exist. The explosive charge ignites the phosphorus and propels it at high velocity through the air where part of it burns to form smoke. The obscurant systems are designed, however, so that a fraction of the material reaches the ground and continues to burn, but more slowly and with much less access to oxygen. In the generator there is a relatively high velocity of air across the burning phosphorus. This mimics conditions that exist during the air burst. Conditions that exist in the static burning apparatus more closely mimic smoldering on the ground.

ANALYTICAL METHODS FOR COMBUSTION PRODUCTS

Aerosol

Aerosol Concentration Determinations. The concentration of the phosphorus aerosol can be expressed as the weight of total aerosol per unit volume of air sampled or as the weight of phosphoric acid per unit volume. Both are satisfactory as measures of aerosol concentration, but the weight concentration is humidity dependent. The aerosol particles absorb water to approach an equilibrium with the water vapor concentration. The phosphoric acid concentration is more directly related to the amount of phosphorus burned. Two methods were used to monitor the weight concentration of the aerosol. Samples drawn from the exposure chamber at known and monitored flow rates onto glass fiber filters (Cambridge Filter Co.) provided average values over the sampling period. To monitor the aerosol concentration continuously, a light scattering technique which has been previously described was used.(5) Briefly, this method relies on a phototransistor to detect light scattered backward from the aerosol particles. The light source is a light emitting diode (LED) mounted beside the phototransistor. The signal produced is amplified and used to drive a digital voltmeter, strip chart recorder, or other signal recording devices. The monitor was calibrated to yield a specific signal to concentration value obtained from filter pad weights.

The phosphoric acid concentration was determined on samples commonly collected for weight concentration measurements. The sample is extracted from the filter pads into NaCl solution containing EDTA. The solution is then analyzed on the flow injection system as described in Appendix B.

Particle Size Distribution. A Mercer-type seven-stage cascade impactor (In Tox Products, Albuquerque, NM) was used to determine the particle size distribution. Glass slide cover slips were used as plates for the individual stages and a glass fiber filter was used after the final stage. The impactor was operated at a flow rate of 1 L/min using flow controlled sampling pumps. Samples were drawn directly from the exposure chamber with the impactor held in a vertical position. Details of this method and the data reduction have been given previously.(6)

Individual substrate plates were analyzed for total phosphoric acid following extraction in NaCl/EDTA solution. These values were then used to determine the weight percentages retained on each stage. The cumulative weight percentages and stage cut-off diameters were plotted on logrithmic probability axes from which mass median diameters (MMD) and associated geometric standard deviations were determined.

Total Phosphate and Phosphorus Speciation. A flow injection analysis (FIA) system was assembled and coupled to a high performance liquid chromatograph for use as a specific post-column detector for linear and cyclic condensed phosphoric acids. The condensed phosphates were separated by anion exchange, hydrolyzed to orthophosphoric acid, and condensed with molybdic acid to form a molybdenum blue complex

which was detected in a flow-through adsorption cell. This system was used to analyze the aerosols from the combustion of red and white phosphorus and to examine the relationship between experimental combustion conditions and the composition of the phosphoric acids. The system was also used for the rapid "batch" analysis of aerosol samples for total phosphoric acid. In the latter case, samples were introduced directly into the stream of molybdic acid reagent without prior separation. The condensed phosphates are hydrolyzed and reacted in a reaction coil maintained at elevated temperatures. A diagram of the system is shown in Figure B-1 and a complete description is given in Appendix B.

Total Organic Carbon (TOC). To determine the concentration levels of organics in the aerosol derived from the combustion and pyrolysis of these formulations, TOC analyses were performed. Aerosol samples were collected using a glass impinger which was fabricated from a flask with a standard tapered mouth and an aerosol inlet tube. Glass fiber filter samples could not be used because of high TOC blank. The end of the tube was constricted to an opening of 0.028 inches and bent so that the aerosol, pulled through the tip, impinged upon the wall of the flask and flowed to the bottom. At a sampling rate of 5 L/m, the Stokes cut-off diameter for this system was calculated to be approximately 0.2 μm which is near the lower limit of the phosphorus aerosol particle size distribution. Experimentally, the collection efficiency was found to be greater than 97 percent based on the weight of material collected on fibrous filters located after the impinger. The aerosol collected in this manner was oxidized to convert all organics to CO_2, which was subsequently measured on a commercially available TOC analyzer using standard procedures.

Vapor Phase and Gas Phase Constituents

Samples for the analysis of gaseous and volatile compounds were collected from the exposure chamber in Tedlar™ bags (SKC Inc., Eighty Four, PA) placed downstream from glass fiber filters. Connections between the sampling bag, pump, filter, and sample source were made with Teflon to minimize contamination. The bags were equipped with stainless steel septum caps and replaceable septums from which samples could be easily removed with a gas tight syringe. Analyses were conducted immediately after collection to minimize compositional changes and sample loss.

Volatile Organic Compounds. Low molecular weight organics and organophosphates were determined by GC on a Perkin Elmer 3920 with a flame ionization detector (FID) and on a Varian 3700 with a nitrogen-phosphorous detector (NPD), respectively. Separations for FID analysis were made on a 1.8 m x 3 mm O.D. glass column packed with 80/100 mesh Carbopack C coated with 0.1 percent SP-1000. The column was operated at 60°C for 2 min, programmed at 8°C/min to 220°C, and held for an additional 8 min at the elevated temperature. NPD analyses were made on a 1.8 m x 3 mm O.D. glass column packed with Carbopack B containing 1 percent SP-1000 (60/80 mesh). The column was programmed from 30°C at 8°C/min to 180°C where it was held for an additional 20 min. Helium

carrier gas flow rates for both columns were 30 mL/min. Flow rates, optimized for the detection of P-containing compounds on the NPD, were 175 mL/min for air and 5.0 mL/min for H_2. The NPD was calculated to have a P to C selectivity of 7500.

Carbon Monoxide and Carbon Dioxide. Carbon dioxide was analyzed on a Carle 111 GC with a thermal conductivity detector and separated from other air constituents on a packed column of Amberlyst 15 resin loaded with reduced nickel. The procedure of Horton and Guerin[7] was used without modification. Concentrations of CO were determined on a Ecolyzer 2000 series continuous CO monitor (Energetics Science, Elmsford, NY). This instrument uses an electrochemical sensor to measure current produced from the oxidation of CO to CO_2. The response is directly proportional to the CO concentration, and levels from 1 to 50 ppm can be determined.

Phosphine. Samples for phosphine analysis were analyzed on a Varian 3700 GC equipped with a NPD. Separations were made isothermally at 30°C on a 1.8 m x 3 mm O.D. column packed with Carbopack B containing 1 percent SP-1000 (60/80 mesh). The helium carrier flow rate was 30 mL/min. All other instrumental parameters (i.e., bead current, hydrogen flow rate, and air flow rate) were the same as in the determination for organophosphates. Samples were injected on-column using a gas tight syringe.

Phosphine (6 ppm) in ultra high purity nitrogen (Linde, Somerset, NJ) was diluted 10-fold with air and used as a standard. The estimated detection limit was less than 0.1 ppm and elution time was approximately one minute.

RESULTS AND DISCUSSION

RPBR FORMULATION

RPBR was analyzed with emphasis on constituents of potential toxicological consequence. Such constituents might transfer to the aerosol during the combustion generation process. Since trace elements are one class of impurities which could be transported, the material was analyzed for these constituents. Results are presented in Table 1. The total concentration of all the trace elements was found to comprise less than 1 percent of the weight of the material analyzed, and the low levels of the individual constituents indicate that they are unlikely to contribute to the toxicity of the smoke. In addition, samples were analyzed specifically for arsenic, since initial results by emission spectroscopy did not provide a sensitive measure of this element and since it has been reported to be a major impurity in white phosphorus.[8] The highest concentration determined was 210 μg As/g of RPBR, which corresponds to approximately 67 μg As/m^3 in the exposure atmosphere at an aerosol concentration of 1 mg/L (as H_3PO_4), assuming all of it transfers to the aerosol. The American Industrial

TABLE 1. TRACE ELEMENTS IN RPBR

Element	Concentration (ppm)[a] Emission	ICP	Element	Concentration (ppm)[a] Emission	ICP
Ag	<5	<0.1	Mg	1500	260
Al	250	470	Mn	10	4.3
As	<1000	180;210	Mo	<5	1500
Au	<50	-	Na	600	2200
B	<5	10	Nb	<10	-
Ba	<10	2	Ni	<15	7.8
Be	<1	0.1	Pb	50	44
Bi	<50	-	Pt	<50	-
Ca	1500	180	Rb	<20	-
Cd	<100	1.1	Sb	<50	23
Co	<50	<0.05	Sc	-	22
Cr	<50	82	Si	1500	240
Cu	50	11	Sn	<50	<0.6
Fe	500	270	Sr	<10	0.5
Ga	<15	<0.1	Ta	<50	-
Hf	-	1.4	Ti	<50	990
Hg	<50	-	V	<10	-
In	<50	-	W	<50	-
K	10	270	Zn	<50	-
Li	<10	<5	Zr	<20	-

[a]Analytical method by emission spectroscopy or inductively coupled plasma.

Hygiene Association (AIHA) occupational health standard for an 8 hr time weighted averaged (TWA) exposure for inorganic As is 200 $\mu g/m^3$. Therefore, it is unlikely that As will significantly contribute to the toxicity of the smoke.

Samples were specifically analyzed for methylene chloride which is used as a softening agent in the initial preparation of the RPBR formulation. Although the material was dried following extrusion into pellet form and it seems likely that most of the methylene chloride would be lost in the drying process, there remains a possibility that enough is retained to be important, particularly since chlorinated hydrocarbons are toxic at low concentration levels. Three pellets, each weighing about one g, were analyzed by both GC/FID and GC/MS techniques. No evidence for methylene chloride was found. In the first case, the detection limit was about 50 $\mu g/g$ of RPBR and, in the second, approximately 3 ng/g of RPBR. Corresponding levels in the exposure chamber would be much lower than the current OSHA environmental standard or the recommended exposure limit.[8]

For quality control of the RPBR supplied to ITTRI for use in the inhalation studies, certain analyses are conducted on a routine basis. The raw material supplied from CRDC is first processed to permit extrusion in the smoke generator systems. The treated material is analyzed for phosphorus and extractables. The percent hexane added for softening is also reported and the lubricating oil concentration is determined periodically. The results for some of these analyses are shown in Table 2. Butyl rubber is calculated as the difference between the extractables and the oil, and averages 4.2 $\pm$ 0.6 percent of the total weight. The lubricating oil is 1.0 percent of the phosphorus or 0.9 percent of the RPBR weight. These values are slightly lower than the military specifications for oiled red phosphorus which require an oil content of 1.22 to 1.28 percent by weight (see Appendix A).

Phosphorus was found to comprise 92 percent of the material. This value is lower than the expected 95 percent. When pure powdered red phosphorus (Matheson, Coleman, and Bell, 98 percent minimum) and a synthetic mixture of 95 percent red phosphorus and 5 percent butyl rubber were analyzed, the results were also low (i.e., 94.6 and 91.6 percent, respectively). The differences may therefore be due to a bias in the analytical method. Since the precision was high, it was satisfactory for determining relative changes in concentration.

COMPOSITION OF CONTINUOUSLY GENERATED AEROSOL FROM THE ORNL COMBUSTION GENERATOR

In this section, we discuss some of the general chemistry of the RPBR aerosol as produced from the ORNL Combustion/Extrusion generator. For these experiments, the generator was operated at an air flow rate of 250 L/min and an air velocity across the burning RPBR of 252 m/min. The relative humidity ranged from 40 to 60 percent depending on laboratory conditions. Temperatures in the chamber were 22 $\pm$ 2°C. Aerosol concentrations in the range from one to two milligrams per liter were used for most analyses. They were controlled by adjusting the extrusion rate of the generator and were monitored on-line with particle monitors.

A typical profile obtained from the on-line monitor for aerosol concentration using the particle sensor is shown in Figure 1. Only minor fluctuations corresponding to less than 10 percent change were detected, which indicates that a relatively even burn rate and uniform concentration level were maintained in the chamber.

The aerosol was found to be composed primarily of phosphoric acids, including orthophosphate, and linear and cyclic condensed phosphates. During the development stages of this project, several methods for resolving and quantitating these polymers were considered. These included thin layer chromatography and nuclear magnetic resonance. Preliminary experiments indicated that neither of these provided the specificity and resolution needed, particularly when compared with the high performance anion exchange chromatographic method that was developed and adopted for routine use.

