2
MASTER

MHSMP-76-27

HNS - IMPURITY AND DECOMPOSITION PRODUCT
ANALYSIS BY TLC

Jacob Sandoval

DEVELOPMENT DIVISION

OCTOBER - DECEMBER 1975
P.O. NO. 64-8043

For
Sandia Laboratories
Albuquerque, New Mexico

Mason & Hanger-Silas Mason Co., Inc.
Partex Plant
P. O. BOX 647
AMARILLO, TEXAS 79177
806-335-1581

operated for the
ENERGY RESEARCH AND DEVELOPMENT ADMINISTRATION
under
U. S. GOVERNMENT Contract DA-11-173-AMC-487(A)

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency Thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

DISCLAIMER

Portions of this document may be illegible in electronic image products. Images are produced from the best available original document.

NOTICE

This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately-owned rights.

HNS - IMPURITY AND DECOMPOSITION PRODUCT
ANALYSIS BY TLC

Jacob Sandoval

DEVELOPMENT DIVISION

October - December 1975
P.O. No. 64-8043

ABSTRACT

This study was pursued with the aim of developing thin-layer chromatography (TLC) analysis techniques to separate, identify and semiquantify the various impurities and decomposition products in HNS, before and after exposure to various environments. This method using visual comparisons was found not to be feasible for the semiquantitation of impurities and decomposition products.

INTRODUCTION

This study was undertaken with a dual objective. The primary aim was to develop TLC analysis techniques to determine impurities and decomposition products in HNS. The ultimate intent was to establish, through utilization of these techniques, the rate of thermal decomposition of HNS.

Thin-layer chromatography (TLC), like all chromatographic techniques, involves the passing of a mobile phase over a stationary support. The mobile phase transports materials at different rates, with each product moving independently of any other component present.

Since materials can migrate only while in the mobile phase, all constituents in the product being surveyed must be soluble in the transportation medium to permit movement and separation of the components in the solute.

The TLC plates were charged by application of solutions of sample and standards in aliquots (μg solute/ μl solution), with calibrated micropipettes, near the base of the plate so that the applied spots were at least 1 cm above the solvent layer. The samples were spotted 2 cm apart.

EXPERIMENTAL

In TLC product evaluation there are numerous qualitative factors to be considered in the choice of support and carrier, thus a preliminary survey was conducted on mobile and stationary phases. In surveying the available solid supports employed in TLC analysis, numerous adsorbents, with or without binder were evaluated. These included cellulose, the aluminas (acidic, basic, neutral), Kieselgur, and modified silica gel layers. Silica gel was found to satisfy the adsorbent requirements.

Four types of silica gel were employed in this study. Their make-up and source are listed in Table I. These adsorbents, either obtained commercially in precoated plates or obtained in bulk for in-plant plate preparation, were used exclusively.

A number of solvents were evaluated. Circular chromatograms were prepared according to procedures developed by Stahl(1), which involve spotting the samples over an adsorbent layer, about 3 cm apart, and applying the solvent with a capillary at the center of each spot. The solvent which moves the sample midway between the origin and the outer edge is classified as good (Fig. 1).

In this endeavor, the principal solvents employed were n,n-dimethylformamide (DMF) and tetrahydrofuran (THF), since these represent the better solvents for HNS. At ambient temperatures the solubility of HNS in DMF is 1.26 g HNS/100 ml solvent(2). Its solubility in THF is lower; however, its rate of solubility has not been determined.

In-plant TLC plates were prepared according to the procedure developed by Stahl(3). The apparatus employed in the coating process consists of a moving applicator traversing over a stationary aligning tray. The plates rest on the tray, and are in line with the spreader which takes the slurry and spreads it uniformly in a thin layer. The spreader holds approximately 60 ml of slurry and can coat six plates (20 x 20 cm, thickness 250 μ).

In TLC compositional analyses, where visual evaluation is employed, equal quantities of the solution to be analyzed and increasing quantities of a standard solution of precisely known content of the pure component to be estimated are applied on the TLC plate and chromatographed. The size and intensity of the spots on the chromatogram are compared, and that most nearly agreeing in size and intensity with the sample under investigation is chosen. At best, these analyses are only semi-quantitative.

