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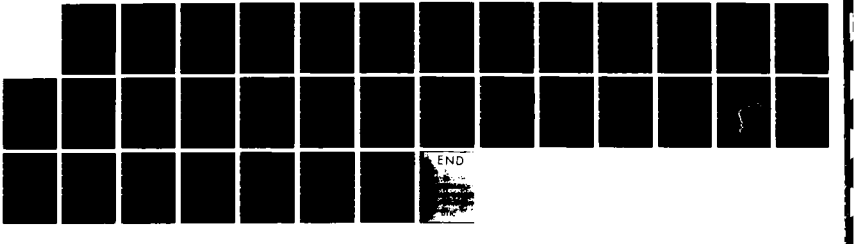

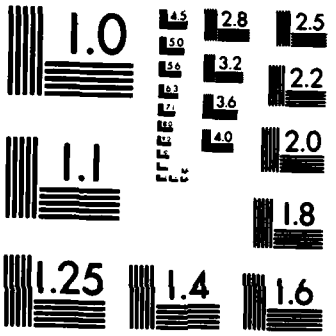

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PREPARATION AND PURIFICATION OF MULTIGRAM QUANTITIES OF SEX & TAX

12

Final Report

Phase IV

Clifford D. Bedford

30 April 1983

Supported by
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1,5-Diacetyloctahydro-3,7-dinitro-1,3,5,7-tetrazocine (DADN)
1,3,5,7-Tetranitro-1,3,5,7-tetrazocine (HMX)
1,3,5-Trinitro-1,3,5-triazine (RDX)
Synthesis Purification Nitrolysis

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)
This final report describes the multigram preparation and purification of 1-acetyloctahydro-3,5,7-trinitro-1,3,5,7-tetrazocine (SEX) needed for toxicological testing. SEX was prepared by nitrolysis of 1,5-diacetyloctahydro-3,7-dinitro-1,3,5,7-tetrazocine (DADN), using a mixture of 30% oleum and 100% nitric acid. The process was conducted batchwise yielding 6.0 kilograms of a HMX/SEX/DADN mixture. The crude SEX was contaminated with up to 5% HMX and up to 20% DADN. Removal of the DADN contamination was accomplished through open hot-column chromatography (90-100°C) on silica gel with a nitromethane eluent. This yielded SEX in 92-95% purity. The resulting SEX/HMX mixture was purified to greater than 98% SEX by recrystallization from

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acetone. A total of 2,170 grams of SEX was prepared by this process.

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SUMMARY

This final report describes the synthesis and purification of 2.0 kilograms of 1-acetyloctahydro-3,5,7-trinitro-1,3,5,7-tetrazocine (SEX). The objective was to provide 2.0 kilograms of SEX in satisfactory purity (>98%) with proper analytical characterization of residual impurities.

Kilogram quantities of SEX, contaminated with 1,5-diacetyloctahydro-3,7-dinitro-1,3,5,7-tetrazocine (DADN) and 1,3,5,7-tetranitrooctahydro-1,3,5,7-tetrazocine (HMX), were prepared by nitrolysis of DADN, using a mixture of 100% nitric acid and 30% oleum. SEX production runs were conducted with a remote batch reactor and mixer apparatus for safety. The crude SEX, contaminated with 2% to 5% HMX and 15% to 30% DADN was purified by hot-column chromatography on silica gel using a nitromethane eluent; this process effectively removes the DADN contaminant. The resulting SEX/HMX mixture was then purified to greater than 98% (as determined by analytical high-pressure liquid chromatography) by recrystallization from acetone.

PREFACE

Citation of trade names in this report does not constitute an official endorsement or approval of the use of such items.

