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SYNTHESIS OF HIGH PURITY HEXANITROSTILBENE

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DEVELOPMENT DIVISION

MASTER

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(P.O. NO. 64-3667)

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ABSTRACT

This report covers the development of a continuous process and the apparatus for the synthesis of high purity hexanitrostilbene type I (HNS I). Optimum solution concentrations and ratios were investigated, and product washing and slurrying procedures were developed to yield a high purity product. The synthesized products were evaluated against the Navy's WS-5003F specification. In addition, other tests suggested by Sandia Laboratory and/or developed in-house, were employed to enable better classification of the explosive and to assure its suitability for ultimate use. Information in this document will enable any facility to synthesize HNS I at a purity level of approximately 99.5%, with yields approaching 38%.

DISCUSSION

GENERAL PROCESS DESCRIPTION

This continuous process for the synthesis of 2,2',4,4',6,6'-hexanitrostilbene, type I (HNS I) was first reported in a U. S. Naval Ordnance Report(*1*). This reference details optimum mixtures as well as the chemistry of the reactions (Fig. 1) involved, and gave a starting point for this effort. The process basically consists of metering two separate solutions, Clorox(*2*) and trinitrotoluene (TNT) dissolved in a solvent mixture of tetrahydrofuran (THF) and methyl alcohol (MeOH), into a common junction and cooling coil held at a temperature of 0 to 5 C. The cooling coil is designed to be of sufficient length to allow a minimum reaction time (exothermic) of one minute at this temperature. After flowing through the cooling coil the mixture is permitted to empty into a holding reservoir and react there (non-exothermic) at ambient temperature for a period of 18 to 24 hours. Following this reaction period, the product is filtered, washed, and dried.

SYNTHESIS SYSTEMS

Laboratory Scale System

A small laboratory system (Fig. 2), capable of producing a net yield of approximately 8 g of HNS at a rate of 4 g/min was used to determine the feasibility of such a process and to investigate and confirm optimum solution concentrations and ratios. A total of seventeen runs using this apparatus was accomplished, and a compilation of these runs is given in Table I. Requirements for a homogeneous mixture(*1*) are 10 mℓ of Clorox solution (5% by weight sodium hypochlorite) and 1 g of TNT dissolved in 10 mℓ of THF and 5 mℓ of MeOH.

(*1*) *Heat Resistant Explosives XVI, A New Synthesis of 2,2',4,4',6,6'-Hexanitrostilbene, HNS (C), K. G. Shipp, NOLTR 64-34 (AD351283L).*

(*2*) *Commercial Household Bleach (5.25% sodium hypochlorite) manufactured by the Clorox Company, Oakland, California.*

This mixture proved to be optimum, and gave a ratio of 1.56 parts by volume of THF/MeOH/TNT solution to 1.0 part 5% Clorox. Deviations from this optimum were employed by varying solvent ratios, TNT and Clorox concentrations, and ratios of the two solutions. In all cases, these deviations resulted in lower product yield and in most cases decreased melting points. At this point in the synthesis development, the process was scaled up to a 1 kg system.

One Kilogram System

Fig. 3 is a photograph and Fig. 4 a process flow diagram of the 1 kg synthesis system. The flow rates of the two reactants used in the laboratory apparatus were scaled initially by a factor of two and finally increased to the rate where it is possible to produce 1 kg of material in approximately 88 minutes. Eleven 1 kg batches have been made to date. Batches 1 and 2 were used to establish the proper flows and correct minor flaws in the design. Batches 3 through 6 were used to further improve the design, to maximize flow rates, and to investigate various washing and slurrying techniques. Batches 7 through 10 were made identically to determine the reproducibility of the overall process. Table II outlines the run to run variation of these batches.

During the reproducibility runs, small dark impurities were apparent as the Clorox solution fed through the flowmeter. (These are the result of a reaction between the Clorox and stainless steel.) Analysis of the final product revealed that, in most cases, water soluble and DMF insoluble results were out of specification and liquid chromatography results showed the purity to be below that desired. The last synthesis run (No. 11) was made incorporating the following improvements:

1. On the Clorox side of the system:
    a. Where possible, Tygon tubing was substituted for stainless steel tubing.
    b. Two stainless steel control valves were removed.
    c. The Clorox solution was fed directly from the upper supply vessel directly to the stainless steel regulating valve.
2. Hot distilled water (95 C) was used instead of warm (70 C) tap water for all product water washes.
3. Two DMF slurry steps were used instead of a single slurry for product purification.

Analysis of Batch 11 showed dramatic improvement since the impurity level and the amount of foreign impurities were significantly reduced. Zeiss particle size analysis of Batch 11 indicated a significant change in particle size when compared to the reproducibility batches. This batch indicates larger crystals were produced. However, B.E.T. specific surface area results are quite close to those of the reproducibility batches. This synthesis procedure has been designated as the present, official Pantex process for the synthesis of 1 kg batches of HNS I. A detailed synthesis procedure is included in this report as Appendix 1.

Ten Kilogram System

Apparatus for the synthesis of HNS I in 10 kg size batches has been designed and is in the process of being fabricated and assembled. This system again is a simple scale-up from the laboratory apparatus, and will make it possible to produce 10 kg of material in approximately 4 hours. (Fig. 5 is a process diagram for this system.)

PRODUCT FILTRATION AND PURIFICATION

Initial effort included washings using cold acetone and tap water. The products, when using this procedure, were of low purity and had significantly lower melting points than desired. Starting with the first material made using the 1 kg system, hot tap water (70 C) was substituted for cold water and one dimethylformamide (DMF) slurry step was incorporated in the procedure. A study of purity as a function of wash cycles was made on Batch 5 by sampling the product following each individual wash or slurry cycle. Figs. 6, 7, and 8 are graphic results of this study.

At this point, and before initiating further improvements, four 1 kg batches of material were produced keeping the synthesis, wash and purification procedures as constant as possible. This established the reproducibility of synthesis conditions, and also determined if the material produced was as uniform as desired.

The purity of the product using the revised wash and slurry methods was approximately 98.5%, still below that desired. Analytical results of the wash cycle study previously referenced and water soluble tests indicated that the two most likely means of improving the product purity were:

1. Substitute hot distilled water (95 C) for hot tap water.
2. Incorporate an additional DMF slurry step in the procedure.

Batch 11 was processed using these changes and analytical results showed a product purity of 99.5%. All other analyses were within specification, foreign particle contamination was greatly reduced, and this process for washing and purification was adopted. The detailed final procedure for product wash and purification is also contained in this report (Appendix 1).

ANALYSIS

On laboratory scale synthesis work, differential thermal analysis (DTA) was the only analytical tool used for product evaluation. The major portion of analytical effort began with the synthesis of the 1 kg size batches. Initially, these batches were tested against portions of the Navy WS-5003F Specification. Tests performed and the specified limits are listed below:

Specific Test	Specification Limits
Melting Point	-2 to +5 C of SCS*
	Maximum % by Weight
Surface Moisture & Volatiles	0.05
Water Soluble Material	0.20
DMF Insolubles	0.10

**Standard Comparison Sample (SCS) specified in WS-5003F supplied by the Quality Evaluation Laboratory (QEL) Naval Ammunition Depot, Crane, Indiana.*

Concurrent with these analyses and the synthesis work, three other analytical areas were being investigated. There were: (1) test revisions by Sandia to the existing Navy Specification, (2) new, additional qualification tests proposed by Sandia for HNS material to be used in ERDA applications, and (3) development of a liquid chromatography test for the rapid purity analysis of HNS samples.

Proposed revisions to the Navy WS 5003F Specification are as follows:

Water Soluble Test: The sample size increased to 10 g and the specification limit be reduced to 0.03%.

DMF Insoluble Test: The sample size increased to 10 g and the specification limit dropped to 0.03%.

Tests proposed for adoption in addition to the Navy Specifications include:

1. Pressure/Density: This involves pressing HNS I at varying pressures with the material meeting minimum density requirements at these pressures.

2. High Z X-Ray: This test is made on the finished material to determine the number of foreign particles present with a density exceeding that of the HNS I.

3. Foreign Particles: An analytical method which allows the physical examination of foreign particles introduced in the synthesis process.

4. Solution Conductivity: A conductivity test to measure the amount of ionic impurities present in the material.

5. Zeiss Particle Size: A microscopic method used in which a representative sample is photomicrographed and approximately 1000 particles are physically measured.

Full development of the liquid chromatography test (included as Appendix 3 in this report) gave a fast, accurate means of not only assessing purity but, also quantifying the amount of major impurities present.