HNS (2,2',4,4',6,6'-hexanitrostilbene), because of its poor and limited solubility in most solvents at ambient temperature, does not lend itself to the usual TLC analytical procedures. Heavy applications on a TLC plate promote excessive tailing. Lighter application minimize the tailing, but in turn reduce the impurity content, if present, below the limit of detection.

During the early stages of mobile and stationary phase evaluations, TLC plates were charged with 1, 3, and 5 λ /spot, of a 1% HNS solution in THF and chromatographed. Heavy tailing, indicating an overcharge, resulted as the material moved up the plate. Consequently, the solutions were diluted to 0.1% concentrations. This eliminated most of the tailing, but no separation was affected. It was later discovered that the impurity content in this particular HNS was below the level of detection.

- (1) Randerath, Kurt, Thin-Layer Chromatography, Academic Press, New York (1966) p 15.
- (2) Jacob Sandoval, "HNS Recrystallization Studies," MHSMP-75-24H (April-June 1975).
- (3) Stahl, Egon, Thin-Layer Chromatography, Academic Press Inc., Publishers, New York - London (1965) pp 5-9.

NOTICE
This report was prepared as an account of work sponsored by the United States Government. Neither the United States nor the United States Energy Research and Development Administration, nor any of their employees, nor any of their contractors, subcontractors, or their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness or usefulness of any information, apparatus, product or process disclosed, or represents that its use would not infringe privately owned rights.

One gram quantities of HNS II (5-178-13-01) were washed in ethanol, ethyl ether, water-ethanol-ether-acetone, and water (25 ml fluid/wash). The wash fluids were condensed by evaporation. A portion of each concentration was removed, for subsequent evaluation, and the balance evaporated to dryness. The dry residues were combined. The wash concentrates and wash residues, along with two HNS samples and three arbitrary standards, were spotted on a TLC plate in aliquots of five λ solution/spot, and chromatographed.

The ensuing chromatograms (Figs. 2a and 2b) indicate some impurity in the wash concentrates (spots 1, 2, 3) and in the wash residue (spot 4); yet the HNS sample from which the impurity was extracted (spot 5) reveals no indication of contamination. The presence of dipicrylethane and 1,3,5-trinitrobenzene is indicated, while the presence of TNT is implied in the impurity concentrate. Since the contamination is found only in the wash and extraction concentrates, one can assume that the same process employed in extracting the impurity can be modified to promote product purification.

An earlier analysis of HNS 4-357-XHNS-1-02 had shown no impurities. Ten grams of this HNS were refluxed in 200 ml benzene for nearly 15 hours. The flask contents were filtered hot and the filtrate was allowed to cool and set at ambient temperature for several hours. A small crop of crystals formed, and after extraction the filtrate was reduced to half volume, which on setting several hours at ambient temperature deposited a second crop. The filtrate was reduced to three-quarter volume and a third crop collected. All three crops of HNS were washed with water, rinsed with methanol, and dried, as was the undissolved HNS in the soxhlet extractor thimble.

These HNS samples, along with the starting material, the condensed filtrate, and standards, were spotted in 5 λ aliquots, on two different TLC plates—silica HR, 250 (Brinkman), and silica gel G, 30/3 Zn, 200 μ m, (in-plant coated). The ensuing chromatograms (Figs. 3a and 3b) were evaluated for product composition and for adsorbent efficiency.

Comparison of plates a and b (Fig. 3) indicates that the silica HR layer is superior to the silica G, 30/3 Zn coating. This is attributed to layer thickness. Neither chromatogram indicates any impurity in the starting HNS, nor in the HNS subjected to benzene extraction. A slight impurity is shown in crystal crops 1 and 2, and becomes more pronounced in the third crop and in the extraction fluid condensate. Four impurities are revealed in the impurity concentrate, with the presence of 1,3,5-trinitrobenzene and TNT implied.

