



TECHNICAL REPORT FCDD-AMT-21-19

# INTERACTIONS OF METAL OXIDE SPECIES ON SIMPLE DOUBLE-BASE (DB) PROPELLANTS

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14. ABSTRACT Efforts at Redstone Arsenal, AL continue work on gaining a stronger understanding of the interactions between known simple Burn Rate Modifiers (BRMs) on simple solventless processed Double-Base (DB) propellants. These include interactions of key nitrate esters with simple metal oxides, creation of multiple DB propellants exploring energy contend, and burn rate effects.					
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## EXECUTIVE SUMMARY

The joint United States (U.S.) Department of Defense (DoD) and United Kingdom (U.K.) Ministry of Defence (MOD) effort under Project Agreement (PA) centered on energetic materials with a focus on Double-Base (DB) propellants continues to make excellent progress with the U.S. Army Combat Capabilities Development Command (DEVCOM) Aviation & Missile Center (AvMC) finishing up the effort. Efforts in-house examined molecular interactions between nitroglycerin (NG) and known Burn Rate Modifiers (BRMs) using attenuated total reflectance infrared spectroscopy, differential scanning calorimetry, and thermal gravimetric analyses. These efforts have screened lead (lead monoxide (PbO), lead dioxide (PbO<sub>2</sub>)), tin (tin monoxide (SnO), tin dioxide (SnO<sub>2</sub>)) and bismuth oxides (Bi<sub>2</sub>O<sub>3</sub>). Due to COVID-19 pandemic work restrictions, only PbO and PbO<sub>2</sub> were further studied in two simple DB propellants and further characterized with stability, initial aging, and burning rate studies.

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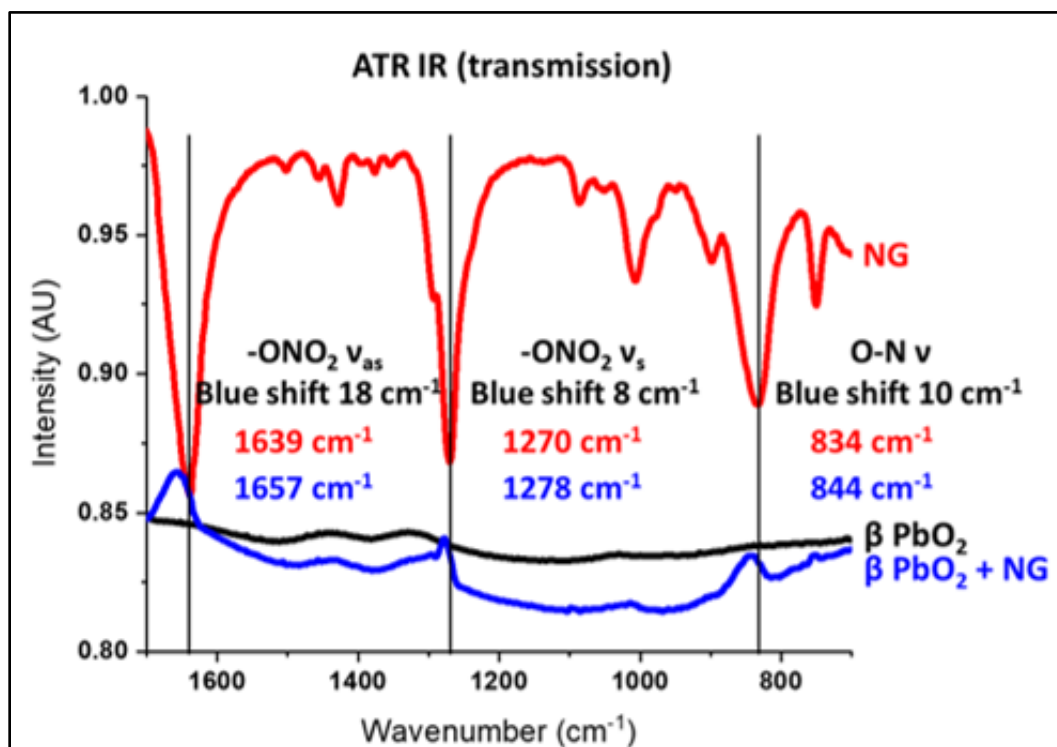
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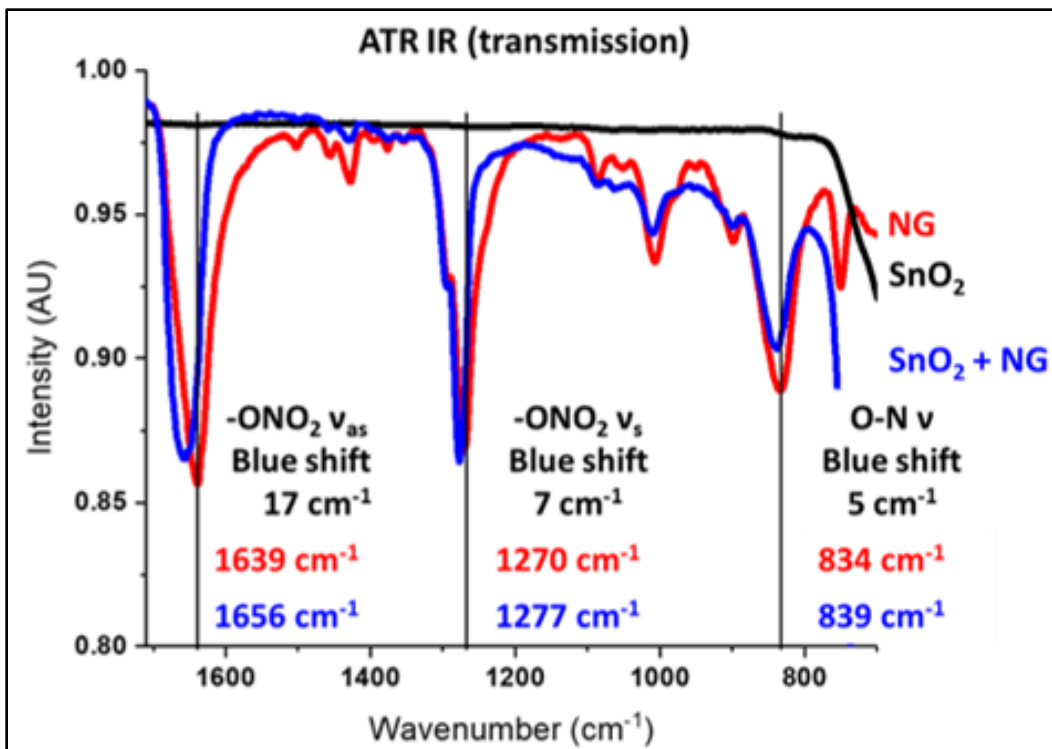
## I. NITRATE ESTER METAL OXIDE INTERACTIONS