The analytical data detailed in this report reflect the concurrent synthesis and analysis effort. Complete data exist only for the last HNS batch synthesized (No. 11) because until that time, full capability for performing all analyses was not attained. The obvious superiority of this batch made the full analysis of previous batches unnecessary.

Fig. 9 is a chronological display of DTA thermogram melting point data starting with the first laboratory batch made and ending with the last 1 kg batch synthesized. Melting points were determined using the tangential method of assessment. (Placed on this figure also are similar results for the Navy standard HNS I and II materials.)

Table III lists liquid chromatography results on ten of the 1 kg batches. The analytical column used separates the three component mixture. However, the results are not considered absolute. The possibility exists that small amounts of other impurities may be present and not separated during the analysis process. Batch 11 is clearly superior and reflects the improvements made in synthesis and washing procedures.

Table IV is a compilation of Navy Specification tests on all of the 1 kg size batches. Again, Batch PX-11 is superior.

Batches 7, 8, 9, and 10 (the reproducibility runs) were analyzed by the Zeiss method to determine the particle reproducibility of the synthesis process. Table V outlines three particle characteristics extracted from the Zeiss particle analysis reports. (The complete Zeiss reports for these and batch PX-11 are included as Appendix 2 in this report.) Results of the four reproducibility batches show the process to have excellent reproducibility. Zeiss analysis results on Batch 11 differ from the previous four batches due to significant changes in wash and slurry methods; however, the improved process should be equally reproducible.

A Beckman Model RX-16B2 Conductivity Meter and a General Radio Decade Capacitor Type 1412 BC were used in conjunction with an LSU type conductance cell to determine the conductivity of HNS samples. Cell constants were determined using three varying concentrations of potassium chloride and readings taken of samples and solutions listed in Table VI. This test is an excellent means of measuring ionic impurities.

Foreign particle contamination of HNS I samples was determined using a procedure outlined by Sandia Laboratory. HNS samples are dissolved in 110 C DMF and passed through Nos. 40, 60 and 100 U.S. Standard sieves. The sieves are then washed, dried and the number of foreign particles are counted on each sieve. Fig. 10 displays photographs of foreign material found in two lots of HNS I. (PX-11 and Chemtronics 66-48).

Table VII contains complete analytical data on the last 1 kg batch synthesized at Pantex (PX-11), Chemtronics Lot 66-48 and partial results on the Navy's HNS I standard material.

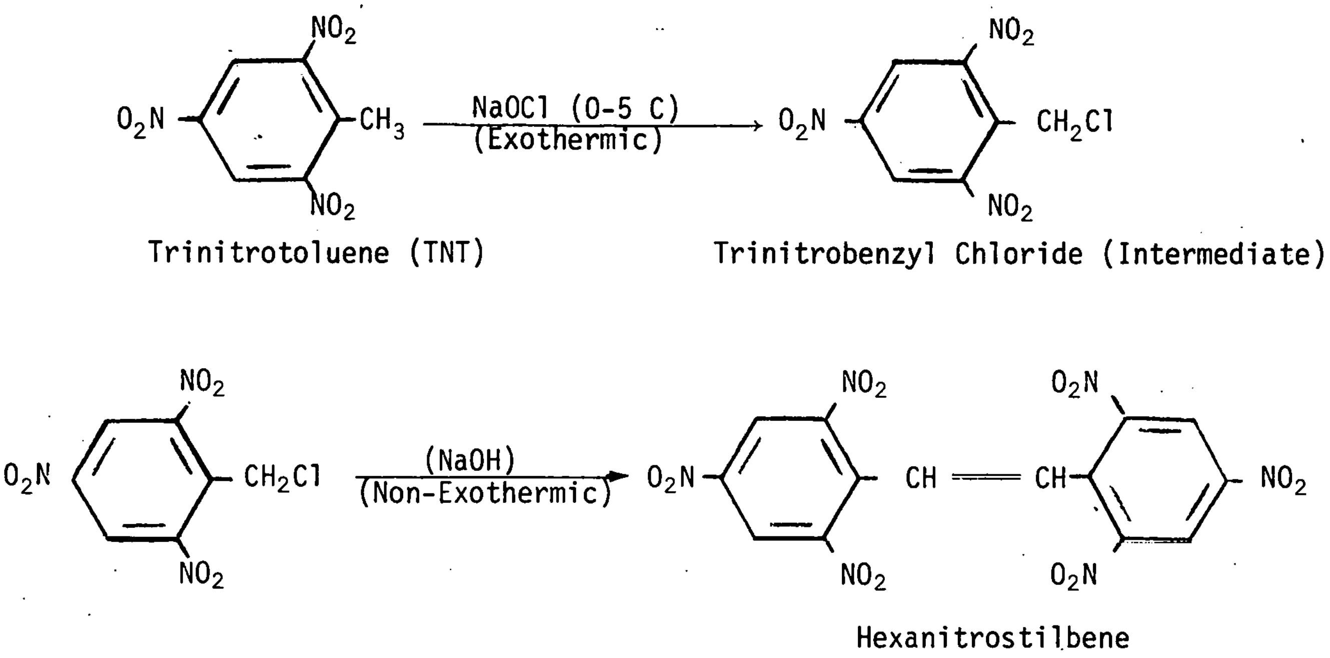
Pantex Batch 11 has been tested in the density range of 1.45 to 1.65 Mg/m^3 for the initiability of compacted HNS II aluminum sheathed MDF of 0.38 g/m core loading. The failure to initiate rate is zero with excess transit times ranging from zero at the lowest density level to 20 nanoseconds at the highest density.

CONCLUSIONS

The synthesis and purification processes outlined and detailed in this report describe procedures to produce hexanitrostilbene, type I (HNS I) with a purity of approximately 99.5% at yields approaching 38%. The process described is simple, has good reproducibility and produces a material that performs adequately and is superior to other HNS I tested to date.

For applications in which this material is used as HNS I, the proposed additional tests of pressure/density, foreign particle, high Z X-ray, and conductivity should be included in tests for material certification. This additional testing, coupled with the revised Navy Specification tests, should insure proper functioning of HNS I components in devices where its application has been tested and approved.

FIGURES



Reference: K. G. Shipp, Heat Resistant Explosives, NOLTR 64-34 (April 22, 1964).