In all subsequent evaluations, HNS impurity concentrates were spotted on TLC plates, along with the HNS samples being analyzed and standards, as an aid in identifying the contaminants.

Two additional plates were charged and developed in an effort to confirm or refute the presence of TNT in the concentrates. These chromatograms (Figs. 4 and 5) reveal that the presence of TNT can be detected in the concentrates.

Analyses of HNS by liquid chromatography indicate the principal impurities in HNS to be 1,3,5-trinitrobenzene and dipicrylethane, yet TLC analysis fails to reveal their presence. In order to establish the limit of detection of these two compounds by TLC procedures, two HNS samples in which no impurity had been detected, were doped with TNB and dipicrylethane. HNS 163-137-02 was adulterated with 1, 5 and 7% TNB, and 0.1% solutions in THF were prepared and chromatographed (Fig. 6). HNS 598-01-5 No. 3 with 5% dipicrylethane was also dissolved in THF in 0.1% concentration and chromatographed (Fig. 7). All samples in Fig. 6 were spotted with 5 and 10 λ of solution. The second plate was charged with 10 λ /spot.

The lowest limit of detection for HNS, through TLC visual evaluation, is about 1 $\mu\text{g}/\mu\text{l}$.

From the chromatogram (Fig. 6), it is noted that TNB in a 7% (0.7 $\mu\text{g}/\mu\text{l}$) solution is not detectable, while dipicrylethane (Fig. 7) is visible in the 1% concentration. Its limit of detection is about 0.1 $\mu\text{g}/\mu\text{l}$. The limit of detection on TNB was not determined.

It became apparent that analysis of HNS through TLC techniques, where visual comparisons are involved in the evaluation, was not feasible; consequently, the analysis effort was shifted to the evaluation of decomposition products in heat-treated HNS. HNS samples, aged over varying time periods and temperatures, were obtained for this study. A number of these samples, along with the corresponding material which had not been exposed to heat-treatment, were analyzed by liquid chromatography (LC) and subsequently subjected to TLC evaluation. The LC analyses values are tabulated in Table II.

One percent solutions of the heat-treated and untreated HNS and of standards were prepared and spotted on a TLC plate. The ensuing chromatogram (Fig. 8) reveals no contamination or decomposition in any of the HNS samples, although analyses of the three heat-treated samples by LC had indicated a dipicrylethane content of 0.5% in sample HNS 5-178-137-01 (spot 2), 0.3% in sample HNS 5-171-137-01/5-178-137-01, mixture (spot 3), and 2.6% in sample HNS I, Chemtronics/HNS 5-134XHNS-1-01, mixture (spot 6).

A following plate was spotted with 1% solutions of heat-treated and untreated HNS I and II (Chemtronics) samples, along with standards. The chromatogram (Fig. 9) failed to reveal any decomposition product in any of the heat-treated samples; however, the presence of dipicrylethane in some of the samples is implied.

A subsequent plate was spotted alternately with HNS I and II (Chemtronics) samples, which had been exposed to identical environments. This chromatogram (Fig. 10) reveals dipicrylethane contamination in all of the HNS I samples, while the HNS II samples are shown to be free of impurities.

Another plate was spotted with heat-treated and untreated HNS I and II (Chemtronics), and this chromatogram (Fig. 11) also reveals the presence of dipicrylethane in the HNS I samples.

Two final samples of heat-treated HNS were evaluated for decomposition products. These consisted of HNS II EB 7-6-73, MDFJ04410, which has been aged for 6 and 12 months at 100 C. The chromatogram of the sample treated at 100 C for 6 month (Fig. 12 and 13) reveals no decomposition products. Dipicrylethane is implied; however, the content in the heat-treated sample appears in the same concentration that is implied for the untreated HNS.

The chromatogram of the same HNS, aged 12 months in a 100 C atmosphere, reveals no decomposition or impurities.

Since no HNS decomposition was detected in the samples above, two lots of HNS (03-76-0329-01, 01-76-0421-01) were selected for thermal treatment at 260 C. Five samples from one lot and two from the accompanying lot were heat-treated for periods up to 60 hours (Table III).