CONTENTS

FIGURES

GLOSSARY

DADN: 1,5-Diacetyloctahydro-3,7-dinitro-1,3,5,7-tetrazocine

DSC: Differential scanning calorimeter

HMX: 1,3,5,7-Tetranitrooctahydro-1,3,5,7-tetrazocine

HPLC: High-pressure liquid chromatography

NMR: Nuclear magnetic resonance

RDX: 1,3,5-Trinitrohexahydro-1,3,5-triazine

SEX: 1-Acetyloctahydro-3,5,7-trinitro-1,3,5,7-tetrazocine

TLC: Thin layer chromatography

I INTRODUCTION

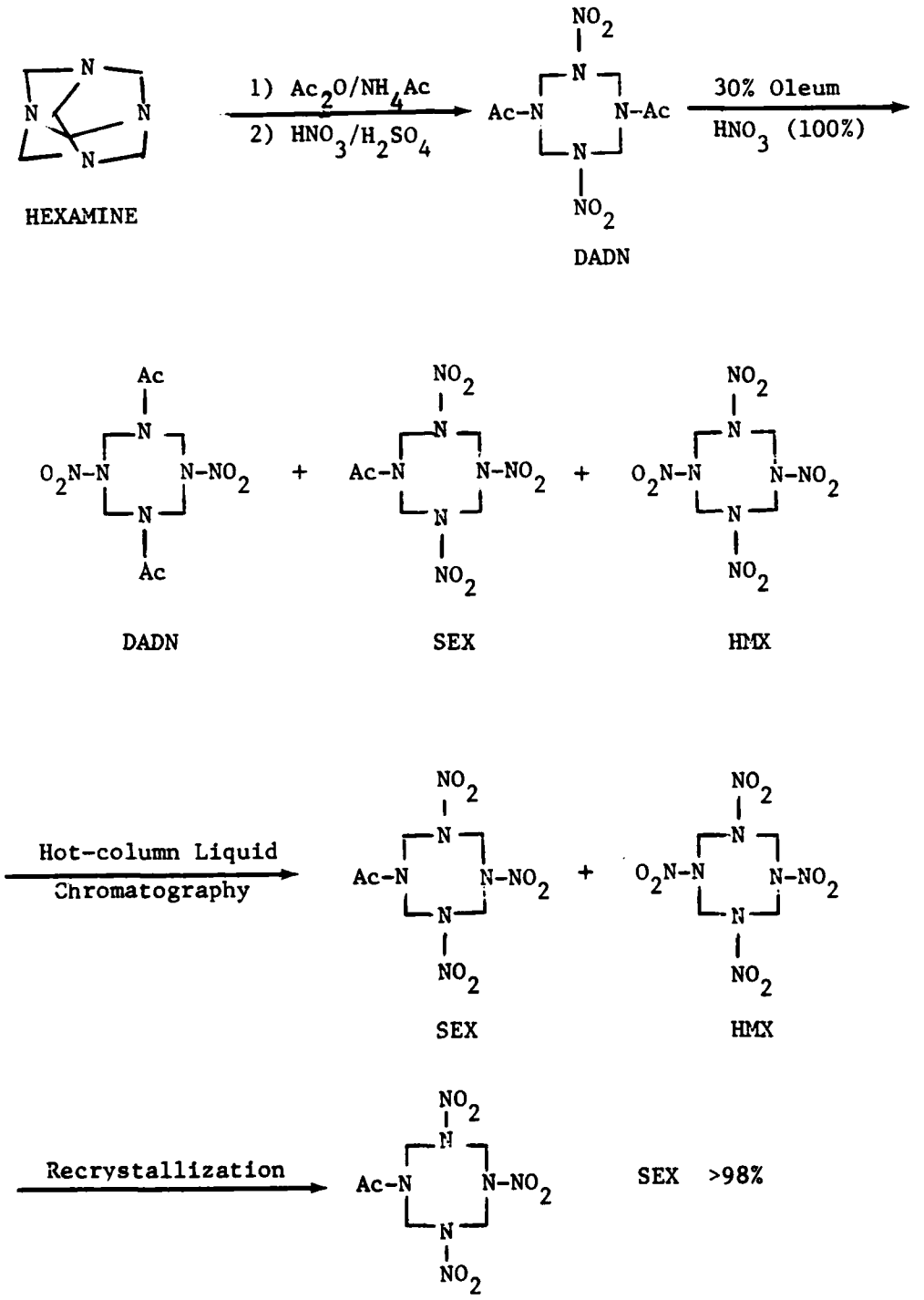
The U.S. Army Medical Research and Development Command is interested in determining the potential environmental and health hazards of wastewaters containing SEX. SEX is an unavoidable coproduct formed during the manufacturing of RDX/HMX. In 1977, 34,000 pounds of HMX were produced, or about 123 pounds per day, at the Holston Army Ammunition Plant. At full production levels, approximately 16 million pounds of RDX and 2 million pounds of HMX can be produced annually, or put another way, more than 1,000 pounds of SEX per day could be generated and discharged. The wastewaters from the manufacturing of RDX/HMX are subject to environmental discharge limitations established by regulatory agencies. Information on major constituents of these wastewaters is a necessary portion of the data base needed to estimate the overall environmental hazards. Because the wastewaters will contain large amounts of SEX, it is important to obtain sufficient quantities of pure SEX for a complete toxicological investigation.

Since SEX has not been shown to be of value as an explosive, little effort has been expended on its deliberate synthesis. However, owing to the present toxicological interest, it was necessary to explore the feasibility of preparing kilogram quantities of SEX in the purity (>98%) necessary for these studies. Our specific objective was to prepare and purify 2.0 kg of SEX, based on earlier investigations.[1]

Our efforts to prepare, purify, and characterize a 2.0 kg quantity of SEX are described in the following sections. The preparation and purification of SEX by an alternative, but more costly, synthesis is described elsewhere.[2,3]

II PREPARATION OF SEX

The total synthesis and purification of SEX, prepared according to the methods described by Gilbert[4] and Coon[5] are shown in Scheme I.



Scheme I

Synthesis and Purification of SEX

Kilogram Production of SEX

On a laboratory scale, the preparation of SEX by the procedure shown in Scheme 1 consistently yielded 23% to 41% crude SEX, contaminated with 2% to 5% HMX and 15% to 30% DADN. The experimental methods developed required that the reaction mixture be cooled during addition of reagents. The resulting mixture was then stirred overnight at ambient temperature.

This previously developed batch method was used to prepare crude SEX mixtures.[1] Thus, a mixture of 1.0 to 1.5 kg of DADN dissolved in 7.5 to 9.0 L of 98% nitric acid and 1.65 to 2.15 L of 30% oleum was stirred overnight at ambient temperature. The exothermic addition of the oleum to the nitric acid was readily controlled with a dry ice/acetone bath. The reaction mixtures were then pumped onto ten gallons of ice and filtered, yielding the crude SEX mixtures. A schematic diagram of the reactor for the SEX synthesis is shown in Figure 1. About 17.0 kg of DADN (supplied by Los Alamos National Laboratories) was converted to about 6.0 kg of a dry DADN/SEX/HMX mixture, which according to HPLC analysis consisted of 3.4% HMX, 78.5% SEX, and 18.1% DADN. The following optimum conditions were established during these batch production runs.

- DADN/nitric acid (100%) feed batches were prepared by dissolving 1.5 kg of anhydrous DADN in 9.0 L of 100% nitric acid, with external cooling.
- A single peristaltic pump cycled cold acetone (-10° to -25°) at 1.5 L/min around the mixing flask.
- Feed lines and cooler lines were insulated to minimize heat losses.
- Both the DADN/nitric acid and 30% oleum reservoirs were cooled in ice baths before mixing.
- The feed pump rates were set at 5 : 1 DADN/nitric acid to 30% oleum.
- DADN/nitric acid feed rates averaged 100 mL/min.
- 30% oleum feed rates averaged 20 mL/min.

