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EXPLOSIVE MATERIAL QUALIFICATION

CHEMISTRY

SUBLIMATION STUDIES OF HEXANITROAZOBENZENE (HNAB)

Purchase Order No. 93-1813

G. L. Clink

August 1970

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SUBLIMATION STUDIES OF HEXANITROAZOBENZENE (HNAB)

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ABSTRACT

Sublimation studies of hexanitroazobenzene (HNAB), Sandia Lot 43-11-B, have shown all sublimation residues to be essentially HNAB (form III), with HNAB (form II) found in the sublimates. The sublimation condensate in the lower temperature ranges (80-130°C) has a non nitro group material, and an HNAB like (nitro group) material was found in the 160-190°C condensates.

The presence of aliphatic impurity(s) in all fractions, from 80 to 220°C, has been determined albeit the concentration decreases significantly at the higher temperature ranges (200-220°C).

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DISCUSSION

Sublimation studies of hexanitroazobenzene (HNAB) were undertaken in an effort to establish optimum temperature/pressure/time relationships for separation of the various fractions of the HNAB system. Whether these fractions contain polymorphs, homologs, impurities, or possible di or tri component combinations of the three has, at the onset of this study, been speculative.

The material under study was Sandia Lot 43-11-B. Fifty grams of the material were placed in a McCarter sublimator (Fig. 1) and maintained for extended periods of time under controlled conditions of temperature and pressure. The sublimator was heated by means of a Dow Corning silicone (SF-96-500) oil bath with Variac control of the mantle. The cold finger (condensing cone) of the sublimator was cooled by means of tap water which varied from 18-22°C. Reduced pressure in the system was effected by means of a Veeco liquid nitrogen diffusion pump. Elapsed time variance among the various runs resulted from the indicated rate decrease of sublimate deposition as a function of the various system conditions imposed.

Results of the study are presented in Table I. Examination of the various sublimes and sublimation residues included the following:

1. Carbon, hydrogen, nitrogen analysis. Hewlett Packard Model 185 Carbon, Hydrogen, and Nitrogen Analyzer. Six samples of each material were run for statistical averaging.
2. Infrared spectral analysis. Perkin-Elmer Model 21 Infrared Spectrophotometer. KBr pellet method.
3. Differential thermal analysis. Du Pont Model 900 Differential Thermal Analyzer. Sample sizes were 1-2 mm x 2 mm, Al₂O₃ reference. Heating rate was 10°C/min.

4. X-ray diffraction. Norelco. Powder method.
5. Macrophotographs (8-10X) and photomicrographs (300X).
6. Spark sensitivity measurements (50% frequency at 5 KV), made only on selected sublimation residues since the sublimates did not afford enough material for complete runs.
7. Weight loss measurements were not made due to the relative massive weight of the McCarter sublimator, tending to give too large an error for meaningful measurements. The matter of weight loss is being undertaken at this time.

Fig. 1
McCarter Sublimator

HNAB, Sandia Lot 43-11-B

Carbon, hydrogen, and nitrogen analysis of the unheated Sandia HNAB (Lot 43-11-B) shows the following comparative values, relative to the theoretical values of pure hexanitroazobenzene;

<u>Material</u>	<u>C</u> <u>(wt.%)</u>	<u>H</u> <u>(wt.%)</u>	<u>N</u> <u>(wt.%)</u>	<u>C/N</u> <u>Molar Ratio</u>	<u>Total %</u> <u>(C+N)</u>
Hexanitroazobenzene (Theor.)	31.88	0.89	24.77	1.50	56.7
Sandia Lot 43-11-B	31.82	0.91	24.80	1.50	56.6

Infrared spectral results are presented in Fig. 2. As is normally the case, band assignments of nitro aromatics is difficult due to the highly inductive effect of the nitro group which tends to cause substantial shifting in the normal position of the ring substitution modes (11-15 μ) and the pronounced damping effects on the ring substitution overtones (5-6 μ). The following band assignments are quite evident, however;

<u>Band (μ)</u>	<u>Mode</u>	<u>Group</u>
2.90	ν	O - H or N - H
3.23	ν	C - H (aromatic)
3.45	$\nu_a + s$	C - H (aliphatic)
6.2 - 6.45	ν_a	N = O
7.4	ν_s	N = O

The remaining absorption bands (9-15 μ) are due to C - N stretching, ring deformation, and the aromatic out of plane deformation of hydrogen. But due to the distorting effect of the nitro group it is not practical to make definitive assignments.

The rather prominent band at $\sim 2.90 \mu$ appears consistently throughout the temperature/pressure range of the numerous sublimation runs ($80-220^\circ\text{C}$, $0.9-10^{-6}$ atm). The structure of hexanitroazobenzene (HNAB) does not allow for a permitted vibrational transition in this wavelength region. Assuming that the potential source of this absorption transition arises from product intermediates and/or solvents, the prime possibilities are O - H from water, ethanol or picrates; and N - H from hydrazine intermediates. The most obvious source indicated by a cursory inspection of the spectrum would be water. However some apparent shortcomings are found in this assumption. Inspection of the spectra of 43-11-B and all resulting sublimation residues and sublimes does not show the normally broad character of the O - H stretching mode usually found for water ($\sim 2.9 \mu$). Nor is there any typical spectral undulation in the $13-15 \mu$ range due to the H - OH wagging deformation. The possibility of this band being due to HOH was further checked by taking several HNAB sublimate fractions and subjecting them to high humidity in a controlled humidity oven at 120°C . Spectral results show no indication of water pickup as a result, but do give the typical HOH stretching, deformation, and wagging mode bands when the fractions are dampened with water. The possibility of interstitially trapped water as a result of cooling occlusion after sublimation could conceivably produce an abnormally sharpened 2.9μ band if relative spatial separation of the water molecules eliminated hydrogen bonding, but the intensity of the 2.9μ band and the lack of the wagging deformation mode makes this doubtful.

The possibility of ethanol is eliminated since the C-O - H stretch occurs at 3.05μ , far too high for the observed 2.9μ band.

In the case of the picrates, the phenolic - OH would normally occur at a lower wavelength when it is hindered (due to lack of hydrogen bonding), but undergoes an opposite shift when hindered by a highly inductive group such as nitro, viz

The absorption band at 2.9μ occurs in the normal wavelength range of N - H stretching. Since intermediate(s) of this type structure were used in the preparation of HNAB (picryl hydrazine, etc.), consideration should be given to the possibility of some N - H system being present.

The absorbance at $\sim 3.45 \mu$ is definitely aliphatic in nature, and is foreign to the HNAB system.

Differential thermal analysis ($10^\circ\text{C}/\text{min.}$) shows endothermic behavior to occur at $\sim 222-223^\circ\text{C}$. The major exothermic peaking occurs at $\sim 336^\circ\text{C}$.

X-ray diffraction results from HNAB 43-11-B appear in Table II-A. Referring to the Sandia coding of HNAB types, it has the d_{hkl} pattern of HNAB-III.

Spark sensitivity of the material has an energy threshold of 1.75 joules at 5 KV.

Photographs (8X and 50X) are presented in Fig. 2.