Vacuum stability values were determined at 20 and 140 minutes from onset of heating while the samples were being aged. Heating was discontinued after 60 hours because the respective sample had become extremely dark.

Analysis by mass spectrometer was conducted on 2 samples, after 20 and 30 hours of aging. Only 2 tubes permitted removal of the volatiles for testing. Mass spec analysis revealed only trace amounts of NO and CO₂.

Three of these samples were analyzed by liquid chromatography and their analyses compared with the values obtained on the same HNS before heat-treatment. No decomposition products were detected.

All of the above samples were evaluated by TLC; however, the ensuing chromatogram (Fig. 14) failed to reveal any extraneous decomposition product.

COMMENTS, CONCLUSIONS

HNS has been subjected to extensive TLC analysis for impurity and decomposition products in materials subjected to various environments. It has also been surveyed to a lesser extent by liquid chromatography. Evaluation through gel permeation was limited to one sample (heat-treated 72 hours/140 C). GP failed to detect any additional products not present in the untreated HNS; thus, it was not pursued further.

HNS was washed or digested with benzene, acetone, alcohol, DMF, and other solvents. The wash or digestion extracts have been condensed and chromatographed. These impurity concentrates reveal some trace contaminants, but these have not been characterized.

From the investigation conducted thus far, it is evident that the present available analytical techniques are inadequate for separation and semi-quantitation of impurity and/or decomposition products in HNS. Development of new analytical techniques or improvement of existing procedures is warranted.

Table I. Silica Gel - Types and Source

<u>Type</u>	<u>Nature</u>	<u>Source</u>
Silica Gel G	Silica gel with plaster of Paris	Brinkman Industries, Inc., Cantiaga Road Westbury, NY 11590
Silica Gel H	Pure silica gel	
Silica Gel HF	Pure silica gel with inorganic fluorescent material	
Silica Gel GF	Silica gel with plaster of Paris and inorganic fluorescent material	

Table II. Liquid Chromatography Analysis

<u>Sample</u>	<u>Heat</u> <u>(C)</u>	<u>Trtmt.</u> <u>(Hrs)</u>	<u>Component (%)</u>			
			<u>TNB</u>	<u>HNS</u>	<u>DPE</u>	<u>Other</u>
HNS I Chemtronics (66-48)	-	-	< 0.1	97.37 ± 0.07	2.63 ± 0.07	-
HNS II Chemtronics (66-47)	-	-	< 0.1	99.61 ± 0.01	0.33 ± 0.01	-
HNS-5178-137-01	260	2	< 0.1	99.45 ± 0.07	0.55 ± 0.07	-
HNS-5178-137-01	260	2	< 0.1	99.44 ± 0.07	0.56 ± 0.07	-
Chemtronics HNS II (66-47)	170	48	< 0.1	99.72 ± 0.01	0.28 ± 0.01	-
Chemtronics HNS II (66-47)	140	72	< 0.1	99.74 ± 0.01	0.26 ± 0.01	-
Chemtronics HNS II (66-47)	0	0	< 0.1	99.68 ± 0.01	0.32 ± 0.01	-
Chemtronics HNS I (66-48)	170	48	-	96.41 ± 0.02	3.59 ± 0.02	-
Chemtronics HNS I (66-48)	140	72	-	95.85 ± 0.04	4.15 ± 0.04	-
Chemtronics HNS I (66-48)	0	0	< 0.01	96.17 ± 0.18	3.83 ± 0.18	-

Table III. Analysis HNS - Heat Treated at 260 C

HNS Lot No.	Sample	Tube	DTA (C)	HE (g)	Vacuum Stability (mg/g/260)		Heated 260 (hrs)	Mass Spectrometer			LC Analysis (%)*				LC Analysis (%)**			
					20 (min)	140 (min)		NO	CO ₂	Other	HNS	DPE	TNB	Other	HNS	DPE	TNB	Other
03-76-0329-01	1	10	316.0	0.1996	1.00	0.275	40											
	2	3		0.1991	1.05	0.449	60				99.4	0.6	-	-	98.9	1.1	-	-
	3	4		0.2002	1.02	0.382	50											
	4	7		0.1973	0.88	0.352	30	T	T	-0-								
	5	5		0.1984	0.91	0.376	20	T	T	-0-	99.4	0.6	-	-	99.0	1.0	-	-
01-76-0421-01	6	7		0.2009			24											
	7	5		0.1925			32				98.2	1.2	-	-	98.5	1.4	-	-

*LC analysis before HNS aging.

