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PYROLYSIS GC-FTIR STUDIES OF A
LOVA PROPELLANT FORMULATION SERIES

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MAY 1989



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19. ABSTRACT (Continue on reverse if necessary and identify by block number) Pyrolysis gas chromatography, Fourier transform infrared spectroscopic (GC-FTIR) techniques are being used to measure the distribution of both permanent gases and less volatile products from the pyrolysis of a Naval Weapons Center (NWC), China Lake, LOVA propellant formulation series containing HMX or RDX, the binders HTPB, GAP, BAMO/AMMO, and BAMO/THF, and the plasticizers BTBN and TMETN. The data obtained will be correlated with the NWC time-to-ignition data to obtain information on the formulation variables that affect the ignitability and stability of this LOVA propellant series.					
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I. INTRODUCTION

A considerable amount of information has been published concerning the mechanisms (i.e., products) of the thermal decomposition of the nitramines cyclotrimethylenetrinitramine (RDX) and cyclotetramethylenetetranitramine (HMX). (References 1-3 are useful reviews of the literature.) Until recently, these studies primarily involved measurement only of the permanent gases (CO_2 , NO_2 , NO , CH_2O , HCN , N_2O , N_2 , etc.) in the products, or involved mass spectral studies under vacuum conditions where it is difficult to distinguish pyrolysis from ionization-induced fragmentation of vaporized nitramine molecules. During the last 3-4 years, two developments have led to the identification of larger fragments in the pyrolysis products. One is the application of fused silica capillary column GC techniques.⁴⁻⁷ The other involves new mass spectral techniques involving time-of-flight measurements to determine the parent peak leading to each ion fragment,^{8,9} or employing atmospheric pressure chemical ionization and tandem mass spectrometric techniques to minimize vaporization and provide information on the structures of the observed product masses.¹⁰

The majority of the published studies have concentrated on the development of mechanisms to explain the formation of the observed decomposition products. There have been very few attempts to correlate pyrolysis product distributions with larger scale performance tests such as ignitability, impact sensitivity, or burn rate. Since definitive mechanistic information has not been forthcoming for the nitramines and nitramine propellants, the search for correlations may be a more fruitful approach. Mechanisms are not required, only a correlation of one or more features in the pyrolysis product distributions with the performance property of interest. Once such a correlation is found, the pyrolysis measurement becomes a small scale screening test for the desired performance property, one that perhaps does not require fabrication on as large a scale, or that might only require (unprocessed) mixtures of potential ingredients. Also, the correlation may suggest a hypothesis for the desired property (e.g., "the addition of a reducing agent that reduces NO to N_2 will raise the burning rate at low to moderate pressures") that does not require a mechanism but can be immediately tested. Such hypotheses, when corroborated by testing, will provide the basis for intelligent formulations design (as opposed to trial-and-error procedures), as well as "rules" that can be used in expert systems for computer assisted formulation design and properties prediction.¹¹ Correlating pyrolysis product distributions with performance is analogous to reported correlations between LOVA propellant sensitivity to ignition by hot fragments and binder/acid DSC decomposition temperature.^{12,13} The "information content" in a product distribution measurement, where perhaps 15 or 20 products are measured, is much greater than in a thermokinetic measurement where only a single property (e.g., decomposition temperature) is measured, so there should be an even greater likelihood of finding a usable correlation.

The principal reason why pyrolysis-performance correlations have not been attempted is that suitable series of systematically varied propellant formulations, with properly documented performance measurements, are "hard to come by". Such a "model" LOVA propellant formulation series has been developed at the Naval Weapons Center (NWC), China Lake, by Dr. Rena Yee,¹⁴⁻¹⁶ who has graciously made both samples and test data available to us for this study. In this formulation series, oxidizer, binder, and plasticizer

were systematically varied; performance test results include burn rate, impact sensitivity and time-to-ignition for radiative-heating. This formulation series contains HMX or RDX as the oxidizer, one of the following binders: hydroxy-terminated polybutadiene (HTPB), glycidyl azide polymer (GAP); 3,3-bis-azidomethyl oxetane/tetrahydrofuran copolymer (BAMO/THF); 3,3-bis-azidomethyl oxetane/3,3-azidomethyl-3-methyl oxetane copolymer (BAMO/AMMO). The azido binders were plasticized by trimethyl ethane trinitrate (TMETN) and 1,2,4 butane trinitrate (BTTN). The formulations obtained from NWC, and the corresponding NWC sample numbers, are as follows:

RDX-based:

RDX + HTPB	16
RDX + GAP	8
RDX + GAP + BTTN	19
RDX + GAP + 2BTTN	9
RDX + GAP + TMETN	25
RDX + GAP + 3TMETN	4

HMX-based:

HMX + HTPB	17
HMX + GAP	14
HMX + GAP + BTTN	20
HMX + GAP + TMETN	24
HMX + BAMO/AMMO + TMETN	22
HMX + BAMO/THF + BTTN	21
HMX + BAMO/THF + TMETN	23

No Oxidizer:

GAP + BTTN	15
GAP + TMETN	18

Samples of HMX, RDX, GAP, and HTPB were also obtained and pyrolyzed as part of the test matrix. Figure 1 shows the formulation variations schematically; Table 1 gives the compositions, as well as some of the NWC performance test results.

These formulations were studied using a pyrolysis gas chromatography-Fourier transform infrared (P-GC-FTIR) apparatus. This is a progress report on this investigation. At the time of writing this report, all of the data has been collected, but data compilation, spectral identification, and correlation with the NWC performance test results has only just begun. We felt it was beneficial to publish a progress report stressing the goals and techniques that are being used. We expect to publish a report with final results and possible correlations within six months of writing this report. This report will therefore stress the goals and techniques being employed, and the type of data that we have obtained, rather than final results or correlations.

II. EXPERIMENTAL

RDX, HMX, HTPB, GAP, and 15 formulations were pyrolyzed using a Chemical Data Systems (CDS) Pyroprobe connected via a heated interface chamber to the injector of a Hewlett Packard 5965 GC-FTIR system equipped with a capillary