Table I

Sublimation Fraction Analyses Results

HNAB Lot 43-11-B

System Conditions			Chemical Analysis			Carbon/ Nitrogen	Infrared	DTA	Photo- graph	X-ray	Spark	Material
Temp. (°C)	Time (hr.)	Pressure (atm x 10 ⁻⁶)	Carbon (wt.%)	Hydrogen (wt.%)	Nitrogen (wt.%)	Molar Ratio	Spectra Fig. No.	Fig. No.	Fig. No.	Diffraction Type	Sensitivity (joules)	Fraction
-	-	-	31.8	0.9	24.8	1.50	2	2	2	A	1.75	-
80	168	Ambient	30.9	0.9	24.2	1.50	3	3	3	A	-	Residue
80	168	Ambient	-	-	-	-	4	-	-	-	-	Sublimate
100	168	Ambient	29.7	0.9	24.3	1.40	5	5	5	A	-	Residue
100	168	Ambient	-	-	-	-	-	-	-	-	-	Sublimate
120	168	Ambient	29.7	1.0	24.4	1.40	6	6	6	A	-	Residue
120	168	Ambient	-	-	-	-	7	-	-	-	-	Sublimate
130	168	6.5	31.0	1.0	24.1	1.51	8	8	8	A	1.83	Residue
130	168	6.5	-	-	-	-	9	-	-	-	-	Sublimate
145	96	10.0	31.4	1.3	24.3	1.51	10	10	10	A	2.00	Residue
145	96	10.0	-	-	-	-	-	-	-	-	-	Sublimate
150	168	Ambient	31.6	1.3	24.3	1.52	11	11	11	A	1.75	Residue
150	168	Ambient	-	-	-	-	-	-	-	-	-	Sublimate
150	216	200.0	31.4	1.3	24.2	1.51	12	12	12	A	2.00	Residue
150	216	200.0	-	-	-	-	-	-	-	-	-	Sublimate
155	216	50.0	31.6	0.9	24.7	1.50	13	13	13	A	2.06	Residue
155	216	50.0	-	-	-	-	-	-	-	-	-	Sublimate
160	48	50.0	31.2	1.1	24.2	1.51	14	14	14	A	1.75	Residue
160	48	50.0	33.7	1.4	23.4	1.68	15	-	15	C	-	Sublimate
170	96	400.0	31.6	0.8	24.9	1.48	16	16	16	A	1.78	Residue
170	96	400.0	-	-	-	-	17	-	-	C	-	Sublimate
170	144	6.5	31.3	0.8	24.8	1.47	18	18	18	A	1.80	Residue
170	144	6.5	32.8	1.0	24.1	1.70	19	19	19	B	-	Sublimate
180*	96	6.5	32.2	0.9	24.2	1.60	20	20	20	A	1.68	Residue
180*	96	6.5	32.3	1.1	23.7	1.56	21	21	21	B	-	Sublimate
175	72	50.0	31.4	0.8	24.7	1.48	22	22	22	A	2.00	Residue
175	72	50.0	32.7	0.8	25.1	1.52	23	23	23	C	-	Sublimate
180	168	Ambient	31.2	1.0	24.2	1.51	24	24	24	A	1.75	Residue
180	168	Ambient	32.1	1.0	24.3	1.55	25	-	-	-	-	Sublimate
180	96	6.0	31.0	1.3	24.1	1.50	26	26	26	A	1.94	Residue
180	96	6.0	34.2	1.7	22.3	1.79	27	27	27	B	-	Sublimate
185	96	80.0	31.7	0.8	24.8	1.49	28	28	28	A	1.78	Residue
185	96	80.0	32.4	0.7	25.0	1.52	29	29	29	B	-	Sublimate
190	168	Ambient	31.6	1.1	24.0	1.54	30	30	30	A	-	Residue
190	168	Ambient	32.2	1.3	23.8	1.61	31	31	31	B	-	Sublimate
195	120	200.0	30.4	0.9	24.6	1.44	32	32	32	A	2.00	Residue
195	120	200.0	30.4	1.0	24.5	1.44	33	33	33	C	-	Sublimate
200	92	Ambient	30.6	0.9	23.9	1.53	34	34	34	A	-	Residue
200	92	Ambient	33.5	2.5	19.8	2.00	35	-	35	B	-	Sublimate
205	90	200.0	32.2	1.1	24.6	1.53	36	36	36	A	-	Residue (light)
205	90	200.0	32.4	0.9	24.7	1.53	37	-	37	A	1.81	Residue (dark)
205	90	200.0	32.2	1.0	24.7	1.53	38	38	38	B	-	Sublimate (light)
205	90	200.0	32.4	1.2	24.7	1.54	39	-	39	B	-	Sublimate (dark)
210	48	500.0	32.3	1.1	24.7	1.52	40	40	40	A	-	Residue
210	48	500.0	32.3	1.0	24.8	1.53	41	41	41	C	-	Sublimate
220	48	400.0	31.8	0.7	24.4	1.53	42	42	42	A	-	Residue
220	48	400.0	32.1	0.8	24.4	1.54	43	43	43	B	-	Sublimate

*The starting material for this sublimation run was the residue from the 170°C, 144 hour, 6.5 x 10⁻⁶ atm run.

Table II-A
X-Ray Diffraction Results

43-11-B		Sandia HNAB-III		Sublimation Fraction Type A		Fractions Having Type A d_{hkl} Pattern				Comments
d_{hkl} (Å)	I/I _o	d_{hkl} (Å)	I/I _o	d_{hkl} (Å)	I/I _o	Fraction Type	Temp. (°C)	Time (hr.)	Pressure (atm x 10 ⁻⁶)	
10.34	90	10.34	90	10.34	90	43-11-B	-	-	-	
7.23	10	7.23	10	7.23	10	Residue	80	168	Ambient	
6.17	75	6.17	75	6.17	75	"	100	168	Ambient	
5.13	10	5.13	10	5.13	10	"	120	168	Ambient	
4.85	75	4.85	75	4.85	75	"	130	168	6.5	
4.39	75	4.39	75	4.39	75	"	145	96	10.0	
4.10	5	4.10	5	4.10	5	"	150	168	Ambient	
3.88	100	3.88	100	3.88	100	"	150	216	200.0	
3.74	10	3.74	10	3.74	10	"	155	216	50.0	
3.62	100	3.62	100	3.62	100	"	160	48	50.0	
3.41	75	3.41	75	3.41	75	"	170	96	400.0	
3.16	75	3.16	75	3.16	75	"	170	144	6.5	
3.04	10	3.04	10	3.04	10	"	180	96	6.5	(From 170°C, 144-hour residue)
2.90	75	2.90	75	2.90	75	"	175	72	50.0	
2.81	10	2.81	10	2.81	10	"	180	168	Ambient	
2.76	20	2.76	20	2.76	20	"	180	96	6.0	
2.66	10	2.66	10	2.66	10	"	185	96	80.0	
2.58	10	2.58	10	2.58	10	"	190	168	Ambient	
2.54	10	2.54	10	2.54	10	"	195	120	200.0	
2.44	20	2.44	20	2.44	20	"	200	92	Ambient	
2.39	5	2.39	5	2.39	5	"	205	90	200.0	Light colored residue
2.31	10	2.31	10	2.31	10	"	205	90	200.0	Dark colored residue
2.20	10	2.20	10	2.20	10	"	210	48	500.0	
2.14	5	2.14	5	2.14	5	"	220	48	400.0	
2.04	10	2.04	10	2.04	10					
2.01	10	2.01	10	2.01	10					
1.93	20	1.93	20	1.93	20					

Table II-B

X-Ray Diffraction Results

Sandia HNAB-II		Sublimation Fraction Type B		Fractions Having Type B d_{hkl} Pattern				Comments
d_{hkl} (Å)	I/I _o	d_{hkl} (Å)	I/I _o	Fraction Type	Temp. (°C)	Time (hr.)	Pressure (atm x 10 ⁻⁶)	
7.41	10	7.41	10	Sublimate	170	144	6.5	(From 170°C 144-hour residue)
6.15	15	6.15	15	"	180	96	6.5	
5.95	15	5.95	15	"	180	96	6.0	
5.72	10	5.72	10	"	185	96	80.0	
5.47	10	5.47	10	"	190	168	Ambient	
4.71	100	4.71	100	"	200	92	Ambient	Light colored sublimate Dark colored sublimate
4.37	40	4.37	40	"	205	90	200.0	
4.25	40	4.25	40	"	205	90	200.0	
4.01	10	4.01	10	"	220	48	400.0	
3.77	50	3.77	50					
3.69	50	3.69	50					
3.41	30	3.41	30					
3.27	15	3.27	15					
3.15	30	3.15	30					
3.07	5	3.07	5					
2.98	10	2.98	10					
2.89	40	2.89	40					
2.83	30	2.83	30					
2.76	20	2.76	20					
2.65	70	2.65	70					
2.57	20	2.57	20					
2.46	30	2.46	30					
2.39	30	2.39	30					
2.31	5(B)	2.31	5(B)					
2.25	10	2.25	10					
2.20	10	2.20	10					
2.14	5	2.14	5					