**LC analysis after HNS aging.

T = Trace

NOTE: Tube 5 and 7 reloaded after 30 and 20 hours aging.
Only tubes permitting withdrawal of volatiles
for analysis.

Fig. 1. Rapid Method for Evaluating Solvents

(a) Plate (under UV light, 24 hrs) before spraying

(b) Plate after spraying

Fig. 2. Chromatogram of HNS Wash Solvents and Wash Residues

Silica Gel, Kieselgel; Solvent, Benzene; Spray DMSO (25%)/
Ethylenediamine

1. Ethanol (HNS Wash)	6. HNS I (Chemtronics (66-48)
2. Ethylether (HNS Wash)	7. Dipicrylethane
3. Water-Ethanol-Ethylether-Acetone (HNS Wash)	8. 1,3,5-Trinitrobenzene
4. Wash Residues	9. TNT
5. HNS-II (5-178-13-01)	10. Water (HNS Wash)
	11. Filtrate

(a) Silica Gel HR, 250 μ ; Solvent-Benzene

(b) Silica Gel G, 30/3 Zn, 200 μ ; Solvent-Benzene

Fig. 3. TLC Chromatograms of HNS and Related Products
Indicator: DMSO/Ethylenediamine (25/75)

1. HNS (4-357-XHNS-1-02)
2. HNS (Subjected to Extraction)
3. First Crystal Crop Fill
4. Second Crystal Crop
5. Third Crystal Crop
6. Condensed Extraction Fluid
7. TNT
8. HNS Acetone Wash (Thimble)
9. 1,3,5-Trinitrobenzene
10. Acetonitrile/Toluene Extraction Fluid from HNS Reflux

Fig. 4. TLC Chromatogram of HNS, Standards, and Impurity Concentrates Silica Gel G, 30/3 Zn, 200 μ ; Solvent, Benzene; Spray, DMSO/Ethylenediamine (25/75)

1. Dipicrylethane
2. TNT 15-61
3. TNB 6-35-5
4. HNS 15-62-5
5. HNS, Benzene Concentrate 10 λ
6. HNS, Benzene Concentrate 5 λ
7. Acetonitrile/Toluene Extract Condensate 10 λ
8. Acetonitrile/Toluene Extract Condensate 5 λ
9. 1,3,5-Trinitrobenzene
10. HNS Wash, Cold Benzene

Fig. 5. TLC Chromatogram - HNS, Standards, Impurity Concentrates
Silica HR, 30/3 Zn, 250 μ ; Solvent, Benzene; Spray, DMSO/
Ethylenediamine (25/75)

1. 2,4,6-Trinitrobenzoic Acid
2. Dipicrylethane 15-40-3
3. TNT 15-6-1
4. TNB 6-35-5
5. HNS 15-62-5
6. Alcohol Soluble, HNS Benzene Condensate
7. Alcohol Soluble, HNS Benzene Condensate
8. TNT
9. Acetonitrile/Toluene HNS Extract
10. Acetone Soluble, HNS Benzene Condensate

Fig. 6. Chromatogram of HNS, Other Products
Silica Gel H, 30/3 Zn, Solvent, Benzene