TABLE 2. QUALITY ASSURANCE ANALYSES OF PROCESSED RPBR

Can Number	*Phosphorus by Hexane Ext.	Phosphorus by Service Lab	Extractables	Lubricating Oil	Butyl Rubber
A1 & A2	94.26	96.27	5.73	0.83	4.9
A3	94.95	91.51	5.05	0.87	4.18
A4	95.54	92.12	4.46	-	-
A5	95.10	90.53	4.90	-	-
A6	95.62	-	4.38	-	-
A7	95.72	-	4.28	-	-
A8	94.97	-	5.03	-	-
B2	94.27	91.63	5.73	1.03	4.70
B3	94.32	91.76	5.68	-	-
B4	95.08	90.93	4.92	0.94	3.98
B5	95.00	91.55	5.00	-	-
B6	95.05	-	4.95	-	-
B7	95.05	-	4.95	-	-
B8	94.73	-	5.27	-	-
D2	96.28	91.40	3.72	-	-
D3	94.74	92.93	5.26	-	-
D4	95.00	92.17	5.00	-	-
D5	94.99	-	5.01	-	-
D6		Shipped to Tom Poston 11/83			
D7	95.61	-	4.39	-	-
D8	95.58	-	4.42	-	-
E1	94.23	90.99	5.77	0.99	4.78
E3	95.30	90.91	4.7	1.03	3.67
Average	95.06	91.90	4.94	0.95	4.37
Std. dev.	0.53	1.46	0.53	0.08	0.50

*All values reported as percent of total weight.

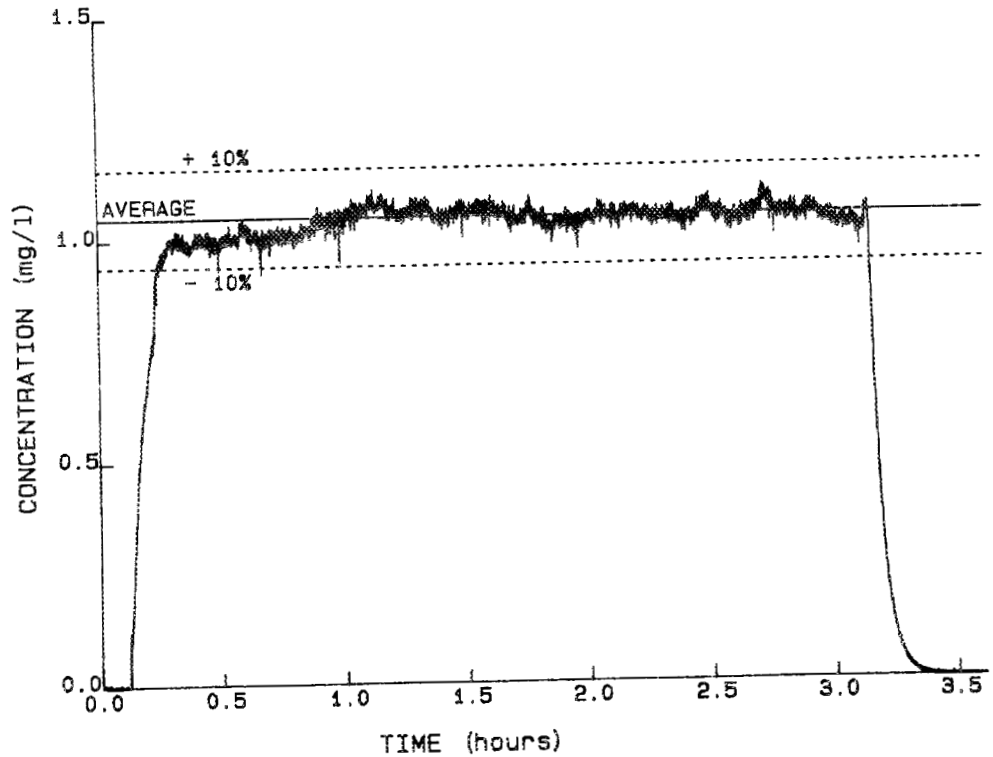


Figure 1. Typical Aerosol Concentration Profile From Extrusion/Combustion Generator. Response of Gayle/ORNL Aerosol Monitor Has Been Converted to Concentration Units.

A typical chromatogram of a generator-produced RPBR aerosol sample showing individual separated phosphoric acids is shown in Figure 2. The sample was collected at an aerosol concentration of 1.8 mg/L (1.4 mg of H_2PO_4/L) and 58 percent relative humidity. A series of polyphosphate species ranging from orthophosphate to the P_{13} polymer was determined. The first peak corresponds to orthophosphoric acid and the remaining peaks to pyrophosphate, tripolyphosphate, etc., up to the P_{13} polymer. All of these peaks are straight chain linear phosphates. With the exception of ortho- and occasionally pyrophosphate, P_5 or P_6 was found in the highest concentration and as the polymer number increased beyond P_6, there was an approximate linear decrease in concentration. The large "envelope" that eluted from the column is believed to contain an unresolved mixture of longer straight chain (> P_{14}), branched, and cyclic phosphates. Analysis of the samples on a column which provided greater resolution (i.e., Aminex A-14) allowed determinations up to the P_{18} polymer. Because the concentration of these phosphates (P_{14}-P_{18}) was very low (i.e., 1 percent of the total phosphate each) and the analysis time very long (i.e., 260 min), the samples were routinely analyzed only for orthophosphate through P_{13}. The concentration of the higher polymers in the envelope was calculated as the difference between the total phosphate concentration and the total of the other distinct peaks which could be quantitated. Small amounts of the cyclic phosphates, tetrameta- and trimetaphosphate were also detected in the generator-produced aerosols. They eluted at 42.5 and 53 min, respectively, and also contributed less than 1 percent of the total phosphate each. The concentrations of the individual components shown in Figure 2 are: 7.1 percent orthophosphate, 2.1 percent pyrophosphate, 3.0 percent tripolyphosphate, 2.6 percent tetrapolyphosphate, 17.2 percent P_5 through P_{13}, and 67.4 percent higher polyphosphates. The variation in the composition of these constituents for the same generator conditions was approximately ten percent.

The vapor phase of the RPBR smoke was analyzed to identify possibly toxic species resulting from the pyrolysis and combustion of the fuel or the organic butyl rubber additive. The direct analysis of gaseous samples (0.5 mL) showed only one peak on the FID which eluted within one minute of when the sample injection was made. The concentration of this peak was calculated based upon the response for pentane and was estimated to be less than 5 ppm (v/v). Judging from the retention time of this peak, it is most likely a low molecular weight hydrocarbon such as methane or ethane. No peaks were detected on the NPD.

To qualitatively determine organics which may be present in the vapor phase at trace levels, samples were also collected on Tenax/Spherocarb cartridges or trapped in a U-shaped tube immersed in a liquid nitrogen-pentane slush bath. The samples were drawn through glass fiber filters, which removed the particulate phase of the aerosol, onto the traps with vacuum sampling pumps. The trapped volatiles were then thermally desorbed at elevated temperature and the eluted volatiles analyzed on the column packed with 1 percent SP-1000 on Carbopack B. Determinations were made both by FID and MS. Figure 3 shows the FID profile of a sample concentrated in liquid nitrogen-pentane and Table 3 lists the compounds identified by MS. The generator and sampling conditions are given in the figure. The major

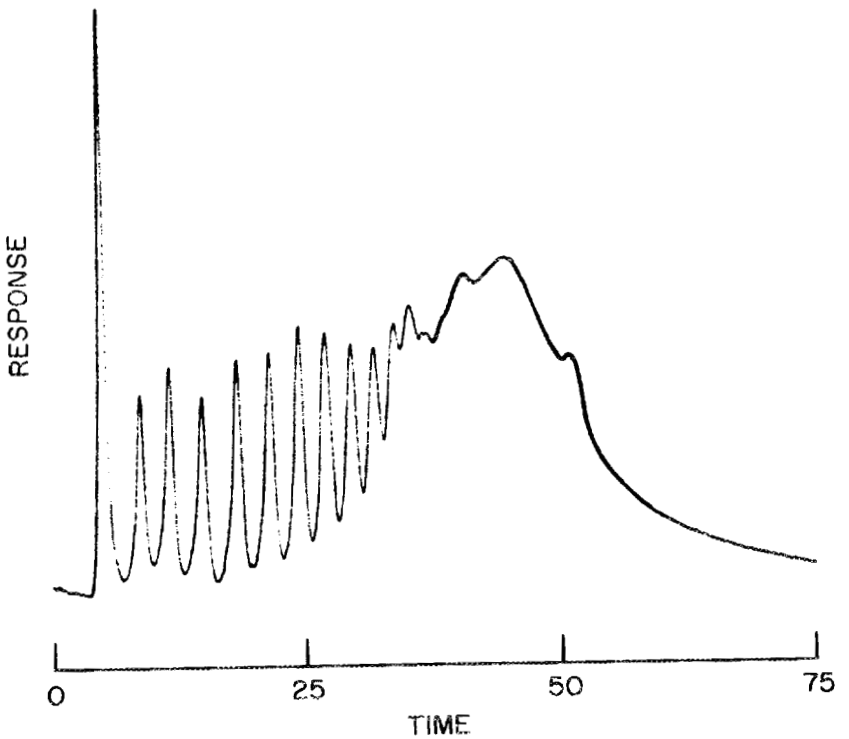


Figure 2. Phosphoric Acid Polymer Speciation Profile of Aerosol from RPBR Extrusion/Combustion Generator. Aerosol Concentration, 1.8 mg/L; Relative Humidity, 58 Percent.

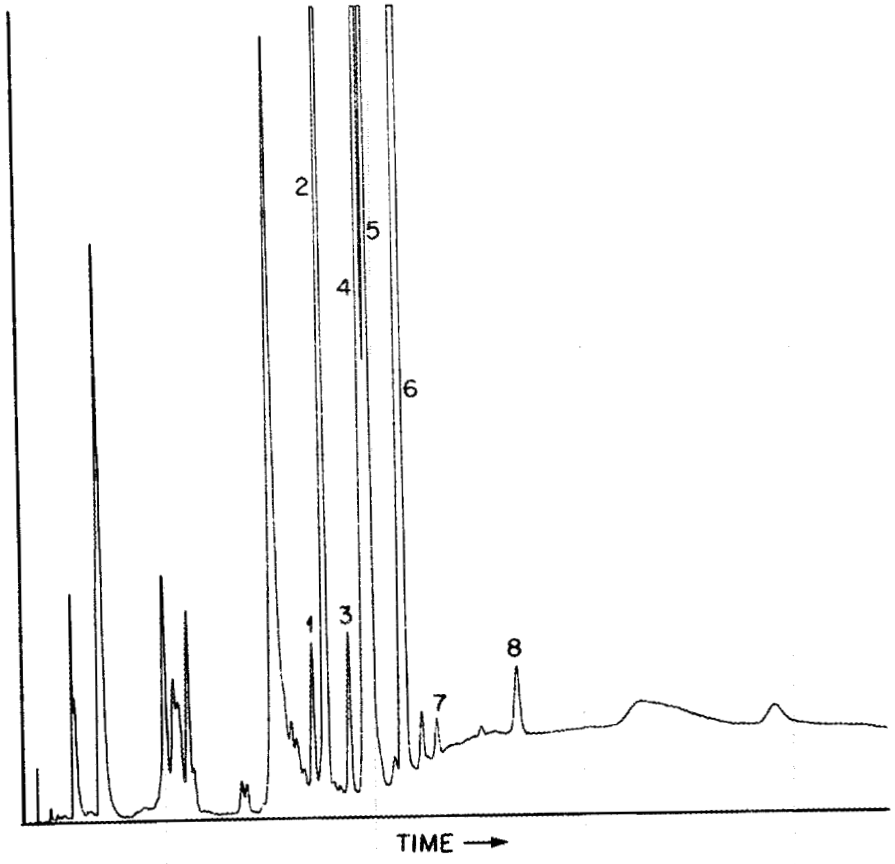


Figure 3. Gas Chromatographic Profile of Organic Volatiles in Aerosol From RPBR Extrusion/Combustion Generator. (Volatiles Concentrated in Liquid N_2/Pentane Cooled Trap.) FID Detector.

TABLE 3. COMPOUNDS IDENTIFIED IN GAS PHASE OF RPBR SMOKE

Peak Number[a]	
	C_4H_{10}
1	Cyclohexane
2	C_6H_{12} Olefin or Cyclo Compound
3	2,3-Dimethylbutane
4	3-Methylpentane
5	2-Methylpentane
6	n-Hexane
7	2,4-Dimethylpentane[b]
8	Toluene
	P_4

[a]Peak numbers refer to Figure 3.
[b]Tentative

constituents in the chamber atmosphere, identified by MS and verified by retention times of standards, were found to be C_6 hydrocarbons. These hexane isomers were also identified in the solvent used to soften the RPBR for extrusion. Since hexane is known to have some neurotoxic effects, and since it is present in elevated concentrations in the treated RPBR, efforts were made to quantitate this compound. Samples were collected on the adsorbent cartridges and the nC_6 peak compared to liquid standards which were analyzed by direct injection. Normalized to an aerosol concentration of 1 mg/L, the average hexane content in the chamber was found to be 4.4 μg/L. Concentration levels in this range are not expected to pose any significant toxicological hazard as the OSHA 8 hr time weighted average limit is 0.18 mg/L.

MS analysis also gave evidence of elemental phosphorus in the gas phase. Since standards for P_4 are not available and could not be easily prepared, this peak was not quantitated. Elemental phosphorus, however, can be detected at low ng levels by MS, indicating that the concentration is in the low ppb range. All of the compounds determined, however, are expected to be very low in concentration since they were not detected by direct analysis.