Table II-C

X-Ray Diffraction Results

Sandia HNAB-II		Sublimation Fraction Type C		Sandia HNAB-III		Fractions Having Type C d_{hkl} Pattern			
d_{hkl} (A)	I/I _o	d_{hkl} (A)	I/I _o	d_{hkl} (A)	I/I _o	Fraction Type	Temp. (°C)	Time (hr.)	Pressure (atm x 10 ⁻⁶)
-	-	10.34	20	10.34	90	Sublimate	160	48	50.0
7.41	10	7.41	10	7.23	10	"	170	96	400.0
6.15	15	6.15	15	6.17	75	"	175	72	50.0
5.95	15	5.95	15	5.13	10	"	195	120	200.0
5.72	10	5.72	10	4.85	75	"	210	48	500.0
5.47	10	5.47	10	4.39	75				
4.71	100	4.71	100	4.10	5				
4.37	40	4.37	40	3.88	100				
4.25	40	4.25	40	3.74	10				
4.01	10	4.01	10	3.62	100				
3.77	50	3.77	50	3.41	75				
3.69	50	3.69	50	3.16	75				
3.41	30	3.61	30	3.04	10				
3.27	15	3.41	30	2.90	75				
3.15	30	3.27	15	2.81	10				
3.07	5	3.15	30	2.76	20				
2.98	10	3.07	5	2.66	10				
2.89	30	2.98	10	2.58	10				
2.83	40	2.89	30	2.54	10				
2.76	20	2.83	40	2.44	20				
2.65	70	2.76	20	2.39	5				
2.57	20	2.65	70	2.31	10				
2.46	30	2.57	20	2.20	10				
2.39	30	2.46	30	2.14	5				
2.31	5(B)	2.39	30	2.04	10				
2.25	10	2.31	5(B)	2.01	10				
2.20	10	2.25	10	1.93	20				
2.14	5	2.20	10						
		2.14	5

HNAB (43-11-B) Original

Fig. 2

80°C, 168 Hours at 670 mm

Residue - The residual portion of this sublimation run remained essentially the same as the original 43-11-B material, based on infrared spectral evidence (Fig. 3). There was, however, the loss of the minor exotherm at $\sim 268^\circ\text{C}$ (Figs. 2, 3). The residue retains the x-ray d_{hkl} pattern (Table II-A) as found in the original material (Sandia HNAB-III). There is a noticeable change in the carbon, hydrogen, and nitrogen percentage composition, even though the carbon/nitrogen molar ratio remains at 1.50 (Table I). Photographs of the residue are presented in Fig. 3.

Sublimate - The yield from a 10 g charge yielded only enough sublimate to obtain an infrared spectrum of the fraction (Fig. 4). The most prominent feature of the spectrum is the absence of nitro group absorption ($\sim 6.4, 7.4 \mu$). Being the most polar group in HNAB these transitions would of necessity be the strongest bands in the spectrum if present in the material. This sublimate is a very dry, intensely dark purple solid, almost like shellac in its consistency. The relative intensity of the 2.9μ band, considering the dry consistency of the material, again makes an assumption of water suspect. The lack of any indication of HOH wagging deformation mode is again evident. Inspection of the spectrum results in the following tentative assignments;

<u>Band (μ)</u>	<u>Mode</u>	<u>Group</u>
2.85	ν	N - H (O - H ?)
3.4 - 3.5	$\nu_a + s$	C - H (aliphatic)
6.10	δ_d	N - H (O - H ?)
7.90	ν	C - N
12.4	δ_w	N - H
(9.0 - 10.0)	C - N stretching and deformation	

At 5.75μ there is a slight indication of the presence of an ester or ketone type carbonyl, $>C=O$.

The spectrum is indicative of an aliphatic amine.

Fig. 3
Sublimation Residue
(80°C, 168 hours, 670 mm)

Fig. 4
Infrared Spectrum of Sublimate
(80°C, 168 Hours, 670 mm)

100°C, 168 Hours at 670 mm

Residue - The infrared spectrum of this fraction (Fig. 5) continues to display the prominent absorption band at $\sim 2.9 \mu$, with no basic change from the spectrum of the previous residue (80°C).

The DTA thermogram is essentially the same as the 80°C residue, showing endothermic behavior at $\sim 222^\circ\text{C}$ with major exothermic behavior cresting at $\sim 353^\circ\text{C}$ (Fig. 5).

X-ray diffraction results (Tables I, II-A) show the residue to have the d_{hkl} pattern of Sandia HNAB-III.

Carbon, hydrogen, and nitrogen analysis does show anomalous behavior relative to the foregoing characteristics (Table I).

<u>Material</u>	<u>C</u> <u>(wt.%)</u>	<u>H</u> <u>(wt.%)</u>	<u>N</u> <u>(wt.%)</u>	<u>C/N</u> <u>Molar Ratio</u>	<u>Total %</u> <u>(C+N)</u>
43-11-B	31.8	0.9	24.8	1.50	56.6
100°C residue	29.7	0.9	24.3	1.40	54.0

Photographs are presented in Fig. 5.

Sublimate - Only enough sublimate was obtained for an infrared spectrum. Spectral results were identical to that of the 80°C sublimate (Fig. 4).

Fig. 5

Sublimation Residue
(100°C, 168 Hours, 670 mm)

120°C, 168 Hours at 670 mm

Residue - Infrared spectral analysis (Fig. 6) shows no appreciable difference from previous residues but maintaining the 2.9 and 3.4 μ bands.

DTA results (Fig. 6) show retention of the $\sim 222^\circ\text{C}$ endotherm with an apparent slight decrease in the temperature of the major exothermic peak maximum (350 vs. 353°C).

X-ray diffraction analysis of the residue produces the Sandia HNAB III d_{hkl} pattern (Tables I, II-A).

Carbon, hydrogen, and nitrogen analysis shows the same elemental percentage change from the 43-11-B as was found with 100°C residue (Table I).

<u>Material</u>	<u>C (wt.%)</u>	<u>H (wt.%)</u>	<u>N (wt.%)</u>	<u>C/N Molar Ratio</u>	<u>Total % (C+N)</u>
43-11-B	31.8	0.9	24.8	1.50	56.6
120°C residue	29.7	1.0	24.4	1.40	54.1

Photographs are presented in Fig. 6.

Sublimate - Only enough material was obtained for infrared spectral analysis (Fig. 7). The spectral pattern appears identical to that of the 80 and 100°C sublimates. The indication of carbonyl is more pronounced (5.75 μ). It is important to note the position of the relatively strong band at 6.05 μ . If the 2.9 μ band was assumed to be due to water (H - OH) the position of the deformation (bending) mode of water is too high to be confused with this band. The following experimental limits are compared,¹ viz

¹K. Nakamoto, *Infrared Spectra of Inorganic & Coordination Compounds*, p. 83, (Wiley, 1963).

<u>Molecule</u>	<u>Deformation Mode (cm⁻¹)</u>
H ₂ O (gas)	1595
H ₂ O (liquid)	1627
H ₂ O (solid, -78°C)	1620
HNAB Sublimate	(1653)

Fig. 6

Sublimation Residue
(120°C, 168 Hours, 670 mm)

10°C/min.

Fig. 7
Infrared Spectrum of Sublimate
(120°C, 168 Hours, 670 mm)

130°C, 168 Hours, 6×10^{-6} atm

Residue - Infrared analysis (Fig. 8) shows the same spectral pattern as unheated 43-11-B, but with a noticeable decrease in the relative intensity of the band at 2.9μ , possibly related to increased sublimation due to increased temperature and reduced pressure of 6.5×10^{-6} atm relative to previous ambient pressure (670 mm).

DTA thermogram of the residue shows retention of the $\sim 233^\circ\text{C}$ endotherm with an increase of $\sim 10^\circ\text{C}$ in the position of the exothermic peak (Fig. 8).