K. G. Shipp, L. A. Kaplan, J. Org. Chem. <u>*31*</u>*, 857 (1966).*

Fig. 1. Synthesis Reactions for Hexanitrostilbene

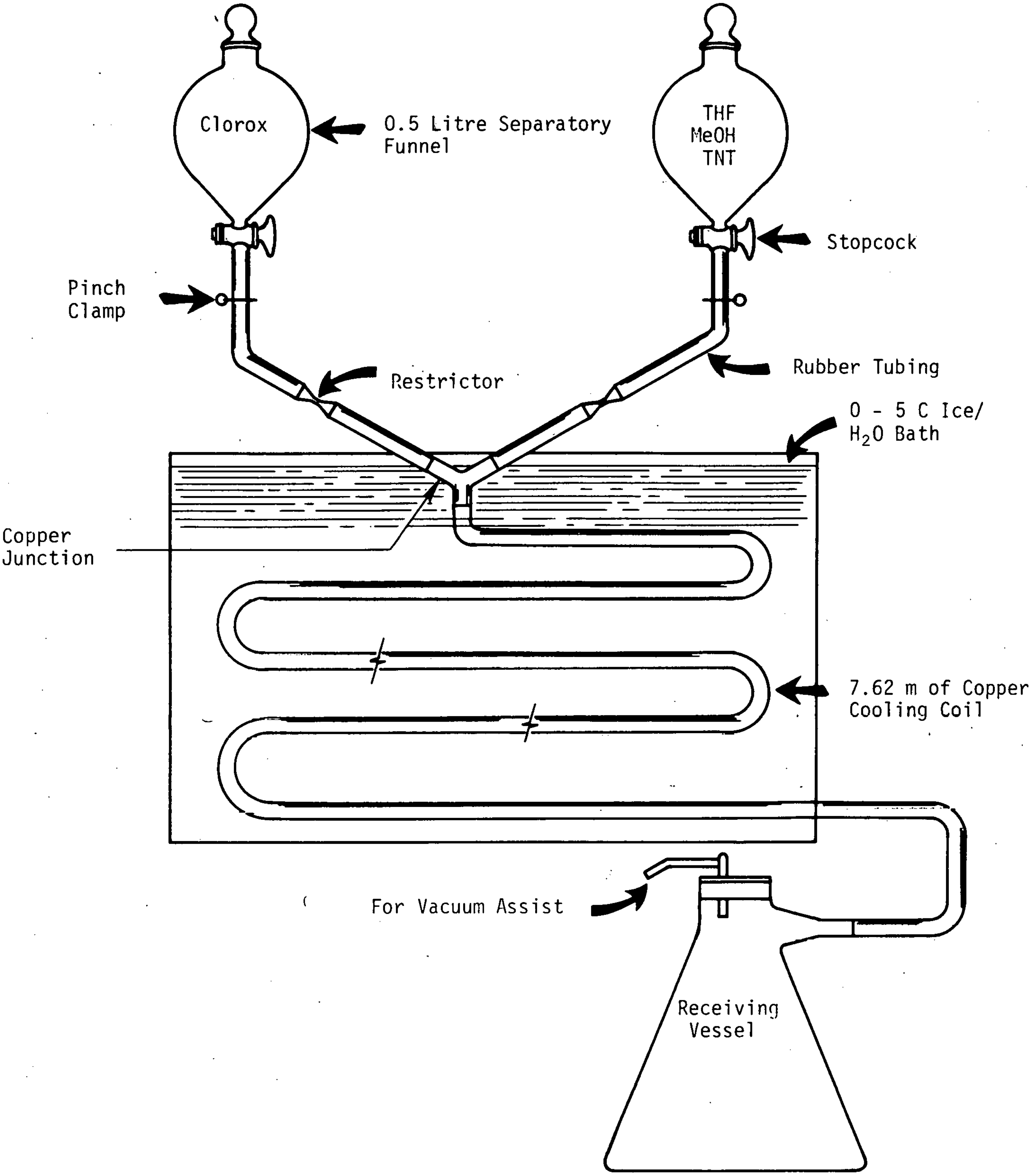


Fig. 2. Continuous HNS Synthesis Apparatus (Laboratory System - Gravity Flow)

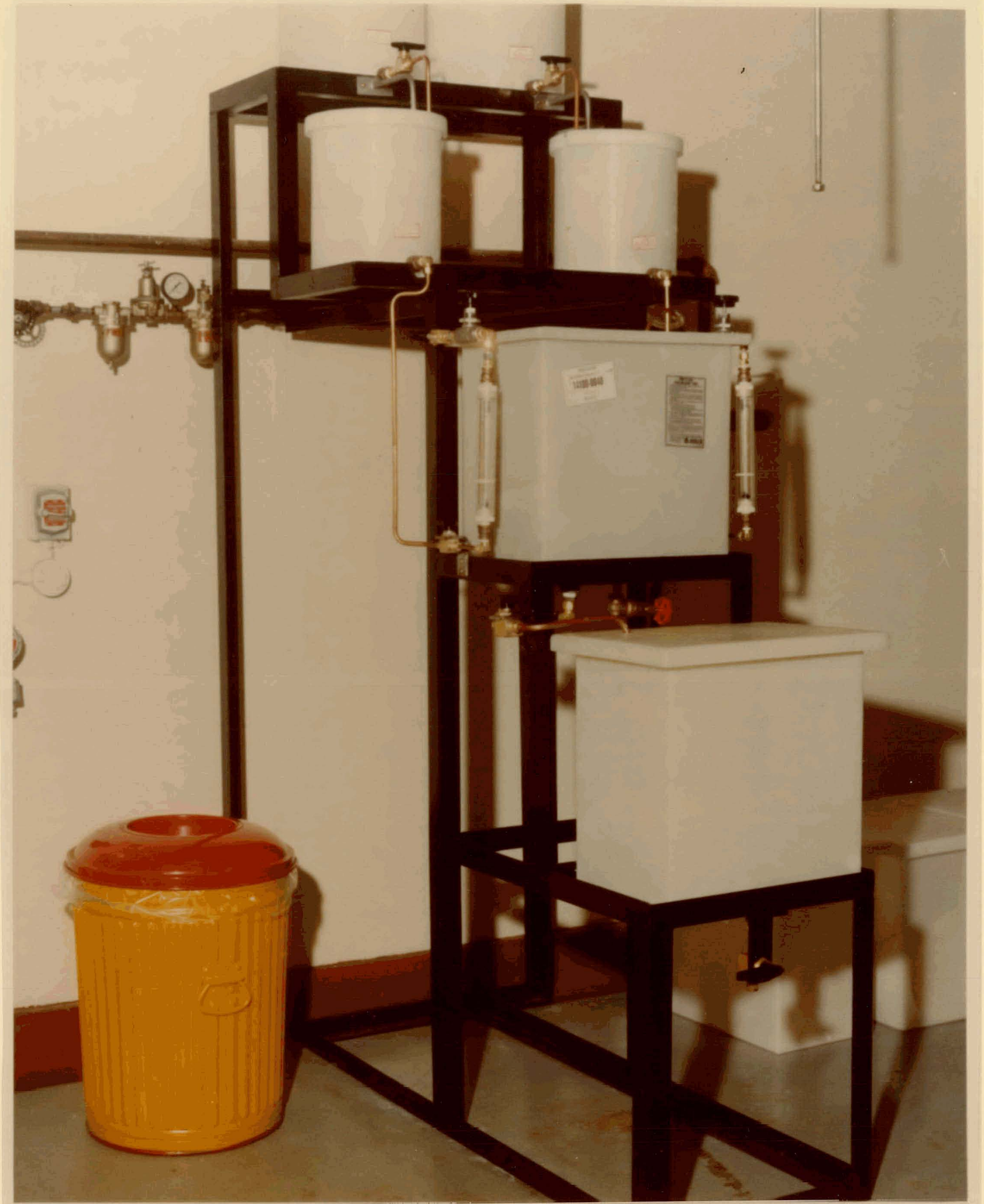
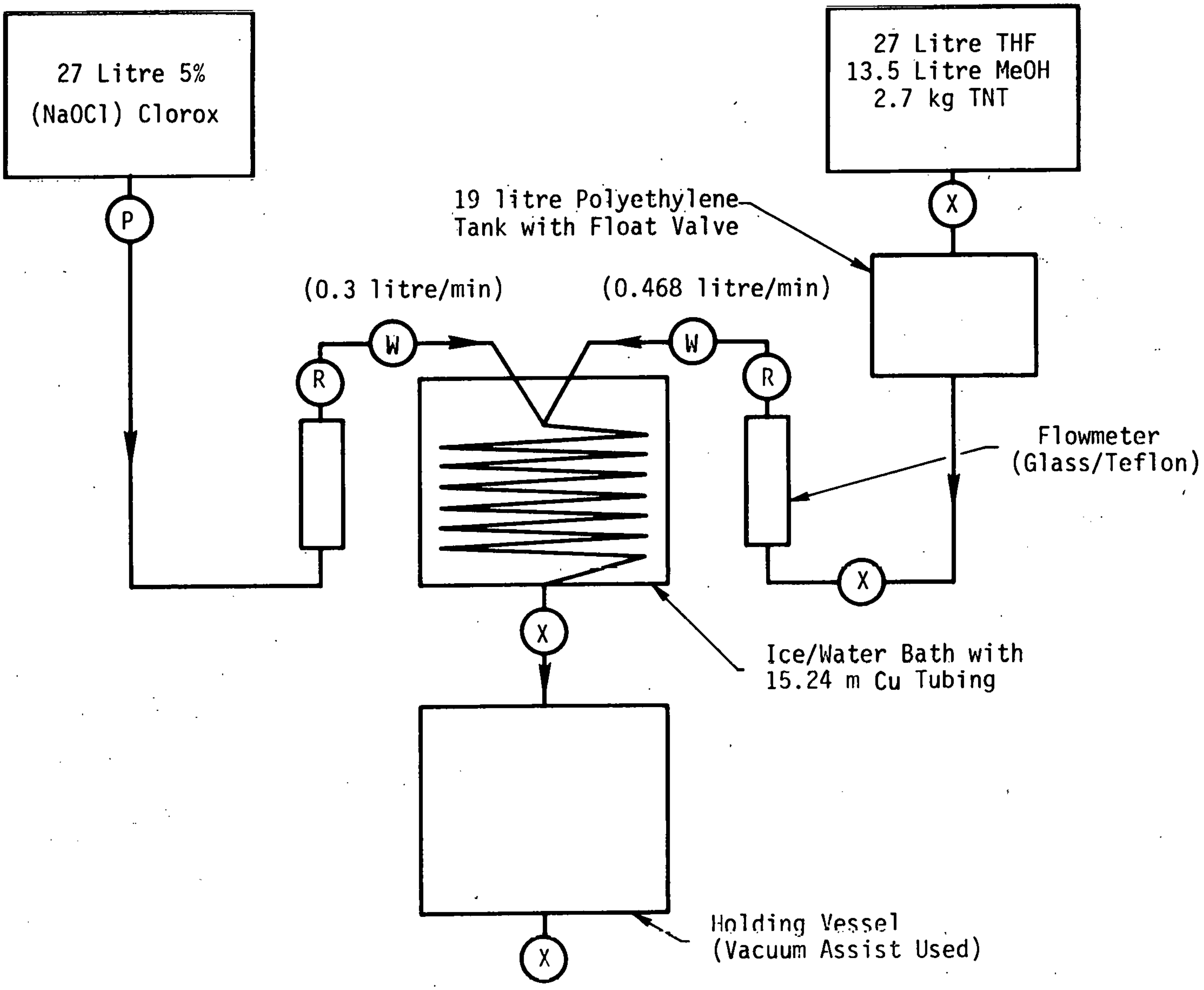
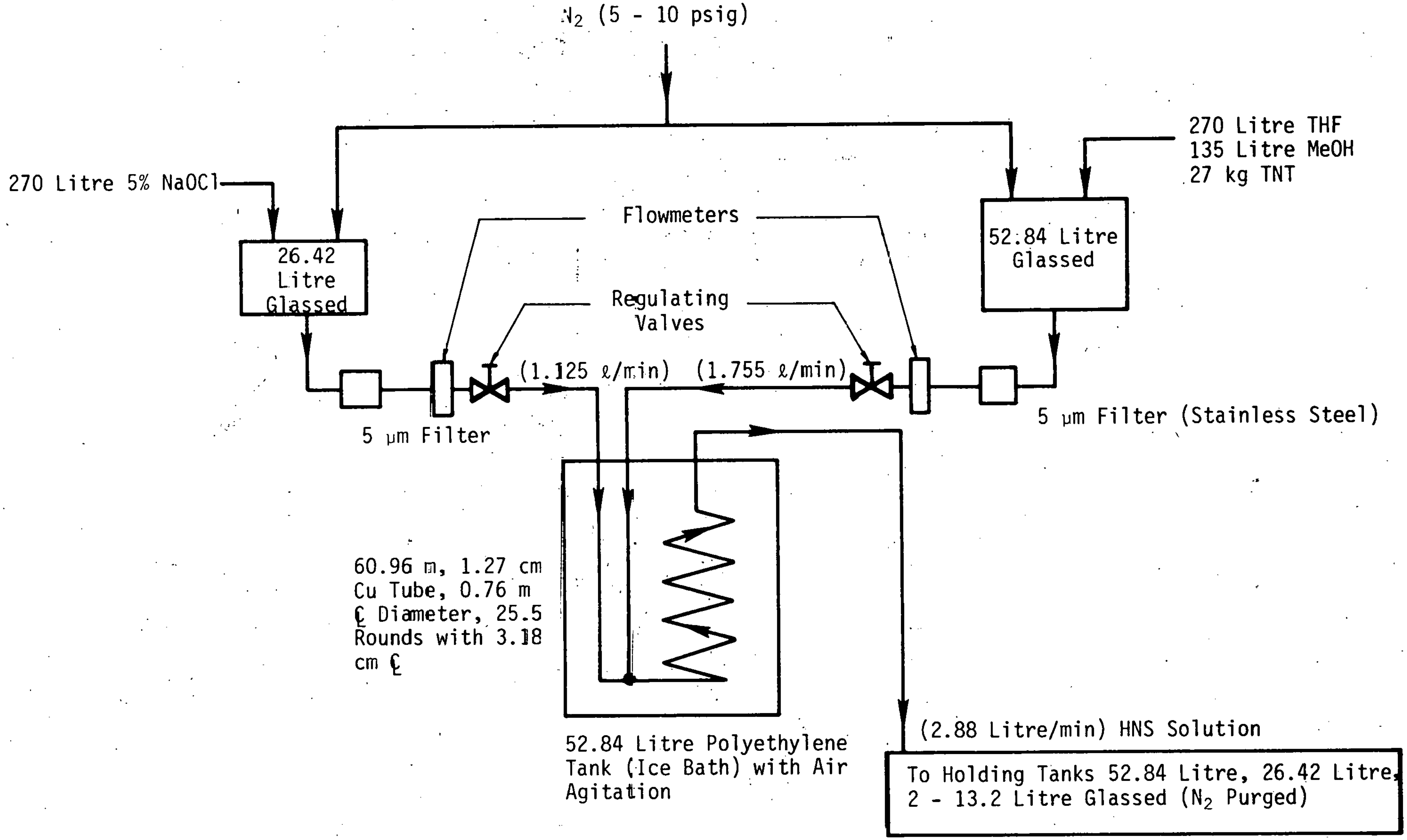