Propellant Formulations

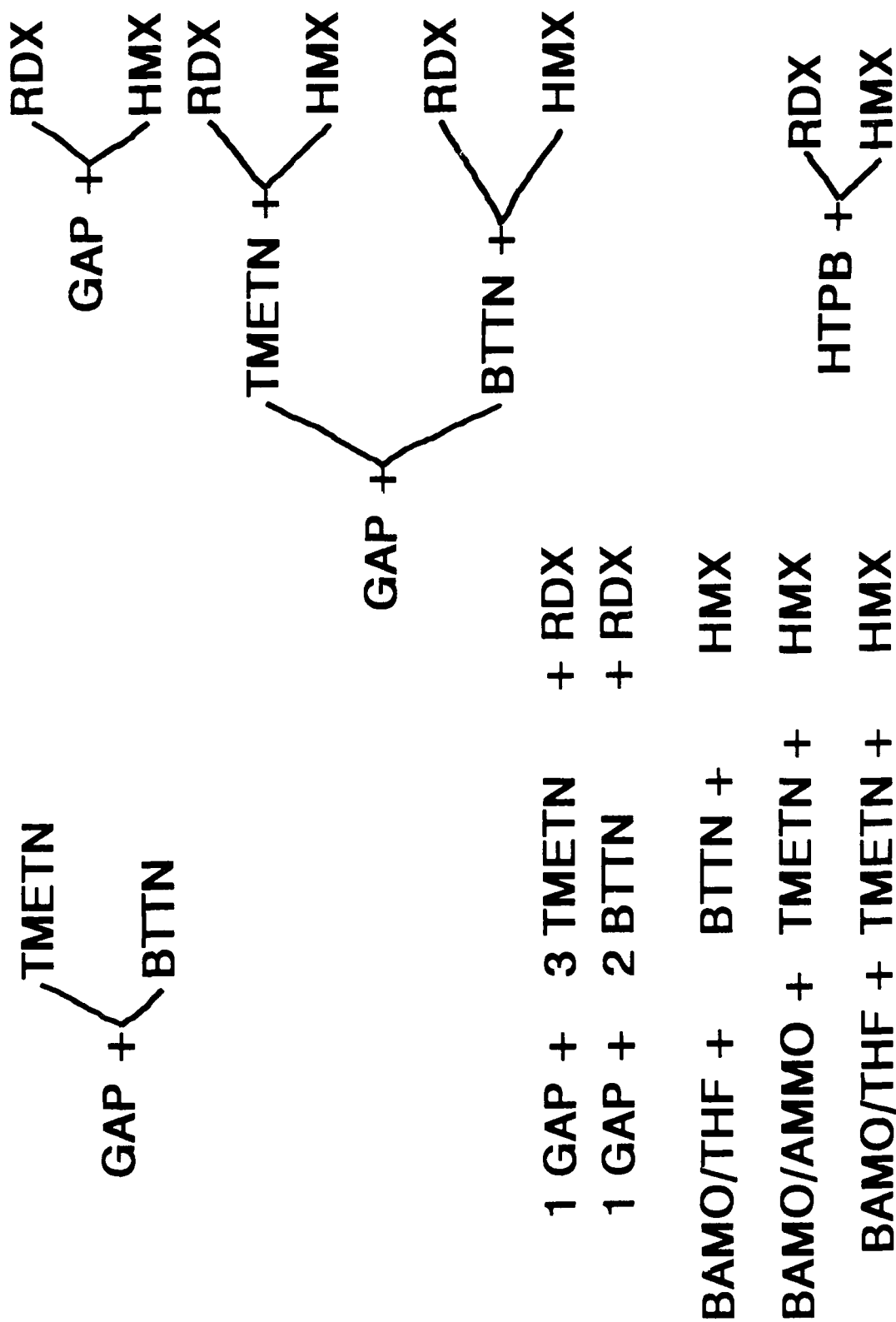


Figure 1. NWC Formulations Used in This Study.

column and liquid-nitrogen cooled Mercury Cadmium Telluride (MCT) detector. Figure 2 shows the system configuration schematically.

The pyrolysis sample (ca 1 mg) was placed in a quartz tube, which was then inserted into a coil-type Pyroprobe. The probe was inserted into the heated interface which was continuously being swept with carrier gas. Once enough time had elapsed to allow the carrier gas to sweep all air from the interface compartment and to allow the sample to reach thermal equilibrium, the sample was flash heated to the final temperature. The pyrolysis products were then passed through the (splitless) injector into the capillary column, which separated the pyrolysis products for detection and identification. As each component eluted from the capillary column, it passed through a light pipe in the beam of the interferometer for spectroscopic analysis by Fourier-transform infrared (FTIR) spectroscopy. Table 2 lists the pyrolysis conditions, chromatographic conditions (type of capillary column and GC oven temperature program), and spectroscopic conditions for the experiments.

Table 1. Propellant Formulations and NWC Performance Test Results*

#	(WT %)	TIMEIN	BTTN	HMX	RDX	ISP (sec ⁻¹)	IMPACT (cm)	BURN RATE (in/sec)	Ignition Times (ms)			
									60 flux		150 flux	
									FL	GNG	FL	GNG
2**	HTPB (20)				80.0	219.0	35.5	0.16	10.4	10.5	2.4	3.75
3**	HTPB (25)				75.0	213.9	46.8	0.14	11.3	11.8	3.1	6.5
4	GAP (5.0)	18.9			74.8	257.8	13.6	0.31	10.3	11.5	2.4	4.7
8	GAP (27.0)				68.4	235.4	30.2	0.26	NA	NA	NA	NA
9	GAP (9.2)		22.6		65.9	257.0	15.6	0.30	8.9	9.9	1.5	3.4
14	GAP (30.3)			69.7		236.8	23.4	0.28	9.1	43.6	2.7	70.4
15	GAP (30.3)			69.7		221.4	33.9	NA	NA	NA	NA	NA
16	HTPB (25)				75.0	213.9	41.6	NA	NA	NA	NA	NA
17	HTPB (24.0)			76.0		214.6	25.7	0.14	7.8	22.4	2.4	17.1
18	GAP (50.0)	50.0				216.9	51.3	NA	NA	NA	NA	NA
19	GAP (14.9)		17.5		65.0	251.0	22.9	0.28	6.3	8.2	2.3	4.2
20	GAP (14.4)		16.9	66.3		251.3	21.9	0.31	6.7	10.2	2.1	10.8
21	BAMO/THF (15.0)		16.2	67.6		246.3	18.6	0.29	7.1	11.5	2.8	8.5
22	BAMO/AMMO (14.7)	15.9		68.2		243.1	17.0	0.27	7.0	15.8	3.2	33.2
23	BAMO/THF (14.0)	15.7		68.6		241.6	20.9	NA	NA	NA	NA	NA
24	GAP (13.0)	15.9		68.3		239.1	20.6	0.26	9.4	14.4	2.7	18.5
25	GAP (13.4)	16.4			67.1	248.8	21.3	0.25	8.0	10.6	2.0	21.6
26**	BAMO/AMMO (28.1)			69.7		226.2	22.7	0.28	7.9	58.1	3.0	48.2

*All data from NWC (Refs. 14-16, R.Y. Yee); all ignition times at specified flux (cal m⁻² s⁻¹) at 1.72 MPa (250 psi), data at 100 and 200 cal m⁻² s⁻¹ also available; burn rate at 6.9 MPa (1000 psi).