Since the United Kingdom (U.K.) Ministry of Defence (MOD) contractor calculations used very low levels of nitroglycerin (NG) molecules in respect to the metal oxide surface at approximately  $1 \times 10^{-6}$  grams (g) per 1 g of metal oxide, there were no available analytical techniques available to measure changes in such small concentration of NG. Based on previous experiments with other classes of molecules, larger amounts of NG could be used with the high surface area metal oxide and still observe NG Infrared (IR) band shifts, if present. A dilute solution of NG of approximately 0.2 percent (%) in methylene chloride ( $\text{CH}_2\text{Cl}_2$ ) was used to deposit 4, 8, 12, and 16 milligrams (mg) of NG onto the target metal oxides at ambient temperatures by measuring respective masses of the  $\text{CH}_2\text{Cl}_2$  solutions onto the respective gram quantities of each metal oxide in an open container. These containers sat at ambient temperatures, which allowed the bulk  $\text{CH}_2\text{Cl}_2$  to evaporate and leave the NG behind. Getting homogenous samples were difficult due to the clumping of NG droplets with the fine metal oxide. This led to an IR spectra that did not demonstrate a repeatable, measurable growth in nitrate ester band intensity based on NG concentration. However, the bands were shifted the same magnitude for each metal oxide tested. A slightly larger sample of 20 mg of NG was deposited upon 1 g of metal oxide. As the  $\text{CH}_2\text{Cl}_2$  sample evaporated from the metal oxide, three fresh aliquots of  $\text{CH}_2\text{Cl}_2$  of approximately 1.5 g each were added to each sample via pipet that washed down the surface and allowed it to fully evaporate. This was repeated three times to ensure that there were more homogenous NG and metal oxide samples. Three types of behavior were noted, as shown in Figures 1 through 3 and Table 1.



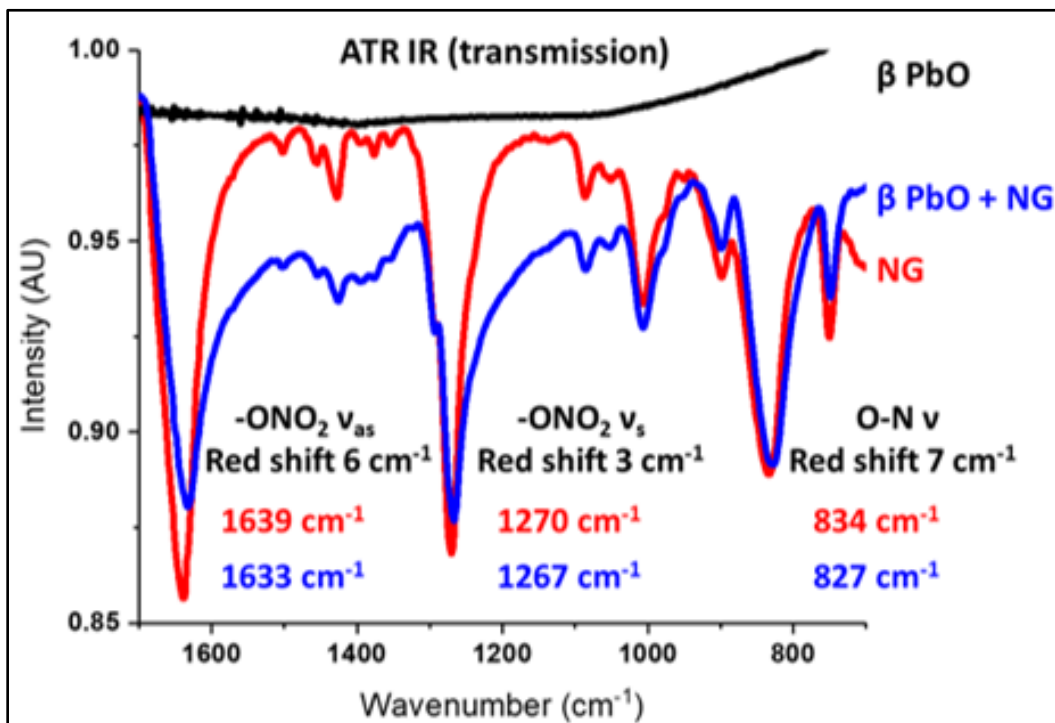
a. NG Adsorbed Onto  $\beta$ -PbO<sub>2</sub>