X-ray diffraction analysis of the material shows the d_{hkl} pattern of Sandia HNAB-III (Tables I, II-A).

Carbon, hydrogen, and nitrogen analysis values are low in carbon and nitrogen relative to HNAB (Table I).

<u>Material</u>	<u>C</u> <u>(wt.%)</u>	<u>H</u> <u>(wt.%)</u>	<u>N</u> <u>(wt.%)</u>	<u>C/N</u> <u>Molar Ratio</u>	<u>Total %</u> <u>(C+N)</u>
HNAB (Theor.)	31.9	0.9	24.8	1.50	56.7
130°C residue	31.0	1.0	24.1	1.51	55.1

Spark sensitivity measurements show a slight increase in the threshold relative to the original material (Table I).

<u>Material</u>	<u>Threshold (joules)</u>
43-11-B	1.75 @ 5 KV
130°C residue	1.83 @ 5 KV

Photographs are presented in Fig. 8.

Sublimate - Sufficient material was not obtained for complete analyses. Infrared spectral analysis shows a functional group departure from the character of the sublimates found in the lower temperature runs (Fig. 9). The 2.9μ band is still prominent but a substantial degree of asymmetric and symmetric stretching of the nitro group is seen at $6.2-6.5$ and $7.4-7.6 \mu$, respectively. Indications are that the sublimate is a mixture of HNAB and lower temperature condensate(s).

Fig. 8

Sublimation Residue
(130°C, 168 Hours, 6.5×10^{-6} atm)

Fig. 9
Infrared Spectrum of Sublimate
(130°C, 168 Hours, 6.5×10^{-6} atm)

145°C, 96 Hours, 10^{-5} atm

Residue - There is no apparent difference in the infrared spectral patterns of the 145°C residue and previous (lower temperature) residues (Fig. 10), with a slight decrease in the relative intensity of the 2.9 μ band.

DTA results show no appreciable variation from previous residual fractions (Fig. 10).

The x-ray diffraction d_{hkl} pattern is that of Sandia HNAB-III (Tables I, II-A).

Carbon, hydrogen, and nitrogen analysis shows slight variation in carbon and nitrogen content from original material values, with appreciable increase in hydrogen content (Table I).

<u>Material</u>	<u>C (wt.%)</u>	<u>H (wt.%)</u>	<u>N (wt.%)</u>	<u>C/N Molar Ratio</u>	<u>Total % (C+N)</u>
43-11-B	31.8	0.9	24.8	1.50	56.6
145°C residue	31.4	1.3	24.3	1.51	55.7

There is an appreciable increase in the spark sensitivity threshold relative to the unheated material (Table I).

<u>Material</u>	<u>Threshold (joules)</u>
43-11-B	1.75 @ 5 KV
145°C residue	2.00 @ 5 KV

Photographs are presented in Fig. 10.

Fig. 10

Sublimation Residue
(145°C, 96 Hours, 10^{-5} atm)

50X

150°C, 168 Hours, 670 mm

Residue - Spectrally there are no apparent anomalies from previous (lower temperature) residues (Fig. 11). The 2.9 μ band is still prominent.

The DTA thermogram shows no change in thermal characteristics (Fig. 11).

The d_{hkl} pattern from x-ray diffraction shows the residue to be Sandia HNAB-III (Tables I, II-A).

Carbon, hydrogen, and nitrogen analysis shows no appreciable difference from the 145°C residue (Table I).

<u>Material</u>	<u>C (wt.%)</u>	<u>H (wt.%)</u>	<u>N (wt.%)</u>	<u>C/N Molar Ratio</u>	<u>Total % (C+N)</u>
43-11-B	31.8	0.9	24.8	1.50	56.6
145°C residue	31.4	1.3	24.3	1.51	55.7
150°C residue	31.6	1.3	24.3	1.52	55.9

Spark sensitivity threshold has undergone an apparent shift to lower values (Table I).

<u>Material</u>	<u>Threshold (joules)</u>
43-11-B	1.75 @ 5 KV
145°C residue	2.00 @ 5 KV
150°C residue	1.75 @ 5 KV

Photographs are presented in Fig. 11.

10°C/min.

Sublimation Residue
(150 C, 168 Hours, 670 mm)

Fig. 11

150°C, 216 Hours, 2×10^{-4} atm

Residue - Maintaining the same temperature as the previous run but subliming at a lower pressure (2×10^{-4} atm) and increasing the elapsed time (168 $\rightarrow$ 216 hours), the infrared spectrum shows a decrease in the 2.9μ band intensity. The remainder of the spectral pattern appears unchanged (Fig. 12).

The DTA thermogram shows essentially no change in the positions of the endo- and exothermal temperature values (Fig. 12). The "endothermic" drift in the baseline is a heat capacity effect in the thermocouples.

The d_{hkl} pattern obtained for the residue is that of Sandia HNAB-III (Tables I, II-A).

Carbon, hydrogen, and nitrogen analysis results are again similar to the two previous sublimation residues (Table I).

<u>Material</u>	<u>C</u> <u>(wt.%)</u>	<u>H</u> <u>(wt.%)</u>	<u>N</u> <u>(wt.%)</u>	<u>C/N</u> <u>Molar Ratio</u>	<u>Total %</u> <u>(C+N)</u>
43-11-B	31.8	0.9	24.8	1.50	56.6
145°C residue	31.4	1.3	24.3	1.51	55.7
150°C (670 mm)	31.6	1.3	24.3	1.52	55.9
150°C (2×10^{-4} atm)	31.4	1.3	24.2	1.51	55.6

Photographs are presented in Fig. 12.

Fig. 12

Sublimation Residue
(150°C, 216 hours, 2×10^{-4} atm)

ENDO $\leftarrow$ Δ T $\rightarrow$ EXO

10°C/min.

8.4X

155°C, 216 Hours, 5×10^{-5} atm

Residue - No infrared spectral evidence of change in the residue from the original material is apparent (Fig. 13). The 2.9μ band is still in evidence.

The DTA thermogram of the fraction shows no change in the endothermic characteristics of the major exotherm ($360 \rightarrow 365^\circ\text{C}$), nor in the appearance of a minor exotherm at 325°C (Fig. 13).

The d_{hkl} pattern of the residue is that of Sandia HNAB-III (Tables I, II-A).

Carbon, hydrogen, and nitrogen results show a substantial decrease in the hydrogen content relative to the previous three fractions (Table I).

<u>Material</u>	<u>C</u> <u>(wt.%)</u>	<u>H</u> <u>(wt.%)</u>	<u>N</u> <u>(wt.%)</u>	<u>C/N</u> <u>Molar Ratio</u>	<u>Total %</u> <u>(C+N)</u>
43-11-B	31.8	0.9	24.8	1.50	56.6
145°C (10^{-5} atm)	31.4	1.3	24.3	1.51	55.7
150°C (670 mm)	31.6	1.3	24.3	1.52	55.9
150°C (2×10^{-4} atm)	31.4	1.3	24.2	1.51	55.6
155°C (5×10^{-5} atm)	31.6	0.9	24.7	1.50	56.3
HNAB (Theor.)	31.9	0.9	24.8	1.50	56.7

Spark sensitivity threshold of this residue has increased to 2.06 joules at 5 KV (Table I).

Photographs are presented in Fig. 13.

Fig. 13

Sublimation Residue
(155°C, 216 hours, 5×10^{-5} atm)

ENDO + ΔT + EXO

10°C/min.

160°C, 48 Hours, 5×10^{-5} atm

Residue - There is no apparent change in the character of the residue fraction based upon infrared spectral or differential thermal analyses (Fig. 14). The d_{hkl} pattern is that of Sandia HNAB-III (Tables, I, II-A).

Carbon, hydrogen, and nitrogen analyses show substantial variations from the theoretical and original HNAB's although the carbon/nitrogen molar ratio remains at ~ 1.50 (Table I).