Two methods have been used to estimate the organic chemical concentration in the particle phase. Initially, bulk liquid condensate from the aerosol was collected, subjected to an extraction procedure, and then analyzed by GC. Only weak peaks were seen. It was not established whether these came from the aerosol, the solvent, or other contaminating influences. Nor does the chromatographic procedure eliminate the possibility of non-chromatographical species. To attain a more quantitative estimate of organics, a conventional total organic carbon analysis (TOC) was performed on the aerosol. For this experiment, to prevent possible contamination from filters, the aerosol was collected by impingement into water using an all glass apparatus. This sample was subjected to TOC analysis. The results obtained at two different aerosol concentrations were as follows:

Aerosol Concentration in Chamber (mg/L)	H_3PO_4 Concentration (mg/L)	TOC ($gC/gH_3PO_4 \times 10^6$)
1.3	1.0	130
3.5	2.8	85

These results indicate only a very slight transfer or transformation of the organic constituents of the RPBR to the particle phase. These analyses were performed to establish an upper limit to the organic content. It indicates that the organic content is approximately 0.01 percent of the particulate phase.

Carbon monoxide and carbon dioxide were also determined in the RPBR generator produced aerosols. The results for three different concentration levels are presented in Table 4.

TABLE 4. CONCENTRATIONS OF CO_2 AND CO IN RPBR GENERATOR SMOKES

Aerosol Concentration (mg/L)	H_3PO_4 (mg/L)	CO_2 ppm (v/v)	CO_2 from RPBR Combustion[a]	CO ppm (v/v)
2.2	1.5	500	150	25
4.0	2.9	570	220	26
5.3	3.7	720	370	24

[a]CO_2 concentrations after subtracting ambient air blanks of 350 ppm.

As the aerosol concentration increased, the CO_2 levels also increased. An average value of 25 ppm was obtained for CO. CO_2 was found to be of the same magnitude as that in the laboratory air. It can be calculated that CO_2 from burning RPBR, assuming complete combustion of the 5 percent butyl rubber and 8 percent hexane, should be 100 ppm for an aerosol of 1 mg H_3PO_4/L. The close agreement between this value and the experimental findings further indicates that most of the organic material is completely oxidized.

An analysis was also performed for phosphine. This substance is extremely toxic, having an eight hour exposure limit established by OSHA of 0.3 ppm. Gas samples were collected and directly injected into a GC with NPD detection. No phosphine was detected in any of the samples. Using standards, we established a low detection limit of approximately 0.1 ppm. Phosphine is formed by reduction of phosphorus. These results tend to confirm a general conjecture that little could be formed in a strongly oxidizing flame. Small amounts of phosphine can be detected by odor from freshly opened cans of raw RPBR. Presumably, it is formed in trace quantities by the reaction of elemental phosphorus with water.

SMOKE COMPOSITION AS A FUNCTION OF GENERATOR CONDITIONS

The effects of humidity, air velocity across the burning phosphorus, aerosol concentration, and time of standing in the chamber (age) on the composition of the aerosol from RPBR under continuous generation conditions were investigated. A range of conditions was examined not only to define the aerosol under potential inhalation exposure conditions, but also to provide some insight to its chemistry in more variable field generation conditions. Generally, to examine the effects of each condition, other parameters were held constant (i.e., as the air velocity was varied, the concentration and humidity were maintained at a fixed level). Only major compositional properties were measured; changes in trace impurities were not investigated in this facet of the study.

Humidity, the moisture content of the air, is a major factor in controlling the composition of a 'hygroscopic' aerosol. Since our aerosol is essentially a water solution of phosphoric acid, it is expected that the individual particles will grow or diminish by absorption or desorption of water from the air that surround them. Their size and their gross composition will adjust until the vapor pressure of water at their surface is the same as the partial pressure of water vapor in the humid air. In addition, as we shall discuss later, the concentrations of the polymeric phosphoric acids also depend on the humidity.

Moisture levels in the incoming air from 20 to approximately 100 percent were produced by mixing dry air with air saturated with water from a steam generator. These streams were combined and well mixed in a mixing chamber located just before the burning chamber of the generator. The humidity of the incoming air was measured here both with conventional psychrometric techniques (e.g, wet/dry bulb thermometry) and by gravimetric absorption of known volumes onto magnesium perchlorate traps. The humidity in the chamber was, of course, not the same as that of the incoming air. Not only does the nascent phosphorus pentoxide absorb some of the water, but the walls of the chamber and the delivery tubing have adsorbed moisture that only slowly adjusts to an equilibrium with the water in the air. In the chamber, with phosphoric acid aerosol present, the conventional techniques were not reliable, and we relied entirely on gravimetric sampling. Detailed analyses of conditions and gross phosphoric acid composition are summarized in Table 5. Relative humidities are temperature-dependent and were calculated from the measured water vapor at the given temperature. The data in the table represent two runs on different days with the generator and air flow (250 L/min) set to produce a constant aerosol concentration. This is reflected in the analytical data of column 8 (Table 5) representing the aerosol concentration measured as phosphoric acid. It will be noted, however, that the weight concentration of the aerosol increases markedly--over a factor of two in the data of Table 5. This is a consequence of increased water content of the aerosol particles and is reflected in the aerosol composition expressed as percent phosphoric acid. The weight percent phosphoric acid in the aerosol as a function of water vapor concentration is shown graphically in Figure 4. The line in the figure represents the weight percent of pure orthophosphoric acid that is in equilibrium with water vapor[9] and is shown

TABLE 5. RPBR AEROSOL AS FUNCTION OF WATER VAPOR CONCENTRATION

Inlet Atmosphere			Exposure Chamber							
Rel Humidity %	Water Vap Conc mg/L	Temp °C	Rel Humidity %	Water Vap Conc mg/L	Temp °C	Aerosol by Total Wt mg/L	Conc as H_3PO_4 mg/L	Percent H_3PO_4	Particle Size MMD	Particle Size g
20	3.8	22	14	3.5	27	1.71	1.42	83.0	.42	1.47
20	3.8	22	12	3.1	27	1.75	1.52	86.9	.37	1.41
33	6.2	22	24	6.3	27	1.86	1.38	74.2	.38	1.41
54	10.2	22	45	11.6	27	2.05	1.11	54.1	.42	1.39
61	12.5	23	44	11.6	28	2.21	1.40	63.3	.44	1.36
87	18.3	24	69	16.9	26	2.83	1.40	49.4	.44	1.38
89	21.9	26	75	20.2	28	3.99	1.32	33.0	.47	1.41
90-100	-	-	84	25.8	30	3.69	1.16	31.4	.43	1.39
						Avg	1.30			
						Std Dev	.14			
						RSD	11%			

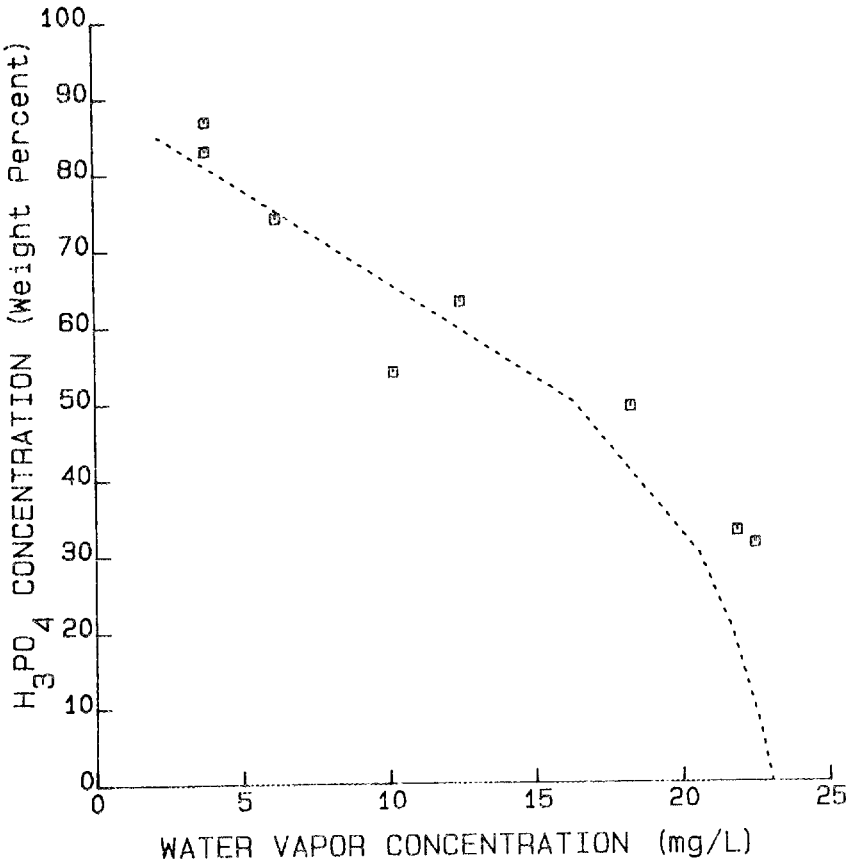


Figure 4. Phosphoric Acid Concentration as a Function of Water Vapor Concentration. Dotted Line is Water Vapor Concentration Over Phosphoric Acid Solutions. (Derived From Data in Ref. 9.)

for comparison purposes. Although the aerosol is not orthophosphoric acid, but contains complex polymeric forms of the acid, one would expect, as a first approximation, the vapor pressures over the two solutions to be very similar at equilibrium.

The detailed resolution of the composition of the aerosol into phosphoric acid polymers is summarized in Table 6. In Figure 5, the results are summarized graphically where the concentrations of orthophosphate, the summation of P_2 to P_{14} linear polymers, and the concentrations of higher polymers are compared. Orthophosphoric acid concentration tends to decrease with increasing humidity. A similar but less pronounced pattern is seen for the straight chain polymers. The chromatographically unresolved 'complex' phophoric acid species, however, increase with increasing humidity. These trends are not completely understood, but are probably related to the rates of depolymerization of these species which are much faster at high acidities. At high humidities, the acidity is lower and the polymeric species survive depolymerization longer.

Particle size distributions of the aerosols were measured using cascade impactor techniques. A complete discussion of the impactor, the sampling techniques and the data reduction steps has been given elsewhere.[6] Briefly, samples were taken into a Mercer/Lovelace type impactor at a flow rate of one liter per minute. The under-stage plates were analyzed for the amount of phosphoric acid collected and from these data cumulative fractions of the material collected were plotted as a function of particle diameter. Stage constants were evaluated using the formalism of Marple[10] as discussed in reference 12. We report here Stokes (physical) diameters. In the calculation of stage constants in terms of Stokes diameters, known values of phosphoric acid solution densities corresponding to the solution composition (percent H_3PO_4) were used. The data are interpreted as logarithmic normal distributions. A typical logarithmic probability plot of the data is shown as Figure 6 and the Stokes mass medium diameters and geometric standard deviations are tabulated in Table 5. As can be seen from the tabulated data, little change of particle diameter was seen in the range of humidities investigated.

A series of tests was also performed to determine the effect of air velocity across the burning RPBR. As the linear velocity of air across the burn increases, the flame temperature increases which can influence oxidation and/or hydration processes involved in the formation of the aerosol. To examine the effects, samples were collected and analyzed at three different velocities: 123, 252, and 493 m/min. The 252 m/min velocity simulates burn conditions used in the exposure studies at IITRI. In that system, 500 L/min unrestricted air flow (corresponding to approximately 250 m/min air velocity at the burn site) is used to deliver the aerosol as it is formed into the environmental exposure chamber. The standard operating condition for the ORNL 0.3 m^3 chamber is 250 L/min air flow through a 1.4 inch diameter glass insert at the inlet of the burn chamber, which provides a velocity of 252 m/min across the burn site. The velocity was changed by removing the 1.4 inch insert (i.e., using no restrictor for the air flow) or replacing it with a 1 inch diameter insert. This changes the velocity to 123 m/min and 493 m/min, respectively. Samples for analysis at all

TABLE 6. COMPOSITION OF THE PHOSPHORIC ACIDS IN PHOSPHORUS SMOKES AS A FUNCTION OF GENERATOR CONDITIONS

Parameter Under Investigation	Generation Conditions			Composition (%)					
	Air Velocity (m/min)	% Relative Humidity	Aerosol Concentration (mg PO_4^{-3}/L)	ortho-Phosphate	pyro-Phosphate	tripoly-Phosphate	tetrapoly-Phosphate	P_5-P_{13}	Higher Polyphosphates
Humidity	252	20	1.4	20.0	7.9	5.4	6.3	27.1	32.8
		45		17.6	4.9	6.0	6.2	34.8	29.1
		58		7.1	2.1	3.0	2.6	17.2	67.4
		80		4.9	1.8	2.6	2.5	17.3	69.8
		100		4.0	1.9	2.5	3.0	17.7	69.7
Air Velocity	123	45	1.3	15.0	3.9	4.7	4.8	30.5	40.7
	252			17.6	4.9	6.0	6.2	34.8	29.1
	493			22.2	5.0	6.3	7.4	43.5	13.4
Aerosol Concentration	252	51	0.8	17.6	7.7	5.7	5.7	26.3	36.9
			2.0	12.4	4.1	4.1	4.5	26.9	48.0
			4.6	16.8	7.7	5.8	6.2	30.3	33.2