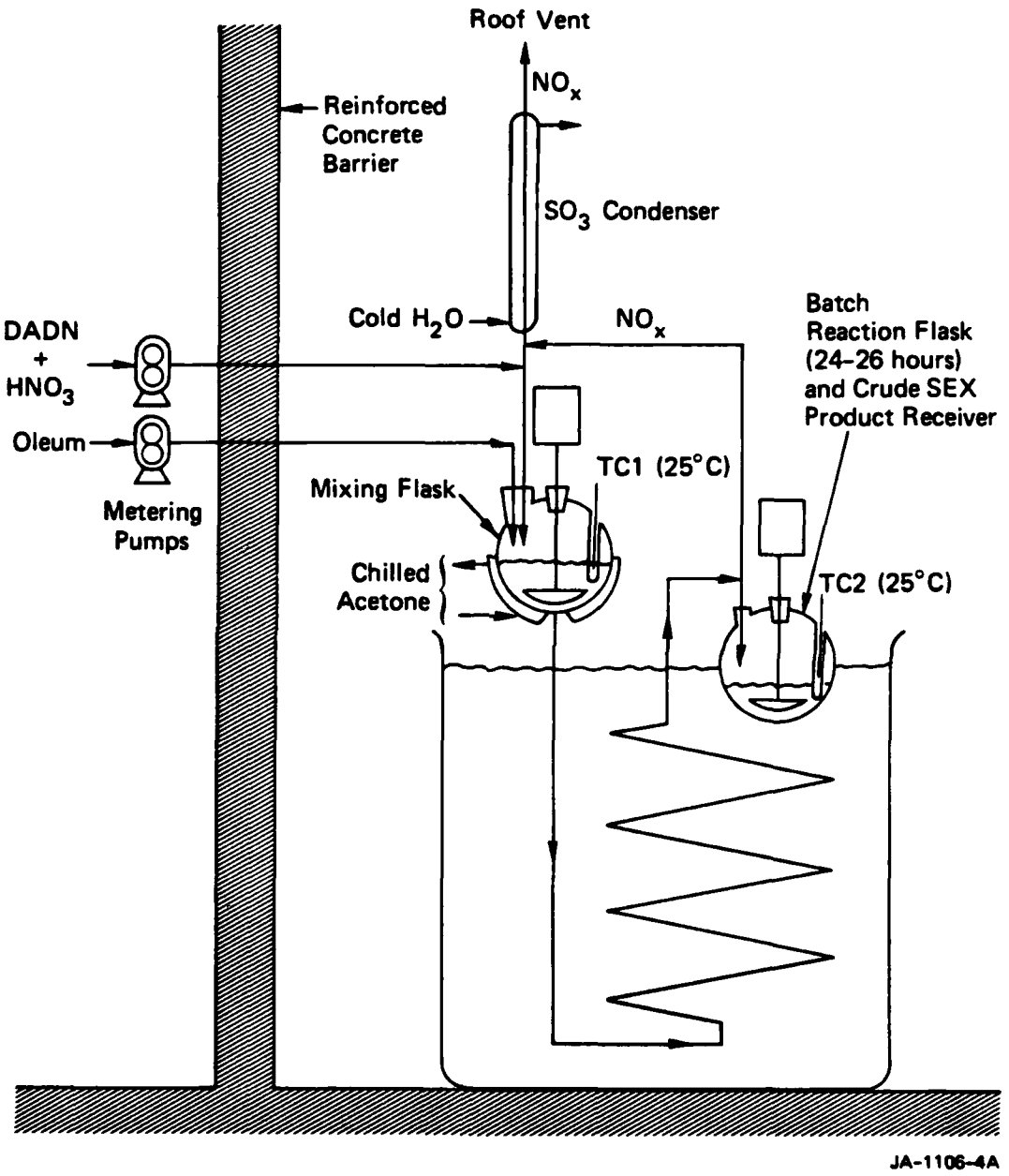


FIGURE 1 BATCH PRODUCTION MINIPLANT FOR MULTIGRAM SYNTHESIS OF SEX

- The temperature of the mixing and holding flasks was maintained by keeping the liquid in the mixing chamber at 500 to 700 mL.

- During the reaction, two temperatures were monitored: (1) the mixer temperature was held at 15° to 25°C with a cooling bath temperature of -10° to -25°C and with the feed rates previously established; (2) the reactor flask remained between 25° to 30°C overnight with mechanical stirring.

- If the temperature in the reactor flask rose above 30°C, an external heat exchanger was used to reduce the reaction temperature.

- After 24 to 26 h the reaction mixture was pumped onto 10 gallons of ice, and stirred until the ice melted.

- The resulting precipitate was filtered, washed several times with one-gallon portions of water, and air dried. The acidic filtrate and washings were filtered through limestone before disposal.

The results of the individual batch runs are shown in Table 1. Runs 1 and 8 fumed off because of a malfunction of the stirrer in the reactor flask. Without the increased heat exchange to the surrounding environment resulting from effective stirring, the temperature of the reaction mixture slowly increased. Ultimately, this gradual heating led to an uncontrollable reaction exotherm after the mixture reached 55°C. Similar results were observed in previous small scale reactions.[1] No product was isolated from either of those runs. It was apparent from these process upsets that additional SEX preparations should incorporate the following mechanical modifications:

- The attachment of the stirrer motor to the stirrer shaft should be improved to prevent slippage; the type of grease used on the stir shaft should be changed to help prevent binding; and the stirrer assembly should be covered to prevent corrosion from acid fumes.

- The reaction flask should be placed in a stand that allows maximum contact between the flask and the air.

- In the event of a stirrer malfunction, an ambient temperature water bath should be installed through which the reaction mixture can be continuously circulated for efficient heat exchange.

