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REDUCED-SMOKE SOLID PROPELLANT COMBUSTION PRODUCTS ANALYSIS

DEVELOPMENT OF A MICROMOTOR COMBUSTOR TECHNIQUE

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OCTOBER 1976

Interim Report for Period 1 February 1976 -
1 July 1976.

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NOTICES

FOREWORD

This report was prepared by the Air Force Rocket Propulsion Laboratory, Edwards AFB, California 93523 under Job Order No. 573010CN and covers the period 1 February to 1 July 1976. The author gratefully acknowledges the support of Lt. Scott Kinkead of the AFRPL Solid Rocket Division, and Thomas W. Owens and Herman H. Martens of the AFRPL Technology Division.

This report has been reviewed by the Information Office/DOZ and is releasable to the National Technical Information Service (NTIS). At NTIS it will be available to the general public, including foreign nations. This report is unclassified and suitable for general public release. This technical report has been reviewed and is approved for publication.

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SECURITY CLASSIFICATION OF THIS PAGE (When Data Entered)

REPORT DOCUMENTATION PAGE

READ INSTRUCTIONS
BEFORE COMPLETING FORM

1. REPORT NUMBER
(14) AFRPL-TR-76-69 ✓

2. GOVT ACCESSION NO.

3. RECIPIENT'S CATALOG NUMBER

4. TITLE (and Subtitle)
(6) REDUCED-SMOKE SOLID PROPELLANT COMBUSTION PRODUCTS ANALYSIS.
Development of a Micromotor Combustor Technique.

5. TYPE OF REPORT & PERIOD COVERED
(9) Interim Report, Feb 76-Jul 76

6. PERFORMING ORG. REPORT NUMBER
1 1

7. AUTHOR(s)
(10) Berge B. Goshgarian

8. CONTRACT OR GRANT NUMBER(s)

9. PERFORMING ORGANIZATION NAME AND ADDRESS
Air Force Rocket propulsion Laboratory/AFSC
Edwards AFB, California 93523

10. PROGRAM ELEMENT, PROJECT, TASK AREA & WORK UNIT NUMBERS
(16) JON 5730 10CN (17) 10

11. CONTROLLING OFFICE NAME AND ADDRESS
(12) 35p.

12. REPORT DATE
(11) Oct[redacted]76 ✓

13. NUMBER OF PAGES
31

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

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)
Micromotor
Solid Propellant
Combustion
Chemical Analysis

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

A low-cost micromotor combustor technique has been devised to support the development of reduced-smoke solid propellant formulations. The technique includes a simple, reusable micromotor capable of high chamber pressures, a combustion products collection system, and procedures for analysis of combustion products. Analytical results for non-condensible combustion products compared favorably with equilibrium calculations. Analysis of solid combustion products revealed that all of the zirconium carbide stability (continued)

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307 720

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additive in the formulation was oxidized to zirconium oxide, however, the graphite additive was not completely oxidized.

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SUMMARY

The development of reduced-smoke solid propellants for the Sidewinder and Maverick missiles has required the addition of acoustic stability additives to the propellant formulation to stabilize combustion. The role of such additives in the combustion process is not thoroughly understood. For this reason the micromotor combustor development program was undertaken to develop a suitable low cost analytical technique to examine the effect of acoustic stability additives on the combustion behavior of reduced-smoke solid propellant formulations. Included were the development of: a simple, reusable micromotor combustor capable of high chamber pressures; a combustion products collection system; and, the techniques for analysis of the combustion products. Identification of all combustion products (solids and gases) was required to determine the effect of various additives on combustion products composition. The micromotor combustor, combustion products collection system, and techniques for analyzing combustion products were successfully developed and demonstrated. Results for non-condensible combustion products compared favorably with equilibrium calculations. Analysis of solid combustion products revealed that all of the zirconium carbide stability additive in the formulation was oxidized to zirconium oxide; however, the graphite additive was not completely oxidized.

Future plans utilizing the micromotor combustor technique include complete analysis of all combustion products from propellant formulations containing different concentrations as well as different types of additives. The data generated will be used to provide guidelines for selecting specific propellant additives to optimize motor performance and stability.

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SECTION I
INTRODUCTION

A thorough evaluation of the combustion behavior of experimental solid propellant involves the use of numerous test techniques. Consequently, it is advantageous to design techniques involving only small quantities of propellant to reduce the cost of propellant ingredients required.

The Rohm and Haas Company (1) developed a 10-gram micromotor for ballistic evaluation of novel propellants. Results obtained from many firings demonstrated that reliable precise ballistic data could be obtained if proper experimental techniques were used.

The behavior of aluminum particles at the surface of burning composite propellants was studied by the Lockheed Propulsion Company (2). Their test techniques included high-speed microcinematography, microscopic observation of extinguished propellant surfaces and of quenched particles collected near the burning surface, and size distribution measurements of collected particles. Their data was used to obtain a better understanding of the behavior of aluminum particles during propellant combustion.

The T-Burner apparatus is a useful technique developed to study unsteady burning of solid propellants. An excellent summary of recent work is presented by Culick (3). The T-Burner has been used to measure response of burning solid propellant to sinusoidal oscillations in the near flow field. It has also been useful for qualitative testing to screen propellants in development work and to compare behavior of different batches of the same propellant. The T-Burner is a successful technique both for application to research and for motor design and development.