<u>Material</u>	<u>C (wt.%)</u>	<u>H (wt.%)</u>	<u>N (wt.%)</u>	<u>C/N Molar Ratio</u>	<u>Total % (C+N)</u>
HNAB (Theor.)	31.9	0.9	24.8	1.50	56.7
HNAB (43-11-B)	31.8	0.9	24.8	1.50	56.6
160°C residue	31.2	1.1	24.2	1.51	55.4

Spark sensitivity threshold (Table I) is 1.75 joules (5 KV).

Photographs are presented in Fig. 14.

Sublimate - This fraction shows substantial deviation from sublimates obtained from lower temperature runs.

Infrared spectral analysis (Fig. 15) shows a substantial increase in the intensity of both the 2.9μ and the $3.4\text{--}3.5 \mu$ bands, relative to the aromatic C-H stretch of HNAB at 3.20μ . Additionally, there is the prominent emergence of bands at 5.75μ , indicative of carbonyl ($C=O$) and at 7.75μ . The ring deformation modes (finger print region) from $9\text{--}15 \mu$ has changed appreciably, particularly the band "envelopes" at $10.5\text{--}11.25 \mu$, $12.1\text{--}12.8 \mu$, and at $13.25\text{--}13.9 \mu$.

The x-ray diffraction pattern of the sublimate shows the material has a predominant number of its d values the same as those of Sandia HNAB-II, but with several spurious d values not found in HNAB-II (Tables I, II-C). Both HNAB-III and this fraction do have a 10.34 Å line in common, not found in HNAB-II.

Carbon, hydrogen, and nitrogen analyses show a substantial deviation from previous (lower temperature) analyzed fractions:

<u>Material</u>	<u>C</u> <u>(wt.%)</u>	<u>H</u> <u>(wt.%)</u>	<u>N</u> <u>(wt.%)</u>	<u>C/N</u> <u>Molar Ratio</u>	<u>Total %</u> <u>(C+N)</u>
43-11-B	31.8	0.9	24.8	1.50	56.6
160°C residue	31.2	1.1	24.2	1.51	55.4
160°C sublimate	33.7	1.4	23.4	1.68	57.1

Photographs are presented in Fig. 15.

Fig. 14

Sublimation Residue
(160°C, 48 Hours, 5×10^{-5} atm)

ENDO ← ΔT → EXO

10°C/min.

Fig. 15
Sublimate
(160°C, 48 Hours, 5×10^{-5} atm)

170°C, 96 Hours, 4×10^{-4} atm

Residue - Infrared spectral results (Fig. 16) indicate no change from the spectral characteristics found with the previous residues, the 2.9μ band is still present.

DTA results show the appearance of an exothermic split of the major exotherm at $\sim 337^\circ\text{C}$ (Fig. 16).

X-ray diffraction results show the residue to have the d_{hkl} pattern of Sandia HNAB-III (Tables I, II-A).

Carbon, hydrogen, and nitrogen analysis (Table I) shows the residue to have the approximate values of the theoretical composition.

<u>Material</u>	<u>C</u> <u>(wt.%)</u>	<u>H</u> <u>(wt.%)</u>	<u>N</u> <u>(wt.%)</u>	<u>C/N</u> <u>Molar Ratio</u>	<u>Total %</u> <u>(C+N)</u>
HNAB (Theor.)	31.9	0.9	24.8	1.50	56.7
43-11-B	31.8	0.9	24.8	1.50	56.6
170°C residue	31.6	0.8	24.9	1.48	56.5

Spark sensitivity threshold is 1.78 joules at 5 KV (Table I).

Photographs are presented in Fig. 16.

Sublimate - Infrared spectral analysis of this fraction (Fig. 17) depicts a continuing change in the character of the ring deformation mode pattern ($9-15 \mu$). However, the bands at 5.75 and 7.75μ , seen in the 160°C sublimate (Fig. 15), are not present indicating that the optimum sublimative action of that component(s) is near 160°C .

The d_{hkl} pattern is the same as found with the 160°C sublimate; basically Sandia HNAB-II but with the 10.34 Å line present (Tables I, II-C).

Fig. 16

Sublimation Residue
(170°C, 96 Hours, 4×10^{-4} atm)

ENDO + ΔT + EXO

10°C/min.

Fig. 17

Infrared Spectrum of Sublimate
(170°C, 96 Hours, 4×10^{-4} atm)

170°C, 144 Hours, 6.5×10^{-6} atm

Residue- Spectral analysis shows no appreciable change from the preceeding sublimation residues (Fig. 18).

DTA results show a definite split in the major exothermic peak at ~ 335 , 350 , and 360°C (Fig. 18).

The x-ray d_{hkl} pattern of the residue is that of Sandia HNAB-III (Tables I, II-A).

Carbon, hydrogen, and nitrogen analysis (Table I) shows a slight decrease in the carbon/nitrogen molar ratio;

<u>Material</u>	<u>C</u> <u>(wt.%)</u>	<u>H</u> <u>(wt.%)</u>	<u>N</u> <u>(wt.%)</u>	<u>C/N</u> <u>Molar Ratio</u>	<u>Total %</u> <u>(C+N)</u>
HNAB (Theor.)	31.9	0.9	24.8	1.50	56.7
43-11-B	31.8	0.9	24.8	1.50	56.6
170°C residue	31.3	0.8	24.8	1.47	56.1

Spark sensitivity threshold was 1.80 joules at 5 KV (Table I).

Photographs are presented in Fig. 18.

Sublimate - Spectral data (Fig. 19) show an additional slight change in the ring deformation modes ($9-15 \mu$) as was seen in the results from the 160°C sublimate (Fig. 15). However, there is a nearly complete absence of the 5.75μ and complete absence of the 7.75μ band which were prominent in the 160°C sublimate. Indications are that this fraction(s) reached an optimum sublimative process in the latter temperature/pressure zone.

DTA results (Fig. 19) of the sublimate show a definite variation in the exothermic character of this sublimate relative to the residual fraction (Fig. 18).

X-ray diffraction shows the material to have the d_{hkl} pattern of Sandia HNAB-II (Tables I, II-B).

Photographs are presented in Fig. 19.

Fig. 26

Sublimation Residue
(180°C, 96 hours, 6×10^{-6} atm)

ENDO → Δ T → EXO

10°C/min.

Fig. 27

Sublimate
(180°C, 96 hours, 6×10^{-6} atm)

ENDO + ΔT + EXO

10°C/min.

8.4X

50X

185°C, 96 Hours, 8×10^{-5} atm

Residue - Spectrally the residue is unchanged from the previous run (180°C) save for the noticeably decreased intensity of the 2.9μ band (Fig. 28). DTA results do not indicate any appreciable changes in the thermal characteristics of the material (Fig. 28).

X-ray analysis shows the material to have the d_{hkl} pattern of Sandia HNAB-III (Tables I, II-B).

Carbon, hydrogen, and nitrogen results show a very close approximation to the theoretical values of HNAB (Table I).

<u>Material</u>	<u>C</u> <u>(wt.%)</u>	<u>H</u> <u>(wt.%)</u>	<u>N</u> <u>(wt.%)</u>	<u>C/N</u> <u>Molar Ratio</u>	<u>Total %</u> <u>(C+N)</u>
HNAB (Theor.)	31.9	0.9	24.8	1.50	56.7
185°C residue	31.7	0.8	24.8	1.49	56.5

Spark sensitivity threshold is 1.78 joules at 5 KV (Table I).

Photographs are presented in Fig. 28.

Sublimate - Spectrally the sublimate is similar to that obtained for Sandia HNAB-II (Fig. 29), noticeably in the skeletal and ring deformation region of $10.5\text{-}15.0 \mu$. There is essentially no change in the DTA thermal pattern of the sublimate from the previous run (180°C, Fig. 27).

X-ray analyses of the sublimate show the d_{hkl} pattern of Sandia HNAB-II (Tables I, II-B).

Carbon and nitrogen compositional percentages are slightly higher than the theoretical values (Table I).