1.	HNS-163-137-02	10λ	8.	HNS-598-01-5 #3 7% TNB	5λ
2.	HNS-163-137-02	5λ	9.	2,4,6-Trinitrobenzoic Acid	10λ
3.	HNS-163-137-02 1% TNB	10λ	10.	2,4,6-Trinitrobenzoic Acid	5λ
4.	HNS-163-137-02 1% TNB	5λ	11.	1,3,5-Trinitrobenzene	10λ
5.	HNS-163-137-02 5% TNB	10λ	12.	1,3,5-Trinitrobenzene	5λ
6.	HNS-163-137-02 5% TNB	5λ	13.	Dipicrylethane 5-40-3	10λ
7.	HNS-598-01-5 #3 7% TNB	10λ	14.	Dipicrylethane 5-40-3	5λ

Fig. 7. Chromatogram of HNS, Other Products Silica Gel H, Solvent Benzene

1. HNS 163-173-02	8. Dipicrylethane 15-40-3
2. 1% Dipicrylethane	9. 1,3,5-Trinitrobenzene
3. 5% Dipicrylethane	10. Wash (HNS Acetone Wash)
4. 10% Dipicrylethane	11. Wash (HNS Acetone-Methanol Wash)
5. Dipicrylethane 15-40-3	12. HNS #28
6. HNS-598-01-5 #3 + 5% DPE	13. HNS #28
7. TNT	

Fig. 8. TLC Chromatogram; HNS (Heat-Treated, Untreated), Standards, Impurity Concentrates, Silica Gel G, 30/3 Zn, 250 μ ; Solvent, Benzene, Spray, DMSO/Ethylenediamine (25/75)

1. HNS-5-178-173-01 (Untreated)	7. 2,4,6-Trinitrobenzoic Acid
2. HNS-5-178-173-01, 140 Min/260 C	8. 1,3,5-Trinitrobenzene
3. HNS (Mix) 5-178, 5-171, 140 Min/260 C	9. Dipicrylethane
4. HNS I (Chemtronics)(Untreated)	10. TNT
5. HNS-5-134 x HNS-1-01 (Untreated)	11. Impurity Concentrate, HNS
6. HNS I (Chemtronics) + 5-134 x HNS-1-01, 140/260 C	12. HNS Wash, Acetone-Methanol
	13. HNS Wash, Acetone-Methanol

Fig. 9. TLC Chromatogram; HNS (Chemtronics) I and II
(Heat-Treated, Untreated), Standards
Silica Gel G, 30/3 Zn, 250 μ ; Solvent Benzene;
Spray DMSO/Ethylenediamine (25/75)

1. HNS I, Untreated	9. 1,3,5-Trinitrobenzene
2. HNS I, Untreated	10. Dipicrylethane 15-40-3
3. HNS I, 48 Hr/170 C	11. Dipicrylethane (New Standard)
4. HNS I, 72 Hr/140 C	12. TNT
5. HNS II, Untreated	13. HNS, Impurity Concentrate
6. HNS II, Untreated	14. HNS Wash, Acetone
7. HNS II, 72 Hr/140 C	15. HNS Wash, Acetone
8. HNS II, 48 Hr/170 C	

Fig. 10. TLC Chromatogram; HNS (Chemtronics) I and II
(Heat-Treated, Untreated), Standards
Silica Gel G, 30/3 Zn, 250 μ , Solvent, Benzene
Spray, DMSO/Ethylenediamine (25/75)

1. HNS II, 16 Hr/170 C	8. HNS II, 8 Hr/140 C
2. HNS I, 16 Hr/170 C	9. HNS II, 96 Hr/140 C
3. HNS II, 48 Hr/170 C	10. HNS I, 96 Hr/140 C
4. HNS I, 48 Hr/170 C	11. Dipicrylethane
5. HNS II, 4 Hr/170 C	12. 2,4,6-Trinitrobenzoic Acid
6. HNS I, 4 Hr/170 C	13. HNS I (Chemtronics)
7. HNS I, 8 Hr/140 C	14. HNS II, 5-178-173-01

Fig. 11. TLC Chromatogram; HNS (Chemtronics) I and II (Heat-Treated, Untreated), Standards
Silica Gel G, 30/3 Zn, 250 μ ; Solvent, Benzene;
Indicator, DMSO/Ethylenediamine (25/75)