At the AFRPL, solid propellant combustion gas analyses have involved both field sampling [(4)] and laboratory scale micromotor combustor [(5)] techniques. The field sampling technique involved the collection of combustion gases during firing of a solid propellant cartridge used to start aircraft engines. Combustion gases were collected in glass cylinders for subsequent analysis in the laboratory. Significant levels of toxic gases were found which were not predicted from theoretical equilibrium calculations. Combustion of small solid propellant grains in the laboratory scale micromotor, with subsequent analysis of the gaseous products, was conducted to study the behavior of hydrogen chloride in controlled atmosphere chambers. Continuous loss of hydrogen chloride from the gas composition occurred, caused by gas-phase reactions forming solids, and reactions with, or absorption on, chamber walls.

This micromotor study was undertaken to develop a suitable low cost analytical technique to examine the effects of acoustic stability additives on the behavior of reduced-smoke propellant formulations during combustion. Included were the development of a simple, reusable micromotor combustor capable of producing chamber pressures to 1500 psi, and the development of gas chromatographic, mass spectrometric, molecular beam mass spectrometric, X-ray, and image analyzer techniques for the detailed analysis of solid propellant combustion products.

SECTION II

EXPERIMENTAL

MICROMOTOR

The micromotor was fabricated from one-inch stainless steel bar stock and Swagelok tube connectors. An exploded view of the motor is shown in Figure 1. Propellant grains bonded to a 0.75" OD phenolic liner were inserted into the motor. Stainless steel spacers were used behind the grains to compensate for variable grain length. A 0.25" OD x 0.125" ID tube welded above and to the side of the propellant surface was used as a port to measure pressure and for overpressure relief. Pressure measurements were made using a 0-3000 psi pressure gauge. Burst discs (2500 psi burst) were fabricated from 0.002" stainless steel shim stock.

The igniter tube was positioned so that the flame from the burning igniter grain impinged on the center of the propellant sample. The igniter consisted of a small piece of propellant grain placed on a nichrome wire filament. Ignition of the propellant grain was achieved by momentarily heating the wire by means of a 15VAC input. The igniter flame then ignited the propellant surface.

The removable nozzle was machined from stainless steel, with the throat diameter sized to provide chamber pressures from 200 to 1000 psi. The entrance angle was machined to provide smooth flow from the combustion chamber to the throat. A polyethylene sheet disc (0.002") was inserted between the nozzle exit and a ball valve fitting to permit

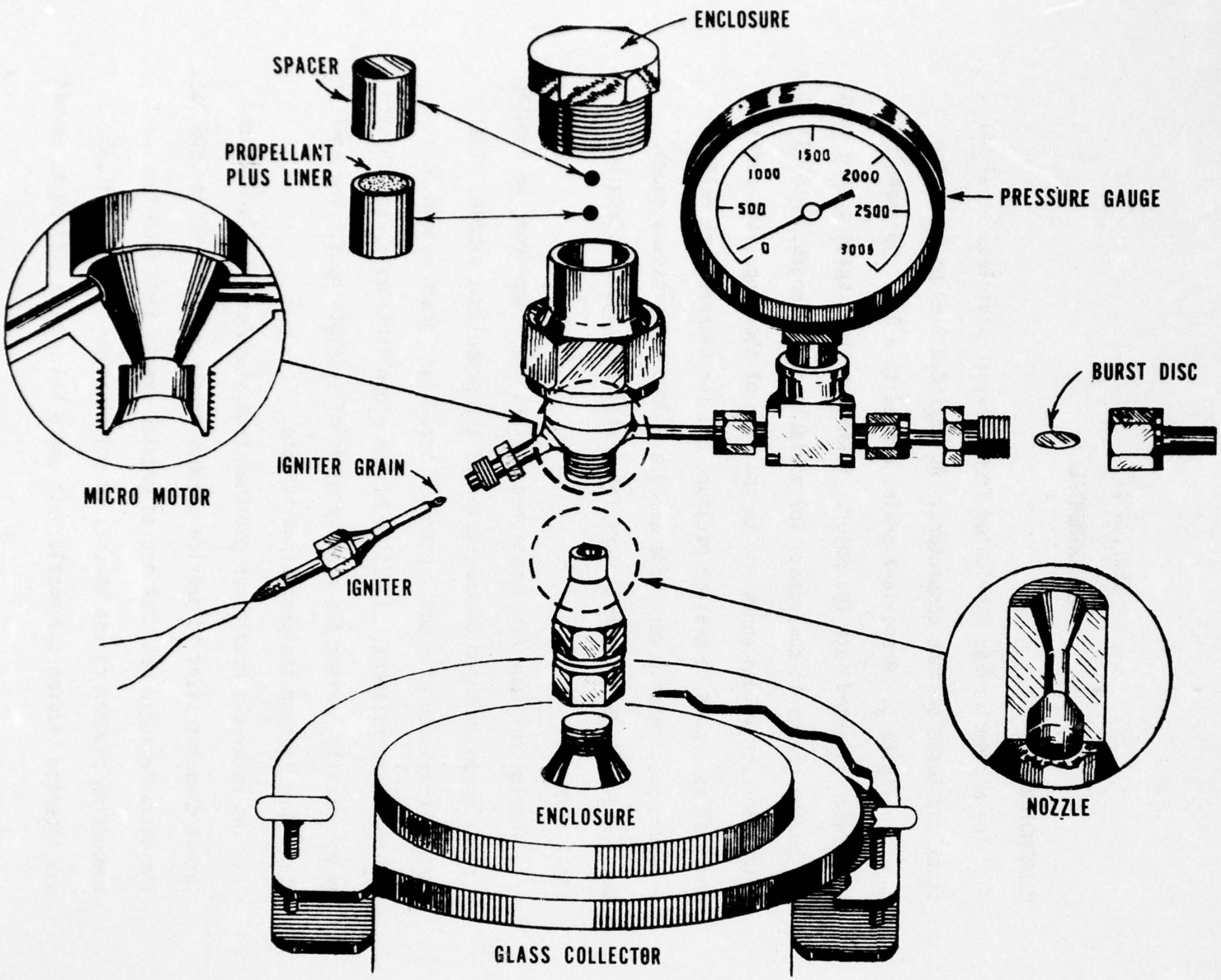

Figure 1. Micromotor and Collector

ignition of the propellant grain while the collection cylinder was under vacuum.