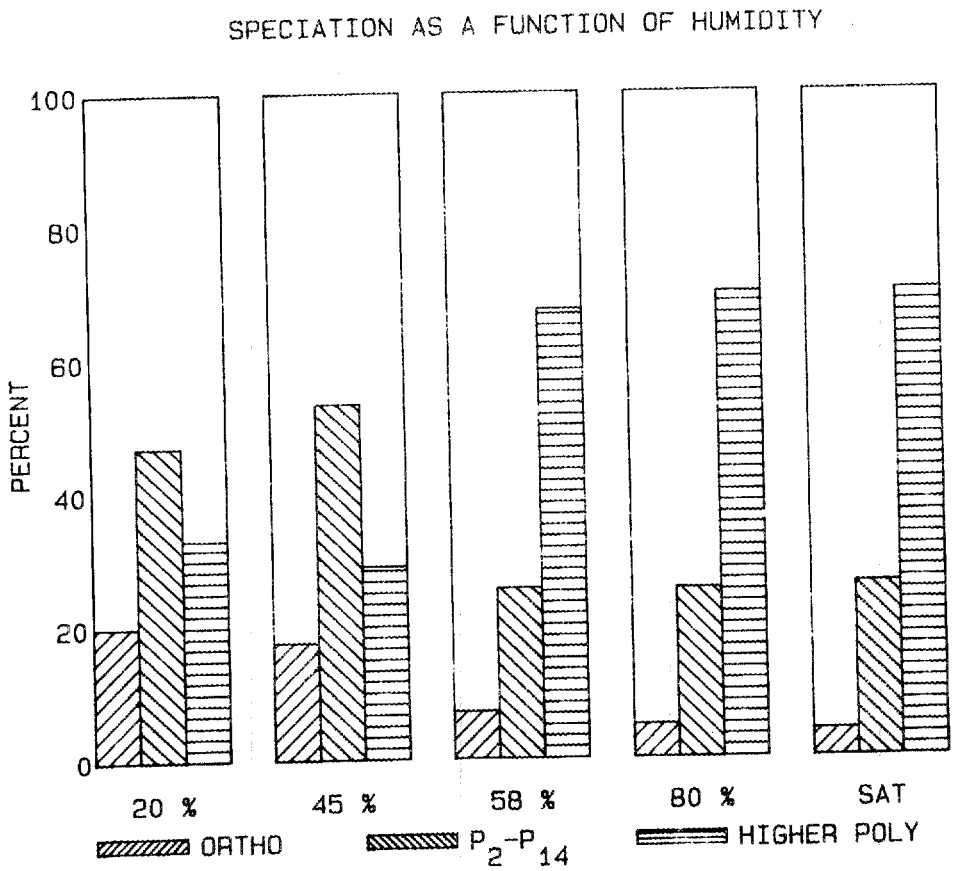


Figure 5. Concentration of Phosphoric Acid Polymers in RPBR Aerosol as a Function of Humidity. Concentrations of o-Phosphorus Acid, Linear Polymers From P2 to P14 and Higher Polymers are Shown.

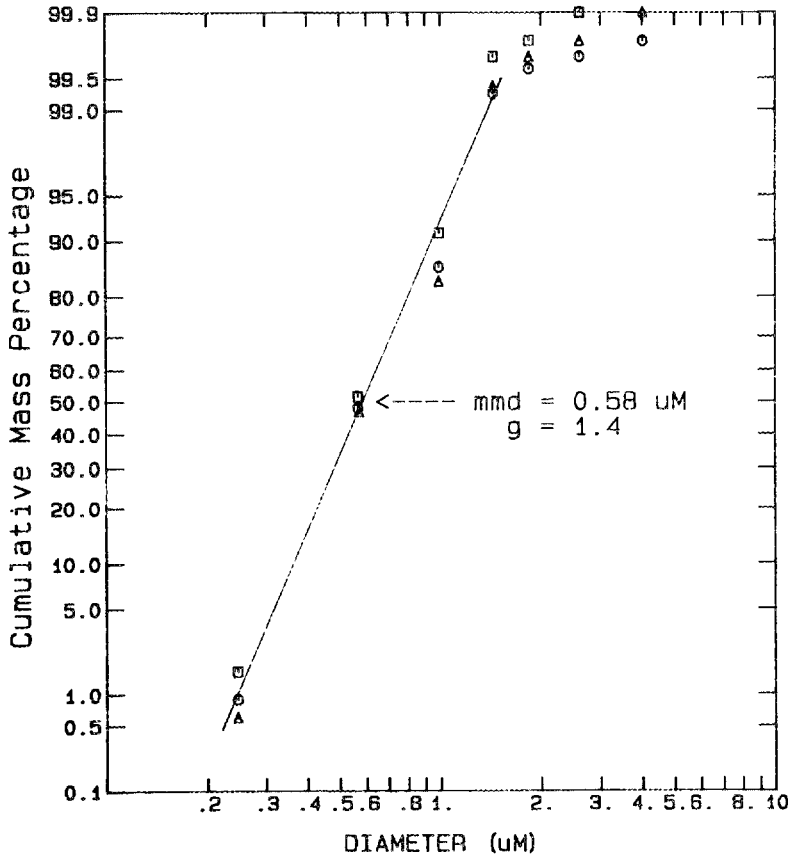


Figure 6. Analysis of RPBR Aerosol Particle Size Distribution From Cascade Impactor Data. Included are Three Determinations Plotted on Logarithmic Probability Coordinates. Aerosol Concentration = 1.8 mg/L; Relative Humidity = 48%; Air Flow 200 L/min.

three velocities were collected at an approximate aerosol concentration of 2 mg/L. The relative humidity in the chamber was 45 percent and the total air flow was maintained at 250 L/min.

The contributions of the various phosphate species toward the total amount of phosphate determined in each sample are given in Table 6 and shown graphically for orthophosphate through P_{12} in Figure 7. The data show that lower quantities of higher polymeric species were formed as the air velocity was increased across the burn site. The concentration of orthophosphate was also slightly elevated at the fastest burn velocity. No appreciable differences were observed in particle size distribution (see Figure 8) and no differences were found in the burn efficiencies since the percent total phosphate remained the same.

RPBR aerosol samples collected at chamber concentrations ranging from approximately 1 mg/L to 8 mg/L were analyzed to determine the effects of concentration on the physical and chemical composition. Data were obtained from different sets of analyses conducted at various times. The results for phosphate speciation indicated that there are no major compositional differences, with only minor variations in the contributions of each species. The results for three different concentrations are shown in Table 6.

The most pronounced change in the aerosol occurred as it was allowed to age. Under usual exposure conditions, the aerosol is formed, then swept into and out of the chamber so that the residence time of the particles is only a few minutes. This dynamic system is used to maintain uniform and reproducible conditions for the biological exposures. In the field, however, the smoke cloud may persist for longer times, particularly in calm weather conditions. To determine the changes that occur with time, a separate study was conducted. The RPBR aerosol was generated continuosly and delivered to the chamber until steady state conditions were reached as evidenced by the light scattering monitors. Samples were collected at this time and arbitrarily designated 'unaged'. The chamber was then sealed at both entrance and exit and samples were periodically taken. For completeness and to emphasize the time dependent changes, the experiment was continued for two hours even though it seemed unlikely that field aerosols would persist that long. Duplicate experiments were performed. The aerosol was generated with incoming relative humidity of 30 percent and an air velocity across the burn of 250 m/min. An aerosol mass concentration of 1.8 mg/L was measured before the chamber was sealed.

Chromatographic profiles of the unaged and 120 min aged aerosol are shown in Figure 9. Generally, the concentrations of orthophosphate and straight chain polymers from P_2 through P_{13} increase with time, while the higher polymers almost completely disappeared. These changes again reflect the rapid rate of depolymerization in the highly acidic aerosol. To further examine the hydrolytic process, pad samples from an unaged aerosol were extracted in water rather than NaCl/EDTA solution which inhibits the depolymerization. The aerosol from which samples were collected for analysis was generated under conditions similar to those used in the aging study. Following extraction, the samples were analyzed every 24 hrs up to 72 hrs. It was determined that hydrolysis is much slower in a dilute solution than in the

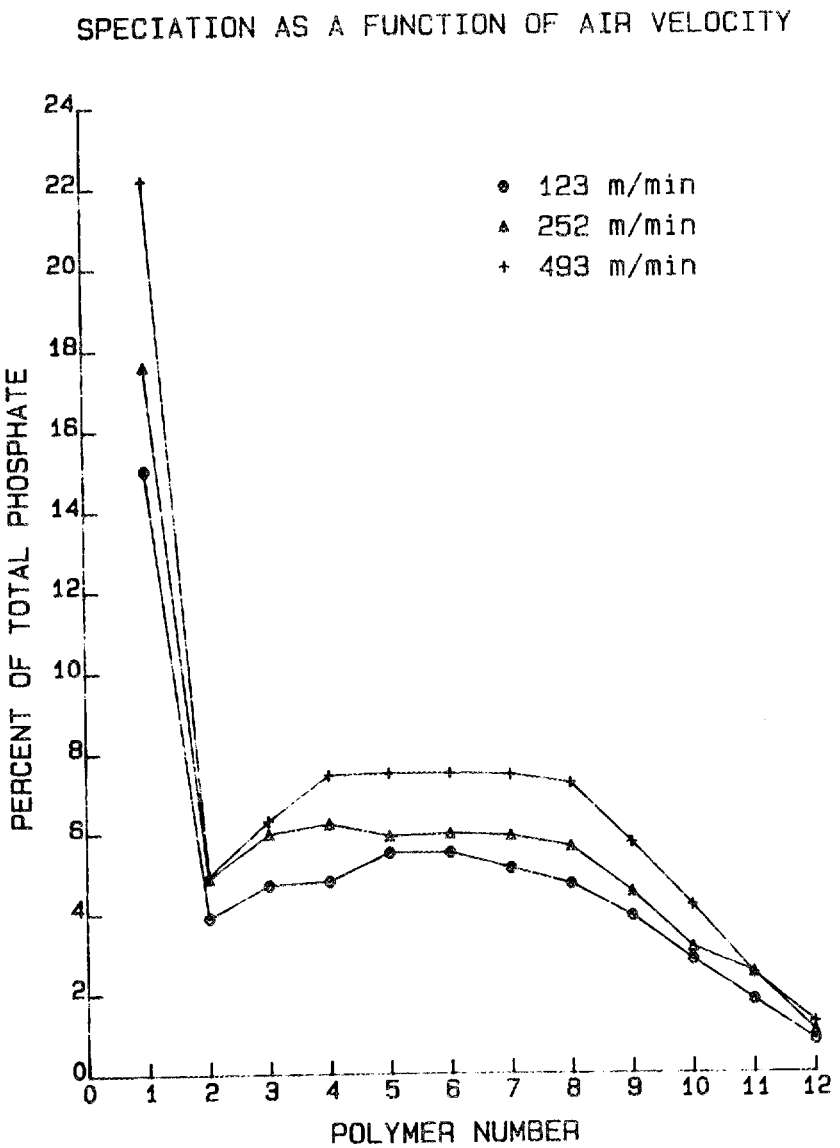


Figure 7. Effect of Air Velocity Across Burning RPBR on Phosphoric Acid Polymer Speciation.

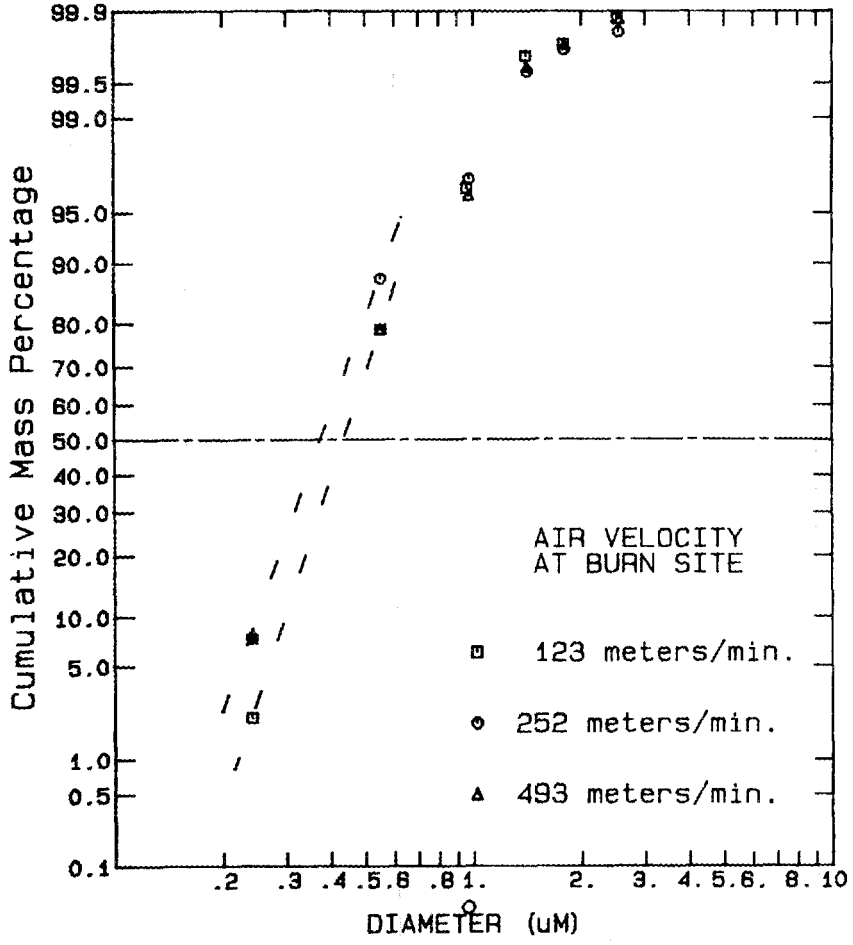


Figure 8. Effect of Air Velocity Across Burning RPBR on Particle Size Distribution.