ISP = specific impulse, FL = first light, GNG = go-no-go

**Samples of these formulations were not available for the pyrolysis studies.

Each of the samples was pyrolyzed at both a "low" and a "high" temperature. For the low temperature runs, RDX and the RDX formulations were flash heated to 400°C, while HMX and the HMX formulations were flash heated to 500°C. For the high temperature runs, all samples were flash heated to 1000°C. GAP and HTPB were only pyrolyzed at the high temperature due to their thermal stability. The temperatures mentioned here are the Pyroprobe "set" temperatures. Thermocouple measurements showed that the actual temperatures experienced by the samples in the quartz tubes were 150-200°C lower; the low

Experimental Apparatus

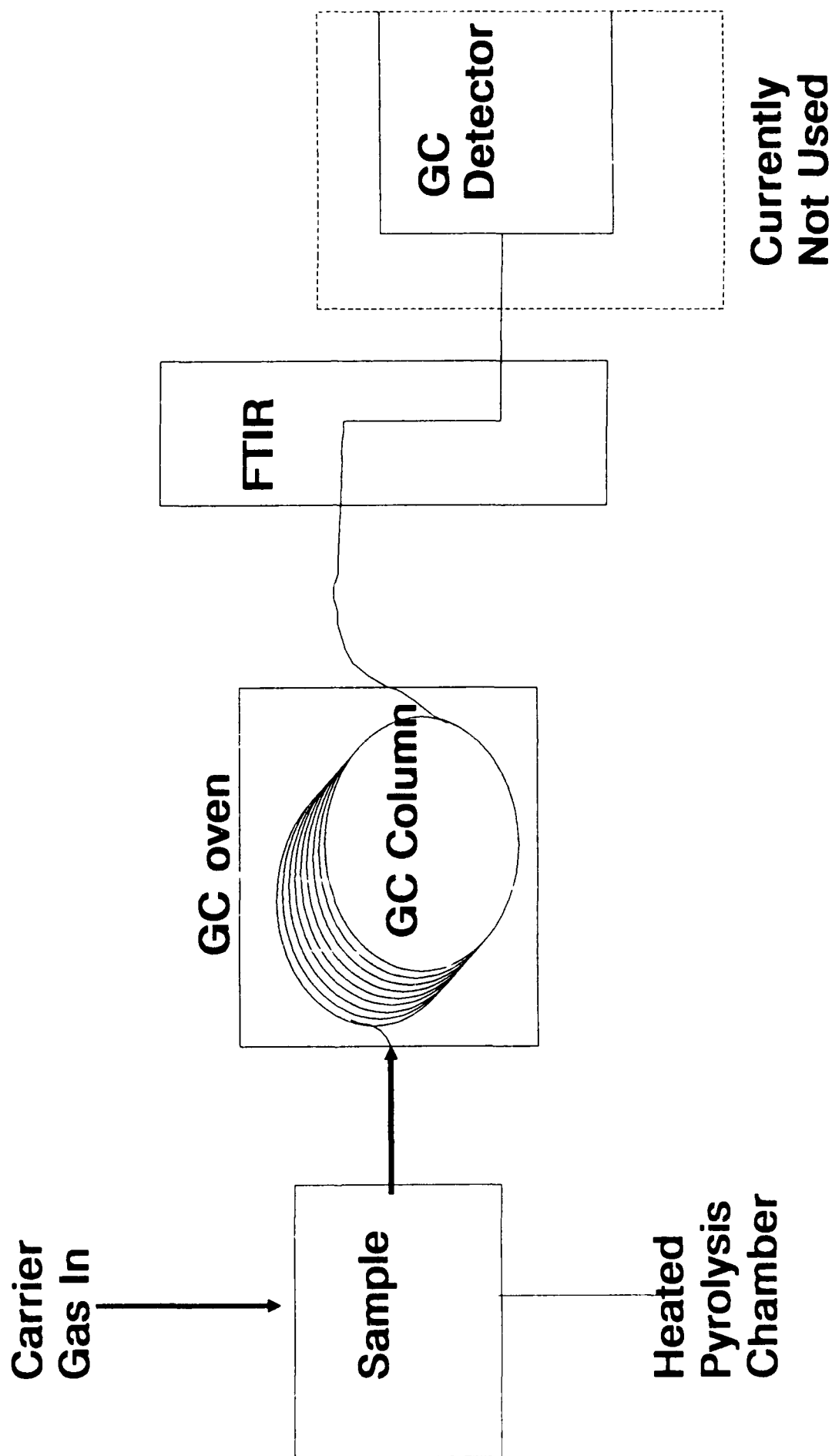


Figure 2. Schematic of Pyrolysis Gas Chromatography-Fourier Transform-Infrared (P-GC-FTIR) Experiment.

temperature runs were therefore just above the RDX and HMX melting temperatures (204 and 280°C, respectively). Three experiments were carried out for each of the samples at each of the two temperatures. The final test matrix therefore consisted of 108 runs.

Table 2. Chromatographic and Spectroscopic Conditions

GC oven/column conditions:	
initial temperature:	50°C
initial (hold) time:	3 minutes
heating rate:	10 deg/min
final temperature:	200°C
final (hold) time:	5 minutes
injection port temp:	200°C
light pipe temp:	250°C
transfer line temp:	250°C
column:	0.32mm x 25m OV-17, 3.0 µm film
(Quadrex Corp)	
FTIR parameters:	
narrow band MCT detector	
8 cm ⁻¹ resolution	
scan rate:	3 scans/sec
Pyroprobe and interface parameters:	
interface temperature:	100°C
configuration:	
1 mg sample in quartz tube	
coil type probe	
heating mode:	flash heating
pyrolysis temp:	400, 500 or 1000°C
heating time:	20 sec

A chromatogram was generated for each run by the instrument showing infrared absorption vs. time. This chromatogram or interferogram was generated by the FTIR detector using the Gram-Schmidt algorithm. After the run, the software integrated this interferogram, generating a peak table listing peak times and associated peak areas for all peaks above a specified threshold. From this table, an automated search of the EPA library of vapor phase infrared spectra was performed for the infrared spectrum corresponding to each peak detected. The results of the library search along with the infrared spectrum at the peak maximum was then printed. A small fraction of the peaks was directly identified by the automated library searches of the infrared spectrum. For those that were not, a frequency-intensity-peak width table for the principal bands in the infrared spectrum was entered into a microcomputer version of the PAIRS expert system for infrared spectral interpretation.¹⁷ The output of this program is a ranked list of possible functionality (e.g., ketone, amide, etc.) for each spectrum. For chromatographic peaks for the different formulations that had similar retention times (measured relative to the permanent gas peak), the infrared spectra were visually compared to determine if the product was in fact the same.

For the permanent gases, a somewhat different procedure was used. These gases elute from the capillary column as a single unresolved peak near the beginning of the chromatogram. In the common GC-mass spectrometric (GC-MS) technique, no analysis of the permanent gases would be possible in this situation with normal (unit mass) resolution, since there are a number of unfortunate coincidences in the ion fragmentation patterns for many of the commonly-observed permanent gases. (For example, m/z 28 could be CO or N_2 , m/z 30 could be CH_2O or NO, m/z 44 could be N_2O or CO_2 , etc.) For GC-FTIR, this is not a problem; most of the gases have absorption bands in several spectral regions, and for each gas there is at least one infrared band for which there is no interference from other species.¹⁸ (The disadvantage with infrared is that the homonuclear diatomics (for propellants primarily N_2 and H_2) are inactive and therefore cannot be measured.) Therefore, from the infrared spectrum of the unresolved permanent gases, a table of selected band absorbances was tabulated. Actually, it was found that the permanent gases were separated slightly; each of the permanent gases "peaked" at a different point in the permanent gas peak, so that the infrared spectrum varied somewhat across this peak. Three spectra were therefore examined for the permanent gas peak: left, center, and right within the peak. The maximum absorbance for the three spectra for each selected band was then tabulated.