Propellant samples were prepared by coring 0.625" diameter grains from one inch thick slabs of solid propellant. The 6.5 gram grains were bonded to 0.625" ID x 0.750" OD x 0.750" to 1.5" long phenolic liners, using a mixture of hydroxy terminated polybutadiene (HTPB) prepolymer and isocyanate curing agent. The samples were placed in an inert atmosphere oven at 60^{o}C for one week to facilitate polymerization of the bonding mixture. The ends of the propellant samples were trimmed even with the ends of the phenolic liner before insertion into the motor. Stainless steel 0.750" diameter spacers were used in the motor behind the propellant grain to compensate for grains of varying lengths as well as to properly align the propellant surface with the igniter tube.
The HTPB propellant formulation used in this study contained the following ingredients:

Ingredient	Percent By Weight
Binder	12.5%
Ammonium Perchlorate	85.0%
Zirconium Carbide	0.5%
Graphite	1.0%
Aluminum Oxide	0.5%
Ferric Fluoride	0.5%

PRODUCT COLLECTION

Two types of collection cylinders were used to collect all combustion products. A glass cylinder was made from a high pressure 4-liter glass reaction kettle and a Teflon enclosure. An O-ring between the enclosure and cylinder was compressed by means of "U" clamps to provide a leak-tight seal. The enclosure contained a 0.375" ball valve for attaching the motor to the collector, a compound pressure measuring gauge, and a valved outlet for sample removal. A Teflon sheet was placed at the bottom of the glass cylinder to prevent chipping of the glass by any large particles emanating from the motor during combustion. A 4-liter stainless steel collection cylinder containing inlet and outlet components similar to those on the glass cylinders was used whenever recovery of solid combustion products was not required.

A polyethylene sheet (0.002") disc was inserted between the fittings of the motor nozzle and the ball valve on top of the collection cylinder, and the fittings were tightened. The sample cylinder was then evacuated to less than 200 microns and leak-tested before each test. The collection cylinder was immersed in a $-15^{o}C$ ice-alcohol bath prior to ignition. Upon ignition, the expanding combustion gases burst the polyethylene disc and were collected in the evacuated cylinder. Immediately after combustion, the ball valve was closed and the collection cylinder, in the cold bath, was taken to the laboratory for gas analysis.

MASS SPECTROMETRY

A DuPont Model 21-490 analytical mass spectrometer was used to analyze the non-condensible combustion gases. Samples at known pressures were expanded to a reservoir in the instrument inlet manifold and then introduced to the ion source through a gold foil leak. Ionizing electron energy was maintained at 70ev in the 200°C heated ion source. At least four complete spectra were obtained per sample introduced and six gas samples were taken from each combustion gas collection cylinder. The data was obtained as peak intensity counts at a specific mass per unit charge. The counts were then divided by sensitivity values obtained from standard gas mixture data to obtain actual gas composition in the combustion gas collection cylinder.

The molecular beam mass spectrometer apparatus has been previously described (6). Combustion gases were analyzed as they exited from the nozzle during combustion. Data was continually recorded for H_2O, $CO+N_2$, CO_2 while spectra of all gases present were recorded every 0.5 second. Longer propellant grains were used for these tests to obtain adequate data.

GAS CHROMATOGRAPHY

A Beckman Instrument Model GC-M gas chromatograph was also used to analyze the non-condensible combustion gases. Instrument parameters were:

Detector:	Thermal Conductivity 300μa
Column:	20' x 1/8" OD Chromosorb 102
Flowrate:	15cc/min Helium

Column Temp:	Room Temperature (Normally 25°C)
Output:	HP3380A Integrator with output in area and area percent
Gas Inlet:	Barocell vacuum gauge and gas sampling valve with 0.5ml loop volume

Calibration gas standard mixtures and combustion gas samples were run under identical conditions. Samples were introduced via the gas-tight valve at pressures between 300-400 mm. Five combustion gas samples were analyzed per test, together with four calibration gas standards. Combustion gas peak area data were converted to concentration using amount-per-area sensitivity values obtained from the calibration gas values.

Both the mass spectrometer and gas chromatograph were calibrated prior to, during, and after analyzing combustion gas with standard gas mixture prepared by partial pressure measurement of the pure gases. The calibration gas mixtures included H_2, CO, N_2, CO_2, O_2, and CH_4. Sensitivity values derived from the analysis of the calibration gases were applied to the combustion gas analysis to obtain quantitative data.

SOLIDS ANALYSIS

The solid combustion products were collected in the glass collection cylinder during combustion. They were then removed with methyl alcohol rinses, separated from the alcohol, dried, weighed, and submitted for particle size distribution and X-ray analysis.

The particle size distributions were performed on a Bausch & Lomb Model QMS Image Analyzer. Between 11,000 to 22,000 particles were measured automatically.

The X-ray analyses were performed by use of a Diano Model XRD 710 X-ray spectrometer equipped with both diffraction and emission capabilities. Emission was used to identify elements present in the solid combustion products, while identification of crystalline material was made by X-ray diffraction. Spectra were compared with reference spectra to identify elements and compounds present in the solid combustion products.