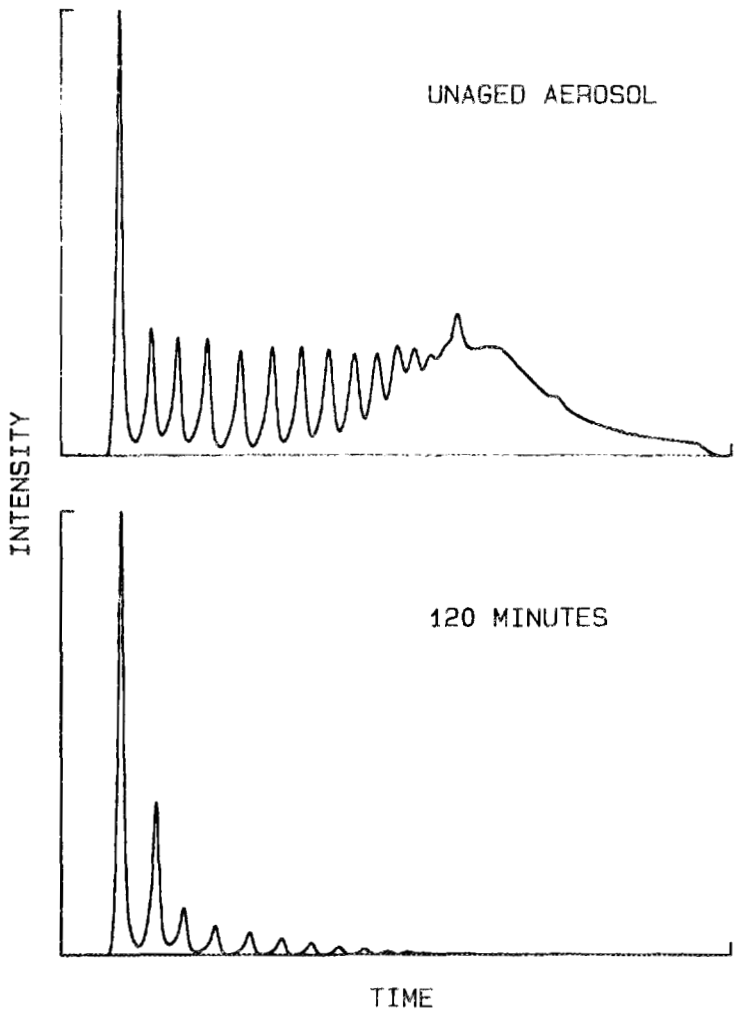


Figure 9. Comparison of Phosphoric Acid Polymer Concentrations in Fresh and Aged RPBR Aerosol.

TABLE 7. COMPOSITION OF THE PHOSPHORIC ACIDS IN PHOSPHORUS SMOKES AS A FUNCTION OF AEROSOL AGE AND SAMPLE ANALYSIS TIME

Parameter Under Investigation	Generation Conditions			Composition (%)							
	Air Velocity (m/min)	% Relative Humidity	Aerosol Concentration (mg PO_4^{-3}/L)	ortho-Phosphate	pyro-Phosphate	tripoly-Phosphate	tetrapoly-Phosphate	P_5-P_{13}	Higher Polyphosphates	tetrameta-Phosphate	trimeta-Phosphate
Aerosol Age	252	30	1.5								
Unaged				9.5	3.6	3.9	4.5	24.3	53.3	—	--
30 min				16.6	7.0	3.4	3.0	12.1	57.9	--	--
60 min				31.6	14.0	5.5	4.7	15.2	29.0	—	--
120 min				49.0	22.1	7.2	5.4	13.9	2.4	--	--
Hydrolysis (Sample Analysis Time)	252	30	1.5								
4 hrs				10.0	3.5	3.8	4.9	27.2	49.5	0.7	0.4
24 hrs				12.0	4.8	6.5	9.8	42.3	16.5	0.9	7.2
48 hrs				15.2	6.5	9.8	13.9	36.3	—	1.4	16.9
72 hrs				16.8	7.5	12.3	16.2	26.2	--	2.3	18.7

concentrated aerosol particles. The concentration of long and branched chain polymers was found to decrease, but the concentration of trimeta- and tetrametaphosphate increased. The level of orthophosphate also increased, but only slightly. The results are reported in Table 7, and profiles of an aged aerosol sample and hydrolyzed sample (i.e., aerosol extracts in water) are shown in Figure 10 for comparative purposes.

The particle size growth with time is tabulated in Table 8 where mass median diameters and geometric standard deviations taken from logarithmic probability plots of cascade impactor data are shown. Diameters increase from about 0.4 μm initially to 1.65 μm after two hours. Such growth patterns are typical of concentrated aerosols and are usually considered to be the result of Brownian coagulation mechanisms. Note also the gradual decrease in aerosol concentration that was particularly evident on long standing. It is probable that this represents losses due to migration to the chamber walls and settling, rather than chamber leaks.

TABLE 8. RPBR MASS MEDIAN PARTICLE SIZE AS A FUNCTION OF AEROSOL AGE

Age min[a]	Mass Median Particle Size μm	μg[b]	Aerosol Mass Concentration (mg/L)
Turret[c]	.38	1.4	
0	.37	1.5	1.81
0	.41	1.4	1.84
5	.95	1.3	1.69
18	1.15	1.3	1.69
29	1.35	1.3	1.62
30	1.40	1.4	1.65
60	1.55	1.3	1.05
120	1.65	1.4	.54

[a]Time after generator stopped and chamber sealed
[b]geometric standard deviation
[c]Sample collected in the turret section of the exposure chamber

COMPARISON OF RPBR AND WPF UNDER FREE BURNING CONDITIONS

In this section we discuss chemical similarities and differences encountered in the smokes when RPBR and WPF formulations are burned under free burning conditions. The primary purpose was to compare the combustion products of the two formulations when burned under similar conditions. In the work discussed so far in this report, RPBR was burned in a strong air flow for delivery into chambers for toxicology testing. No such generator was available for WPF. Hence, a simpler system for burning these materials was devised so that they could be compared as burned under similar conditions. The device is diagrammed in Figure 11. Pellets of the materials were placed on a bed of clean

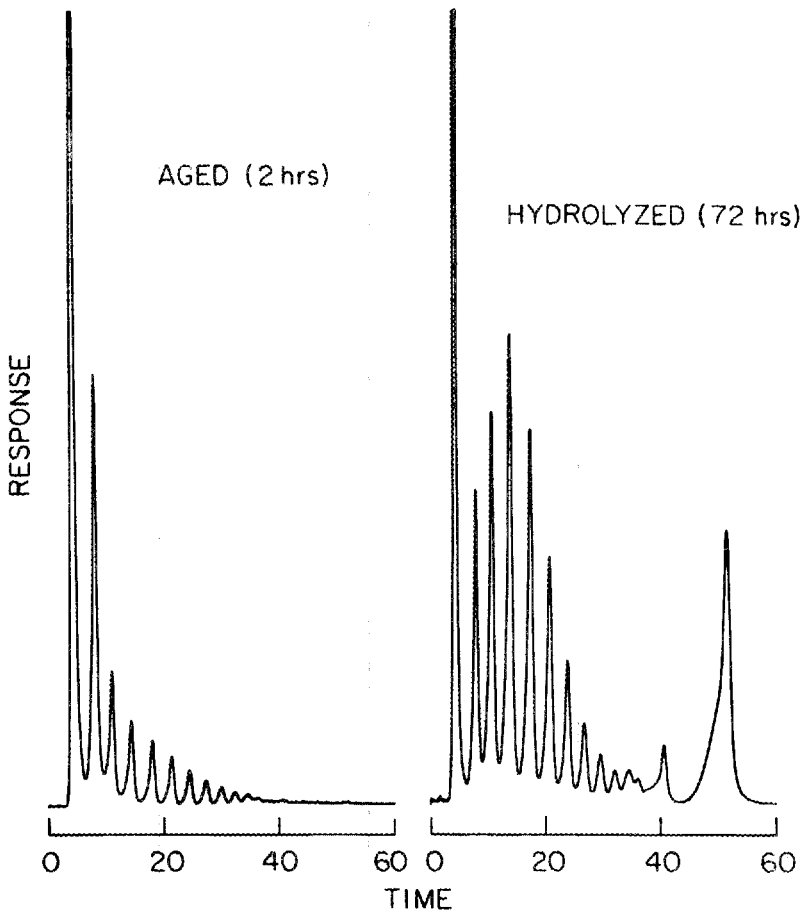
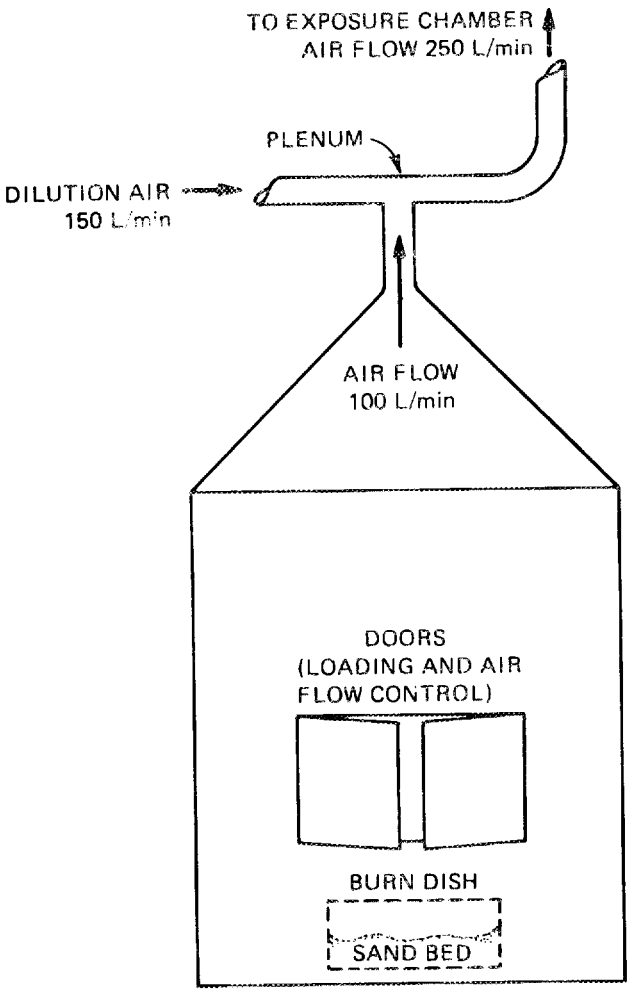


Figure 10. Comparison of Phosphoric Acid Polymers in Aged RPBR Aerosol and a Hydrolyzed RPBR Aerosol Sample.



STATIC BURN CHAMBER

Figure 11. Static Burn Chamber.

sand in a canopy chamber, the pellets were ignited and the aerosol carried to the exposure chamber for sampling. The canopy chamber was designed so that excess air was always available, but so that direct drafts across the material were minimized. The air entering the canopy chamber was controlled by a window located just above the burning zone. To help regulate the aerosol concentration, dilution air was added through a plenum in the line leading to the sampling chamber. Much of the phosphorus from a munition detonation burns on the ground under conditions which are simulated by this apparatus. Particles of RPBR were used as received. The WPF was cut under water into similarly sized pieces (ca. 0.5 g). The concentration of smoke in the sampling chamber was controlled with the aid of on-line aerosol concentration monitors. As the burning of one fragment subsided, another was manually added. As expected, the smoke concentration fluctuated as is shown in Figure 12. For the WPF, the aerosol concentrations ranged from 2 to 8 mg/L and for the RPBR 2 to 6 mg/L. Typically, the WPF burned more vigorously than the RPBR. The combustion was never complete. At the end of a run there was a considerable amount of charred and unburned residue that contained some elemental phosphorus.

The smokes generated from the free-burning conditions were analyzed to define their physical and chemical properties for qualitative and quantitative comparisons of the various constituents present in the smokes. A series of analyses including phosphate speciation, volatile organics, and particle size distribution were conducted on experimental burns performed under nearly identical conditions. These generation parameters are given in Table 9.