III. RESULTS

A. Selection of Performance Data for Correlation

The performance data for these formulations measured at the Naval Weapons Center¹⁴⁻¹⁶ consists of burn rate from 1.4 to 10.3 MPa (200 to 1500 psi), impact sensitivity (height for 50% initiation), and time to ignition at 1.7 MPa (250 psi) at four radiant flux levels (60, 100, 150, and 200 cal/(m² sec), as well as (theoretically computed) specific impulse (Isp). In order to determine which data would be most promising for correlation with pyrolysis product distributions, a number of plots were made of the NWC data. A plot of burn rate vs. specific impulse shows a good linear correlation (Figure 3), indicating that the burn rate is largely thermodynamically controlled; the biggest deviation is the high burning rate for #26 (HMX/(BAMO/AMMO)). The drop weight test results also roughly correlate (inversely) with specific impulse (Figure 4), suggesting that this property is also largely thermodynamically controlled. (For a large number of nitro compounds, Yee¹⁹ has developed correlations between impact sensitivity and parameters such as oxygen balance and chemical group functionality.) On the other hand, the ignition data do not correlate at all with specific impulse, as shown in Figure 5, suggesting that they are not thermodynamically controlled, and therefore might be kinetically or mechanistically controlled. (This assumes that physical factors like absorptivity/reflectivity, thermal conductivity, etc., are not greatly different for the samples.) Therefore, our approach in analyzing the pyrolysis data will be to try to explain/correlate the ignition data in terms of the pyrolysis results. For example, why do certain formulations, namely HMX/GAP (#14), HMX/(BAMO/AMMO)/TMETN (#22) and RDX/GAP/TMETN (#25) exhibit increasing go-no-go ignition times with increasing flux, while the first-light ignition times for these same formulations decrease with increasing flux? Since pyrolysis is part of the ignition process, some correlations should be found that would form the basis for propellant formulation guidelines.

burn rate vs specific impulse

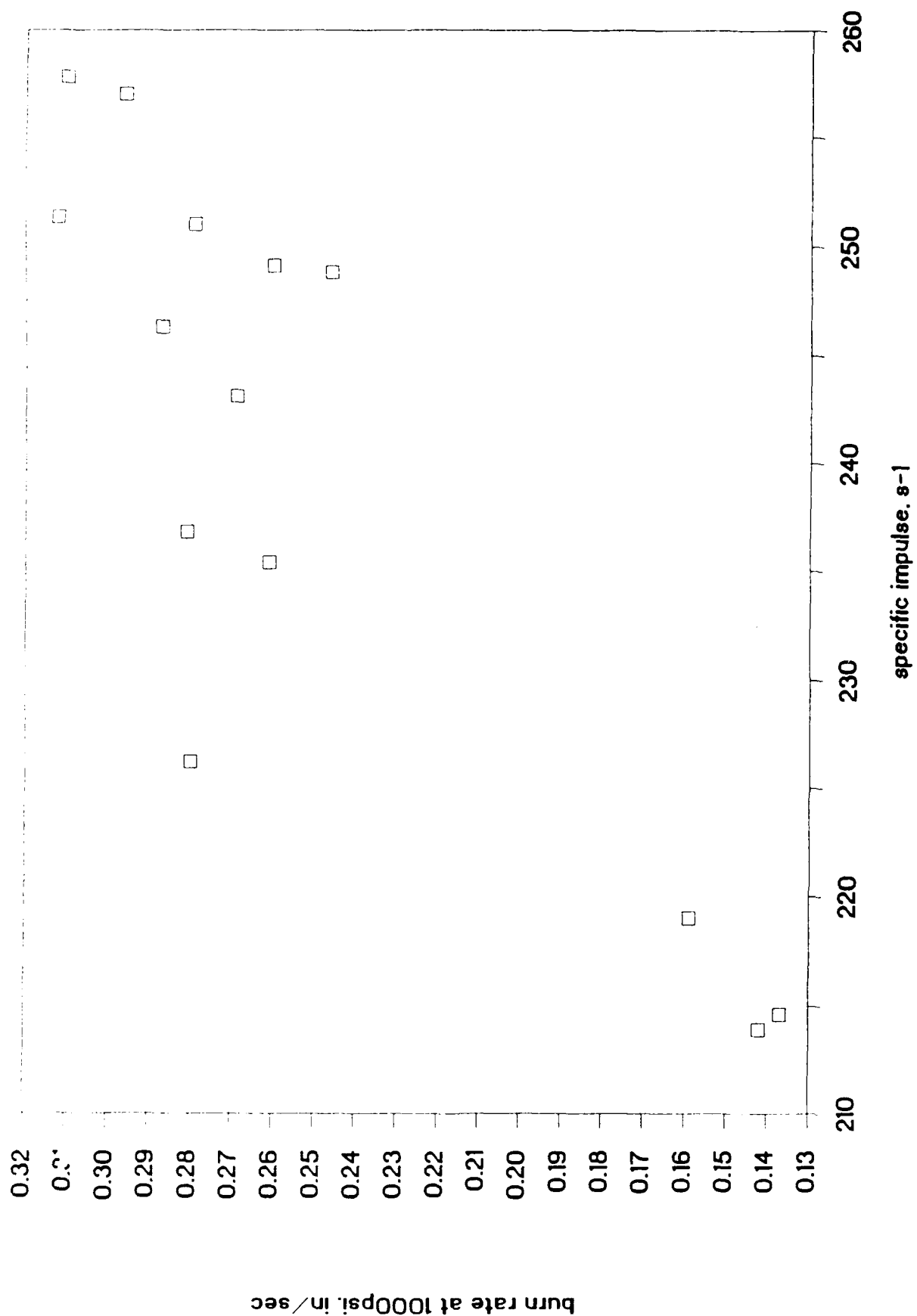


Figure 3. NWC Burn Rate Data vs. Theoretical Specific Impulse.