SECTION III

RESULTS

MICROMOTOR

Once initial problems were corrected, reliable firings were routinely made. One problem was rapid burning down the propellant-liner interface in advance of surface regression which resulted in rapid pressure rise with subsequent burst disc rupture. This was prevented by adequate bonding of the phenolic liner with the propellant grain. Another problem encountered in one test was the loss of the aft motor closure immediately upon propellant ignition. This was caused by a rapid pressure increase due to an improperly formulated and uncured propellant grain. Physical inspection and simple mechanical property determinations were made on subsequent propellant grains prior to liner bonding.

The nozzle throat diameters used in these studies to produce a specific chamber pressure in the micromotor are given in Table 1 and are plotted in Figure 2 as area ratio of burning surface to throat area A_B/A_T vs chamber pressure P_c.

Table 1. MEASURED CHAMBER PRESSURE
VS THROAT DIAMETER

P_c(psi)	Throat Diameter (inches)
200	0.080
350	0.067
500	0.057
600	0.055
800	0.052
1000	0.051

Propellant diameter = 0.625 inches

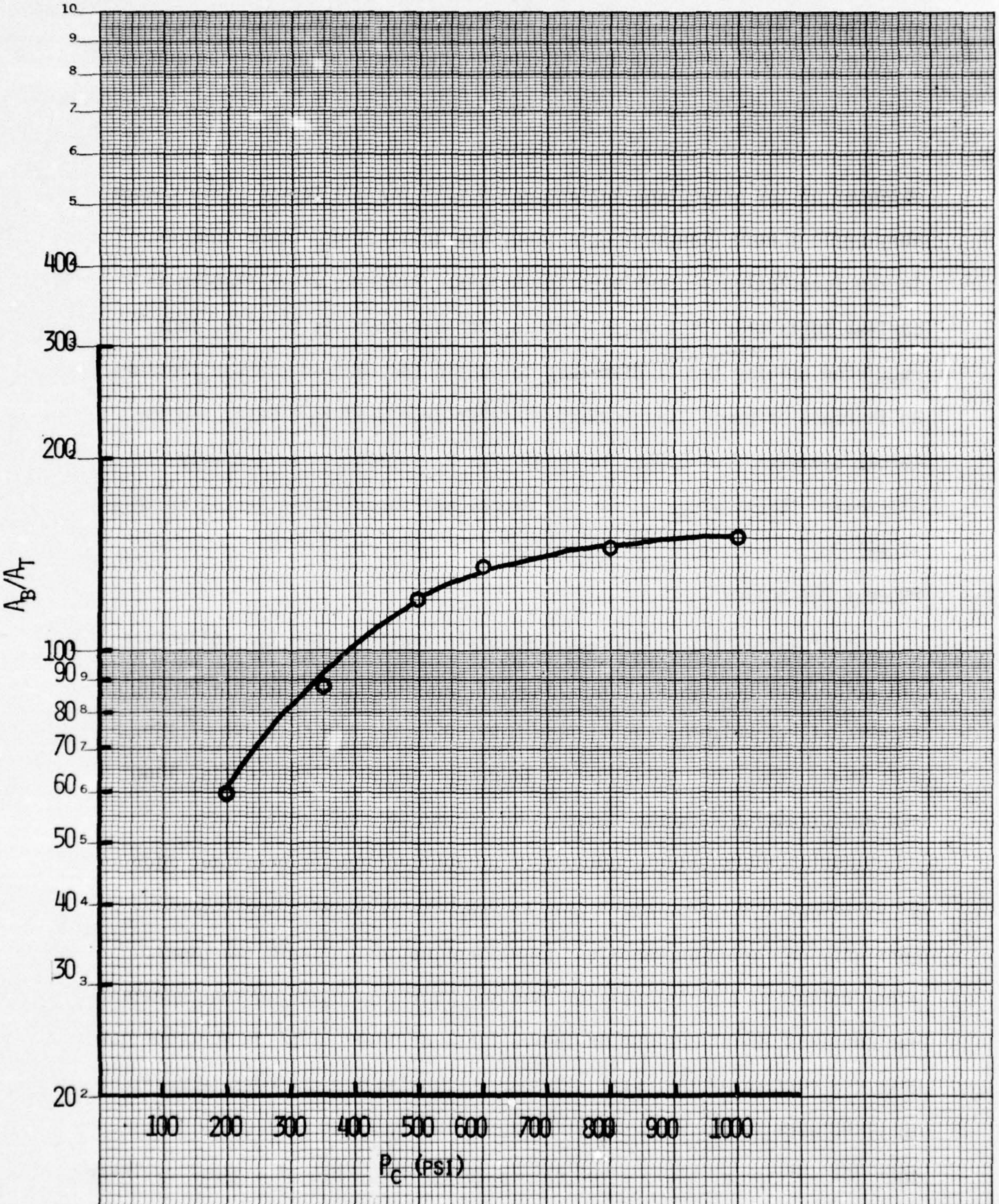

Figure 2. Area Ratio vs Chamber Pressure

Diameter of the propellant surface was 0.625" for all tests. Even though very small throat diameters were used, the 2.5% solids, other than AP, in the formulation did not plug the throat. Plugging was a problem in earlier tests where the propellant surface diameter was smaller, thus, requiring smaller throat diameters to obtain the desired chamber pressure. An increase of propellant surface diameter from 0.5" to 0.625", and the throat diameter from 0.040" to 0.051" for P_C = 1000 psi effectively eliminated throat plugging for the propellant formulations tested in this study.

PRODUCT COLLECTION

Early difficulty with propellant grain ignition when the collection cylinder was under vacuum was eliminated by isolation of the micromotor chamber with a polyethylene disc as previously discussed. Lack of the disc would cause the igniter gases to expand rapidly, thus cooling them and not providing adequate temperature for grain ignition.