TABLE 9. GENERATION CONDITIONS FOR FREE-BURNING RPBR AND WPF

Average concentration:	2.5 mg/L for RPBR and 2.9 mg/L for WP-F
Relative humidity:	40 percent
Air flow through burn chamber:	100 L/min
Dilution air flow:	150 L/min
Chamber temperature:	21°C

Figure 13 shows the results obtained for the phosphate speciation. The profiles were very similar with regard to the number of compounds detected and their concentration levels. Contributions for individual phosphates are given in Table 10. The slightly elevated concentrations of the higher polymeric forms (beyond P_5) in the RPBR may reflect the differences in burn temperature and rate of burning. Overall, however, the results of burning the RPBR and WPF were very similar. The highest polymeric phosphate found was P_{11}, and none of the complex cyclic compounds were seen when either RPBR or WPF were burned under these conditions. This is in distinct contrast to the results obtained with RPBR as generated from the continuous generator. Further experimental work would be necessary to begin to understand the causes of this interesting difference.

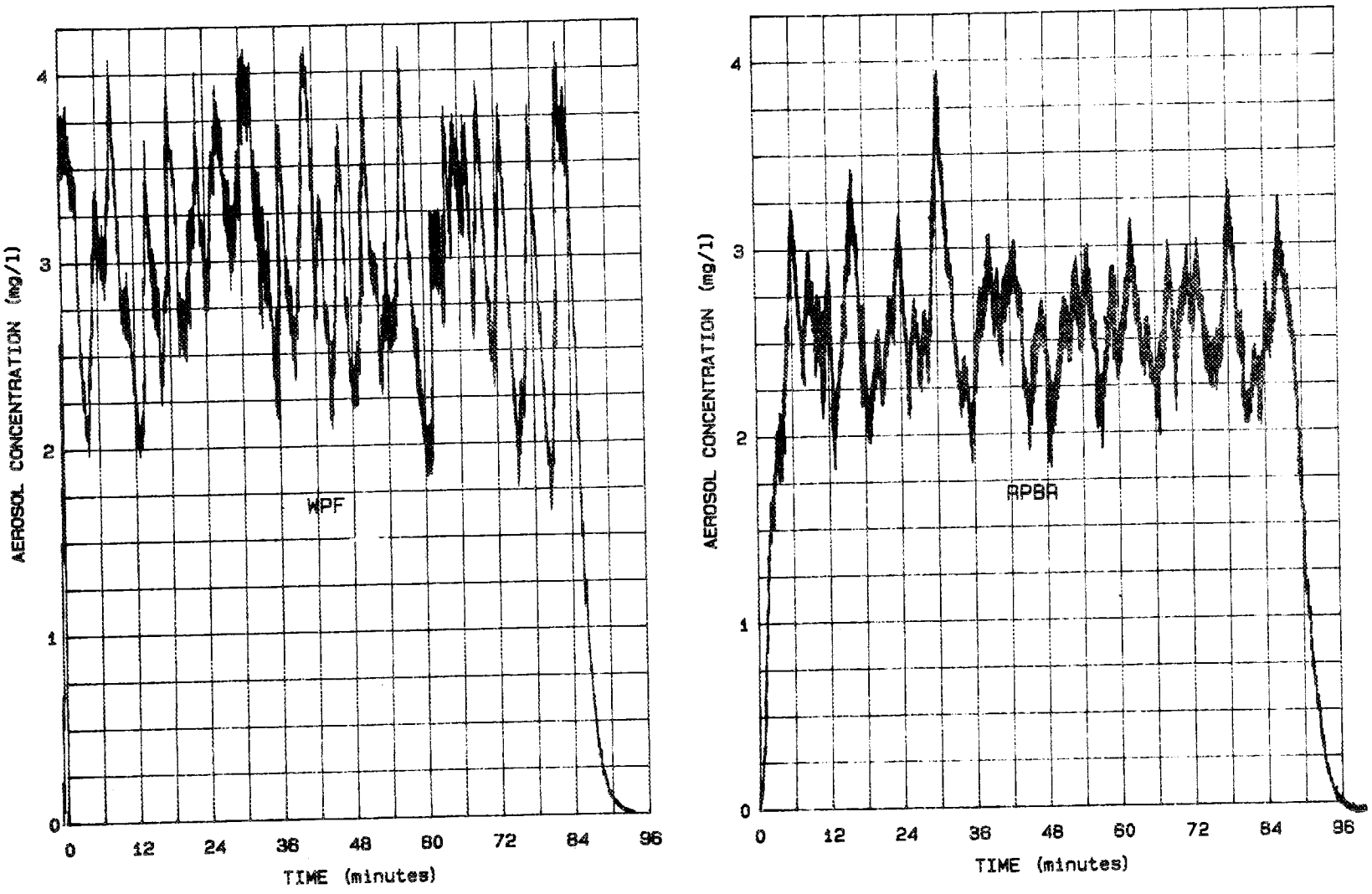


Figure 12. Time Dependent Aerosol Concentrations From RPBR and WPF as Produced in the Free Burn System.

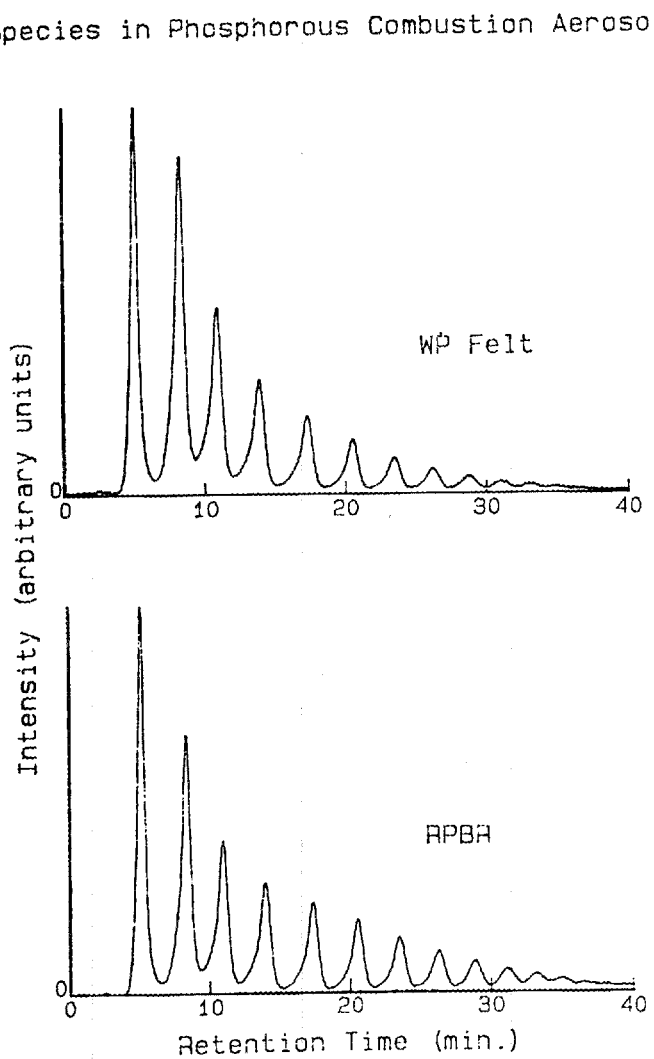


Figure 13. Phosphoric Acid Polymer Concentrations From WPF and RPBR Aerosols Under Static Burning Conditions.

TABLE 10. COMPOSITION OF THE PHOSPHORIC ACIDS IN PHOSPHORUS SMOKES PRODUCED FROM STATICALLY BURNED RPBR AND WPF

	RPBR	WPF
	Composition in Percent	
Orthophosphate	22.8	23.8
Pyrophosphate	19.6	26.6
Tripolyphosphate	13.3	16.3
Tetrapolyphosphate	11.5	11.3
P_5-P_{13}	32.8	22.0
Higher Polyphosphates	low	low

A gas chromatographic search for volatile organics and organophosphates was carried out by direct injection of 0.5 mL gas samples collected from the smoke filled chamber. No organic compounds were seen using FID with the exception of a small peak eluting within one minute of the start of the analysis in both the RPBR and WPF samples. The concentration of this peak was less than 5 ppm (calculated as pentane) and is likely a low molecular weight hydrocarbon such as methane or ethane. Similarly, chromatographic profiles using NPD detection showed no major peaks. A compound eluting from the column at 29 min was seen but proved to be an artifact. It outgassed from unused gas sampling bags. When the WPF volatiles were examined at much higher sensitivity, a trace of phosphine (approximately 1 ppm) and elemental phosphorus was seen. No standards were available for elemental phosphorus, but the concentration was estimated to be in the low ppb range. The identity as P_4 was confirmed by comparison of the retention time with that found in the nitrogen headspace over WPF. A mass spectrographic analysis of a gas sample drawn from the chamber and condensed in a U-tube placed in a liquid nitrogen bath, also detected P_4. Neither P_4 nor phosphine were detected in the gas phase of RPBR aerosols.

Duplicate particle size determinations were made for each of the formulations. Results are shown in Figure 14 for the RPBR and WPF. There was little difference between the two smokes with the mass median particle diameter for each being just below 1 μm.

To detect non-chromatographable organic compounds and establish an upper limit to the organic content of the particulate phase, TOC analyses were conducted. For RPBR, at an aerosol concentration of 3.5 mg/L (2.9 mg/L as H_3PO_4), total organic carbon (TOC) was 27 μg/g H_3PO_4. For WPF, at an aerosol concentration of 5.0 mg/L (4.2 mg/L as H_3PO_4), a signficantly higher value of 415 μg TOC/g H_3PO_4 was found. This higher level was expected since the WPF contains a higher percentage of organic material.

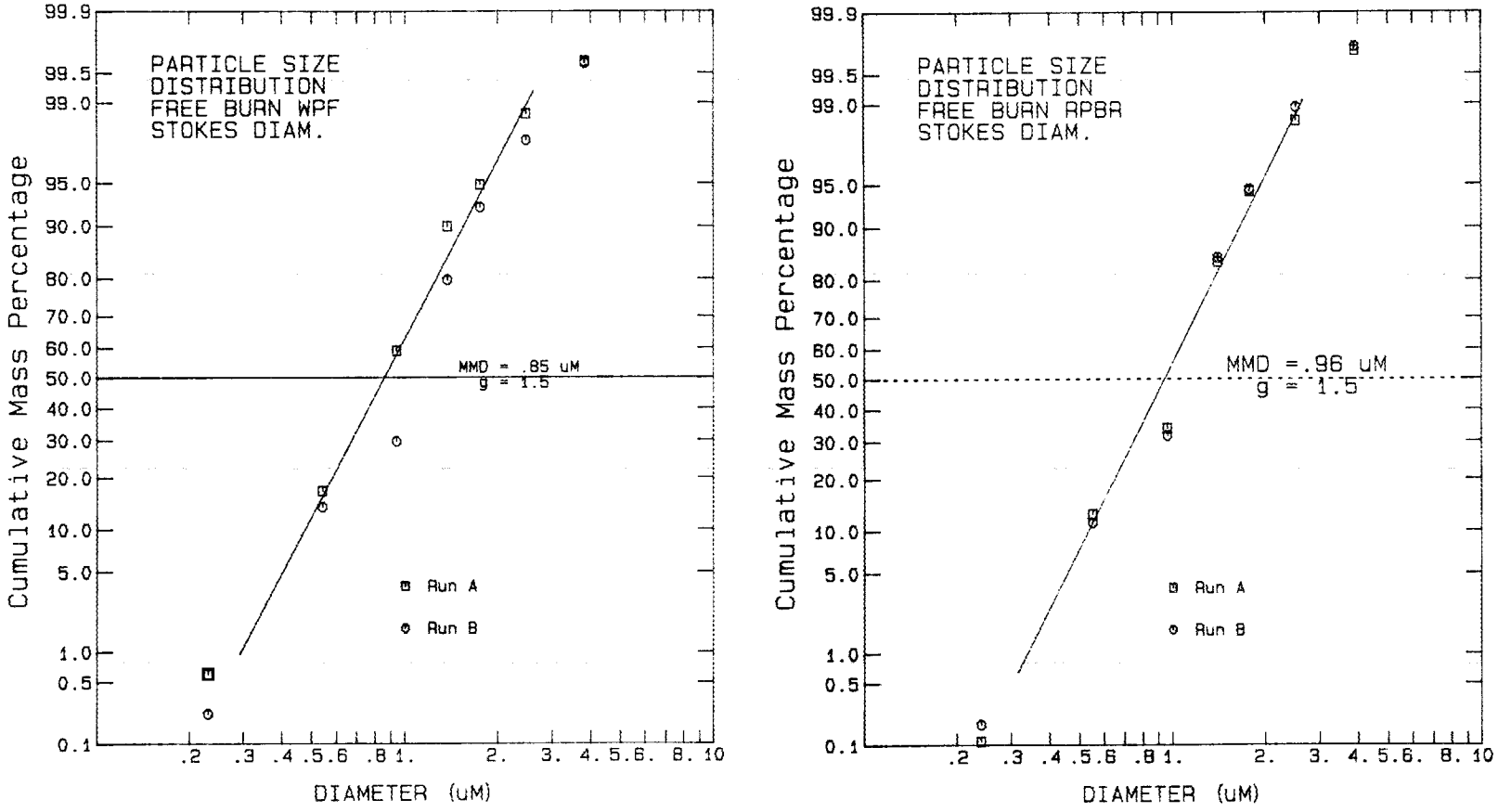


Figure 14. Aerosol Particle Size Distribution in Free Burn of RPBR and WPF.