Fig. 3. HNS I Synthesis System (1 kg batches)



NOTES:
1. Plastic Valve (P)
2. On-Off Stainless Valves (X)
3. Regulating Stainless Valves (R)
4. Three way Stainless Valves (W)
5. All Tubing Cu Except on Clorox Side (Tygon and Stainless)

Fig. 4. HNS I Synthesis System (1 kg)



1. All valves stainless steel; seals, packing, etc., stainless or Teflon.
2. All tubing other than junction, reaction coil and clorox feed lines: 1.21 cm stainless.
3. All seals in contact with THF: Teflon or metallic.

Fig. 5. HNS I Synthesis System (10 kg)

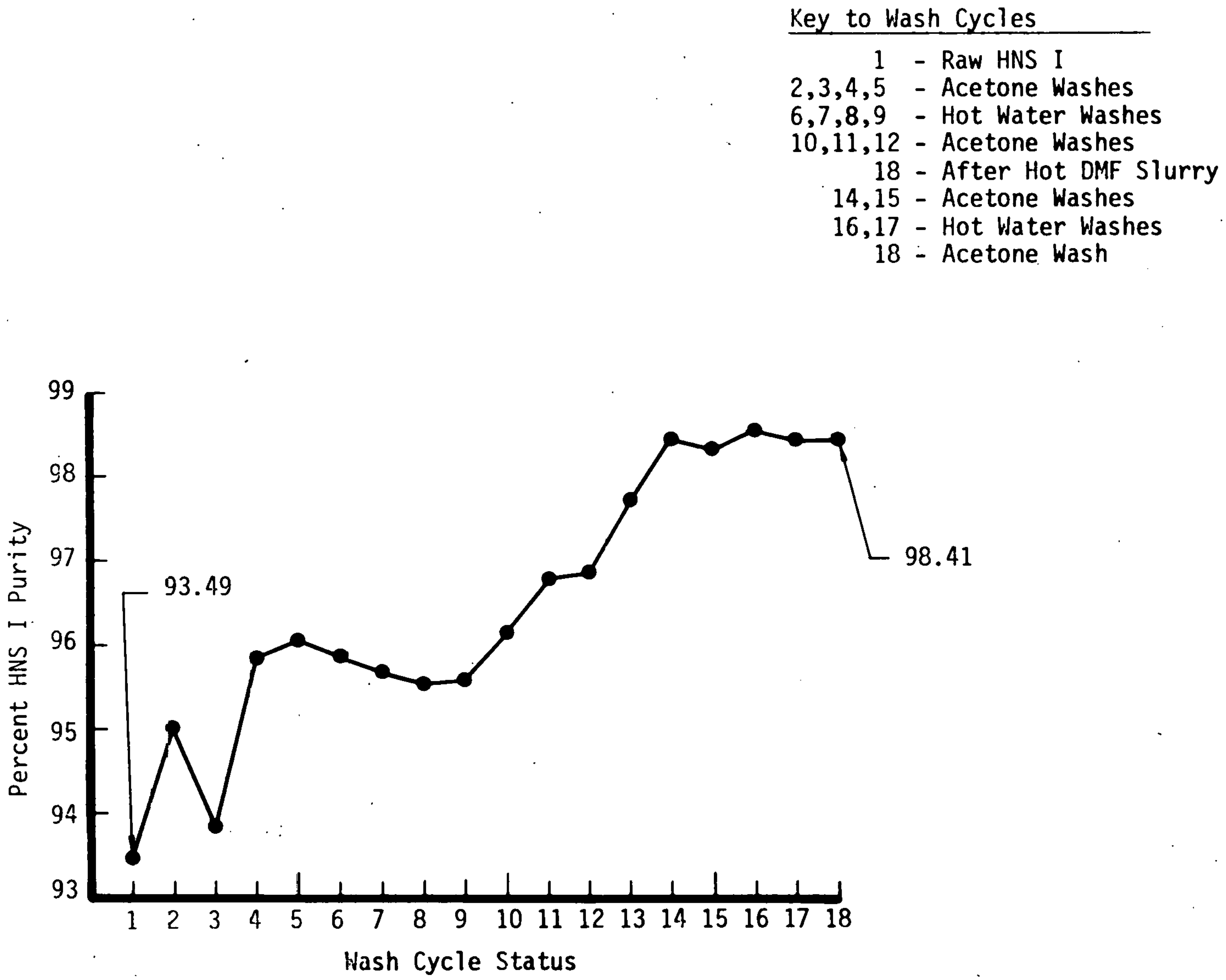


Fig. 6. Purity of HNS I as a Function of Wash Cycles (Batch No. PX-05)