Table 1

PRODUCTION RUNS OF CRUDE SEX

Run	HNO_3 (L)	30% Oleum (L)	DADN (kg)	Temp. (°C)	Time (h)	Product Composition[a] % HMX	% SEX	% DADN	Total Yield (g)	% Yield SEX
1	7.5	1.65	1.0	--	--		--		--	--
2	7.5	1.65	1.0	18-25	24	3.6	76.0	20.0	370	28.0
3	11.25	2.35	1.5	18-25	26	4.0	80.1	15.9	510	27.2
4	9.75	2.15	1.5	18-25	26	3.1	77.5	19.5	620	32.0
5	9.00	2.15	1.5	20-23	24	2.4	80.0	17.5	700	37.3
6	9.00	2.15	1.5	24-26	24	4.1	82.9	13.0	440	23.9
7	9.00	2.15	1.5	24-26	26	4.4	85.2	10.1	400	22.7
8	9.00	2.15	1.5	--	--		--		--	--
9	9.00	2.15	1.5	20-22	24	2.4	67.6	29.9	800	36.1
10	9.00	2.15	1.5	20-24	24	2.9	73.7	23.1	750	36.8
11	9.00	2.15	1.5	22-26	24	3.3	76.4	20.3	660	33.4
12	9.00	2.15	1.5	24-26	24	3.5	85.6	11.0	725	40.8
Total	118.0	25.0	17.0	--	--	3.4	78.5	18.0	5,975	27.6

[a]Compositions determined by analytical HPLC.

Purification of SEX

The SEX prepared as described above was purified in a two-step process. First, the crude DADN/SEX/HMX mixtures were chromatographed on silica gel using a nitromethane eluent. This process effectively removes all residual DADN. Furthermore, as shown in Table 2, the purification procedure was quite reproducible and directly yielded small quantities of 98+% SEX. In general, up to 90% of the SEX originally placed on the column was recovered after removal of solvent. We were able to purify 75- to 200-g quantities of crude SEX (composition determined by analytical HPLC: 3.4% HMX, 78.5% SEX, and 18.1% DADN) using the jacketed metal column apparatus. Concentration of the chromatographed SEX samples yielded 1,133 g of 98+% SEX, 2,283 g of 92-95% SEX contaminated with HMX, and 256 g of 82-85% SEX contaminated with DADN (Table 2). All chromatographed samples were examined by TLC, and like fractions were combined before removal of the nitromethane to ensure sample uniformity.

To obtain the required 2.0 kg of 98% SEX, the remaining 2,283 g of 92-95% SEX contaminated with HMX was recrystallized from acetone. In general, 30 g of 92-95% SEX was dissolved in 3.0 L of acetone. The resulting solution was filtered hot and stored at ambient temperature for 7 to 10 days. The precipitate was filtered and dried in vacuo yielding, on the average, 12 to 15 g. The purity of the recrystallized SEX (as determined by analytical HPLC) was greater than 99%. A total of 1,037.6 g of recrystallized SEX was collected (Table 3).

In total, 2,170 g of 98+% SEX was recovered from the initial crude 6.0 kg mixture, a 36.6% yield. The major impurity proved to be HMX, approximately 1.0%, with a 0.1% residual impurity of DADN. No other impurities could be detected using either normal-phase or reverse-phase analytical HPLC. The process described above was an effective solution to preparing and purifying multigram quantities of SEX.

Table 2

HOT COLUMN PURIFICATION OF SEX MIXTURES[a]

Run No.[c]	Fraction[b] No.	Compositions High in SEX				Compositions Low in DADN				Compositions Low in HMX			
		g	HMX %	SEX %	DADN %	g	HMX %	SEX %	DADN %	g	HMX %	SEX %	DADN %
1	1-7					37.8	2.6	96.2	1.2				
2	3-6					33.7	4.8	95.2	0.0				
2	7									7.6	0.8	92.6	6.6
2	8-10									12.6	1.3	67.3	31.4
3	2-5					35.7	3.6	96.2	0.2				
3	6									8.5	2.1	90.1	7.7
3	7-12									19.3	3.2	51.1	45.7
4	2-5					45.2	3.6	96.2	0.2				
4										2.1	1.4	91.6	7.0
4	-10									13.3	0.8	22.4	76.4
5	2-4					32.6	4.6	94.5	0.8				
5	5-6									13.0	2.8	86.2	10.9
6	2-4					20.0	5.4	94.5	0.0				
6	5	16.3	1.6	98.4	0.0								
6	6-7	10.1	0.6	99.4	0.0								
6	8-10									4.5	0.9	54.0	45.0
7	1-3	49.5	0.4	99.4	0.1								
7	4	4.8	0.6	99.2	0.1								
7	5-6									1.1	1.0	66.0	33.0
8	1-3	36.8	1.2	98.2	0.1								
8	4	-		-									
8	5	2.5	0.7	98.1	1.2								
8	6									0.6	0.8	57.6	41.6
9	2-4					26.0	3.0	97.0	0.0				
9	5-8	16.9	0.8	99.1	0.1								
10	2-3					46.1	3.7	96.3	0.0				
10	4-8									8.9	0.6	93.7	5.8
11	2-4					39.6	3.2	96.8	0.0				
11	5-8	13.4	0.2	99.0	0.8								

(continued)

Table 2 (continued)

Run No.[c]	Fraction[b] No.	Compositions High in SEX				Compositions Low in DADN				Compositions Low in HMX			
		g	HMX %	SEX %	DADN %	g	HMX %	SEX %	DADN %	g	HMX %	SEX %	DADN %
12	2-4					48.6	2.9	97.1	0.0				
12	5-9	8.3	0.4	99.6	0.0								
13	2-3					32.0	5.0	95.0	0.0				
13	4-8	21.0	1.0	98.9	0.2								
14	2-3					30.8	3.2	96.8	0.0				
14	4-9									18.4	1.1	96.0	3.0
15	2-3												
16	1-3												
17	1-4												
18	2-3												
						151.4	4.0	95.5	0.5				
15	4-9												
16	4-8												
17	5-8												
18	4-9												
		31.8	0.7	98.4	0.8								
19	2-3												
20	2-3												
21	2-3												
22	2-3												
23	1-3												
24	1-2												
						205.1	4.6	95.1	0.2				
19	4												
20	4-5												
21	--												
22	4-6												
23	3-5												
24	3-5												
		70.0	0.6	99.1	0.3								

(continued)

Table 2 (continued)