Initial tests using a combustion products collection cylinder made of stainless steel and immersed in an ice bath revealed a continuous generation of hydrogen gas after sample collection. Within two hours after collection, an increase of nearly 100% in hydrogen gas concentration was measured, which was due to the reaction of "wet" hydrogen chloride gas with the surface of the metal cylinder. Lowering the cylinder temperature to -15°C with an ice-alcohol bath reduced the hydrogen buildup to less than 10% within two hours after sample collection. Use of a glass cylinder with a Teflon closure completely eliminated this problem. For ease of removing solid combustion products, glass collection cylinders were used when solids as well as gases were to be analyzed. The stainless steel cylinders were used for analysis of non-condensible combustion gases only.

Initial pressure in the 4-liter collection cylinder during combustion of a 6.5 gram propellant grain would rise above one atmosphere, then drop after combustion to approximately 450 mm. The water and most of the hydrogen chloride condensed upon the cold surface of the collection cylinder, thus reducing the pressure of collected gas.

MASS SPECTRAL DATA

To determine if air had leaked into the collection cylinder, the concentration of argon and oxygen in the non-condensible combustion products were first measured by mass spectrometry. If argon was absent, gas chromatographic analysis was then performed.

Table 2 presents combined mass spectra data for seven firings of the same propellant formulation at P_c ranging from 350-1000 psi. The non-condensible gases H_2, CO, N_2, CO_2, and O_2 in the combustion products were expected. The unexpected formation of CH_4 and C_2H_2 may have occurred either before steady state combustion and during tailoff, or because of non-equilibrium combustion.

Replicate analysis of a single firing provides greater precision than the combined replicate analysis of seven firings. Theoretical equilibrium calculations for combustion products show very little change of non-condensible gas composition from 500-1500 psi chamber pressure.

Table 2. MASS SPECTRAL DATA

Reduced-Smoke Propellant

Mole Percent Combustion Gas Composition

	SAMPLE NUMBER								STD DEV	STD DEV
SPECIE	6081	6091	6092	6101	6180	6181	6231	Mean	Seven Tests	One Analysis
H_2	20.6	20.8	20.6	19.9	19.5	19.5	19.7	20.1	0.56	0.28
$CO+N_2$	52.6	53.4	53.3	53.9	52.9	54.4	53.1	53.4	0.61	0.29
CO_2	26.1	25.3	25.6	25.5	27.2	25.7	26.6	26.0	0.68	0.12
O_2	0.26	0.24	0.22	0.22	0.20	0.20	0.30	0.23	0.04	0.05
CH_4	0.18	0.14	0.13	0.25	0.26	0.25	0.13	0.19	0.06	0.01
C_2H_4	0.20	0.12	0.12	0.20	0.15	0.16	0.12	0.15	0.04	0.02
Configuration										
Pc(Psi)	600	500	500	1000	1000	1000	350			
Grain Length (in.)	1	3/4	3/4	3/4	3/4	3/4	3/4			
Collector	Metal	Metal	Metal	Metal	Glass	Glass	Glass			

Therefore, such parameters as variations in propellant formulation, motor test conditions, sampling procedure and instrument calibration and stability could contribute to data variation for combined replicate analysis.

GAS CHROMATOGRAPHIC DATA

Data for non-condensible combustion gas compositions derived from gas chromatographic (GC) data are presented in Table 3. The N_2 and CO peaks were resolved on the Chromosorb 102 column; however, any O_2 present was unresolved from the CO peak. Consequently, the CO concentration derived from the GC data had to be corrected for any O_2 found in the mass spectral analysis.

The precision appears equivalent to that derived from the mass spectral analysis. The advantage of the GC analysis is complete resolution of the N_2 and CO peaks; however, unresolved O_2 would result in a higher calculated concentration for CO. Use of a molecular sieve column would resolve H_2, N_2, O_2, and CO; however, the CO_2 would be absorbed. Therefore, a dual column analysis of the same sample using both molecular sieve and Chromosorb 102 columns would resolve this difficulty.

COMBINED ANALYTICAL DATA

The combined mass spectral and gas chromatographic analytical data for non-condensible combustion gas composition were compared to theoretically predicted equilibrium compositions and are presented in Table 4. The experimentally derived N_2/CO_2 and CO/CO_2 ratios compare

Table 3. GAS CHROMATOGRAPHIC DATA

Reduced-Smoke Propellant

Mole Percent Combustion Gas Composition

	SAMPLE NUMBER								STD DEV	STD DEV
SPECIE	6081	6091	6092	6101	6180	6181	6231	Mean	Seven Tests	One Analysis
H_2	19.9	20.7	20.3	20.0	19.9	19.8	20.0	20.1	0.31	0.11
N_2	21.8	21.4	21.3	21.9	20.0	22.1	22.7	21.6	0.84	0.51
CO	30.7	31.3	31.6	31.3	31.9	31.8	30.0	31.2	0.67	0.27
CO_2	27.3	26.4	26.8	26.7	27.8	26.0	27.2	26.9	0.60	0.34
CH_4	0.11	0.07	0.08	0.20	0.20	0.19	0.07	0.13	0.06	0.03
C_2H_2	0.08	-	-	0.06	0.08	0.05	-	0.06	0.02	0.01
Configuration										
Pc (psi)										
	600	500	500	1000	1000	1000	350			
Grain Length (in.)										
	1	3/4	3/4	3/4	3/4	3/4	3/4			
Collector										
	Metal	Metal	Metal	Metal	Glass	Glass	Glass			