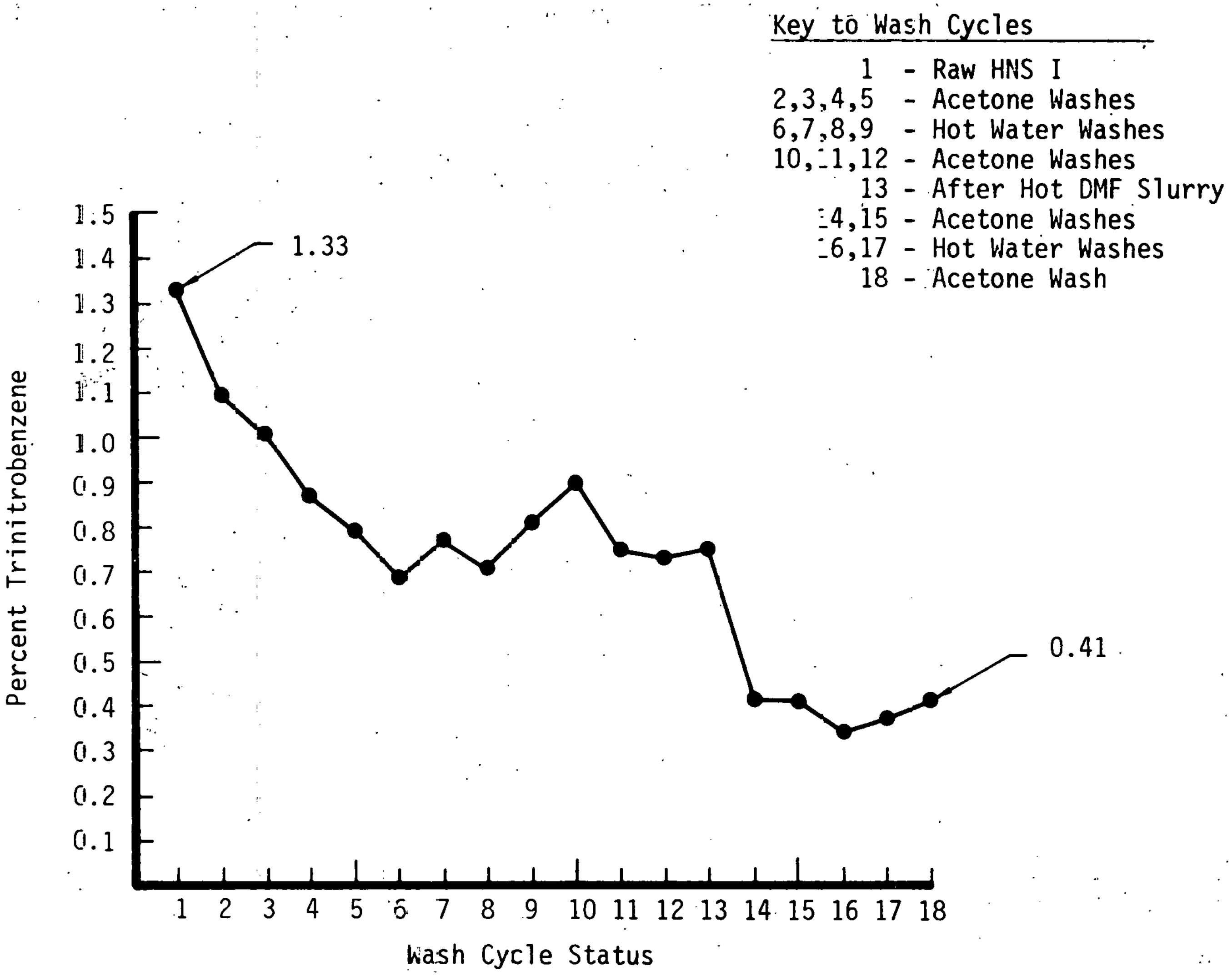


Fig. 7. Reduction of Trinitrobenzene During Wash Cycles of HNS I (Batch No. PX-05)

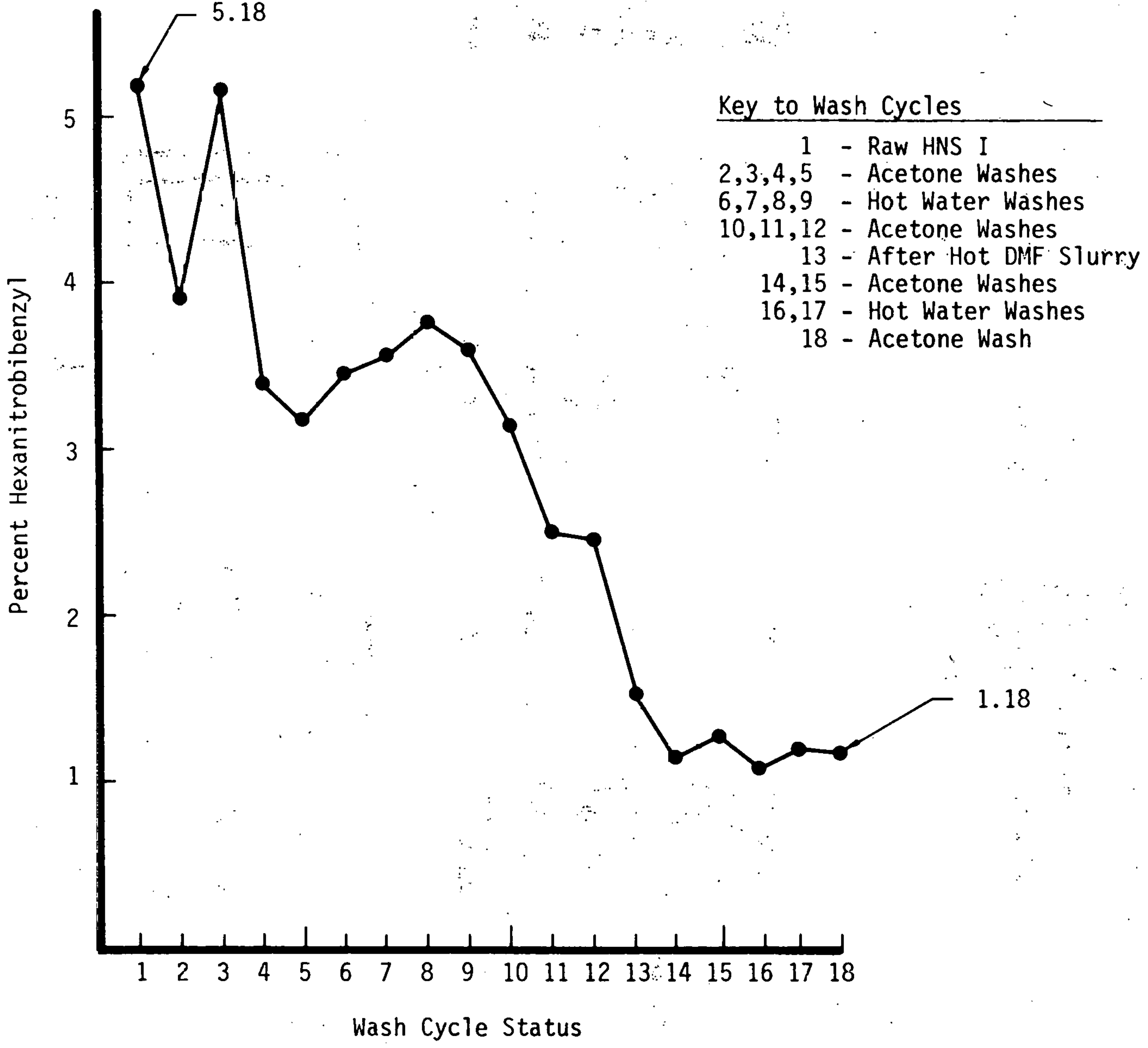
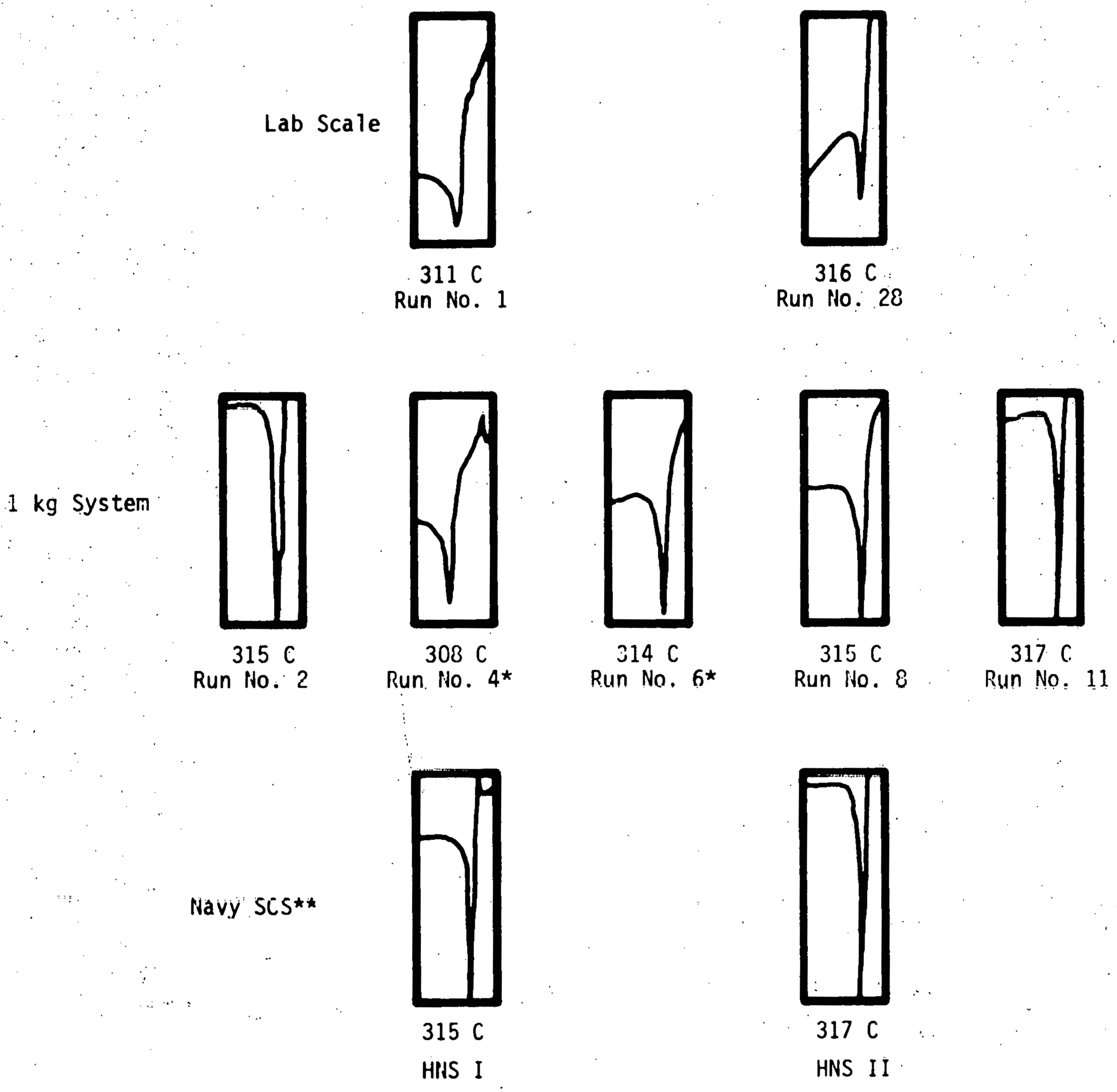