impact height vs specific impulse

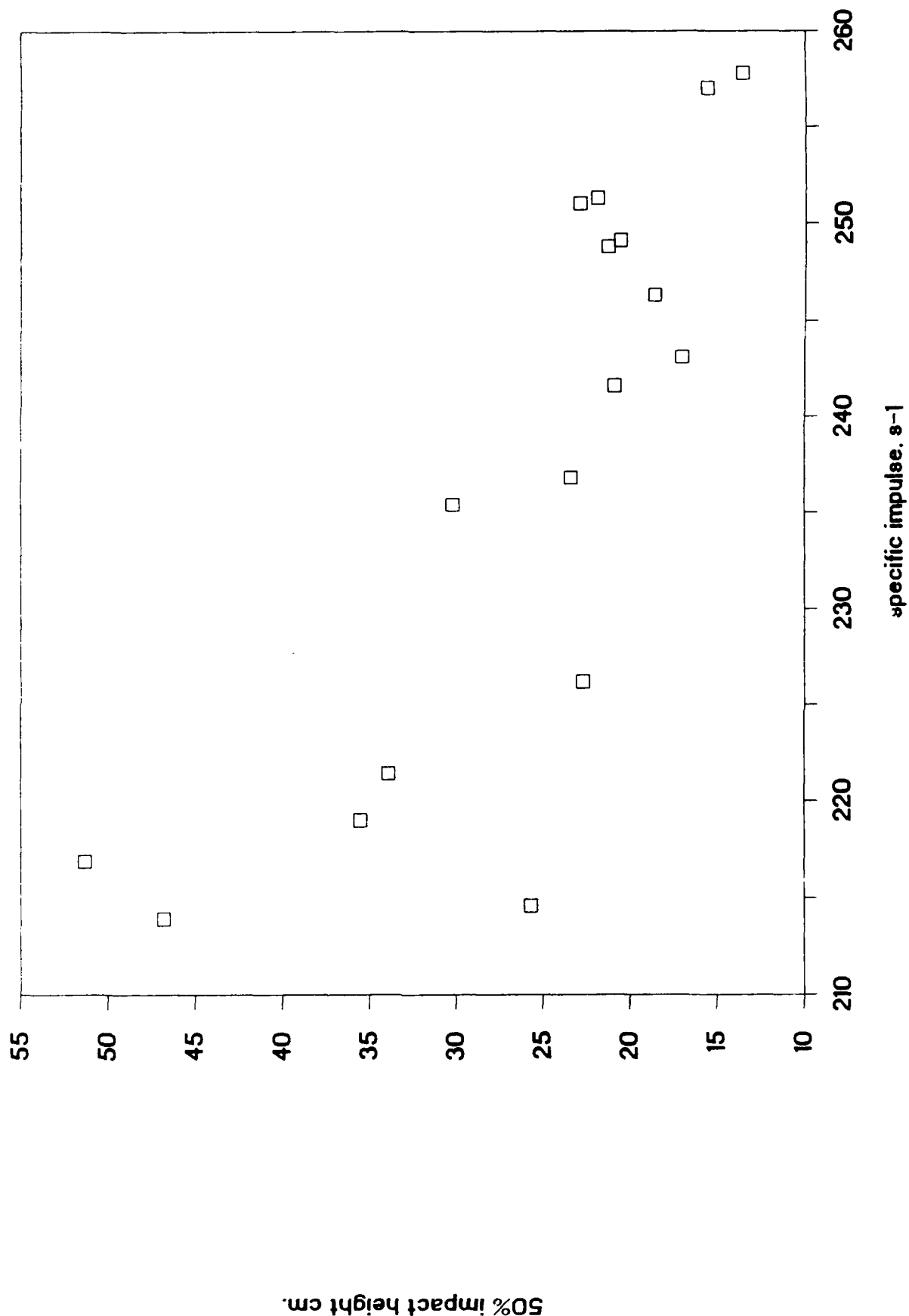


Figure 4. NWC Impact Sensitivity vs. Theoretical Specific Impulse.

ignition time (flux 150) vs sp. impulse

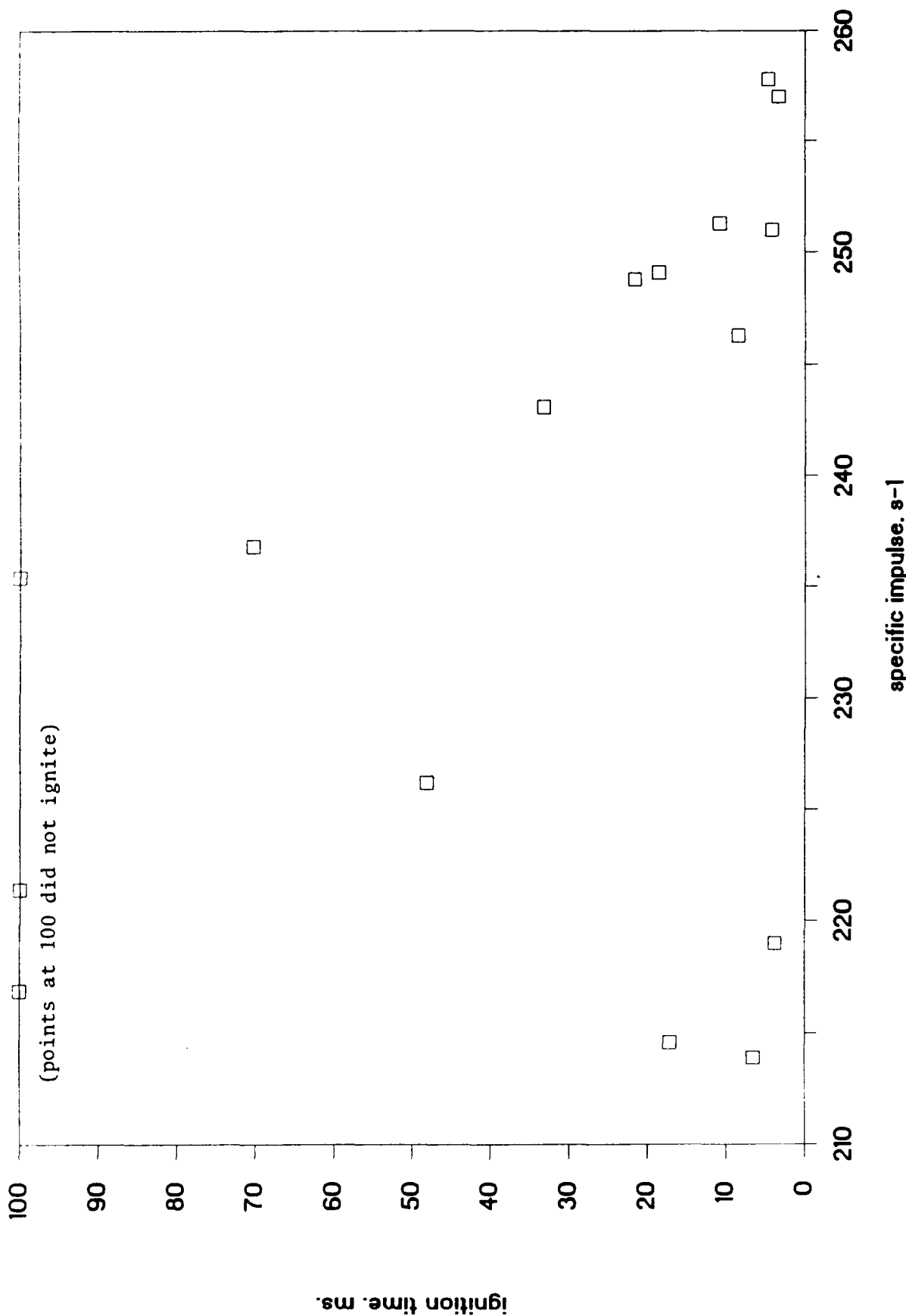


Figure 5. NWC Go-No-Go Time to Ignition Data at 150 cal/(m² sec) vs. Theoretical Specific Impulse.