Run No.[c]	Fraction[b] No.	Compositions High in SEX				Compositions Low in DADN				Compositions Low in HMX			
		g	HMX %	SEX %	DADN %	g	HMX %	SEX %	DADN %	g	HMX %	SEX %	DADN %
19	5-8												
20	--												
21	4-6												
22	--												
23	6												
24	6-7									6.8	0.6	82.5	16.9
25	3-6					74.3	3.7	96.3	0.0				
25	7-15	34.4	0.5	99.3	0.2								
26	2-6												
27	1-3												
28	1-5												
29	3-7												
30	2-4												
31	--					339.0	4.9	95.1	0.0				
26	7-14												
27	4-6												
28	6-14												
29	8-12												
30	4-7												
30	4-7												
31	0-4	265.5	1.1	98.9	0.0								

(continued)

Table 2 (continued)

Run No.[c]	Fraction[b] No.	Compositions High in SEX				Compositions Low in DADN				Compositions Low in HMX			
		g	HMX %	SEX %	DADN %	g	HMX %	SEC %	DADN %	g	HMX %	SEX %	DADN %
32	1-3												
33	3-6												
34	0-3												
35	2-3												
36	1-4					409.71	6.9	93.2	0.0				
32	4-9												
33	11-15												
34	9-13									139.70	4.6	85.1	10.3
37	1-4												
38	1-3												
39	2-4												
40	1-5												
41	1-2												
42	1-4												
43	1-4					676.1	7.8	92.2					

(continued)

Table 2 (concluded)

Run No.[c]	Fraction[b] No.	Compositions High in SEX				Compositions Low in DADN				Compositions Low in HMX			
		g	HMX %	SEX %	DADN %	g	HMX %	SEX %	DADN %	g	HMX %	SEX %	DADN %
33	7-10												
34	4-8												
35	4-10												
36	5-6												
37	5-11												
38	5-11												
39	5-11												
40	6-7												
41	3-6												
42	5-7												
43	5-10												
		552.0	1.9	98.1	0.0								
Totals		1,133.3				2,283.1				256.4			

[a]Initial SEX composition 3.4% HMX, 78.5% SEX, and 18.1% DADN.

[b]One-liter aliquots were collected in each fraction.

[c]Like fractions were combined after TLC analysis and concentrated. Runs in brackets represent combined fractions.

Table 3

RECRYSTALLIZATION OF 92-95% SEX/HMX MIXTURES FROM ACETONE[a]

Run	92-95% SEX (g)	Acetone (L)	Recrystallized[b] % HMX	Recrystallized[b] % SEX	Yield (g)	Yield (%)
1	115	12	0.7	99.3	62.1	54.0
2	120	12	0.6	99.4	68.9	57.4
3	120	12	0.7	99.3	62.9	52.3
4	120	12	0.6	99.4	68.9	57.4
5	120	12	0.6	99.4	66.7	55.6
6	120	12	0.7	99.3	65.3	54.4
7[c]	--	--	0.8	99.7	67.9	--
8	120	12	0.6	99.4	65.0	54.2
9	240	24	0.7	99.3	142.0	59.2
10	240	24	0.8	99.2	127.9	53.3
11	240	24	0.9	99.1	128.2	53.4
12	180	18	0.7	99.3	111.4	61.9
Total Recrystallized SEX					1,037.6	
Total Column Purified SEX					1,133.3	
Total Purified SEX					2,170.9	

[a]Saturated solutions are allowed to sit for 7 days before filtration.

[b]Composition determined by analytical HPLC.

[c]SEX obtained from the stored mother liquors.

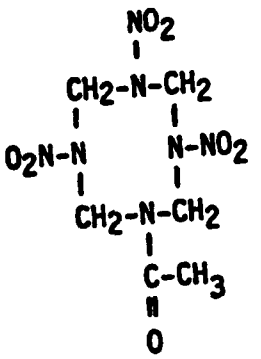
III RESULTS AND CONCLUSIONS

Crude SEX was prepared in kilogram quantities by a batch reaction method. Purification by hot-column liquid chromatography followed by recrystallization from acetone yielded SEX with a purity greater than 98%. A total of 2,170 g of 98+% SEX was prepared, 500 g of which was delivered to Dr. White of Letterman Army Institute of Research for testing and evaluation.

IV CHARACTERIZATION OF SEX[6]

SEX is the trivial designation for the compound 1-aceto-3,5,7-trinitro-1,3,5,7-tetrazacyclooctane, or alternatively, 1-(N)-acetyl-3,5,7-trinitrocyclotetramethylenetetramine. SEX appears sufficiently stable in normal nitrolysis media to exist as a contaminant in RDX/HMX.

Structural Formula:



Empirical Formula: $C_6H_{11}N_7O_7$

Elemental Analyses (Calculated): C,24.57%; H,3.76%; N,33.5%
(Found): C,24.21%; H,3.76%; N,33.45%

Melting Point: 224.2° - 224.7°C (DEC).

Molecular Weight: 293 (Calculated). Typical experimental values by Rast camphor method: 207 to 377

Density: 1.785 g/cm^3 at 21°C

Solubility: Soluble in dimethylsulfoxide.
Slightly soluble in pyridine, acetone, and nitromethane.
Almost insoluble in ethanol, benzene, and ether.
Limited solubility in acetic acid.

Impact Sensitivity (drop weight test): Greater than 300 kg-cm compared with 148 kg-cm for pure HMX. SEX is sensitive to direct strong hammer blows. During our investigations SEX has exhibited no instability, but because of the hammer results, SEX should be handled like HMX--as a potential explosive.

Infrared Spectrum: Attached (Figure 2).

Nuclear Magnetic Resonance Spectrum: Attached (Figure 3).

Chemical Properties: SEX gives a positive Franchimont nitramine reaction, but a negative Liebermann nitroso test. Decomposition in sodium hydroxide fails to produce free CH_3COO^- for a lanthanum nitrate test. However, if SEX is decomposed in 96% sulfuric acid, the distillate gives a lanthanum nitrate test.