Analyses for CO and CO_2 were made at an average aerosol concentration of 3.2 mg/L for the RPBR (corresponding to 2.4 mg of H_3PO_4/ μL) and 3.5 mg/L for the WPF (corresponding to 2.2 mg of H_3PO_4/L). The results were as follows:

	CO_2 mL/mg H_3PO_4	CO_2 ppm (v/v)	CO ppm (v/v)
RPBR	0.05	120	4-8
WPF	0.11	250	26

The CO_2 concentrations were obtained by subtracting the ambient air levels. CO was monitored continuously in the chamber, and the values reported represent the average concentration during the burns. It was noted that as the WPF aerosol concentration fluctuated the CO levels decreased or increased correspondingly. For the RPBR burns the CO levels did not vary with the aerosol concentration but increased as additional fuel was added and decreased as the rate of combustion increased. Overall the levels for CO_2 and CO indicate that most of the organic material is completely oxidized. The CO concentrations are sufficiently low that they are not expected to pose any exposure hazard.

Smoke produced from statically burned red phosphorus containing no butyl rubber was also analyzed to allow comparisons with the aerosols produced from WPF and the RPBR formulation burned under similar conditions and using the extrusion generator. These analyses were conducted to determine the effects, if any, of the butyl rubber on the combustion products and physical properties of the smoke. The powdered RP was first pressed into small pellets to facilitate handling. These pellets were then burned in the manner described for free-burning RPBR. Chamber conditions were as follows: 51 percent relative humidity, 252 m/min air velocity, and 2 mg/L aerosol concentration. Samples were collected and analyzed for total phosphate concentration, particle size distributions, and phosphoric acid species. Since the vapor phase organic content in RPBR smoke was previously found to be very low in concentration, no additional samples were collected for this analysis.

Particle size distribution, determined by cascade impaction, appeared to be log normal with a mass median diameter just below 1 μm. A comparison of RPBR, WPF and red phosphorus free burns is shown in Table 11.

The HPLC profiles for the phosphoric acids were similar to those obtained for RPBR generator produced smokes. Orthophosphate contributed approximately 13 percent to the total phosphate concentration, P_2 through P_{12} - 54 percent, and higher polymers - 33 percent. This differs from the WPF and RPBR free burns where the higher polymers in

the unresolved envelope were not present. The absence of higher polymeric forms, however, may be a reflection of the chamber humidity rather than the nature of the material being combusted. Samples from free-burning RPBR and WPF were collected at lower humidities which influence the acidity of individual particles and accelerates depolymerization of long chained phosphates. Overall there were no major compositional differences and the profiles obtained were as expected.

TABLE 11. PARTICLE SIZE DISTRIBUTION FOR FREE BURN CONDITIONS

	Mass Median Diameter µm	Geometric Std. Dev.
RPBR	.95	1.6
WPF	.85	1.6
Red Phosphorus	.7	1.6

In summary the chemical character of the aerosols formed from burning RPBR and WPF are very similar. In both, particles are primarily concentrated phosphoric acid, present as a complex mixture of polymeric forms. The distribution of these polymers is very similar when RPBR and WPF are burned under similar conditions. Significant differences in polymer distribution were seen when aerosols were formed from RPBR under free-burning and extrusion-burning conditions.

The organic constituents of the raw materials are, for the most part, completely burned. Organic compounds constitute only a minor fraction of the aerosol particles. For example, the total organic content of the aerosol from WPF was ca. 400 µg/g H_3PO_4 and was ca. 15 times less in RPBR. The difference is parallel to the organic content of the starting material.

Aerosol particle size was found to be larger with the free burning of both RPBR and WPF than with generator-produced RPBR aerosol. This is thought to be due to the delay time (aging) in transfer of the aerosol from the free-burn chamber to the exposure chamber where the measurements were made. Even so, the particle diameters remain below 1 µm and are well within the respirable range.

LITERATURE CITED

1. Jameson, R. F., J. Chem. Soc., 752-759 (1959).

2. Holmberg, R. W. and J. H. Moneyhun, "A System for the Continuous Generation of Phosphorus Aerosol of Red Phosphorus-Butyl Rubber," Proceedings, Smoke/Obscurants Symposium VI, Adelphi, MD, April 27-29, 1984, pp. 767-775.

3. Holmberg, R. W., J. H. Moneyhun and T. M. Gayle, "A System for the Continuous Generation of Phosphorus Aerosol from Red Phosphorus Butyl Rubber," Oak Ridge National Laboratory, Oak Ridge, TN, Final Report (to be issued), U. S. Army Project Order 0027 (in preparation).

4. Hildebrand, W. F. and G. E. F. Lundell, in Applied Inorganic Analysis, 2nd Ed., John Wiley and Sons, Inc., New York, 1953, pp. 703-704.

5. Gayle, T. M., C. E. Higgins and J. R. Stokely, "A Cigarette Smoke Monitoring Device for Continuous Animal Exposure Systems," in Tobacco Smoke Inhalation Bioassay Chemistry, Guerin, Stokely, Higgins, Eds., ORNL-5424, Oak Ridge National Laboratory, Oak Ridge, TN, 1979, pp. 63-74.

6. Jenkins, R. A., R. W. Holmberg, J. S. Wike, J. H. Moneyhun and R. S. Brazell, "Chemical Characterization and Toxicologic Evaluation of Airborne Mixtures: Chemical and Physical Characterization of Diesel Fuel Smoke," ORNL/TM-9196, Oak Ridge National Laboratory, Oak Ridge, TN, 1983, AD A 142718.

7. Horton, A. D. and M. R. Guerin, J. Assoc. Off. Anal. Chem. 57, 1-7 (1974).

8. NIOSH, Summary of NIOSH Recommendations for Occupational Health Standards, Department of Health, Education and Welfare. Center for Disease Control, Robert A. Taft Laboratories, Cincinnati, OH, October 1978.

9. Van Wazer, J. R., in Phosphorus and Its Compounds, Vol. 1, Interscience Publications, Inc., New York, 1958, p. 485.

10. Marple, V. A. and Y. H. Liu, "Characteristics of Laminar Jet Impactors," Environ. Sci. and Techn. 8, 648 (1974).

11. Hirai, Y., N. Yoza and S. Ohashi, Anal. Chim. Acta 115, 269 (1980).

PERSONNEL

The following personnel received support from the U. S. Army Medical Research and Development Command under Army Project Order No. 9600 in performance of the work described in this report:

R. S. Brazell
R. W. Holmberg
J. H. Moneyhun
D. D. Pair

PUBLICATIONS

The following publications resulted from the work described in this report:

Brazell, R. S., R. W. Holmberg and J. H. Moneyhun. 1983. Chemical Characterization of Selected Military Obscurants. Proceedings, 1983 CSL Scientific Conference on Obscuration and Aerosol Research, Chemical Systems Laboratory, Aberdeen Proving Ground, MD, 20-24 June, 1983. R. H. Kahl Proceedings Editor, Aberdeen Proving Ground, MD. (In Press)

Brazell, R. S., R. W. Holmberg and J. H. Moneyhun. 1983. Application of HPLC/Flow Injection Analysis for the Determination of Polyphosphoric Aicds in Phosphorous Smokes. J. of Chromatogr. (In Press)

Holmberg, R. W. and J. H. Moneyhun. 1982. A System for the Continuous Generation of Phosphorous Aerosol from Red Phosphorus-Butyl Rubber. Proceedings, Smoke/Obscurants Symposium VI, Harry Diamond Laboratories, Adelphi, MD, 27-29 April, 1982. OPM Smoke/Obscurants Technical Report DRCPM-SMK-T-001-82 (Vol. II), pp. 767-775.

LIST OF ABBREVIATIONS

AIHA	American Industrial Hygiene Association
CRDC	U. S. Army Chemical Research and Development Center
ECD	Effective cutoff diameter
FIA	Flow injection analysis
FID	Flame ionization detector
GC	Gas chromatography
ICP	Inductively coupled plasma
IITRI	IIT Research Institute
LC	Liquid chromatography
LDC	Laboratory Data Control
MMD	Mass median diameter
MS	Mass spectrometry
NPD	Nitrogen phosphorus detector
OSHA	Occupational Safety and Health Administration
RPBR	Red phosphorous-butyl rubber
THF	Tetrahydrofuran
TOC	Total organic Carbon
TWA	Time weighted average
WPF	White phosphorous-felt

APPENDIX A

[METRIC]

G-92-50
DOD-P-51463(EA)
12 February 1980

MILITARY SPECIFICATION

PHOSPHORUS, RED, OILED, TECHNICAL (METRIC)

This specification is approved for use by US Army Armament Research and Development Command, Department of the Army, and is available for use by all Departments and Agencies of the Department of Defense.

1. SCOPE

1.1 Scope. This specification covers one technical grade of oiled red phosphorus.

2. APPLICABLE DOCUMENTS

2.1 Issues of documents. The following documents of the issue in effect on date of invitation for bids or request for proposal form a part of this specification to the extent specified herein.

SPECIFICATIONS

FEDERAL

NN-P-71 - Pallets, Material Handling, Wood, Stringer Construction, 2-Way and 4-Way (Partial)
VV-L-820 - Lubricating Oil, General Purpose (Light)

MILITARY

MIL-P-211 - Phosphorus, Red, Technical (Metric)
MIL-B-82647 - Bag, Conductive Plastic, Heat-Sealable, Flexible

FSC 1365

: Beneficial comments (recommendations, additions, deletions) and any pertinent data which may be of use in improving this document should be addressed to: Commander, US Army Armament Research and Development Command, ATTN: DRDAR-TSC-S, Aberdeen Proving Ground, MD 21010 by using the self-addressed Standardization Document Improvement Proposal (DD Form 1426) appearing at the end of this document or by letter. :

STANDARDS

MILITARY

MIL-STD-105 - Sampling Procedures and Tables for Inspection by Attributes
MIL-STD-129 - Marking for Shipment and Storage
MIL-STD-147 - Palletized Unit Loads for 40" by 48" Pallets

(Copies of specifications, standards, drawings and publications required by contractors in connection with specific procurement functions should be obtained from the procuring activity or as directed by the contracting officer.)

2.2 Other publications. The following documents form a part of this specification to the extent specified herein. Unless otherwise indicated, the issue in effect on date of invitation for bids or request for proposal shall apply.

CODE OF FEDERAL REGULATIONS (CFR)

49 CFR 171 to 179 - Department of Transportation Hazardous Materials Regulations.

(The Code of Federal Regulations is available from the Superintendent of Documents, US Government Printing Office, Washington, DC 20402. Orders for the above publication should cite "49 CFR 171 to 179.")

AMERICAN SOCIETY FOR TESTING AND MATERIALS (ASTM) STANDARDS

E11 - Wire-Cloth Sieves for Testing Purposes

(Application for copies should be addressed to the American Society for Testing and Materials, 1916 Race Street, Philadelphia, PA 19103.)

(Technical society and technical association specifications and standards are generally available for reference from libraries. They are also distributed among technical groups and using Federal agencies.)

3. REQUIREMENTS

3.1 Composition. Oiled red phosphorus shall consist of red phosphorus conforming to class 3 of MIL-P-211 which has been uniformly coated with lubricating oil conforming to VV-L-820. No other material shall be used in the manufacture of the oiled red phosphorus. The contractor shall certify that this requirement has been met.

3.2 Appearance. Oiled red phosphorus shall be free from foreign matter and visible impurities when tested as specified in 4.2.4.1.

3.3 Chemical and physical characteristics. Oiled red phosphorus shall conform to the chemical and physical characteristics of table I when tested as specified therein.

TABLE I. Chemical and physical characteristics

Characteristic	Percent by weight	Test paragraph
Oil content	1.22 to 1.28	4.2.4.2
Volatile matter, maximum	0.25	4.2.4.3
Particle size: retained on a No. 60 (250 micrometer) sieve, maximum	0.5	4.2.4.4

4. QUALITY ASSURANCE PROVISIONS

4.1 Responsibility for inspection. Unless otherwise specified in the contract, the contractor is responsible for the performance of all inspection requirements as specified herein. Except as otherwise specified in the contract, the contractor may use his own or any other facilities suitable for the performance of the inspection requirements specified herein, unless disapproved by the Government. The Government reserves the right to perform any of the inspections set forth in the specification where such inspections are deemed necessary to assure supplies and services conform to specified requirements.

4.2 Quality conformance inspection.

4.2.1 Lotting. A lot shall consist of the oiled red phosphorus produced by one manufacturer, at one plant, from the same materials, and under essentially the same manufacturing conditions provided the operation is continuous. No more than one lot of red phosphorus and one lot of lubricating oil shall be used to produce the lot of oiled red phosphorus. In the event the process is a batch operation, each batch shall constitute a lot (see 6.3).