B. Examples of Pyrolysis GC-FTIR Results

Figures 6a-6f and 7a-7f show representative chromatograms for HMX, GAP, HTPB, and some of the HMX-based formulations at the high pyrolysis temperature (1000°C). For typical formulations, it can be seen that there are several chromatographic peaks in addition to the permanent gas peak. Figure 8a shows a typical infrared spectrum for the permanent gas peak, with bands labeled for the different observed components. Figure 8b and 8c show examples of infrared spectra for products eluting later in the chromatograms. The spectrum for the peak observed about 6 minutes after the permanent gas peak (Figure 8b) corresponds to formic acid (HCOOH); the spectrum of the peak commonly observed 8.6 minutes after the permanent gas peak (Figure 8c) corresponds to acetamide (CH_3CONH_2). Similarly, the important peak at 12.6 minutes is due to N-methyl formamide (HCONHCH_3). A number of the products from GAP and HTPB have also been identified with fair certainty. Table 3 shows the component (if known or else the functional group), the corresponding retention time, and the peak area. In addition to the acid and the amides, ketones appear to also be important in the low-volatile components: HMX's peaks at 3.7, 14.7 (strong) and 16.7 minutes appear to be ketones, as does the important peak at 8.1 minutes that is not present for HMX alone but is produced by most of the HMX-containing formulations (both HTPB and azido). A number of peaks remain unidentified at the present time, although PAIRS results have been obtained for most of them. For some of the single-component systems, good library search results were obtained for a large fraction of the observed peaks. For example, for HTPB the peaks eluting during the first few minutes after the permanent gas peak correspond to cyclic hydrocarbons, while those later in the chromatogram (e.g., 15-20 minutes after the permanent gas peak) correspond to long chain (e.g., C_6 to C_9) hydrocarbons.

Table 4 shows the tabulated absorbances for the permanent gases in these high temperature HMX-series runs. As examples of some of the trends in the data with formulation variations, the following can be seen in Figures 6 and 7, and Tables 3 and 4 for HTPB and GAP-based formulations: HMX produces the permanent gases (NO , N_2O , and CO_2), plus HCN as a separately-resolved peak, and a variety of amides and ketones, as mentioned above. HTPB produces a small permanent gas peak (CO , CO_2 , CH_4 , and C_2H_4), a major peak due to bivinyl ($\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$), and a range of cyclic and linear hydrocarbons at longer retention times. When the two are mixed (HMX/HTPB), the permanent gases show intermediate behavior except for an increase in HCN ; hydrocarbons of HTPB are almost all eliminated, as are the high molecular weight (longer retention time) amides and ketones of HMX. GAP alone produces (CO , NH_3 , CO_2 , and CH_4), a large amount of an early-eluted ester, plus other esters, amides and amines. Mixed with HMX (HMX/GAP), GAP also removes the longer-retained HMX products. Plasticized (with BTTN or TMETN) GAP binder (without oxidizer) produces (CO , CO_2 , NO , CH_4 , and C_2H_4) and much less of the early ester than for GAP alone; TMETN-plasticized GAP produces more formic acid and other later-eluted products than does GAP plasticized with BTTN. For the plasticized HMX/GAP formulations (#20, #24), on the other hand, these trends are reversed: the TMETN removes the heavier HMX products more completely than does BTTN, while the BTTN-plasticized propellant produces much more formic acid than the corresponding TMETN one. These trends may be related to the observed shorter ignition times for BTTN-plasticized formulations. Interestingly, all of the plasticized azido formulations produce large amounts of the same ketone (observed 8.1 minutes after the permanent gas peak) that is

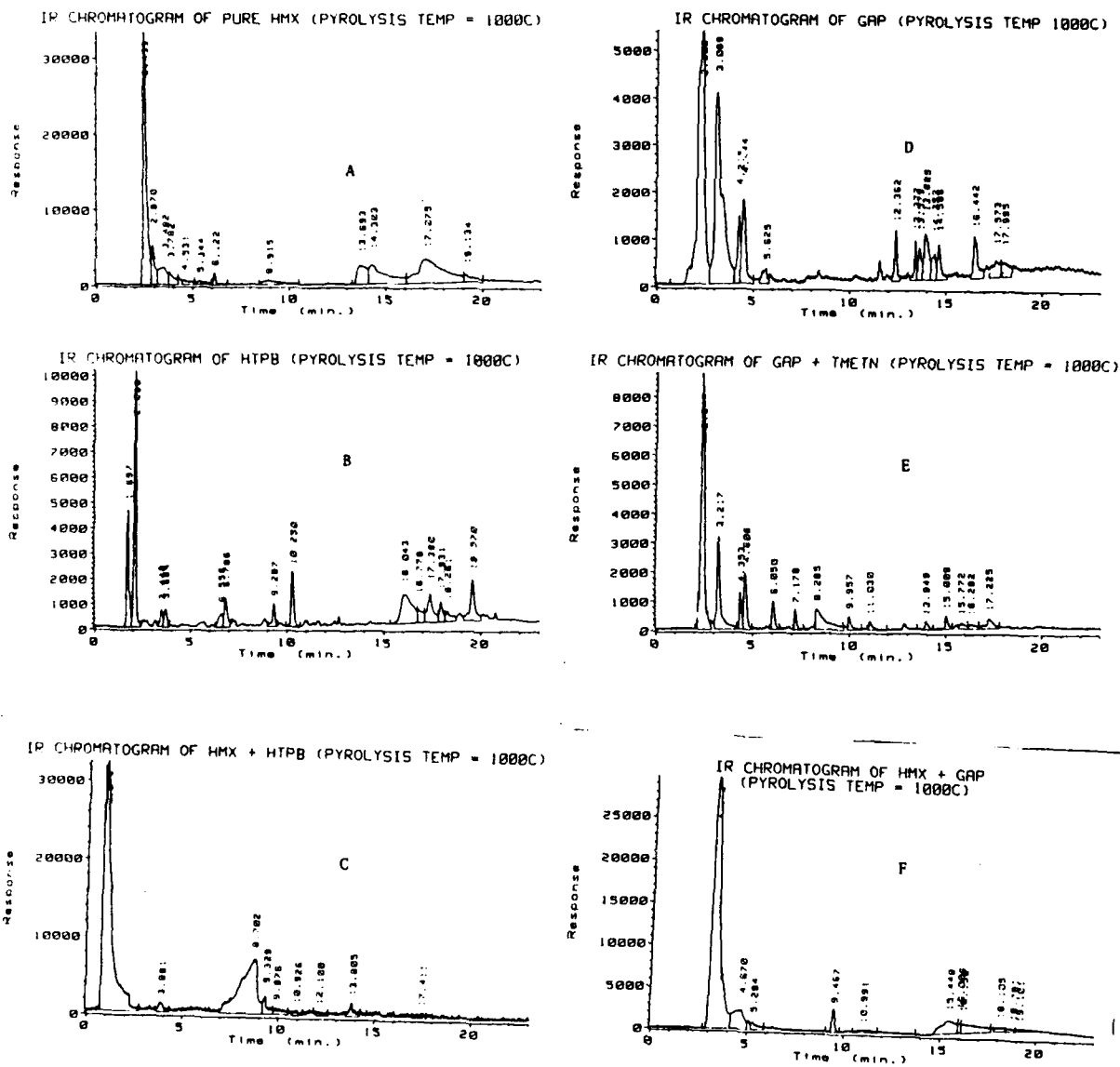


Figure 6. Infrared Chromatograms for Ingredients and Formulations (see Table 4).