SEX appears inert to boiling acetic anhydride and unaffected by treatment with ammonium nitrate-nitric acid mixtures. Absolute nitric acid at 50°-60°C converts SEX to HMX. Warm 70% Nitric acid destroys the compound rapidly, as do 10% aqueous sodium hydroxide and 28% ammonia.

Unconfined Burning: Supports combustion in air (does not explode).

DSC: Exo peak 232°C: Attached (Figure 4). After 48 hours at 75°C there was no change (nmr, ir, and color) or weight loss in SEX samples. Furthermore, no change in composition could be detected after 72 hours under these prescribed conditions.

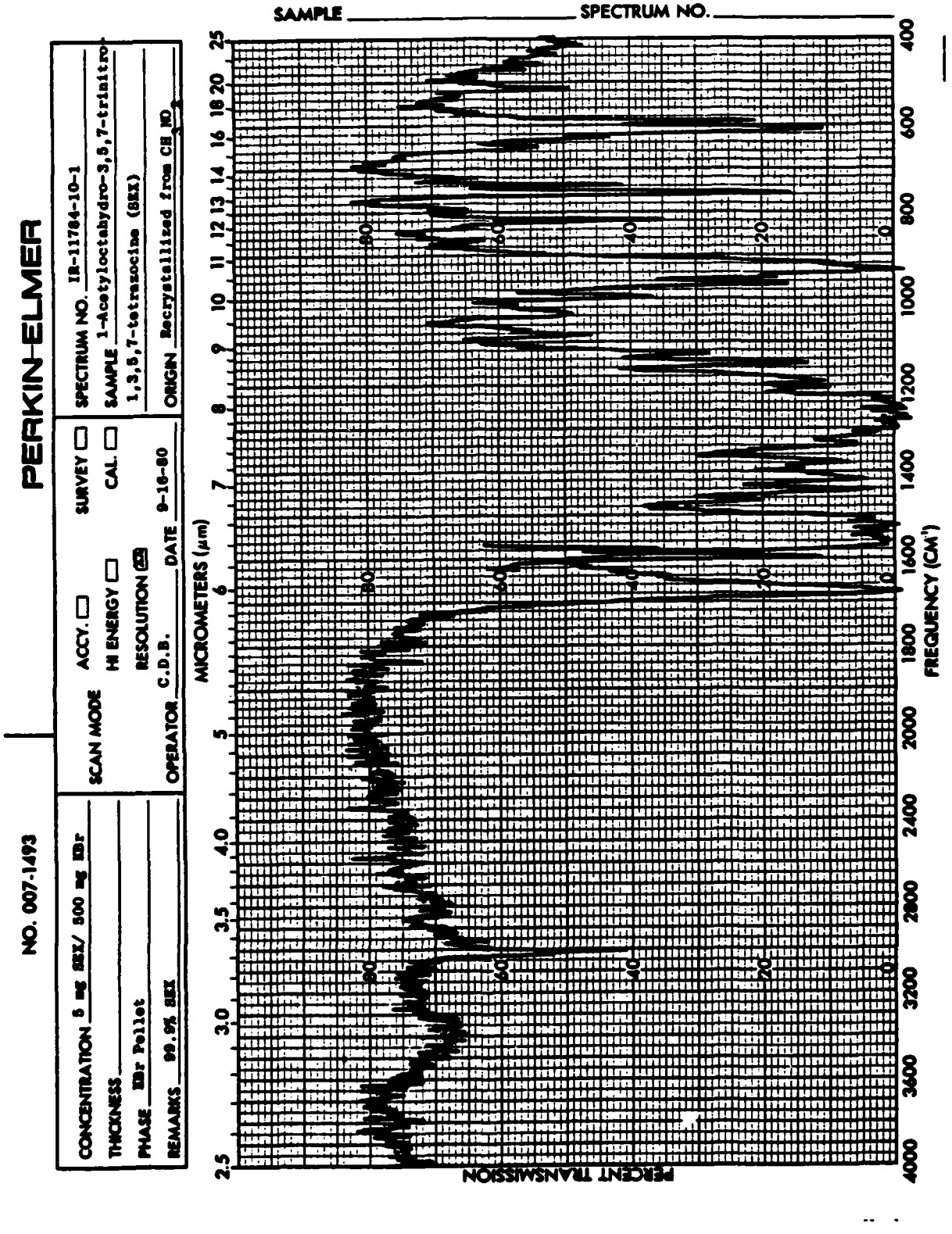


FIGURE 2 INFRARED SPECTRUM OF 99.9% SEX

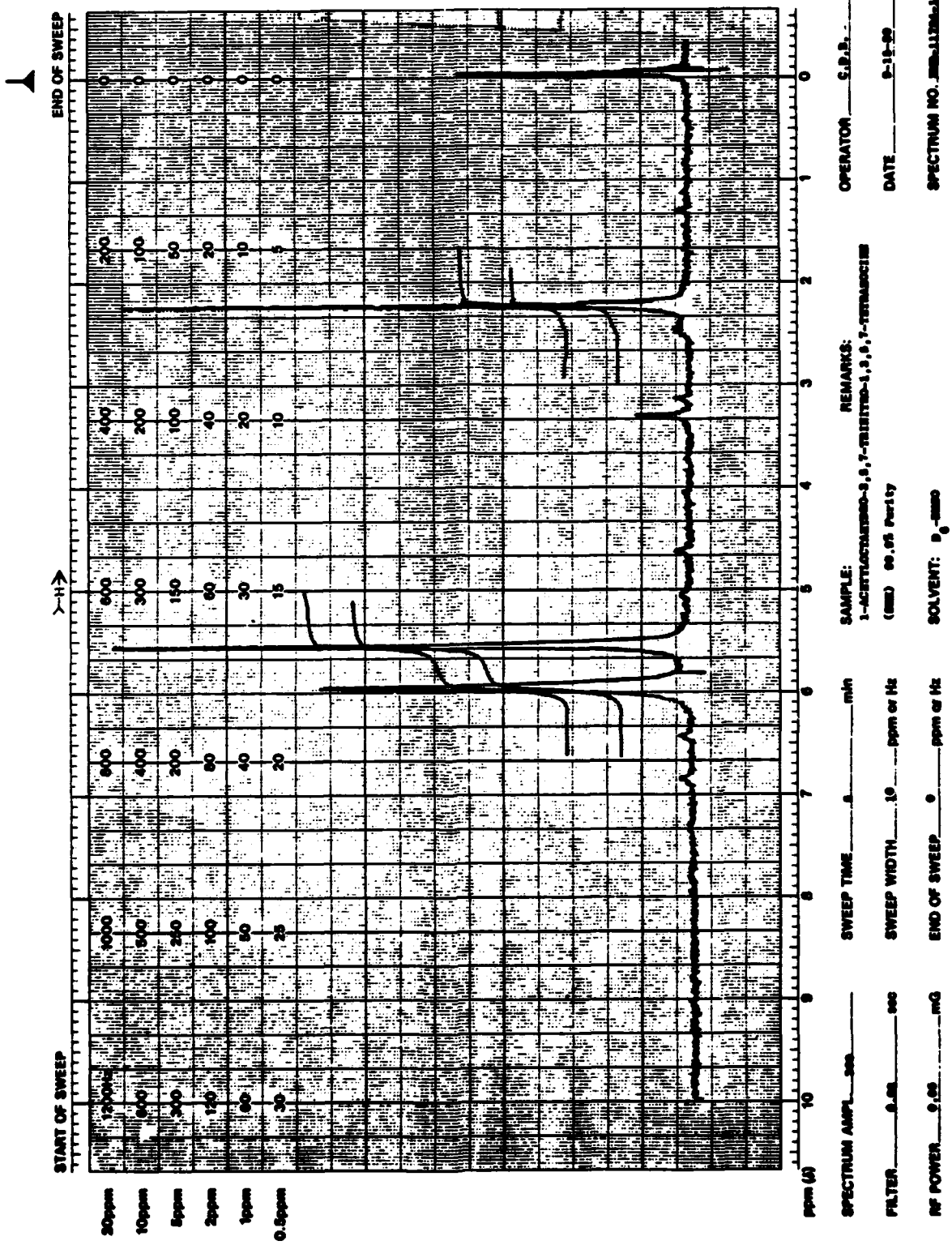


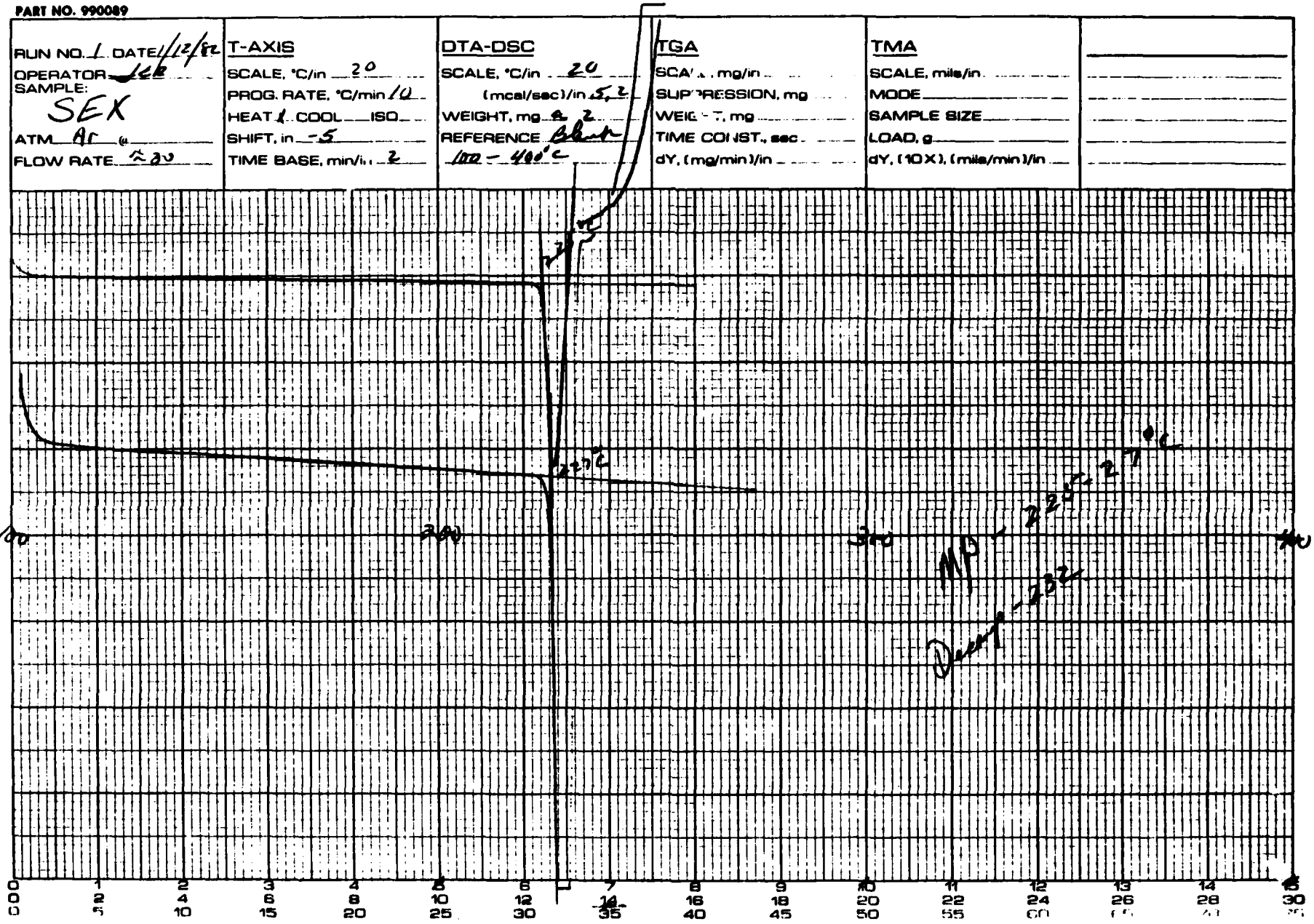
FIGURE 3 PROTON NMR SPECTRUM OF 99.9% SEX