<u>Material</u>	<u>C</u> <u>(wt.%)</u>	<u>H</u> <u>(wt.%)</u>	<u>N</u> <u>(wt.%)</u>	<u>C/N</u> <u>Molar Ratio</u>	<u>Total %</u> <u>(C+N)</u>
HNAB (Theor.)	31.9	0.9	24.8	1.50	56.7
185°C sublimate	32.4	0.7	25.0	1.52	56.4

Photographs are presented in Fig. 29.

10°C/min.

Sublimation Residue
(185°C, 96 hours, 8×10^{-5} atm)

Fig. 28

Fig. 29

Sublimate
(185°C, 96 hours, 8×10^{-5} atm)

ENDO + ΔT → EXO

10°C/min.

8.4X

50X

190°C, 168 Hours, 670 mm

Residue - Infrared spectral analysis indicates no functional or skeletal changes, but a noticeable decrease in the intensity of the 2.9 μ band (Fig. 30). DTA results show no discernable changes in the thermal characteristics of the material (Fig. 30).

X-ray analysis shows the material to give the d_{hkl} pattern of Sandia HNAB-III (Tables I, II-A).

Carbon, hydrogen and nitrogen analyses (Table I) show an appreciable decrease in the nitrogen content.

<u>Material</u>	<u>C</u> <u>(wt.%)</u>	<u>H</u> <u>(wt.%)</u>	<u>N</u> <u>(wt.%)</u>	<u>C/N</u> <u>Molar Ratio</u>	<u>Total %</u> <u>(C+N)</u>
HNAB (Theor.)	31.9	0.9	24.8	1.50	56.7
190°C residue	31.6	1.1	24.0	1.54	55.6

Photographs are presented in Fig. 30.

Sublimate - Infrared spectral results show a continuance of the Sandia HNAB-II skeletal/ring deformation pattern in the 10.5-15.0 μ range (Fig. 31). The 2.9 μ band is still prominent. DTA results indicate no appreciable change in the exothermal characteristics of the material (Fig. 31).

X-ray data show the sublimate to have the d_{hkl} pattern of Sandia HNAB-II (Tables I, II-B).

Carbon, hydrogen, and nitrogen results show a continuing decrease in the nitrogen content relative to the theoretical accompanied by a substantial increase in the carbon/nitrogen molar ratio (Table I).

<u>Material</u>	<u>C</u> <u>(wt.%)</u>	<u>H</u> <u>(wt.%)</u>	<u>N</u> <u>(wt.%)</u>	<u>C/N</u> <u>Molar Ratio</u>	<u>Total %</u> <u>(C+N)</u>
HNAB (Theor.)	31.9	0.9	24.8	1.50	56.7
190°C sublimate	32.2	1.3	23.8	1.61	56.0

Photographs are presented in Fig. 31.

Sublimation Residue
(190°C, 168 hours, 670 mm)

Fig. 30

Fig. 31

Sublimate
(190°C, 168 hours, 670 mm)

8.4X

50X

195°C, 120 Hours, 2×10^{-4} atm

Residue - Spectrally there is no change from previous residues (Fig. 31), but a noticeable decrease in the 2.9μ band. DTA results show no change in the thermal characteristics of the residue (Fig. 32).

X-ray diffraction results show the Sandia HNAB-III d_{hkl} pattern (Tables I, II-A).

Carbon, hydrogen, and nitrogen results show a substantial decrease in the carbon and slight decrease in the nitrogen percentage composition accompanied by a sizeable decrease in the C/N molar ratio (Table I).

<u>Material</u>	<u>C (wt.%)</u>	<u>H (wt.%)</u>	<u>N (wt.%)</u>	<u>C/N Molar Ratio</u>	<u>Total % (C+N)</u>
HNAB (Theor.)	31.9	0.9	24.8	1.50	56.7
195°C residue	30.4	0.9	24.6	1.44	55.0

Spark sensitivity threshold is 2.0 joules at 5 KV (Table I).

Photographs are presented in Fig. 32.

Sublimate - This fraction is spectrally the same as Sandia HNAB-II (Fig. 33), the 2.9μ band still prominent. DTA results indicate no change in the thermal characteristics of the sublimate (Fig. 33).

X-ray diffraction results show a trend anomaly in that the d_{hkl} pattern is basically the Sandia HNAB-II but the $10.34 \text{ \AA}$ line is again present (Tables I, II-C).

Carbon, hydrogen, and nitrogen results are nearly identical to that obtained for the residue (Table I).

<u>Material</u>	<u>C</u> <u>(wt.%)</u>	<u>H</u> <u>(wt.%)</u>	<u>N</u> <u>(wt.%)</u>	<u>C/N</u> <u>Molar Ratio</u>	<u>Total %</u> <u>(C+N)</u>
HNAB (Theor.)	31.9	0.9	24.8	1.50	56.7
195°C residue	30.4	0.9	24.6	1.44	55.0
195°C sublimate	30.4	1.0	24.5	1.44	54.9

Photographs are presented in Fig. 33.

Fig. 32

Sublimation Residue
(195°C, 120 hours, 2×10^{-4} atm)

(195°C, 120 hours, 2×10^{-4} atm)

Sublimate

Fig. 33

200°C, 92 Hours, 670 mm

Residue - Spectrally there is no change from the previous residue (Fig. 34). DTA results show slight variation in the exothermal trace but no appreciable change in the temperature position of the major exothermic peak ($\sim 360^\circ\text{C}$).

X-ray diffraction results show the d_{hkl} pattern of Sandia HNAB-III (Tables I, II-A).

Carbon, hydrogen, and nitrogen analysis shows a continued decrease in the nitrogen percentage composition (Table I).

<u>Material</u>	<u>C</u> <u>(wt.%)</u>	<u>H</u> <u>(wt.%)</u>	<u>N</u> <u>(wt.%)</u>	<u>C/N</u> <u>Molar Ratio</u>	<u>Total %</u> <u>(C+N)</u>
HNAB (Theor.)	31.9	0.9	24.8	1.50	56.7
200°C residue	30.6	0.9	23.9	1.53	54.5

Photographs are presented in Fig. 34.

Sublimate - The infrared spectral pattern is basically that of Sandia HNAB-II (Fig. 35). The $2.9\ \mu$ band is prominent. The 7.9 and $9.75\ \mu$ bands are again in evidence.

The d_{hkl} pattern from x-ray diffraction analysis is that of Sandia HNAB-II (Tables I, II-B).

The carbon, hydrogen, and nitrogen analysis of the sublimate shows a sizeable decrease in the nitrogen percentage resulting in an accompanying increase in the carbon/nitrogen molar ratio (Table I).

<u>Material</u>	<u>C</u> <u>(wt.%)</u>	<u>H</u> <u>(wt.%)</u>	<u>N</u> <u>(wt.%)</u>	<u>C/N</u> <u>Molar Ratio</u>	<u>Total %</u> <u>(C+N)</u>
HNAB (Theor.)	31.9	0.9	24.8	1.50	56.7
200°C sublimate	33.5	2.5	19.8	2.00	53.3

Photographs are presented in Fig. 35.

Fig. 34
Sublimation Residue
(200°C, 92 hours, 670 mm)

Fig. 35

Sublimate
(200°C, 92 hours, 670 mm)

205°C, 90 Hours, 2×10^{-4} atm

Residue - The residue formed in definite zones of light orange and dark reddish orange. As a result the color zones were analyzed individually.

The spectral analyses (Figs. 36, 37) show both residue fractions to be essentially the same as previous residues (Sandia HNAB-III). The only apparent spectral anomaly between the two occurs with the 2.9μ band with substantially less prominence in the dark portion of the residue. There is no apparent difference in the DTA thermograms, and no change from the previous residue (200°C, Fig. 35).

X-ray analyses show both fractions to be of the Sandia HNAB-III d_{hkl} pattern (Tables I, II-A).

Carbon, hydrogen, and nitrogen analyses are virtually identical (Table I).