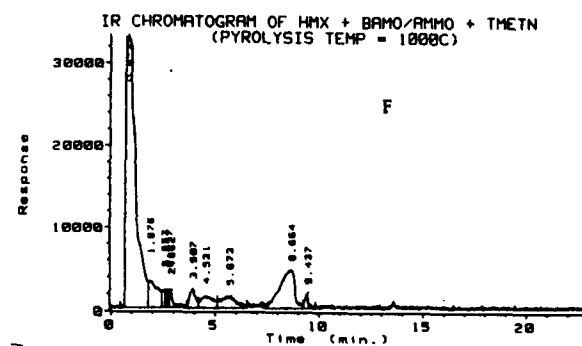
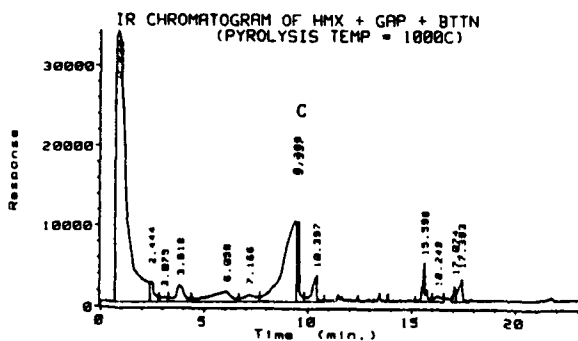
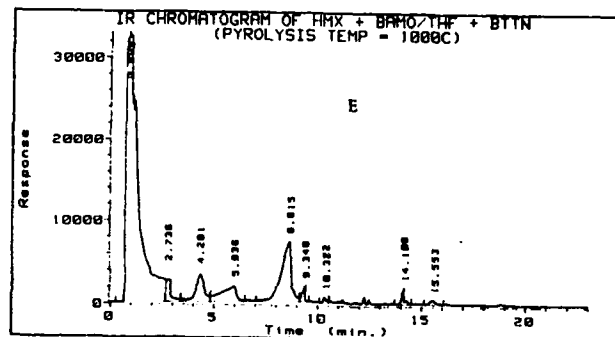
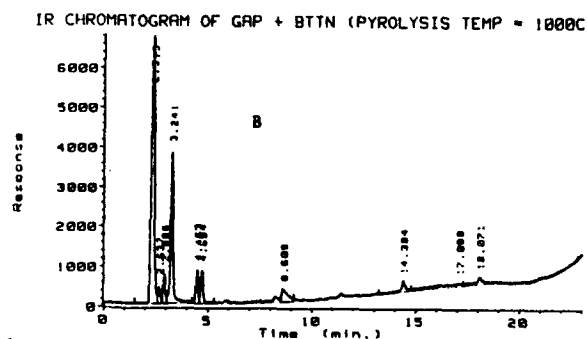
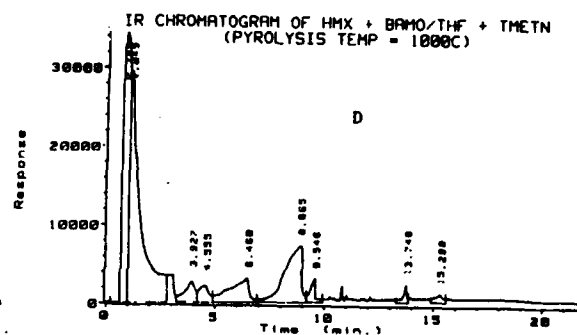
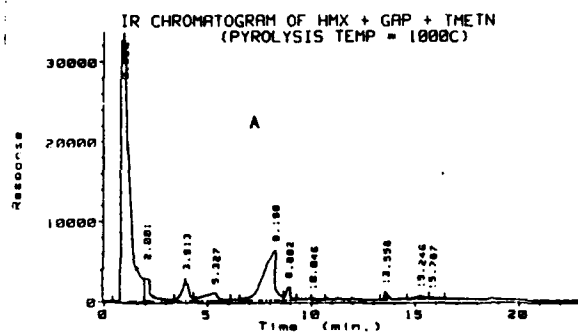


Figure 7. Infrared Chromatograms (1000 C pyrolysis) for Formulations (see Table 4).

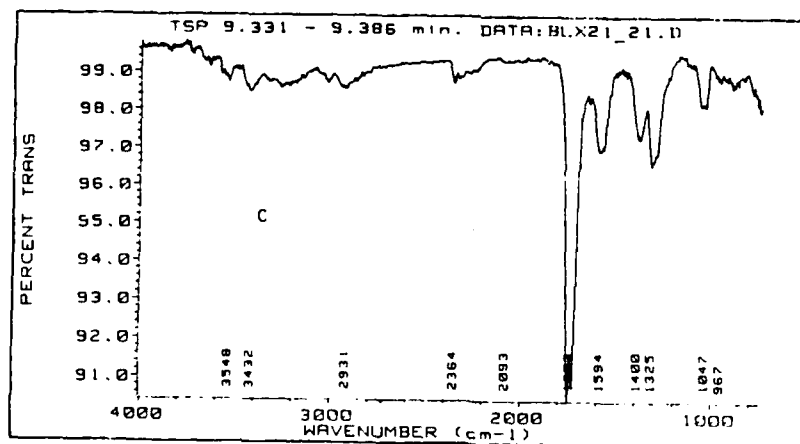
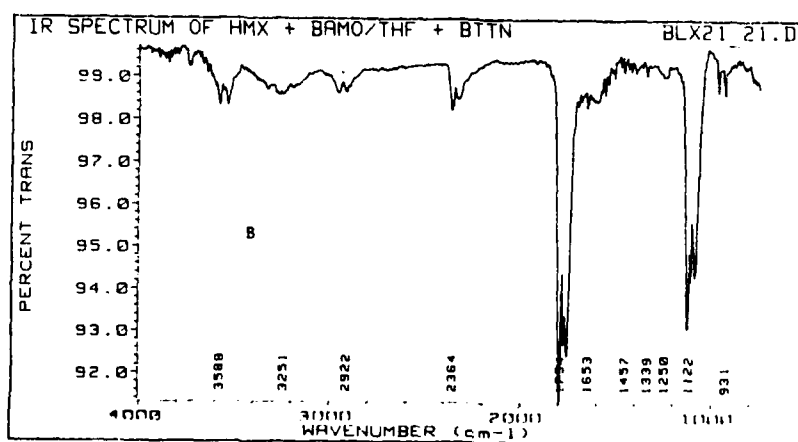
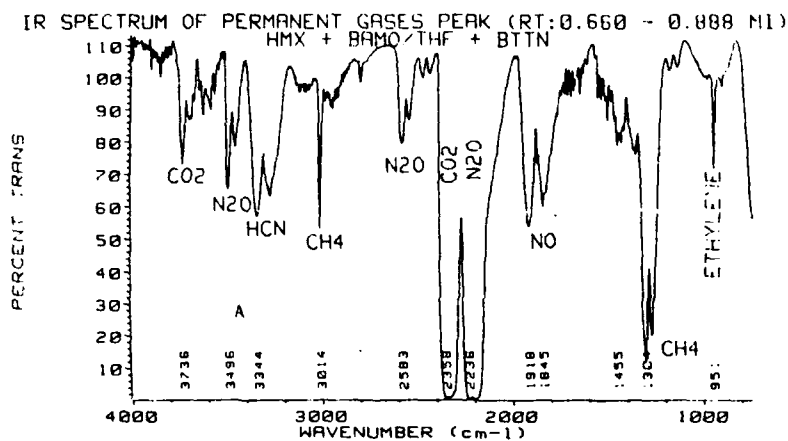


Figure 8. Examples of FTIR Spectra of Pyrolysis GC-FTIR Peaks for Propellant Formulations.
a) Permanent Gas Peak, b) Peak at 6 min due to Formic Acid, c) Peak at 8.6 min due to Acetamide.