Figure 1. IR Spectra Revealing Shifted NG Bands



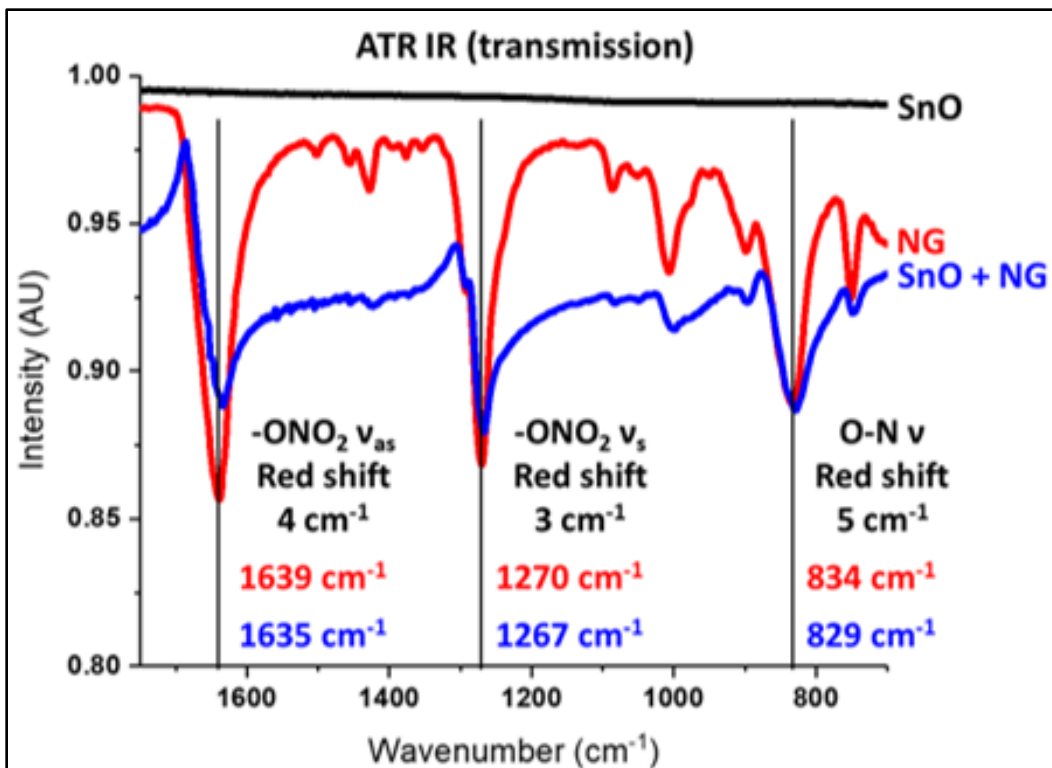
*b. NG Adsorbed Onto SnO<sub>2</sub>*

*Figure 1. IR Spectra Revealing Shifted NG Bands (Concluded)*



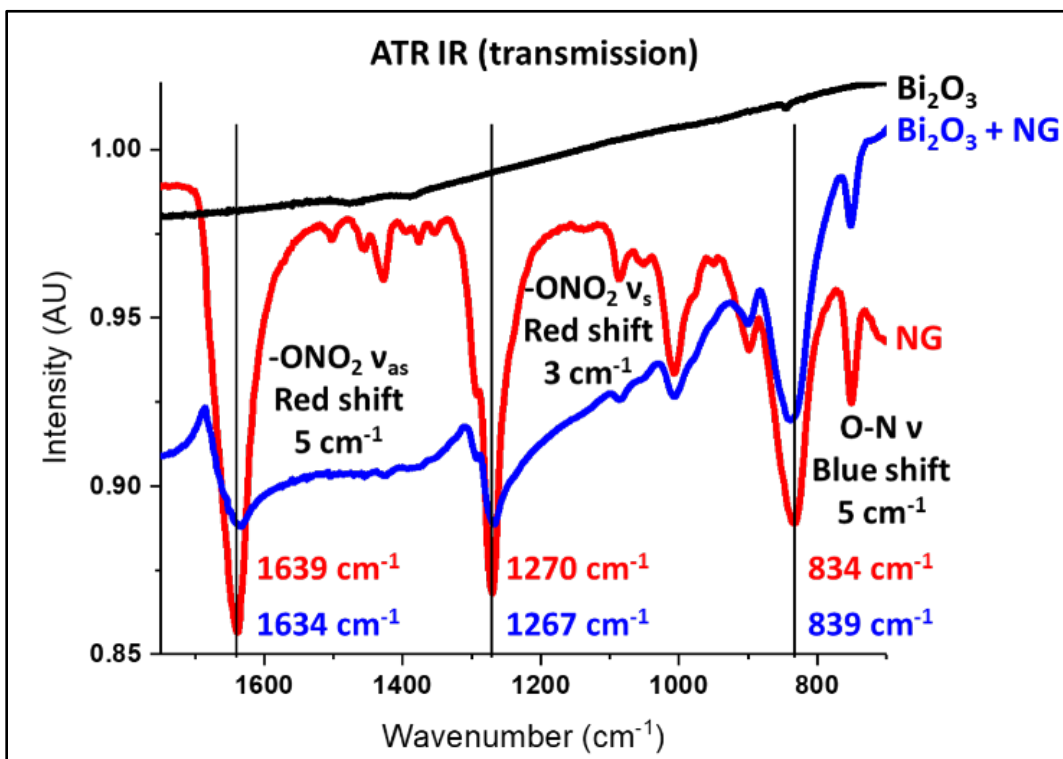
*a. NG Adsorbed Onto β-PbO*

*Figure 2. IR Spectra Revealing Red Shifted Bands*



*b. NG Adsorbed Onto SnO*

*Figure 2. IR Spectra Revealing Red Shifted Bands (Concluded)*



*Figure 3. IR Spectra of NG Adsorbed Onto Bi<sub>2</sub>O<sub>3</sub> Revealing no Small and Variant Shifts*