<u>Material</u>	<u>C</u> <u>(wt.%)</u>	<u>H</u> <u>(wt.%)</u>	<u>N</u> <u>(wt.%)</u>	<u>C/N</u> <u>Molar Ratio</u>	<u>Total %</u> <u>(C+N)</u>
HNAB (Theor.)	31.9	0.9	24.8	1.50	56.7
205°C residue (dk.)	32.4	0.9	24.7	1.53	57.1
205°C residue (lt.)	32.2	1.1	24.6	1.53	56.8

Spark sensitivity threshold is 1.81 at 5 KV (Table I).

Photographs are presented in Figs. 36 and 37.

Fig. 36
Sublimation Residue
(205°C, 90 hours, 2×10^{-4} atm)

Fig. 37

Dark Portion of Sublimation Residue
(205°C, 90 hours, 2×10^{-4} atm)

Sublimate - Similar to the residue, definite dark and light color zones were formed in the sublimate (Figs. 38 and 39). They are spectrally the same as Sandia HNAB-II. As with the residue, the light portion has a relatively more intense 2.9 μ band than the dark portion of the fraction. DTA results show no significant anomalies from the previous sublimate (Figs. 38 and 39).

X-ray results show both light and dark zones of the sublimate have the Sandia HNAB-II d_{hkl} pattern (Tables I, II-B).

Carbon, hydrogen, and nitrogen analyses indicate a slight increase in the carbon percentages of both fractions (Table I).

<u>Material</u>	<u>C</u> <u>(wt.%)</u>	<u>H</u> <u>(wt.%)</u>	<u>N</u> <u>(wt.%)</u>	<u>C/N</u> <u>Molar Ratio</u>	<u>Total %</u> <u>(C+N)</u>
HNAB (Theor.)	31.9	0.9	24.8	1.50	56.7
Sublimate (lt.)	32.2	1.0	24.7	1.53	56.9
Sublimate (dk.)	32.4	1.2	24.7	1.54	57.1

Photographs are presented in Figs. 38 and 39.

Sublimate
(205°C, 90 hours, 2×10^{-4} atm)

Fig. 38

Fig. 39

Dark Portion of Sublimate
(205°C, 90 hours, 2×10^{-4} atm)

210°C, 48 Hours, 5×10^{-4} atm

Residue- Spectrally there is no change from previous residues (Fig. 40), quite similar to spectral pattern of Sandia HNAB-III. DTA results show no appreciable differences from previous residues (Fig. 40).

X-ray diffraction shows the d_{hkl} pattern of Sandia HNAB-III Tables I, II-A).

Carbon, hydrogen, and nitrogen analyses show a slight increase in the carbon percentage relative to theoretical values (Table I).

<u>Material</u>	<u>C</u> <u>(wt.%)</u>	<u>H</u> <u>(wt.%)</u>	<u>N</u> <u>(wt.%)</u>	<u>C/N</u> <u>Molar Ratio</u>	<u>Total %</u> <u>(C+N)</u>
HNAB (Theor.)	31.9	0.9	24.8	1.50	56.7
210°C residue	32.3	1.1	24.7	1.52	56.0

Photographs are presented in Fig. 40.

Sublimate - Spectrally the sublimate is similar to Sandia HNAB-II (Fig. 41), with a substantial intensity of the 2.9μ band. DTA shows no appreciable difference from previous sublimate (205°C, Figs. 39 and 41).

X-ray diffraction shows the d_{hkl} pattern to be that of Sandia HNAB-II, but with the spurious $10.34 \text{ \AA}$ line (Table I, II-C).

Carbon, hydrogen, and nitrogen results show the sublimate to have essentially the same percentage composition and carbon/nitrogen molar ratio as the residue, which was also found to occur in the 205°C residues and sublimates (Table I).

<u>Material</u>	<u>C</u> <u>(wt.%)</u>	<u>H</u> <u>(wt.%)</u>	<u>N</u> <u>(wt.%)</u>	<u>C/N</u> <u>Molar Ratio</u>	<u>Total %</u> <u>(C+N)</u>
HNAB (Theor.)	31.9	0.9	24.8	1.50	56.7
210°C residue	32.3	1.1	24.7	1.52	57.0
210°C sublimate	32.3	1.0	24.8	1.53	57.1

Photographs are presented in Fig. 41.

Fig. 40

Sublimation Residue
(210°C, 48 hours, 5×10^{-4} atm)

Fig. 41

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Sublimate
(210°C, 48 hours, 5×10^{-4} atm)

ENDO $\leftrightarrow$ Δ T $\rightarrow$ EXO

10°C/min.

220°C, 48 Hours, 4×10^{-4} atm

Residue - Infrared spectral pattern is essentially that of Sandia HNAB-III (Fig. 42), with noticeable decrease in the intensity of the 2.9μ band. DTA results show no significant change in the thermal characteristics from previously analyzed residues (Fig. 42). A split does occur in the major exotherm region at $\sim 340^\circ\text{C}$ and $\sim 355^\circ\text{C}$.

X-ray diffraction results show the d_{hkl} pattern of Sandia HNAB-III (Tables I, II-A).

Carbon, hydrogen, and nitrogen analyses show slight deviations from theoretical values (Table I).

<u>Material</u>	<u>C (wt.%)</u>	<u>H (wt.%)</u>	<u>N (wt.%)</u>	<u>C/N Molar Ratio</u>	<u>Total % (C+N)</u>
HNAB (Theor.)	31.9	0.9	24.8	1.50	56.7
220°C residue	31.8	0.7	24.4	1.53	56.2

Photographs are presented in Fig. 42.

Sublimate - Spectrally the sublimate is similar to Sandia HNAB-II, with significant decrease in the intensity of the 2.9μ band (Fig. 43). DTA results indicate no change from the 210°C sublimate (Fig. 43).

The x-ray d_{hkl} pattern is that of Sandia HNAB-II (Tables I, II-B).

Carbon, hydrogen, and nitrogen results are quite similar to those obtained for the 220°C residue, as was found to be the case in both the 205 and 210°C runs (Table I).

<u>Material</u>	<u>C</u> <u>(wt.%)</u>	<u>H</u> <u>(wt.%)</u>	<u>N</u> <u>(wt.%)</u>	<u>C/N</u> <u>Molar Ratio</u>	<u>Total %</u> <u>(C+N)</u>
HNAB (Theor.)	31.9	0.9	24.8	1.50	56.7
220°C residue	31.8	0.7	24.4	1.53	56.2
220°C sublimate	32.1	0.8	24.4	1.54	56.5

Photographs are presented in Fig. 43.

Fig. 42

Sublimation Residue
(220°C, 48 hours, 4×10^{-4} atm)

Fig. 43

Sublimate
(220°C, 48 hours, 4×10^{-4} atm)

10°C/min.

The variation of characteristics of the sublimation residues is minimal relative to the sublimate fractions.

From the infrared spectral results there appears to be no appreciable changes seen in the residues as a result of various temperature and pressure conditions imposed during the sublimative processes. The infrared spectral patterns of all the residues are essentially the same as that of the original unheated material (Sandia 43-11-B) and Sandia HNAB-III. This observation is given added credence by the results of x-ray diffraction studies which show the residues to all be of the Sandia HNAB-III d_{hkl} pattern, as is Sandia 43-11-B. However, due to the limits of detection of both methods, IR and x-ray diffraction would not necessarily show the presence of a multi component system if these components were less than 2-4%, or if their individual vibrational functionality frequencies were coincidental to those of the HNAB-III.

There is some variation in the carbon and nitrogen percentage composition, relative to theoretical, which tends to be on the low side in the lower temperature residues (80- ~ 200°C) and on the high side for carbon from 200 to 220°C. The carbon to nitrogen molar ratio varies from 1.40 to 1.60 relative to the theoretical value of 1.50.

Spark sensitivity thresholds vary from 1.68 joules up to 2.06 joules relative to 1.75 joules in the Sandia 43-11-B material.

DTA thermograms do show some variation in the peak position of the exothermal temperature, varying from ~ 340 up to ~ 370°C. There is some very definite sporadic splitting of the exotherm occurring at ~ 335°C.