Table 3. Chromatographic Peak Areas for RMK Formulation Series Pyrolyzed at 1000°C*

formulation number		RMK A	HTPB B	RMK HTPB 17	GAP C	RMK GAP 14	GAP BTIN 15	RMK GAP BTIN 20	RMK BAND/ AMMO BTIN 21	GAP TME TN 18	RMK GAP TME TN 24	RMK BAND/ AMMO TME TN 22	RMK BAND/ THF TME TN 23
species	time (min)	areas											
permanent gases		4060	144	7680	1711	8510	715	14710	13410	1151	12180	10661	16740
HCN(A);biviny(B)	0.4	616	299 ^a				35						
	0.6						57						
ester	0.9				1244		346			412			
H ₂ O	1.1	673		NM		947					NM	<956	
ester	1.9				314	98		NM	NM	98		<692	
acetone(A);ketone	2.1	161 ^a			215	202	65			95			NM
	2.4						73						
nitramine (17,20)	3.0	147		246		57		516			573	427	
ketone,ether	3.7	164						279		98		555	670
vinyl cyclohexene	3.9		188										
	4.7									56			NM
formic acid	6.3	354		<177		293	69	2872	941	255	426	656	1922
toluene(B);ketone	8.1		41 ^a	2809				4362	2453	52 ^a	2497	2305	3934
acetamide	8.6		75	241				358	182	37	261	227	532
toluene(B);ketone	9.4		30				21	61	63				81
	9.6							77	22				87
amine	10.4				140			65	25	29			119
formamide ?	11.3	816		58	197			90	48				76
amide	11.8				277		42		32	35			
n-methyl formamide	12.6	1550		199		<789		303	118	54		99	
	13.2			56		720		177		<38			
urea ?	13.8			33				192		<38			
ketone ?	14.7	2956				NM	77	646	108	92	305		290
amide(C);HC(C)	15.2		62		166		51						
hydrocarbon	15.3		93										
hydrocarbon	15.6		59										
hydrocarbon	15.9		77										
hydrocarbon	16.2		52										
ketone ?	16.7	318								23			
	17.6		179					124					
hydrocarbon	19.6				163								

*Preliminary results; not all peaks listed on same line due to same species; retention times relative to first (permanent gas) peak; areas in arbitrary units; HC=hydrocarbon, NM: small peak, area not measured by software; "a" indicates that the species (infrared spectrum) is different from the others appearing on the same line.

produced by HMX/HTPB, while this product is not produced by HMX, GAP, or HMX/GAP. A similar trend is observed in the permanent gases: the plasticized formulations produce copious amounts of HCN (plus NO, CO₂, N₂O, and CH₄), more HCN in fact than for HMX alone (leading to the broadened permanent gas peak compared to that for HMX), whereas HMX/GAP produces almost no HCN.

Table 4. Peak Absorbances at Selected Frequencies for Permanent Gases - HMX Formulation Series at 1000°C*

formulation number		HMX A	HTPB B	HMX HTPB 17	GAP C	HMX GAP 14	GAP BTIN 15	HMX GAP BTIN 20	HMX BAMO/ AMMO BTIN 21	GAP TMETN 18	HMX GAP TMETN 24	HMX BAMO/ AMMO TMETN 22	HMX BAMO/ THF TMETN 23
cm ⁻¹	species	absorbances											
3497	N ₂ O	64		46		48		87	68		76	93	36
3275	HCN	38		78			55	189	212		177	159	93
2805	CH ₂ O	5					12						
2583	N ₂ O	34		27		25	5	44	26		36	49	
2361	CO ₂	549	149	596	225	798	471	1446	803	365	1144	1217	487
2238	N ₂ O	803		618		873	169	1240	680	106	1140	1315	449
2212	N ₂ CO	723		571		780		304	633		1054	1215	420
2180	CO	103	13		74		202			131	129		
2114	CO	36	9		55	57	80	100	14	54	69	55	
1915	NO	126		100		94	85	185	144	58	155	183	82
1844	NO	84		90		68	63	161	137	43	133	155	77
1761	CH ₂ O	21	46		96	34		67			62	53	
1518	H ₂ O	78		70	45	73	13	154	156		121	96	123
1271	N ₂ O	234	8	173		217	25	340	217		315	376	145
1088	NH ₃ +CH ₂ O		125		36								
965	NH ₃				201							54	
951	CH ₂ CH ₂		205	91			176				53		83

*Preliminary results; values listed are maximum absorbances recorded in spectra at three positions in the permanent gas peak; values shown are not proportional to concentrations due to major differences in extinction coefficients for different species.

These are just some of the (preliminary) trends observed for the high temperature HMX formulation series. This series represents only one "quadrant" of the experimental test matrix; as might be expected, different product distributions are observed at the lower temperature, and some differences are observed between RDX-based and HMX-based formulations. These results will be presented in the final report in conjunction with a discussion of observed product distribution/performance correlations. In particular, an attempt will be made to correlate data of these types with the NWC time-to-ignition data. We will also be comparing our results to the low molecular weight (permanent gas) products reported by other investigators for these and other azido-polymer based formulations.²⁰⁻²²

In looking for correlations, several techniques and tools are being used: (1) Visual examination: chromatograms are "laid out" as in Figures 6 and 7, perhaps labeled with an indication of their ignitability, and examined for trends. (2) Simple plots: the tabulated data (peak areas or absorbances and corresponding time-to-ignition values) are entered into a spreadsheet program (SYMPHONY) and different components- or ratios of components-plotted against the ignition results to look for correlations; a correlation coefficient near zero in the histograms indicates no correlation, while a coefficient near 1 (or -1 for an inverse relationship) would indicate a strong correlation. (3) Multivariate analysis: "Pattern recognition" and principal component analysis provide valuable tools for analyzing data involving a large

number of independent variables. In this case, the independent variables are the absorbances or peak areas. Principal component software (EINSIGHT, running on a microcomputer) will be used to look at the data in n-dimensional (up to about 20, based on the number of products typically observed) space as a series of two dimensional "slices" or windows; boundaries in these "projections" of the data correspond to correlations or "classifications" in the data. Yee has already used these techniques to correlate impact sensitivity with molecular structural parameters.¹⁹ Note that it is not necessary to develop chemical mechanisms, or even to identify the observed products, in order to obtain practical results (e.g., a small scale screening test) from the derived correlations.

IV. CONCLUSION

Pyrolysis gas chromatography Fourier transform infrared (P-GC-FTIR) techniques are being used to study the distribution of both permanent gases and less volatile components in a "model" LOVA propellant formulation series developed at the NWC, China Lake. It is expected that correlation of the observed pyrolysis products with the NWC time-to-ignition data will provide insight into the chemical factors that affect LOVA propellant ignitability and sensitivity, and ultimately lead to formulation guidelines (ingredient "selection rules") and data for input to expert systems for computer assisted formulation design and propellant property prediction.

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