Table 1. ATR IR Band Frequency and Shift Relative to NG

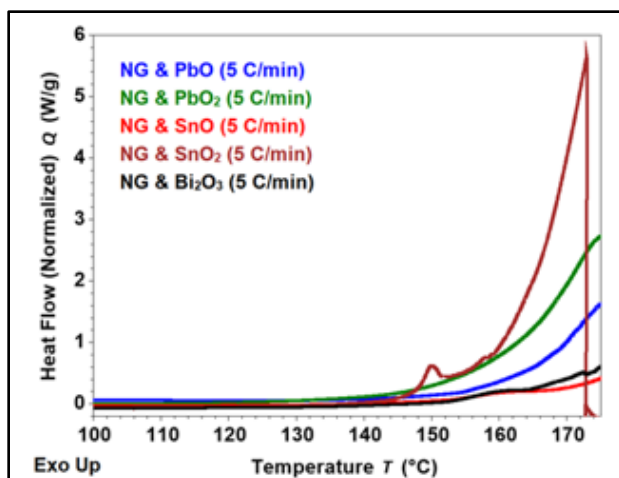
	<b>-ONO<sub>2</sub> v<sub>as</sub> (cm<sup>-1</sup>)</b>		<b>-ONO<sub>2</sub> v<sub>s</sub> (cm<sup>-1</sup>)</b>		<b>O-N v (cm<sup>-1</sup>)</b>	
<b>NG</b>	<b>1639</b>		<b>1270</b>		<b>834</b>	
NG PbO <sub>2</sub>	1657	(18 blue)	1278	(8 blue)	844	(10 blue)
NG SnO <sub>2</sub>	1656	(17 blue)	1277	(7 blue)	839	(5 blue)
NG PbO	1633	(6 red)	1267	(3 red)	827	(7 red)
NG SnO	1635	(4 red)	1267	(3 red)	829	(5 red)
NG Bi <sub>2</sub> O <sub>3</sub>	1634	(5 red)	1267	(3 red)	839	(5 blue)

In the case of lead dioxide (PbO<sub>2</sub>) and tin dioxide (SnO<sub>2</sub>), as shown in Figure 1, IR spectral bands blue shifts were observed. The Abnormal Infrared Effect (AIRE) [1] band inversion observed with NG on PbO<sub>2</sub> is unusual but has been noted previously in other metallic and semimetallic systems and also has been cited as evidence of strong molecular interactions [2].

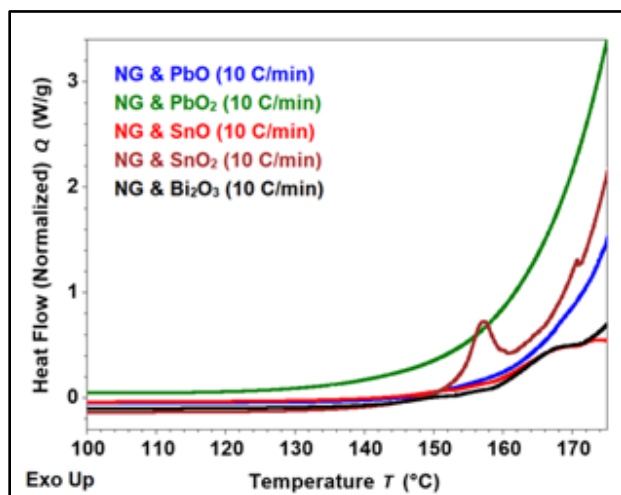
In the case of lead monoxide (PbO) and tin monoxide (SnO), as shown in Figure 2, less drastic IR band red shifts are observed yet are evidences of molecular interactions between NG and respective metal oxide.

In the case of bismuth oxide (Bi<sub>2</sub>O<sub>3</sub>), as shown in Figure 3, small and divergent, that is, red and blue, IR band shifts are observed, which suggests that there is little evidence of molecular interactions between NG and Bi<sub>2</sub>O<sub>3</sub>.

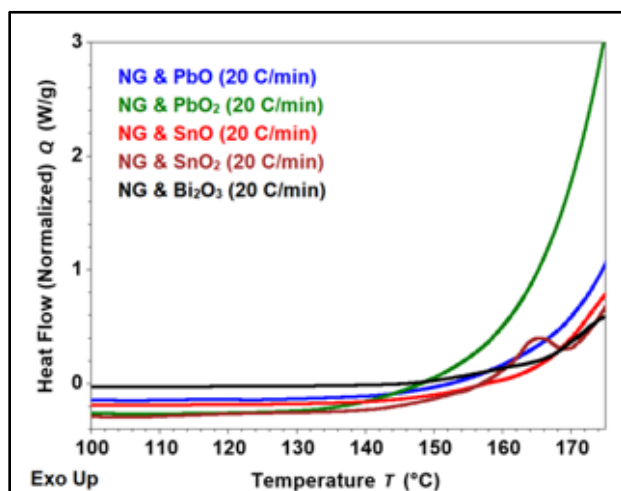
Secondly, Differential Scanning Calorimetry (DSC) can sometimes be used to infer that there is reactivity between intimate mixtures of two materials. In the case of NG [3-5], it demonstrates irreversible exothermic decomposition, which begins at approximately 145 °C to 150 °C at nominal heating rates of 10 degrees Celsius per minute (°C/min). Intimate mixtures of metal oxide of approximately 1.0 mg to 1.5 mg and neat NG of 1.0 mg to 1.5 mg were mixed in DSC pans and then hermetically sealed. Separate samples were heated at 20, 10, and 5 °C/min to get an idea of any catalytic behavior between NG and metal oxide, as shown in Figure 4. In regard to exothermic behavior onsets of metal oxides mixed with NG, a trend exists with SnO<sub>2</sub>>PbO<sub>2</sub>>>PbO~SnO >Bi<sub>2</sub>O<sub>3</sub> with SnO<sub>2</sub> and PbO<sub>2</sub> having the strongest effect upon NG. These DSC results are in agreement with the IR results, that is, no bond weakening concomitant with an energy input reduction needed for exothermic decomposition.