Table 4. COMBINED ANALYTICAL DATA

Reduced-Smoke Propellant

Combustion Gas Composition

Mole Percent Concentration

Specie	Mass Spectral Mean	Gas Chrom Mean	Combined Mean	Theoretical Data
H_2	20.1	20.1	20.1	16.1
N_2	53.4	21.6	21.6	23.2
CO		31.2	31.2	33.2
CO_2	26.0	26.9	26.5	27.6
CH_4	0.19	0.13	0.16	-
C_2H_2	0.15	0.06	0.11	-
O_2	0.23	-	0.23	0.21
Ratio				
CO/CO_2			1.177	1.202
N_2/CO_2			0.815	0.841
H_2/CO_2			0.758	0.583

favorably with those predicted. However, the hydrogen concentration found in the experimental analysis is 23% greater than the amount predicted. The difference may be due to non-equilibrium combustion in the micromotor or reaction of O_2 with other combustion species to reduce the amount of water formed. Because a complete analysis of the combustion products was not performed, a mass balance was not obtained. Therefore, further studies of the combustion products must be performed to resolve the difference in H_2 concentration between experimental and theoretical data.

PRESSURE EFFECT

Some combustion tests resulted in chamber pressures increasing above 1500 psi caused by rapid burning of the propellant between the liner and grain. Combined data for these tests are presented in Table 5.

One obvious difference between tests at high pressure (>1500 psi) and standard pressure (350 psi - 1000 psi) was the increase of CO relative to CO_2. Fifer and Lannon,(7) in their studies of double base propellant combustion also noted an increase of CO relative to CO_2 with increasing reaction pressure. They suggest this is due to the oxidation of formaldehyde and hydrocarbon species. Also, the small decrease in CO_2 with increasing pressure may result from the reaction:

$$C(solid)+CO_2 \longrightarrow 2CO$$

This occurs in the secondary flame zone where solid carbon or graphite particles, expelled from the burning surface by evolving gases, pass through the secondary flame zone and are then oxidized by the reaction with CO_2.

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Table 5. HIGH PRESSURE COMBUSTION GAS CORRELATION

Mole Percent Concentration

Specie	High Pressure (>1500 psi)	Average Pressure (350-1000 psi)	Theoretical (500-1500 psi)
H_2	22.0	20.1	16.1
N_2	20.3	21.6	23.2
CO	33.1	31.2	33.2
CO_2	24.2	26.5	27.6
CH_4	0.16	0.16	-
C_2H_2	-	0.11	-
O_2	0.14	0.23	0.21
Ratio			
CO/CO_2	1.37	1.18	1.20
N_2/CO_2	0.84	0.82	0.84
H_2/CO_2	0.91	0.76	0.58

MOLECULAR BEAM SPECTRAL DATA

The combustion gases from a 1.5" length of burning solid propellant grain were monitored by exhausting them directly into the orifice of the water-cooled sampling cone. Rapid quenching of the gases occurs immediately upon sampling due to rapid expansion of the gases from exhaust pressure to 10^{-4} torr. Further reactions of the combustion products are effectively stopped. Mass spectra of the quenched combustion gases were obtained downstream of the skimmer nozzle which formed a molecular beam of combustion gases. Complete spectra of all gases present were obtained every 0.5 second together with continuous monitoring of the H_2O, $CO + N_2$, and CO_2 species. Data for the combustion gases H_2O, $CO + N_2$, CO_2, HCl, and NO are plotted in Figure 3. Initial chamber pressure for approximately 1.3 seconds after ignition was 500 psi; however, it increased to over 1500 psi before the burst disc ruptured. Apparently the propellant grain contained a void or rapid burning occurred down the side of the propellant. This increase in pressure before rupture can be observed in Figure 3. The continuous increase in combustion gas composition starting at 1.3 seconds after ignition would indicate increased pressure at the sampling orifice. Once the burst disc ruptured, the composition of the combustion gases changed. The most obvious change was the appearance of nitric oxide (NO). The rapid drop in chamber pressure would reduce the temperature of the burning propellant with subsequent decrease in