1. HNS I, Untreated	9. 1,3,5-Trinitrobenzene
2. HNS I, Untreated	10. Dipicrylethane 15-4-3
3. HNS I, 48 Hr/170 C	11. Dipicrylethane 15-4-3 (New Standard)
4. HNS I, 72 Hr/140 C	12. TNT
5. HNS II, Untreated	13. Impurity Concentrate
6. HNS II, Untreated	14. HNS, CS ₂ Soluble
7. HNS II, 72 Hr/140 C	15. HNS I, Methanol Wash
8. HNS II, 48 Hr/170 C	16. HNS I, Methanol Wash

Fig. 12. TLC Chromatogram; HNS (Heat-Treated, Untreated), Standards
Silica Gel G, 30/3 Zn; Solvent Benzene
Indicator, DMSO/Ethylenediamine (25/75)

1.	1,3,5-Trinitrobenzene	3λ
2.	HNS Extract, Acetone	5λ
3.	HNS Extract, Methanol	5λ
4.	TNT	3λ
5.	Dipicrylethane	3λ
6.	HNS II, EB 7-6-73 MFD JO 4410 (Untreated)	10λ
7.	HNS II, EB 7-6-73 MFD JO 4410 (Untreated)	7λ
8.	HNS II, EB 7-6-73 MFD JO 4410 (Untreated)	5λ
9.	HNS II, EB 7-6-73 MFD JO 4410 (100 C/6 Mos.)	10λ
10.	HNS II, EB 7-6-73 MFD JO 4410 (100 C/6 Mos.)	7λ
11.	HNS II, EB 7-6-73 MFD JO 4410 (100 C/6 Mos.)	5λ

Fig. 13. TLC Chromatogram; HNS (Heat-Treated, Untreated), Standards
Silica Gel G, 30/3 Zn; Solvent, Benzene;
Indicator, DMSO/Ethylenediamine (25/75)

1.	HNS II, 163-137-02	5λ
2.	HNS II, 163-137-02 w/1% Dipicrylethane	5λ
3.	HNS II, 163-137-02 w/5% Dipicrylethane	5λ
4.	TNT	5λ
5.	Dipicrylethane	5λ
6.	1,3,5-Trinitrobenzene	5λ
7.	HNS I Chemtronics (66-48)	5λ
8.	HNS II Chemtronics (66-47)	5λ
9.	HNS II EB 5737	5λ
10.	HNS II 5157-137-02	5λ
11.	HNS II EB 7-6-73 MFD JO 4410 (100 C/12 Mos.)	10λ
12.	HNS II EB 7-6-73 MFD JO 4410 (100 C/12 Mos.)	7λ
13.	HNS II EB 7-6-73 MFD JO 4410 (100 C/12 Mos.)	3λ
14.	HNS II EB 7-6-73 MFD JO 4410 (100 C/12 Mos.)	1λ

Fig. 14. Chromatogram of HNS, Heated-Treated at 260 C
[Silica Gel-GF (Kontes); Solvent, Benzene;
Spray DMSO-EDA (1:1)]

1.	TNT	25 μ g
2.	TNT	15 μ g
3.	Trinitrobenzene	25 μ g
4.	Trinitrobenzene	15 μ g
5.	Dipicrylethane	25 μ g
6.	Dipicrylethane	15 μ g
7.	HNS, Thermal Aging, 60 hrs	25 μ g
8.	HNS, Thermal Aging, 60 hrs	15 μ g
9.	HNS, Thermal Aging, 40 hrs	25 μ g
10.	HNS, Thermal Aging, 40 hrs	15 μ g
11.	HNS, Thermal Aging, 32 hrs	25 μ g
12.	HNS, Thermal Aging, 32 hrs	15 μ g
13.	HNS, Thermal Aging, 30 hrs	25 μ g
14.	HNS, Thermal Aging, 30 hrs	15 μ g
15.	HNS, Thermal Aging, 20 hrs	25 μ g
16.	HNS, Thermal Aging, 20 hrs	15 μ g