a. 5 °C



b. 10 °C



c. 20 °C

Figure 4. DSC Traces of Metal Oxide Mixed With NG per Minute Heating Rates

Burn Rate Modifiers (BRMs) are capable of interacting with key nitrate bonds, as illustrated by IR, by often reducing the energy required for thermal decomposition, as illustrated by DSC, to better understand BRM roles on NG thermal decomposition products. A Pyrolysis (Py) Gas Chromatography Mass Spectrometry (GCMS) was conducted. As NG on various metal oxides is thermally decomposed, gaseous products are collected, chromatographically separated, and identified by mass spectrometry, as shown in Figure 5. For all samples studied, as shown in Figures 5a through e, no significant changes were observed for the nitric oxide (NO) and nitrous oxide (N<sub>2</sub>O) of approximately 1.57 minutes per peak, formaldehyde (CH<sub>2</sub>O) and water of approximately 2.00 minutes per peak, and nitrate ester species of approximately 2.45 minutes per peak. Relative to the Gas Chromatography (GC) of pure NG pyrolysis in the presence of all metal oxides studied in Figures 5 b through e, CH<sub>2</sub>O and nitrogen dioxide (NO<sub>2</sub>) at approximately 1.60 minutes per peak slightly decreases in intensity, methyl nitrate (CH<sub>3</sub>NO<sub>3</sub>) and glyoxal of approximately 1.67 minutes per peak is not observed, and NO<sub>2</sub> with very small amounts of glyoxal of approximately 1.64 minutes per peak emerges with no distinct trend or ordering among the metal oxide samples. In the results from samples with PbO<sub>2</sub> and SnO<sub>2</sub>, as shown in Figures 5b and c, relative to those of pure NG, Figure 5a shows no change in the CH<sub>3</sub>NO<sub>3</sub> of approximately 1.70 minutes per peak or a shift from glyoxal trimer to dimer of approximately 3.71 minutes to approximately 3.51 minutes per peak. The results from samples with PbO, SnO, and Bi<sub>2</sub>O<sub>3</sub>, as shown in Figures 5d and e, relative to those of pure NG, as shown in Figure 5a, show a broadening of the CH<sub>3</sub>NO<sub>3</sub> of approximately 1.70 minutes per peak and no significant shift from glyoxal trimer to dimer of approximately 3.71 minutes to approximately 3.51 minutes per peak.

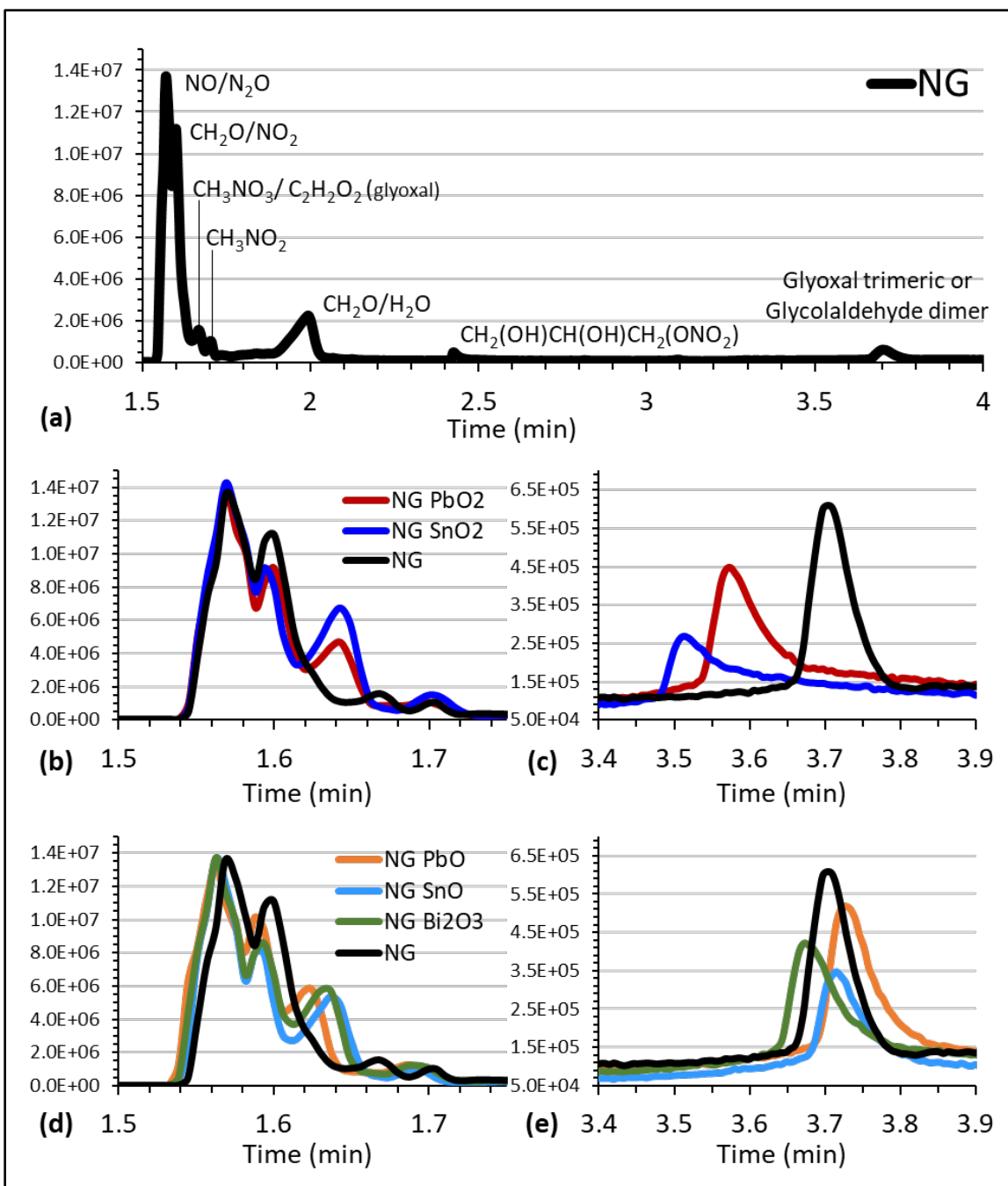


Figure 5. GC Y-Axis Abundance (Counts) of Pyrolysis Products of NG on Various Metal Oxides

Previous efforts [4, 6-8] report various decomposition products based on the thermal decomposition of neat NG at various pyrolysis rates. There are not many references of neat NG decomposition studies with various materials as binary systems alone.