PART NO. 990089

	T-AXIS	DTA-DSC	TGA	TMA	
RUN NO. 1 DATE 1/12/82	SCALE, °C/in 20	SCALE, °C/in 20	SCALE, mg/in	SCALE, mils/in	
OPERATOR Lab	PROG. RATE, °C/min 10	(mcal/sec)/in 5.2	SUPPRESSION, mg	MODE	
SAMPLE: SEX	HEAT 1 COOL ISO	WEIGHT, mg 2	WEIGHT, mg	SAMPLE SIZE	
ATM Ar @	SHIFT, in -5	REFERENCE Blank	TIME CONST., sec	LOAD, g	
FLOW RATE ~20	TIME BASE, min/in 2	100 - 400°C	dY, (mg/min)/in	dY, (10X), (mils/min)/in	

DUPONT Instruments

MEASURED VARIABLE



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EXPERIMENTAL PROCEDURES

Materials

Melting points were determined in glass capillaries with a Laboratory Devices Mel-Temp apparatus or on a Fisher-Johns melting point apparatus and are uncorrected. Infrared (IR) spectra were obtained on Perkin-Elmer Model 281 and 735B spectrophotometers. Nuclear magnetic resonance (NMR) spectra were recorded on a Varian Associates EM-360 spectrometer, and chemical shifts are reported in parts per million (δ) relative to an internal tetramethylsilane reference. Microanalyses were performed with a Perkin-Elmer 240 elemental analyzer (C, H, N), and by Galbraith Laboratories, Inc., Knoxville, Tennessee.

1,5-Diacetyloctahydro-3,7-dinitro-1,3,5,7-tetrazocine (DADN) was supplied by Los Alamos National Laboratory and used without further purification. Nitric acid (100%) was supplied by the Holston Army Ammunition Plant, Kingsport, Tennessee. Hot-column chromatography was performed on 90-200 mesh silica gel supplied by Accurate Chemical and Scientific Corp., Hicksville, NY using a nitromethane eluent purchased from International Minerals and Chemical Corp., Des Plaines, Il.

Analysis Procedures for SEX

The composition of reaction products obtained from the nitration of DADN, hot-column chromatography, and SEX recrystallizations from acetone was determined by HPLC. A waters system consisting of a pair of Model 6000 Pumps, a U6K Injector, Model 440 UV Absorbance Detector, Data Module and System Controller was used. A waters micro-Porasil column using a 50/50 acetonitrile methylene chloride eluent at a flow rate of 2 ml per minute was employed. Under these conditions, baseline separation achieved, and the entire analysis of a sample requires less than ten minutes. Standard solutions of each of the pure compounds, and a known composition mixture of the three were injected to determine

the retention time and the relative response factors for each component. The relative response factors for the three compounds are: SEX-0.515; HMX-0.430; and DADN-0.571. By this method we can determine the percent composition of a sample with an accuracy of about two tenths of one percent.

1-Acetyl-3,5,7-trinitro-1,3,5,7-octahydrotetrazocine (SEX)

DADN (100.0 g, 0.138 mole) was dissolved in 750 mL of 100% HNO_3 at 20°C. With cooling (dry ice/acetone bath), 165 mL of 30% oleum was added at such a rate that the temperature of the mixture did not exceed 25°C. At the end of the addition, the flask was stirred at room temperature for 19.5 hours. The mixture was then poured into ice/water and stirred for 30 min, which precipitated the crude SEX. The precipitate was filtered, washed with several large portions of water, and dried over P_2O_5 in vacuo, yielding 42.5 g (38%) SEX. Analytical HPLC of the product indicated the following composition: 14.2% DADN, 84.0% SEX, 1.8% HMX.

Purification of SEX. The crude SEX produced by the nitration of DADN consists of about 75-80% SEX, 15-20% DADN, and less than 5% HMX. Separation of all three components was possible by TLC using nitromethane as the solvent and silica gel as the stationary phase. However, neither ordinary column chromatography nor preparative HPLC could be employed for preparative separations because of low solubilities of crude SEX mixtures. Open hot-column chromatography using nitromethane did prove effective in removing the DADN, and recrystallization of the resulting SEX/HMX mixture yields 98+% SEX.

The apparatus for the removal of the DADN consists of an aluminum, steam jacketed column, 4 feet in length and 3 inches in diameter. A 1 liter steam jacketed addition funnel was used as a reservoir for pre-heating the nitromethane eluent. A water aspirator was connected at the bottom of the column, and a 1 liter flask attached for collection. The aspirator speeds up the flow of solvent but does not significantly impair the separation.

Four and one-half pounds of silica are added to the column as a slurry in nitromethane. The steam is turned on to preheat the column. A 75 g sample of the crude SEX dissolved in 1800-2000 mL of boiling nitromethane is added to the column. After the removal of the first 2 L of solvent, 750 mL fractions are collected. These are analyzed by TLC, like fractions combined, and solvent removed. Collection continues until SEX no longer appears on the TLC. In general, the first 5 to 7 fractions contain only HMX/SEX, and fractions 8 to 10 contain SEX and DADN.

The recovered product consists of 95-96% SEX with less than 0.5% DADN as determined by analytical HPLC.

The SEX/HMX mixture is then dissolved in a minimum of refluxing acetone (approximately 10 g/L) and allowed to cool slowly. Precipitate forms over a period of several days, removing most of the HMX and yielding 98+% SEX.

Elemental analysis: Calculated for $C_6H_{11}N_7O_7$: C, 24.57, H, 3.75; N, 33.45
Found: C, 24.21; H, 3.76; N, 33.45

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PERSONNEL RECEIVING CONTRACT SUPPORT

The following persons received support under Contract No. DAMD17-82-C-2092:

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