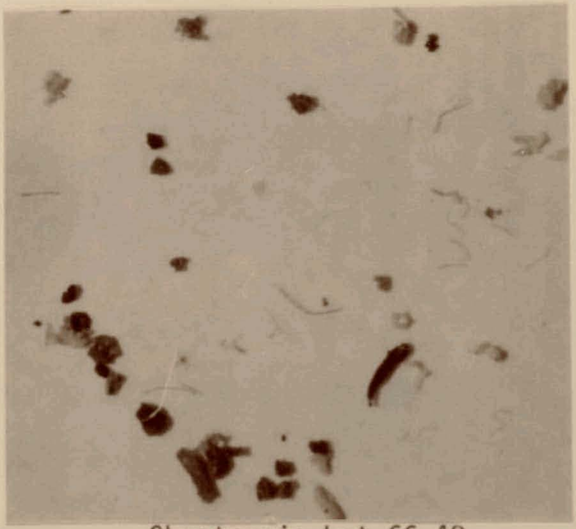
Fig. 8. Reduction of Hexanitrobibenzyl During Wash Cycles of HNS I (Batch No. PX-05)



**Batches where the filter press was used for initial filtering and washing.*

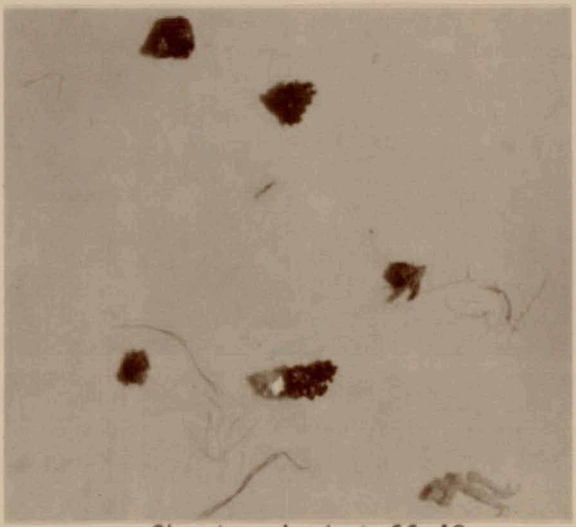
***Navy Standard Certification Samples*

Fig. 9. DTA Thermograms of Synthesized HNS (Melting Points)

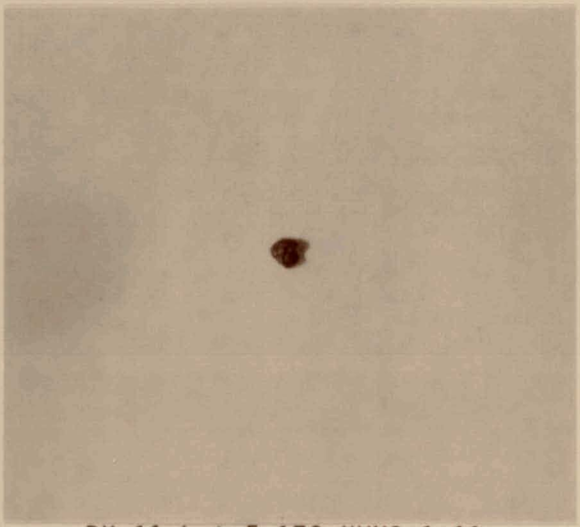


Chemtronic Lot 66-48
100 μm Sieve

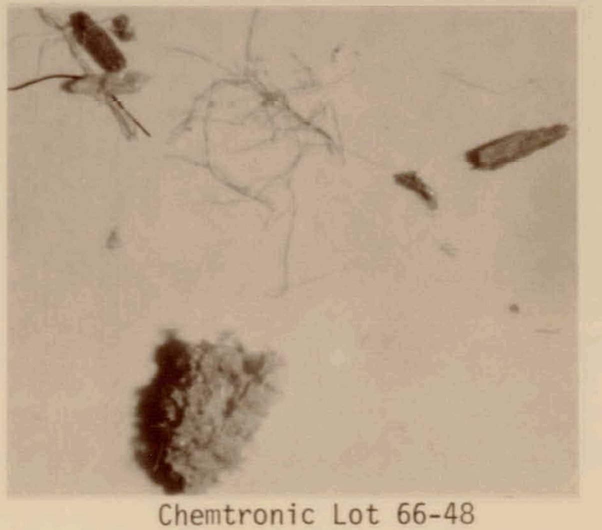
PX-11 Lot 5-173-XHNS-1-11
100 μm Sieve



Chemtronic Lot 66-48
60 μm Sieve



PX-11 Lot 5-173-XHNS-1-11
60 μm Sieve



Chemtronic Lot 66-48
40 μm Sieve

PX-11 Lot 5-173-XHNS-1-11
40 μm Sieve (No Particles Found)

Fig. 10. Foreign Material in HNS I Samples
(All Mag. ∿ 12X)