## II. PROPELLANT EFFORTS

Historically, lead and other metal compounds have been found to have significant effects upon Double-Base (DB) combustion in literature [7-32]. Few solventless DB propellant burning rate studies, including those containing only nitrocellulose (NC), NG, and BRM with no diluents, such as phthalates, dinitrotoluene, and technical additives, have been illustrated and often with carbon black additions of these simple metal oxides upon combustion behavior [33, 15]. These simplistic studies were necessary to collect data for comparison with models being developed for simple DB interactions. A few examples of similar NG/NC based formulations have been reported, but actual burning rate data are limited for comparison. Two solventless DB propellant slurry baselines were created—one a lower calorific base with an NG/NC ratio of 0.6 and another with NG/NC 1.5 ratio, as shown in Table 2.

Table 2. Formulation (Mass Percent) of Simple DB Propellants in Study

$\Delta H_{\text{exp}}$ (calc) cal/g	1173	1132	1138	1262	1221	1225
12.15% N NC	58.8	57	57	39.2	38	38
NG	39.2	38	38	58.8	57	57
2-NDPA	2	2	2	2	2	2
PbO	--	3	--	--	3	--
PbO <sub>2</sub>	--	--	3	--	--	3

Due to the unexpected and schedule debilitating effects of COVID 19 pandemic restrictions on workplace schedules, PbO<sub>2</sub> and PbO were chosen and downselected for incorporation into these two simple DB propellants. These propellants were developed by well-known solventless procedures by creating DB pastes with the addition of NG to NC under water and after filtering. BRMs were thoroughly dispersed through the water wet DB paste until deemed homogenous by visual inspection. The slurries were remotely pressed into 4-x-4 inches (") approximately 0.150" sheets in a custom designed stainless steel, two part die set under several hundred pressures per square inch (psi) static pressure multiple times similar to methods, which are described in References 8, 15, 24, 34, and 35. Characterization, decomposition studies, and propellant strand burning rates were carried out on cut samples of these propellant sheets. In the case strand data, burning rates were determined from a 3" run distance in externally deterred propellant using three tests at each pressure measured.

DSC studies were conducted using small cut circles of each of the DB propellants. Separate samples in DSC pans were hermetically sealed and heated at 5, 10, and 20 °C/min each to get an idea of any catalytic behavior between the metal oxide and two differing propellants. The DSC traces at 5, 10, and 20 °C/min heating rates, respectively, are overlaid, as shown in Figure 6. No major conclusions are drawn from varying the NG/NC ratio. This discussion is limited to rate and catalyst type. More evident at slower rates, the presence of a BRM catalyst, that is, PbO<sub>2</sub> (blue) and PbO (green), results in a DSC exothermic onset temperature reduction relative to that of the uncatalyzed propellant (red). Generally, the presence of PbO<sub>2</sub> is associated with the greatest reduction of DSC exothermic onset temperature in these simple propellants. Attempts at using Attenuated Total Reflectance (ATR) IR spectroscopy were rather uninformative in the homogenous, amorphous thermoplastic propellants due to nature of the sample coloring coupled with relatively low metal oxide weight

percent of 3%, and no spectral variations were observed between any of the samples besides the typical broad fingerprint bands of nitrate esters.

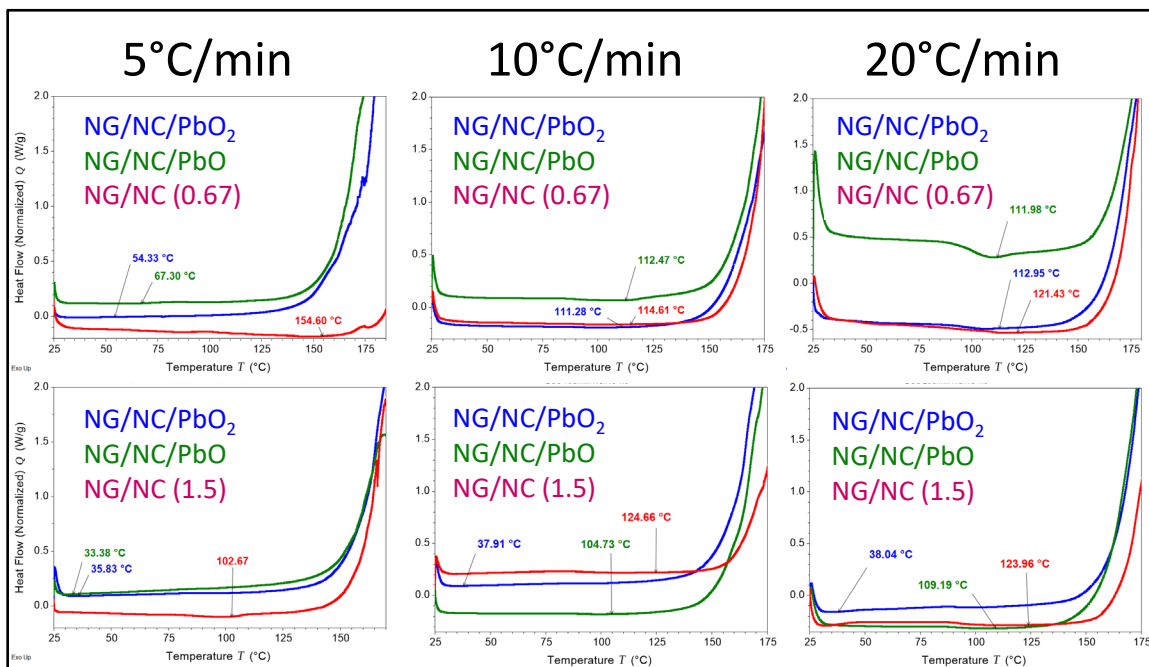


Figure 6. DSC Heating Profiles of DB Propellants With NG/NC Weight Ratios With Labeled Exothermic Onset Temperatures