Photographs of the residues (8X and 50X) show slight color variations at higher temperatures (200°C, Fig. 34). At 205°C there is dark and light color zoning found in the residue, quite probably the result of crystal size differences, because spectral and x-ray results indicate them to be the same material.

Investigation of the spectral results of representative materials (Fig. 44) show the residues are not spectrally dissimilar from the original Sandia Lot 43-11-B (Spectra 1 and 2). There is variation in the relative intensities of the 2.9 and the 3.4 μ bands (O - H or N - H and C - H, aliphatic; respectively) as a function of prolonged heating, but no discernible differences in the HNAB theoretical functionality (6.20-14.5 μ). All sublimation residues display this general spectral pattern regardless of temperature, pressure, or elapsed time conditions. These spectral patterns are the same as that of Sandia HNAB-III.

The sublimates show appreciable spectral pattern changes from those of the residues and Lot 43-11-B (Fig. 44, Spectra 2 and 3). These changes in the skeletal and ring deformation (hydrogen out of plane) modes are seen quite clearly by visual comparison of the band envelopes at 10.5-11.3 μ and at 13.25-14.75 μ . The resulting changes in these spectral regions are found to be consistent with the spectral pattern of Sandia HNAB-II. Of significant spectral consistency is the "saw tooth" pattern of the band envelope from 13.25-13.6 μ , found in all HNAB sublimates and in Sandia HNAB-II. This spectral uniqueness is consistently noted in the region from 10.5-11.3 μ .

Spectrum 4 of Fig. 44 is representative of the sublimate whose x-ray d_{hkl} pattern contains the spurious 10.34 Å line. The overall spectral pattern is that of

Sandia HNAB-II and other sublimates but with obvious spectral anomalies. These can be seen at 5.75μ ($C=O$?), 7.75μ , and 8.8μ . The 2.9μ band ($O-H$ or $N-H$) and that at $3.4-3.5 \mu$ ($C-H$, aliphatic) are significantly more intense.

The DTA thermograms of these four materials are presented in Fig. 45 (1-4). There seems to be little effect on the temperature of the endotherm as a result of heating although the temperature has decreased slightly in the Type C material to approximately $218^{\circ}C$ from the nominal value of $\sim 223^{\circ}C$ (Thermogram 4). There is slight exothermic excursion seen in the original material (43-11-B) at $\sim 268^{\circ}C$ (Thermogram 1). There is appreciable shifting and splitting seen to occur in the major exotherm among the various fractions ($\sim 300-375^{\circ}C$, Thermograms 1-4).

Comparison of the spectral patterns (Fig. 46, Spectra 1-4) shows a pattern consistency which exists between the original unheated 43-11-B material and the sublimation residue (Spectra 1 and 2). There are essentially no spectral differences except for the relative intensities of the bands at ~ 2.9 and $\sim 3.4 \mu$. Spectra 3 and 4 show significant similarities consistently found with Sandia HNAB-II (Spectrum 3) and higher temperature sublimates (Spectrum 4). This is quite apparent in the comparative spectral patterns from $10.5-14.2 \mu$.

Close inspection of the spectral results from the lower temperature sublimates (i.e., $120^{\circ}C$, 168 hours, 670 mm; Fig. 47) show anomalous spectral absorbance not inherent to the normal functionality frequencies of hexanitroazobenzene. The several prominent absorption bands are considered (Fig. 47);

Fig. 44

Infrared Spectra of Sublimation Fraction Types

- 1) HNAB 43-11-B (original)
- 2) Type A
- 3) Type B
- 4) Type C

Fig. 45

DTA Thermograms of Sublimation Fraction Types

1) UNP 40-11-L (Original)

2) Type A

3) Type B

4) Type C

Fig. 46
Infrared Spectra of HNAB Types

- 1) Sandia 43-11-B
- 2) Residue (205°C)
- 3) Sandia HNAB II
- 4) Sublimate (205°C)

Band 1 (2.9 μ) - This band is obviously due to the stretching mode of O - H or N - H. The band shape does not indicate it is due to O - H unless the hydroxyl group were spatially hindered to remove the hydrogen bonding effect which presents a normally broad band envelope.

Band 2 (3.4-3.5 μ) - This band is due to the aliphatic C - H stretching mode. The presence of the band shoulder ($\sim 3.45 \mu$) indicates the presence of both the methylene (CH_2) and the methyl (CH_3) groups, substantiated by the weak bands at $\sim 6.8 \mu$ and 7.25μ , due to the C - CH_3 asymmetric and symmetric deformation modes.

Band 3 (5.75 μ) - Although not the typical sharp band shape usually found with the carbonyl group, this band appears at the approximate wavelength of an ester or ketone carbonyl.

Band 4 (6.05 μ) - This band is probably due to the bending (deformation) mode related to the 2.9 μ band. If it is a bending deformation it occurs as a result of angular deformation and not bond deformation, hence would necessitate an AB_2 or AB_3 angular grouping. This would dictate that a possible O - H would be due to H - O - H. The wavelength position of this band does not indicate it is due to H - O - H bending. Experimentally the wavelength of the bending mode of water is too high to be assigned to this band. The following experimental limits are compared.²

<u>Molecule</u>	Deformation (bending)
	<u>Mode (cm^{-1})</u>
H ₂ O (gas)	1595
H ₂ O (liquid)	1627
H ₂ O (solid, -78°C)	1620
HNAB Sublimate (120°C)	1653

Band 5 ($\sim 7.75 \mu$) - Possible C - N stretching mode

Bands 6 ($\sim 9.25 \mu$) and 7 (11.9 μ) - These bands are in the appropriate range for the N - H wagging deformation and the NH_2 wagging deformation modes, respectively.

²K. Nakamoto, *Infrared Spectra of Inorganic & Coordination Compounds*, p. 83, (Wiley, 1963).

Fig. 47

Infrared Spectrum of Sublimate
(120°C, 168 hours, 670 mm)

Spectral inspection of the sublimate obtained at 160°C shows significant anomalous functionality modes (Fig. 48) which are not inherent to HNAB.

Band 1 (2.9 μ) - Referring to the discussion of Fig. 47, O - H_v or N - H_v.

Band 2 ($\sim$ 3.4 μ) - Due to band shape, indications are of the presence of methylene (CH₂) and the methyl (CH₃) group.

Band 3 (5.75 μ) - Strongly indicative of the ester or ketone carbonyl group.

Band 4 (7.75 μ) - No tentative mode assignment but band is not inherent to HNAB as a vibrational or deformational mode.

Band 5 ($\sim$ 8.8 μ) - No tentative mode assignment but again, is not an inherent HNAB vibrational or deformational mode.

Fig. 48

Infrared Spectra of Sublimate
(160°C, 48 hours, 5×10^{-5} atm)

COMMENTS

The spectral evidence in this study shows quite definitely the appreciable presence of non-HNAB components in Sandia Lot 43-11-B.

There appears to have been established temperature ranges for the potential isolation of these components. The lower temperature component appears to sublime off at 80°C (Fig. 47). The higher temperature component was found in its highest concentration at 160°C. X-ray diffraction results also show a maximum concentration of the Type C sublimate in the 160°C fraction.

X-ray diffraction results indicate a basic three fraction trend. All of the sublimation residues are of the Sandia HNAB-III d_{hkl} pattern. The sublimates, exclusive of the non-nitro fractions isolated up to 130°C, are of the Sandia HNAB-II type and fall into two types: (1) apparently clean HNAB-II and (2) HNAB-II with the spurious 10.34 Å line present. The strongest d_{hkl} pattern of the latter is also found in the same sublimate which presented the strongest infrared spectrum of non-HNAB functionality, namely 160°C.

Elemental analyses (carbon, hydrogen, and nitrogen) present carbon and nitrogen percentage composition data which is not complementary to a high purity HNAB in the 200°C + sublimates. As can be seen by the infrared spectrum of the 220°C sublimate (Fig. 43), there is still substantial evidence for the presence of an aliphatic impurity(s) by the persistence of the 3.45 μ band, albeit substantially diminished in intensity. If one assumes that water were responsible for fluctuating elemental percentage composition, the carbon percentage would be less