Table I. Compilation of HNS I Runs

Run No.	Solution 1			Solution 2			Solution Ratio Sol. 2/Sol. 1	Product Data	
	Clorox (mℓ)	Wt. % NaOCl	H_2O (mℓ)	THF (mℓ)	MeOH (mℓ)	TNT (g)		Yield (%)	M.P. (C)
1	200	4.78	20	200	100	20	1.69	41	314
2	200	4.78	20	200	100	25	1.53	31.6	307
3	200	4.78	20	250	50	20	1.60	5.5	305
4	200	4.78	20	300	-0-	20	2.46	SCRAPPED	
5	200	4.78	20	200	100	20	1.58	40	313
6	200	4.78	20	200	100	20	1.55	-	313
7	200	4.78	20	200	100	20	1.56	Avg. 39.7	312
8	200	4.78	20	200	100	20	1.49	-	312
9	200	4.58	30	200	100	20	1.49	31.5	310
10	200	4.99	10	200	100	20	1.56	42.5	314
11	200	5.10	5	200	100	20	1.55	41.5	314
12	200	5.05	7.5	200	100	20	1.59	41.5	312
13	200	4.99	10	200	100	20	1.56	43.5	313
14	200	4.88	15	200	100	20	1.57	40.5	312
15	200	5.01	9	200	100	20	1.53	36	315
16	200	4.99	10	200	100	20	1.57	40.5	316
17	200	4.97	11	200	100	20	1.55	40.5	315

NOTE: Underscored data indicate changes from previous run

Table II. Reproducibility Run Details

Batch No.	Run Time (min)	Clorox Flow (mℓ/min)	Flow of THF MeOH & TNT (mℓ/min)	Flow Ratio	Final Yield (g)	Yield (%)
PX-07	87.4	293.7	478.4	1.629	1045	38.95
PX-08	87.5	295.6	478.4	1.618	1029	38.40
PX-09	86.5	298.1	484.6	1.626	1072	39.90
PX-10	87.8	296.4	478.0	1.613	1030	38.28
Average	87.3	296.0	479.8	1.622*	1044	38.88
Range	1.3	4.4	6.6	0.016	**	**

**Not optimum flow ratio of 1.56 because at this time the main concern was in run detail and particle size reproducibility. (The deviation from optimum (0.06) results in slightly reduced yield.)*

***The variation in yield figures are not indicative of reproducibility. Loss of material during the filtering process varies to the extent that these figures are listed for comparison purposes only.*

Table III. HNS I Synthesis-Liquid Chromatography Results

Batch No.	% HNS	% Hexanitrobibenzyl	% Trinitrobenzene
PX-02	98.12	1.71	< 0.3
PX-03*	92.39	7.61	< 0.3
PX-04*	92.19	7.81	< 0.3
PX-05	97.58	2.00	0.42
PX-06*	97.86	1.70	0.44
PX-07***	98.35	1.33	0.32
PX-08***	98.04	1.59	0.37
PX-09***	97.71	1.88	0.41
PX-10***	97.63	2.00	0.37
PX-11**	99.54	0.43	< 0.1
Navy HNS I Std.	95.61	4.24	0.15
Navy HNS II Std.	98.55	1.45	< 0.1

**Batches in which the filter press was used for initial filtering and washing.*

***Last batch made using improved slurrying and washing techniques.*

****Reproducibility batches.*

Table IV. Navy Specification Test Results on Ten Batches of HNS I

Batch No.	Surface Moisture & Volatiles (Wt. %)	Water Solubles (Wt. %)	DMF Insolubles (Wt. %)	Melting Point (C)
PX-02	0.03	0.05	0.02	316
PX-03	0.017	0.00	0.12	312
PX-04	0.0	0.16	0.09	308
PX-05	0.002	0.15	0.07	316
PX-06	0.001	0.07	0.17	314
PX-07	0.05	0.03	0.15	315
PX-08	0.03	0.05	0.11	315
PX-09	0.01	0.06	0.21	315
PX-10	0.02	0.06	0.17	315
PX-11*	0.001	0.028	0.004	317

**Last 1 kg batch made using improved synthesis and washing procedures.*

Table V. Zeiss Analysis for Four Reproducibility Runs of HNS I

(Particle Size Data)

Batch No.	Average Length (μm)	Average Width (μm)	Equivalent Spherical Diameter (μm)
PX-07	22.02	11.59	10.31
PX-08	22.28	11.25	10.14
PX-09	22.66	11.46	10.32
PX-10	22.00	11.02	9.95
Average	22.24	11.33	10.18
Range	0.66	0.57	0.37
Std. Dev.	0.31	0.25	0.17

Table VI. Conductivity Tests of HNS I and Other Solutions

Sample Solution	Conductance (mhos)
1 ppm NaCl*	5.21×10^{-6}
Fisher Distilled Water	1.55×10^{-6}
Navy Standard HNS I	4.24×10^{-6}
Chemtronics Lot 66-48 (HNS I)	6.27×10^{-6}
PX-11 (HNS I)	2.11×10^{-6}
Last Water Wash on PX-11	3.27×10^{-6}

Proposed to be the maximum permissible conductance of a 0.5 g sample of HNS I when mixed with 50 mℓ of distilled water.

Table VII. Comparison Analysis of HNS I Samples

Specific Test	PX-11	Chemtronics 66-48	Navy (SCS)
Bulk Density (Mg/m^3)	0.24	0.27	0.31
Melting Point Range (C)	317-319	315-317	312-315
Surface Moisture & Volatiles (wt. %)	0.001	0.002	-
Water Solubles (wt. %)	0.028	0.054	-
DMF Insolubles (wt. %)	0.004	0.031	-
Liquid Chromatography			
% HNS	99.54	97.37	95.61
% Hexanitrobibenzyl	0.43	2.63	4.24
% Trinitrobenzene	< 0.1	< 0.1	0.15
Conductivity (mhos x 10^{-6})	2.11	6.27	4.24
Foreign Particles Retained On			
U.S.S. 40 Sieve	0	9	-
U.S.S. 60 Sieve	1	9	-
U.S.S. 90 Sieve	11	50	-
X-Ray Analysis of High Z Particles			
> 0.003-inch < 0.010-inch	0	50	-
> 0.010-inch	4	10	-

- Not analyzed due to insufficient sample.

**Tentative specification limits are that a 0.5 g sample of HNS with 50 mℓ distilled water shall not exceed that of 1 ppm sodium chloride solution. (Ran with the above tests this 1 ppm NaCl had a conductivity reading of 5.21 x 10^{-6} mhos.)*

APPENDIX 1

APPENDIX 1

DETAILED PROCEDURES FOR PRODUCING HEXANITROSTILBENE (HNS I)

(1 kg Batch Size)

I. APPARATUS, CHEMICALS AND SAFETY EQUIPMENT

A. Apparatus

1. Tank, linear polyethylene with cover, 57 litre capacity
2. Tank, linear polyethylene with cover and spigot, 38 litre capacity
3. Tank, same as above except 19 litre capacity
4. Coil, cooling, copper, 9.525 mm OD, 15.24 m long
5. Flowmeter, glass/Teflon, shielded, Cole-Palmer size 5
6. Float valve, polypropylene
7. Valve, stainless steel (SS), regulating, Whitey No. SS6HTRS6
8. Valve, Ball, 12.7 mm, Whitey No. SS45S6
9. Valve, Ball, 9.525 mm, Whitey No. SS44S6
10. Valve, Ball, 9.525 mm, three-way, Whitey No. SS44XS6
11. SS tubing, 9.525 mm OD
12. Tygon tubing, 9.525 mm OD
13. Bottles, polypropylene, 19 litre capacity
14. Filter Cloth, Nylon, 15 μm opening
15. Buchner Funnel, fixed perforated plate
16. Steam or electrically approved hot-plate
17. Scale, 25 kg capacity
18. Scale, 2 kg capacity
19. Oven, vacuum
20. Building air and vacuum
21. Spatulas, carbon filled

B. Chemicals

1. Acetone, Fisher certified
2. Dimethylformamide, Fisher certified
3. Methanol, Fisher certified
4. Tetrahydrofuran, Histological grade
5. Clorox, (Commercial household bleach, minimum of 5.25 weight percent sodium hypochlorite)
6. Distilled water

C. Safety Equipment

1. Exhaust ventilation for synthesis and washing areas
2. Full face respirators and shields
3. Rubber gloves, aprons
4. Miscellaneous (Normal safety equipment and facilities for handling explosives and flammable solvents)

II. PRE-RUN OPERATIONS

A. Thoroughly clean all solution tanks and sample lines as follows:

1. Rinse Clorox side of the system with distilled water and drain.

2. Rinse all tanks and sample lines on the THF/MeOH/TNT side with acetone and flush with compressed air until dry. (Insure that the Rotocone is operating and turned on before using acetone.)