To better understand BRM roles on NG thermal decomposition products, a Py-GCMS was conducted using the six propellant samples. A small propellant discs sample of 0.5 mg was used. Experiments were run in duplicate to verify results due to the small sample size. Figure 7 contains the GCs of NG, as shown in Figure 7a, which were labeled with a mass spectrometry analyzed composition and various time plots of NG/NC 0.67 (purple), as shown in Figures 7b through d; NG/NC 0.67 with 3% PbO<sub>2</sub> (navy), NG/NC 0.67 with 3% PbO (blue), and NG/NC 1.5 (black), as shown in Figures 7e through g; NG/NC 1.5 with 3% PbO<sub>2</sub> (orange); and NG/NC 1.5 with 3% PbO (green). Upon decomposition with heat, NG exhibits a peak approximately 2.5 minutes on the GC plot assigned to CH<sub>2</sub>(OH)CH(OH)CH<sub>2</sub>(ONO<sub>2</sub>) by a Minimum Signature (MS) propellant, as shown in Figure 3a. Heavily plasticized propellant samples, despite BRM, as shown in Figure 3d, exhibit an analogous peak of similar mass fraction. GC plots of less plasticized propellant, despite BRM, as shown in Figure 3g, are absent of an analogous peak. Otherwise, condensable, stable species, as seen in the decomposition of NG and DB propellants, were observed. The GC Y-axis abundance (counts) of pyrolysis products of NG are shown in Figure 7a, and DB propellants with various metal oxides are shown in Figures 7b through g with labeled mass spectrometry assigned compositions.

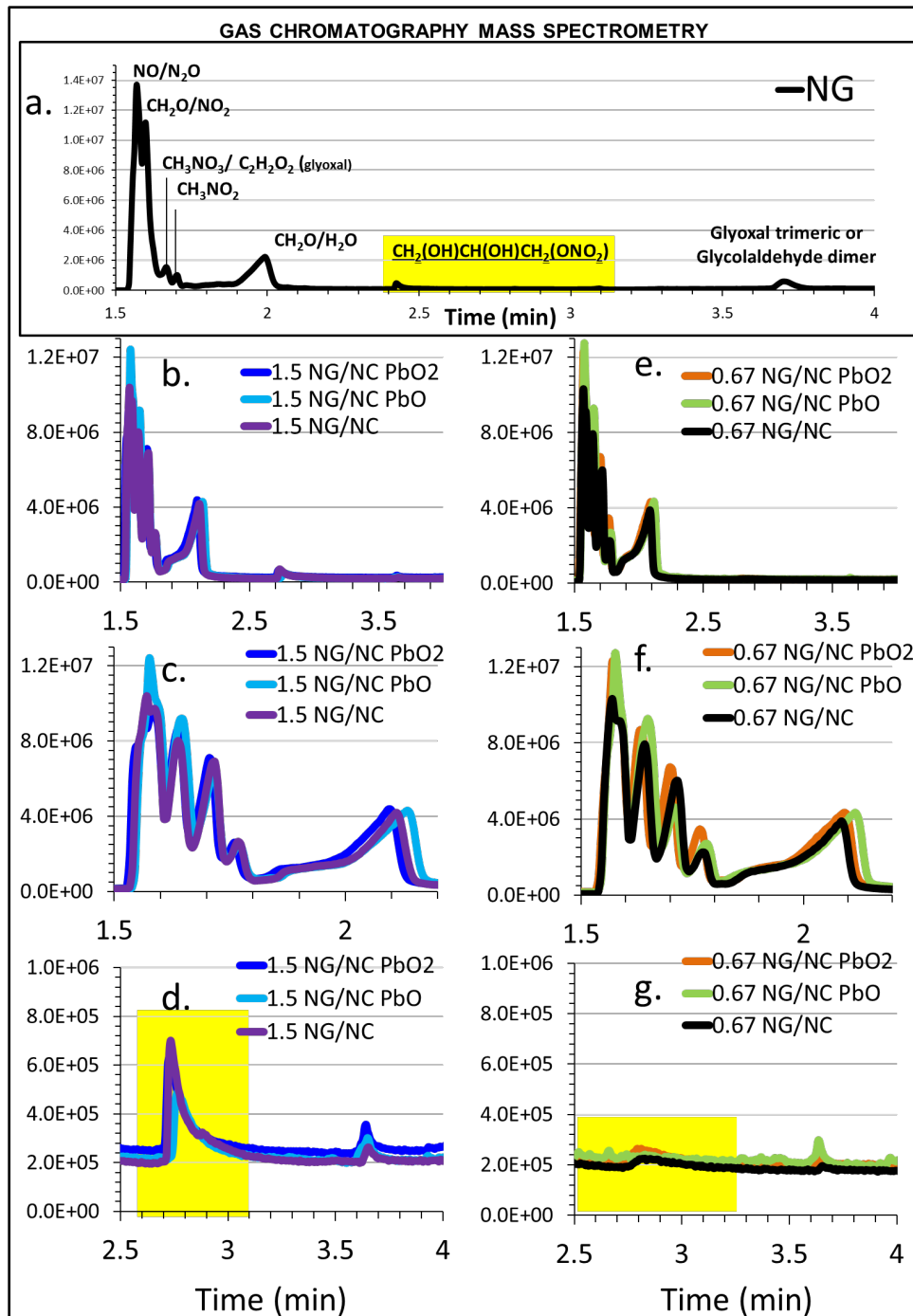
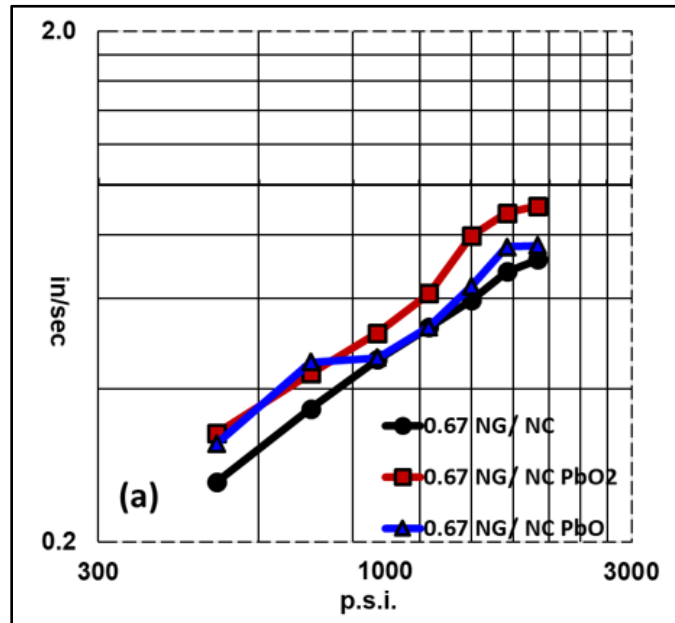