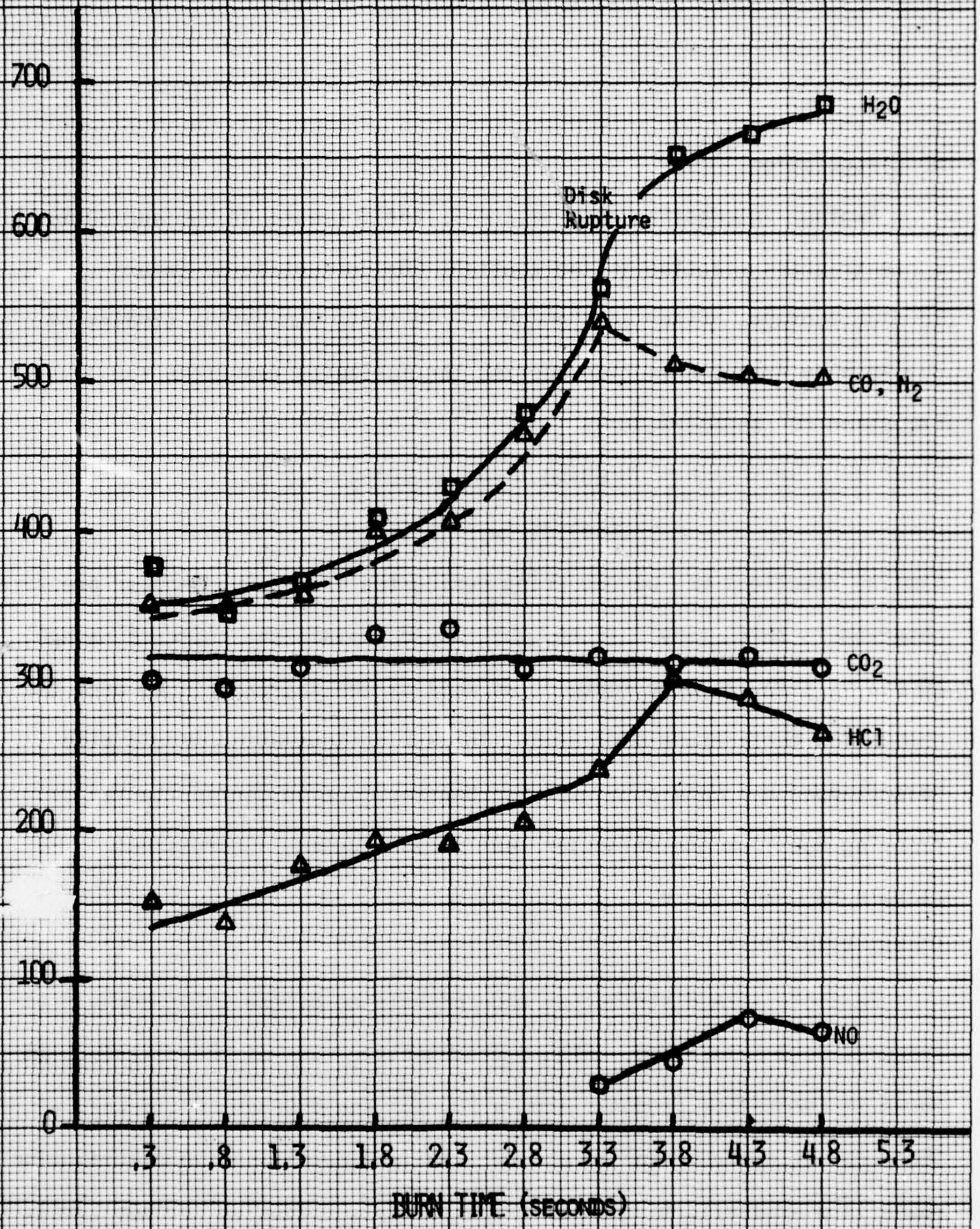

Figure 3. Molecular Beam Mass Spectral Data

NO dissociation (7).

Another interesting observation is the increase of H_2O and $CO+N_2$ concentrations relative to the constant CO_2 concentration prior to disc rupture. Fifer and Lannon (7) in their combustion studies of double base propellants hypothesized the following reactions for increased CO concentrations:

$$HCHO+NO \longrightarrow CO+H_2O+1/2\ N_2$$

$$C(solid)+CO_2 \longrightarrow 2CO$$

Similar reactions may be occurring during the increasing chamber pressure observed in this study. If so, this would explain the increase in H_2O, CO and N_2 prior to disc rupture, as well as the increase in NO once the combustion temperature decreased. The H_2O concentration should also have dropped off upon disc rupture; however, due to difficulty in removing H_2O from the molecular beam vacuum system, a persistent background would occur.

SOLIDS ANALYSIS

Particle size distribution and composition of the solid combustion products were determined. Figure 4 presents curves of the distribution found in combustion products from a 200 psi and 1000 psi Pc firing. These curves are compared to one derived from particle size distribution found in a synthetic mixture of graphite (C_s), zirconium carbide (ZrC), and aluminum oxide (Al_2O_3). The synthetic mixture was a well-mixed sample of the three ingredients in the ratios expected in the propellant