4.2.2 Sampling.

4.2.2.1 For examination of packaging. Sampling shall be conducted in accordance with MIL-STD-105.

4.2.2.2 For test. Sampling shall be conducted in accordance with table II. A representative specimen of approximately 50 grams (g) shall be removed from each sample container and placed in a suitable clean, dry container labeled to identify the lot and container from which it was taken.

TABLE II. Sampling for test

Number of containers in batch or lot	Number of sample containers
2 to 25	2
26 to 150	3
151 to 1,200	5
1,201 to 7,000	8
7,001 to 20,000	10
Over 20,000	20

4.2.3 Inspection procedure.

4.2.3.1 For examination of packaging. The sample unit shall be one filled shipping container ready for shipment. Sample shipping containers shall be examined for the following defects using an AQL of 2.5 percent defective:

(a) Contents per container not as specified
(b) Container not as specified
(c) Container closure not as specified
(d) Container damaged or leaking
(e) Bag liner missing or not as specified
(f) Marking incorrect, missing, or illegible
(g) Evidence of oiled red phosphorus on bag liner exterior
(h) Unitization not as specified (when required)

4.2.3.2 For test. Each sample specimen taken in 4.2.2.2 shall be tested as specified in 4.2.4. Failure of any test by any specimen shall be cause for rejection of the lot represented.

4.2.4 Tests. Reagent grade chemicals shall be used throughout the tests. Where applicable, blank determinations shall be run and corrections applied where significant. Tests shall be conducted as follows:

4.2.4.1 Appearance. Visually examine the specimen for evidence of foreign matter and impurities.

4.2.4.2 Oil content. Weigh to the nearest milligram approximately 5 g of the specimen into a 100-milliliter (ml) beaker. Add 50 ml of methylene chloride and stir for 30 minutes with a mechanical stirrer. Filter through a double thickness of 12.5-centimeter Whatman No. 42 or equal filter paper

into a clean, tared, glass evaporating dish. Wash with 50 ml of methylene chloride. Place the evaporating dish containing the methylene chloride and oil on a steam bath and evaporate to approximately 3 ml of solution. Remove the remaining methylene chloride in an air stream. Dry off traces of outside moisture, cool, and weigh. Calculate the percent by weight oil content as follows:

$$\text{Percent oil} = \frac{100\ (A - B)}{W}$$

where: A = Weight of dish and residue in grams,
B = Weight of dish in grams, and
W = Weight of specimen in grams.

4.2.4.3 Volatile matter. Heat a flat-bottomed glass or aluminum dish with a loosely fitting cover in a hot water bath for at least 30 minutes. Cool the dish and cover in a desiccator for 30 minutes and weigh them together. Immediately transfer 5 g of specimen to the dish, cover it, and accurately weigh. Place the dish, with cover removed, in a vacuum desiccator over freshly activated silica gel and maintain a substantial vacuum for 24 hours. Release the vacuum slowly and pass the incoming air through a suitable drying vessel filled with activated silica gel. Replace the dish cover and weigh. Calculate the percent by weight volatile matter as follows:

$$\text{Percent volatile matter} = \frac{100\ (A - B)}{(A - C)}$$

where: A = Weight of dish, cover, and specimen before evaporation, in grams,
B = Weight of dish, cover, and specimen after evaporation in grams, and
C = Weight of empty dish and cover in grams.

4.2.4.4 Particle size. Transfer 10 g of specimen onto a tared No. 60 sieve conforming to ASTM E11. Tap the sieve over a sheet of white paper until no significant amount of material passes through the sieve. Add an additional 10 g of specimen and repeat the sieving procedure. Brush any remaining residue on the sieve with a 25-millimeter varnish brush until no material passes through the sieve. Weigh the sieve and material retained on it. Calculate the percent by weight material retained on the sieve as follows:

$$\text{Percent retained on sieve} = \frac{100\ (A - B)}{W}$$

where: A = Weight of sieve and material retained in grams,
B = Weight of sieve in grams, and
W = Total weight of specimen in grams.

5. PACKAGING

5.1 Packing, level D. A quantity of 27.20 ± 0.25 kilograms of oiled red phosphorus shall be packed in a removable-head, gasketed-head steel drum which provides moisture resistance and is furnished with an electrically conductive, close-fitting bag liner. The drum shall conform to Department of Transportation (DOT) Specification 6A or 6B. The bag shall conform to MIL-B-22847 and shall be formed from film having a minimum thickness of 0.7620 millimeter. The bag shall be closed by tying or knotting. There shall be no evidence of red phosphorus on the exterior of the bag. The drum shall be closed in accordance with DOT regulations.

5.2 Unitization. When specified (see 6.2), shipping containers shall be palletized in accordance with the applicable requirements of MIL-STD-147. Pallets shall conform to type IV of NN-P-71. A horizontal strap shall be applied to each tier and tie-down straps parallel to the 1.016-meter dimension only of the pallet shall be used. When specified (see 6.2), the pallet and any wood storage aids shall be treated with a wood preservative as specified in NN-P-71.

5.3 Marking. Each container shall be marked in accordance with MIL-STD-129 and DOT regulations and shall bear the special prominent marking: "When emptying, clamp the bag to the bare inner surface of the drum and make good electrical connection to ground."

6. NOTES

6.1 Intended use. Oiled red phosphorus is intended for use as an ingredient in smoke compositions.

6.2 Ordering data. Procurement documents should specify the following:

(a) Title, number, and date of this specification.
(b) If unitization and wood preservative are required (see 5.2).

6.3 Batch. A batch is defined as that quantity of material which has been manufactured by some unit chemical process or subjected to some physical mixing operation intended to make the final product substantially uniform.

6.4 Significant places. For the purpose of determining conformance with this specification, an observed or calculated value should be rounded off "to the nearest unit" in the last right-hand place of figures used in expressing the limiting value, in accordance with the rounding-off method of ASTM E29.

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Project No. 1355-A065

U.S. GOVERNMENT PRINTING OFFICE 1969 — 603-121/1491

APPENDIX B

TOTAL PHOSPHATE AND PHOSPHORUS SPECIATION

Sampling

Samples were drawn directly from the exposure chamber with a vacuum pump onto 47 mm glass fiber filter pads. Following collection, the samples were immediately extracted by placing the pads in 100 mL of 0.22 M NaCl containing 5 mM Na_4 EDTA. The pads remained in solution for a minimum of 2 hours prior to analysis to assure maximum recovery. Samples placed in NaCl/EDTA preserved the polyphosphate species for a minimum of 72 hours at room temperature.

Reagents

All chemicals were reagent grade and were used as received. Pyrophosphate, trimetaphosphate, tripolyphosphate, and tetrapolyphosphate were purchased from Sigma Chemical Co. (St. Louis, MO). Sodium tetrametaphosphate was donated by E. J. Griffith (Monsanto, St. Louis, MO). Orthophosphate standards were prepared from sodium hydrogen phosphate purchased from the Office of Standard Reference Materials, National Bureau of Standards (Washington, DC). All standards were prepared in 0.22 M NaCl containing 5 mM Na_4 EDTA.

The reagent used in the flow injection system for the determination of phosphates was a 5 to 1 mixture of 5.7×10^{-3} M ammonium molybdate, $(NH_4)_6 Mo_7O_{24} \cdot 4H_2O$, in 1.8 M H_2SO_4 and 0.05 M L-ascorbic acid containing 5 percent (v/v) acetone. The ascorbic acid partially reduces the Mo(VI) to Mo(V). The Mo(V)-Mo(VI) complex combines with orthophosphate to form the heteropolyblue complex.

Flow Injection Analysis

The flow injection system was adapted from Hirai, et al.,[11] with a few modifications. An Eldex Model E-120-S pump (Menlo Park, CA) delivers the molybdenum reagent at a flow of 0.5 mL/min. Samples for total phosphate analysis are introduced into the reagent stream with a Rheodyne Model 7125 6-port injection valve equipped with a 20 µL sampling loop. The sample and reagent react in a 10 m PTFE coil heated to 140°C. This coil is wrapped around a 2 in. O.D. x 6 in. glass pipe which is then wrapped with electrical heating tape. The temperature is controlled with a Barber Coleman Model 520 Solid State Controller. At 140°C the hydrolysis of the polyphosphate species to orthophosphate is 95 percent or greater. The reacted sample passes through a 1 m coil cooled by chilled water before flowing through an Altex Model 153 UV detector (8 µL volume, 10 mm path). Absorption of the phosphate complex is measured at 660 nm. Although the maximum absorption of the heteropoly blue complex is at 820 nm, the sensitivity was satisfactory at the lower wavelength, thus eliminating the need to make costly modifications on the fixed wavelength detector. A 10 m backpressure

coil attached to the exit of the detector prevents anomalous responses due to bubble formation caused by heating the reaction coil.

Total phosphate determinations could be made at a rate of 25 samples per hour. The relative standard deviation for replicate injections was less than 1 percent and the linear range was from 1.5 to 105 ppm.

Chromatographic Separations of Condensed Phosphates

A Spectra Physics 8700 solvent delivery system was used for programming and delivering the solvent at a constant flow of 1 mL/min through the analytical column. Samples were injected with a Rheodyne 7125 6 port injection valve with a 50 μL sample loop onto a Vydac SC anion guard column (4 cm x 4 mm I.D., Varian, Palo Alto, CA). The polyphosphates were separated on an Aminex A-27 8 percent crosslinked quaternary ammonium anion exchange column (30 cm x 4 mm I.D., BioRad, Richmond, CA) using NaCl solutions (pH 10) containing 5 mM Na_4 EDTA. A linear gradient from 0.28 M NaCl to 0.53 M NaCl over a 40 min time interval was used and the final eluent concentration was held for an additional 15 min. Some analyses were also conducted on an Aminex A-14 column (4 percent crosslinked resin, 30 cm x 7.8 mm I.D., BioRad). In this case, the solvent was programmed from 0.31 M NaCl to 0.53 M NaCl at a linear rate over a 260 min time interval. The effluent from the analytical columns was introduced directly into the stream of reagent used for FIA. A diagram of the complete system is shown in Figure B-1.

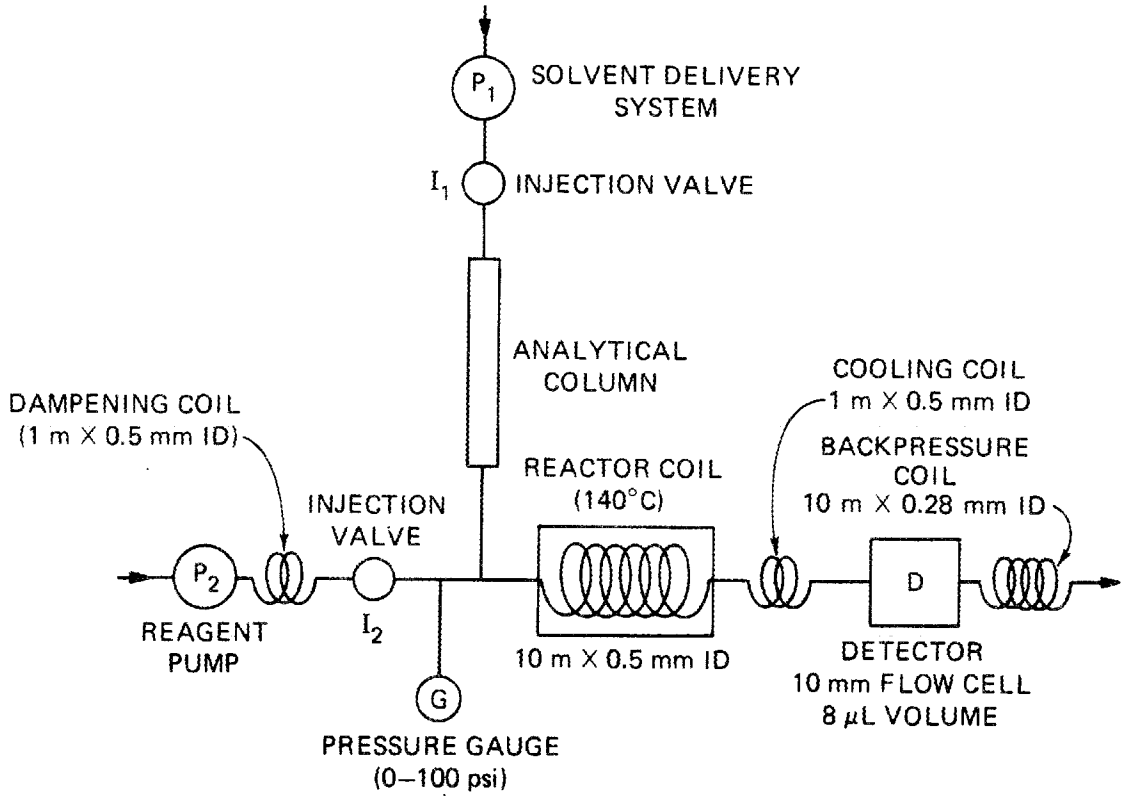

Figure B1. Flow Injection System for Determination of Phosphoric Acid and Phosphoric Acid Polymers.

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