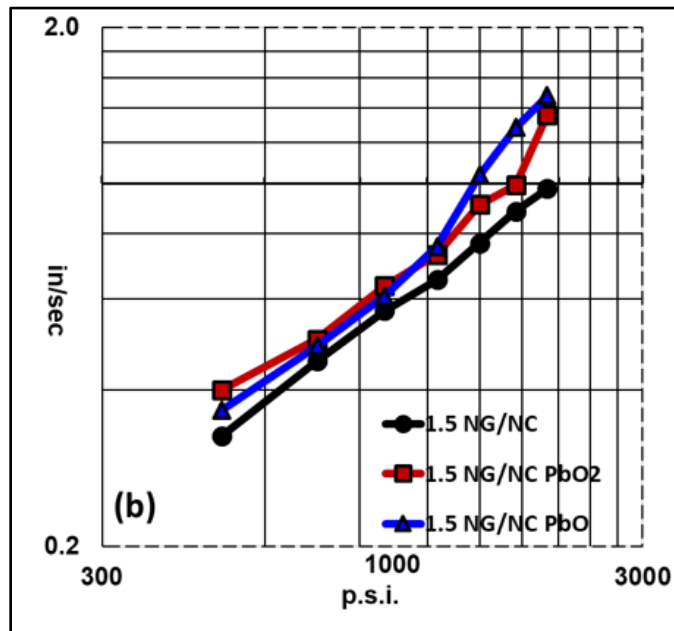
Figure 7. GC Y-Axis Abundance (Counts) of Pyrolysis Products With Labeled Mass Spectrometry Assigned Compositions

The propellant strand burning data are plotted, as shown in Figure 8. In the uncatalyzed propellant with 0.67 (circle) and 1.5 (circle) NG/NC ratio in Figures 8a and b, respectively, burning rates are linear lacking mesa and plateau features as expected from literature and in light of the simple binary mixture. The uncatalyzed propellant with a 1.5 (circle) NG/NC ratio burning rate, as shown in Figure 8b, is greater than that of 0.67 (circle), as shown in Figure 8a,

as expected since better oxygen balanced formulations typically burn faster. Relative to the uncatalyzed propellant burning rates, the catalyzed propellant burning rates are elevated exhibiting weak plateau features, as shown in Table 3. These burning rate and exponent effects are very comparable to those previously reported in References 15 through 17 with  $PbO_2$  and  $PbO$  at modest levels (1-3%) without carbon black or diluents in similar calorific value DB propellants. As previously reported, burn rate alterations by various BRMs are weakened by rising calorific value of the propellant base [9, 20, 21].



a. 0.67 NG/NC Ratio



b. 1.5 NG/NC Ratio

Figure 8. DB Propellant Strand Burning Rates

Table 3. DB Propellant Strand Burning Rates (75 °F) Values and Calculated Exponents

Sample	Propellant Burning Rates (in/s)			n
	500 psi	1,000 psi	1,500 psi	
NG/NC 1.5 PbO <sub>2</sub>	.40	.64	1.0	.83
NG/NC 1.5 PbO	.37	.61	1.0	1.0
NG/NC 1.5	.32	.61	.77	.78
NG/NC 0.67 PbO <sub>2</sub>	.33	.51	.80	.78
NG/NC 0.67 PbO	.31	.46	.63	.64
NG/NC 0.67	.26	.46	.60	.73

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## LIST OF ABBREVIATIONS, ACRONYMS, AND SYMBOLS

%	percent
~	Approximately
“	inch
$\beta$	beta
$\Delta H_{\text{exp}}$	heat of explosion
$\nu_{\text{as}}$	stretching frequency, asymmetric
$\nu_{\text{s}}$	stretching frequency, symmetric
$^{\circ}\text{C}$	degree Celsius
2-NDPA	2-nitrodiphenylamine
AIRE	Abnormal Infrared Effect
ATR	Attenuated Total Reflection
AU	Absorbance Unit
$\text{Bi}_2\text{O}_3$	bismuth oxide
BRM	Burn Rate Modifier
calc	Calculated
cal/g	calorie per gram
$\text{C}_2\text{H}_2\text{O}_2$	acetylenediol
$\text{CH}_2\text{Cl}_2$	methylene chloride
$\text{CH}_3\text{NO}_2$	nitromethane
$\text{CH}_3\text{NO}_3$	methyl nitrate
$\text{CH}_2\text{O}$	Formaldehyde
$\text{cm}^{-1}$	Wavenumber
C/min, $^{\circ}\text{C}/\text{min}$	degree Celsius per minute
DB	Double-Base

## LIST OF ABBREVIATIONS, ACRONYMS, AND SYMBOLS (CONTINUED)

DSC	Differential Scanning Calorimetry
Exo	Exothermic
g	gram
GC	Gas Chromatography
H <sub>2</sub> O	water
in/s	inch per second
IR	Infrared
mg	milligram
min	minute
MOD	Ministry of Defence
MS	Minimum Signature
N	Percent nitrogen Content
n	burning rate exponent
N <sub>2</sub> O	nitrous dioxide
NC	nitrocellulose
NG	nitroglycerin
NO	nitric oxide
NO <sub>2</sub>	nitrogen oxide
PbO	lead monoxide
PbO <sub>2</sub>	lead dioxide
p.s.i, psi	pressure per square inch
Py-GCMS	Pyrolysis Gas Chromatography Mass Spectrometry
SnO	tin monoxide
SnO <sub>2</sub>	tin dioxide

## **LIST OF ABBREVIATIONS, ACRONYMS, AND SYMBOLS (CONCLUDED)**

T	Temperature
U.K.	United Kingdom
W/g	watt per gram