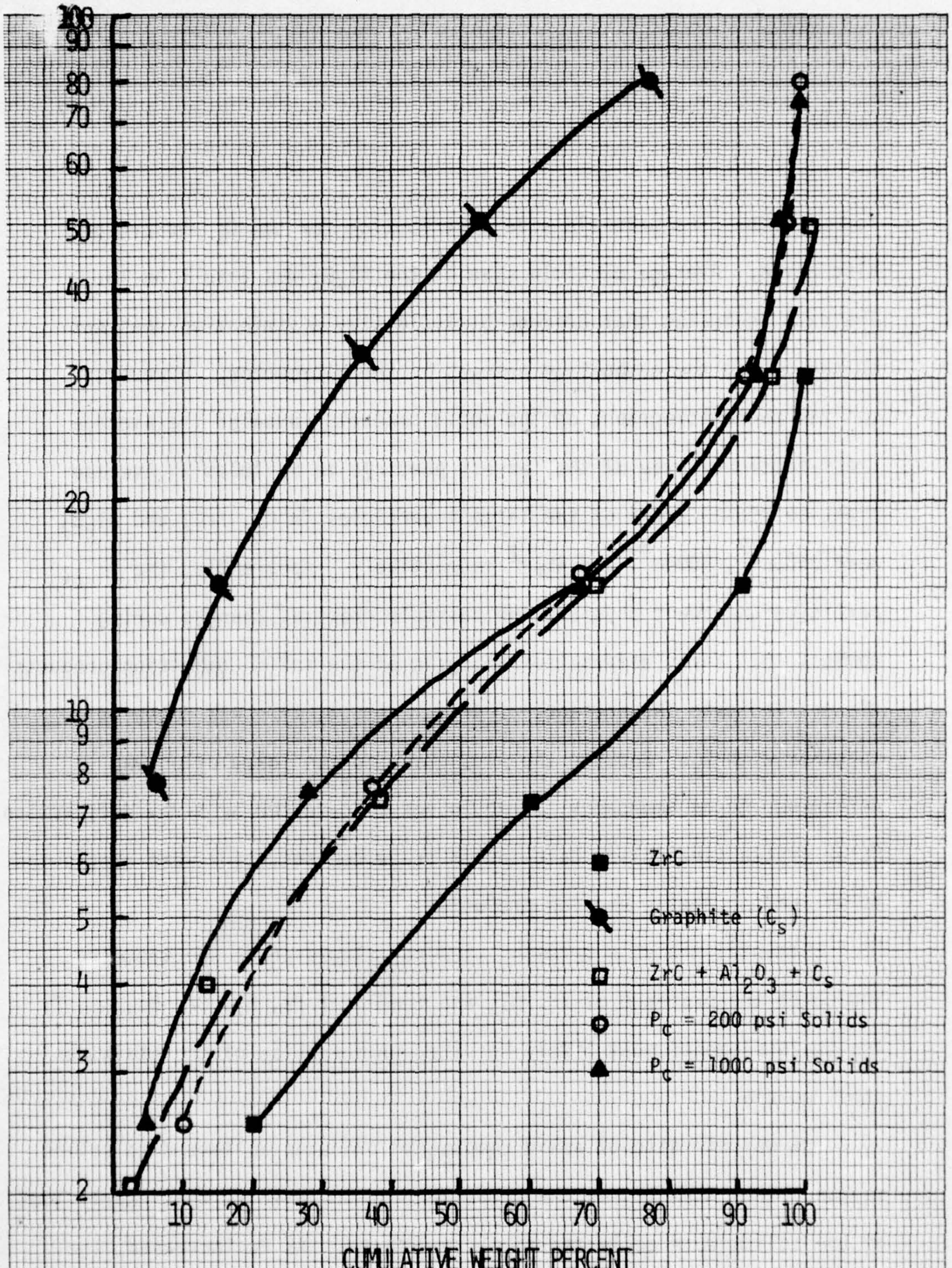

Figure 4. Particle Size Distribution of Solid Combustion Products

formulation. The particle size distribution for the C_s and ZrC are also given. Average particle size of the Al_2O_3 was less than 1μ. The data indicates that average particle size distribution does not change during the combustion process in the micromotor. However, optical photomicrographs of the solid products revealed the average cross-sectional area of the largest particle to be $180 \mu m^2$. Average cross-sectional areas of the largest particles in C_s, ZrC, and Al_2O_3 were $3500 \mu m^2$, $100 \mu m^2$, and $45 \mu m^2$ respectively. Apparently, the particles underwent physical and possible chemical changes during combustion. X-ray diffraction analysis of the solid combustion products did not indicate the presence of ZrC. Instead, ZrO_2 was detected together with C_s. Because the Al_2O_3 used in the formulation was determined to be amorphous, it would not be detected by X-ray diffraction. Other crystalline solids detected in trace concentration were attributed to micromotor nozzle erosion products.

Elemental analysis by means of X-ray fluorescence spectrometry indicated the presence of Zr, Al, and traces of Fe, Ni, Cr, Ca, and Ti. The trace elements most likely resulted from erosion of the stainless steel nozzle.

The weight ratio of solid combustion products collected to solids weight, other than AP, in the propellant grain revealed that nearly 100% of the solids were collected for Pc = 200 psi. As Pc increased, the amount of solids collected decreased, with the ratio being 30%-40% for Pc = 1000 psi. More efficient combustion of C_s in the case of Pc = 1000 psi may account for most of the difference in the weight of solid combustion products collected.

SECTION IV

CONCLUSIONS

The development and demonstration of a small scale micromotor combustor, combustion products collection systems, and analytical techniques for analyzing most of the combustion products have been conducted. Chamber pressures as high as 1500 psi were achieved and all resulting combustion products were collected. The analytical procedures used to analyze combustion products provided information on non-condensible gas composition, particle size distribution, and solid product identification. Combustion data for the propellant formulation studied compared favorably with theoretically predicted equilibrium compositions, except for the hydrogen concentration. Further analytical methods must be developed for complete chemical analysis of combustion products so that a mass balance can be obtained. Results can then be used to identify differences in combustion characteristics of solid propellant formulations containing different concentrations as well as different types of acoustical stability additives.

SECTION V

RECOMMENDATIONS

Recommendations for future programs utilizing the developed micromotor combustor technique include complete analysis of all combustion products from propellant formulations containing different concentrations and types of additives. Future programs should also include the study of combustion products not only from reduced-smoke propellant formulations but also metallized and high energy NF plasticizer formulations. Results obtained from the micromotor tests should be continually reviewed by user organizations to provide feedback for planning further micromotor tests.

SECTION VI

REFERENCES

1. "Ballistic Evaluation of Propellants in Micro-Motors", Byron L. Cockrell, AD451-357, 1964.

2. "Aluminum Behavior In Solid Propellant Combustion", Hans L. Churchill, Rebecca W. Fleming, and Norman S. Cohen, AFRPL-TR-74-13, 1974.

3. "T-Burner Testing of Metallized Solid Propellants" F.E.C. Culick, AFRPL-TR-74-28, 1974.

4. "Exhaust Gas Analysis of Jet Engine Starter Cartridge", L. A. Dee and B. B. Goshgarian, AFRPL-TR-76-43, 1976.

5. "Solid Propellant Combustion Gas Analysis Using A Micromotor Technique", B. B. Goshgarian, AFRPL-TR-69-53, 1969.

6. "Molecular Beam Mass Spectrometric Apparatus For Studying One-Atmosphere Flames", B. B. Goshgarian, AFRPL-TR-72-30, 1972.

7. "Effect of Pressure and Some Lead Salts on the Chemistry of Solid Propellant Combustion", R. A. Fifer and J. A. Lannon, Combustion and Flame 24 369-380, 1975.