B. Prepare feed solutions as follows:

1. THF/MeOH/TNT solution

a. Into three each polypropylene 19-litre containers place the following:

9 litres of THF (17 pounds 9 ounces)
4.5 litres of MeOH (7 pounds 13 ounces)
0.9 kg of TNT

Note: Solvents are weighed directly into the polypropylene containers placed on a platform scale located in Bay 214. The TNT is weighed on a 2 kg single pan balance.

When weighing out the solvents, wear the solvent respirator.

2. Clorox solution

a. Determine weight percent sodium hypochlorite of the clorox solution. Calculate the volume of distilled water necessary to reduce the hypochlorite solution to 5.00%.

b. Measure out the prescribed quantity of distilled water and transfer it to a clean 3.8-litre container. (The amount of distilled water varies according to the Clorox strength, and the exact amount necessary will be specified by the supervisor involved.)

C. Solvent loading of system

1. Insure all the TNT is dissolved in the three containers before proceeding.

2. During this phase of the operation rubber gloves and full face respirators are to be worn, and operations are not to start until it is insured the Rotocone unit is exhausting properly.

3. Check and close, if necessary, all system valves.

4. Place the portable loading platform on the right side of the synthesis stand. Remove the cover from the supply tank.

5. Place the nylon filtering cloth so all solvent going into the vessel is filtered.

6. Transfer, by pouring slowly, the contents of two of the 19-litre containers of the THF/MeOH/TNT into the supply tank.

7. Open main supply valve and let it drain into the flow control tank until the float closes, thus stopping the flow. (Insure flow stops at this point before proceeding.)

8. Transfer the last of the three THF/MeOH/TNT solutions into the main supply tank and replace the tank cover.

9. Place the loading platform on the left side of the synthesis stand, remove the cover on the Clorox tank, install the nylon filter and carefully pour the Clorox and water into the vessel.

10. Open the main Clorox vessel supply valve and allow the Clorox solution to flow to the stainless steel regulating valve.

D. Adjustment of flow rates

1. The procedure for flow adjustment is identical for both solutions, therefore, detailed instructions given here for the Clorox side are followed for the other solution.

2. Place the three way valve to the bypass position, place a vessel for containing the solution effluent and open the regulating valve. (This allows the solution to feed into the flow meter through the regulating valve and exit the system.) Regulate the Clorox flow until the flow meter ball position is located at the 18.5 division position (0.305 litre/minute).

   NOTE: The bottom of the ball rests on this position.

3. Turn the three way valve to the OFF position.

4. For the THF side, open the regulating valve, place the three way valve to the bypass position and regulate the flow until the bottom of the ball in the float valve rests at the 20 division position (0.470 litre/minute).

5. Turn the three way valve to the OFF position.

6. Place the metered solutions back into their respective containers.

7. Fill the tank containing the cooling coil with an ice/water mixture. (Approximately 20 kg of ice is placed in the tank and then water added until the level reaches the top of the cooling vessel.) As the synthesis run progresses the addition of more ice is necessary to maintain the desired temperature (0 - 2 C).

8. Place a metal thermometer in the ice/water solution.

9. Adjust the air agitation system for the cooling tank until adequate mixing is evident.

AT THIS POINT YOU ARE READY FOR THE ACTUAL SYNTHESIS OPERATION

III. SYNTHESIS OPERATION

A. Initial checks and operations

1. Insure the column exit valve is in the open position.

2. Adjust the vacuum valve of the receiving vessel until 12.7 mm of vacuum is constant.

3. Record the temperature of the ice/H_2O bath.

B. Start-Up

1. Record the time to the nearest minute and simultaneously turn the 2/3 way valves to the coil position.

2. Adjust regulating valves until the positions specified are attained.

3. Record the time the first appearance of effluent from the coil occurs.

C. Checks during the synthesis run

1. Keep a constant check on the flow meters to insure they remain at their intended positions.

2. Insure the float valve on the THF side of the system does not stick in the open position.

3. Periodically, check the ice/H_2O bath and add ice as necessary.

D. Changing receiving vessels

1. Close column exit valve.

2. Release vacuum and remove the vessel.

3. Position the next vessel and apply vacuum to 12.7 mm.

4. Open column exit valve.

5. Recheck flow meter ball positions and adjust if necessary.

E. Stopping synthesis run

1. Close the three way valves when the first bubble appears in either flow meter. Record time to the nearest minute.

2. Allow vacuum to operate until flow from the reaction coil ceases.

3. The resulting reaction mixture is allowed to react at ambient temperature for a minimum period of 18 hours before filtering and washing operations are initiated.

IV. SYSTEM CLEANUP

A. Remove the last receiving vessel from the system and place a vessel so any dripping that occurs will be caught.

B. Isolate the reaction coil from the system by breaking the fittings on the coil side of regulating valves.

C. Using vacuum and a solvent trap, clean the reaction coil by pulling acetone up through the coil from both solution sides of the system. Flush until the acetone becomes free of contamination (colorless).

D. Thoroughly rinse all tanks and lines on the THF side with acetone.

E. Thoroughly rinse all tanks and lines on the Clorox side with distilled water.

F. Clean the respective nylon filters and replace all tank covers.

G. When all the system has been cleaned, reconnect the coil to the regulating valves.

V. PRODUCT FILTERING, WASHING, AND PURIFICATION PROCEDURES

The amount of product plus solvent involved in initial filtering operation is approximately 64 litres. This volume is distributed in four 19 litre receiving vessels and is filtered using vacuum and four 270 mm diameter Buchner funnels. Initial washing using acetone and hot water is done in these same funnels without removing the HNS from the funnels. After this is accomplished, the HNS is removed, dried, weighed, slurried with warm DMF, transferred to one large Buchner funnel and rewashed with more acetone and hot water.

Transfer the four 19 litre containers to filtration area. Insure the Rotocone is operating. (Respirators must be worn during initial filtering.)

A. Connect the four Buchner funnels to four 4 litre vacuum flasks.

B. Install the nylon filtering cloth in the funnels and begin filtering operations.

C. Product plus solvent is carefully poured into each of the funnels and this process is continued until all the HNS I has been trapped on the filter and the waste solvent has been pulled into the vacuum flasks.

D. After all the initial solvent is removed, four washings of acetone, three of boiling hot water, and the three more acetone washings are applied to the product.

E. Washing procedures

Four acetone washes are accomplished as follows:

1. After breaking the vacuum, add 1 litre of acetone to each of the Buchner funnels.

2. Using a carbon-filled plastic spatula, slurry the HNS and acetone until the HNS is fully suspended.

3. Apply vacuum and remove the acetone.

4. Add 1.5 litre of 95 C distilled water, slurry and apply vacuum.

5. Accomplish step 4 two additional times.

6. Repeat steps 1 through 3 three more times.

7. Transfer the crude HNS to metal drying trays, cover with aluminum foil and dry at 100 C in the steam vacuum oven in Bay 215. (Approximately three hours with an air bleed allowed to enter the system.)

F. DMF slurrying procedure

1. Remove the HNS from the vacuum oven and allow it to cool. Cool until ambient temperature is attained.

2. Weigh to determine the yield of crude HNS.

3. For slurrying, the ratio of DMF to HNS used is 2.09 litre per kg of HNS.

4. Heat the DMF in a stainless steel vessel to 70 C on a steam hot plate or on an approved electric unit. (This should be done in a well ventilated area or in a hood where fumes may be controlled.)

5. Transfer the 1 kg of HNS (approximate) to a 2-gallon stainless steel vessel, and add the hot DMF and slurry until uniform.

6. Allow to cool to 30 C or less and filter using the large Buchner funnel and nylon filter cloth.

7. Repeat steps 4 through 6 with a second portion of DMF.

8. The material now in the large Buchner funnel is then washed as in steps A through G in the washing procedure section of this SOP with the following exceptions.

   a. 3 litre of acetone is used for each acetone wash.

   b. 3 litre of hot distilled water is used for each water wash.

c. Sequence of washing cycles is as follows:

Three acetone washes
Four water washes
Three acetone washes

9. The material is then removed from the Buchner funnel, placed on metal trays and dried at 100 C in the vacuum oven in Bay 215 overnight.

APPENDIX 2

APPENDIX 2

PANTEX SYNTHESIZED HNS

Density 1.7400 Mg/m^3

PX-07 Hot DMF Slurried

Zeiss Arithmetic Means

	Frequency	Weight
Length (μm)	22	58
Width (μm)	11	36
Length/Width Ratio	2.00	1.87
Cross-Sectional Area (μm^2)	315	2775
Volume (μm^3)	1400	35000
Equivalent Spherical Diameter (μm)	10	31
Surface Area (μm^2)	830	7500
Degree of Sphericity	0.51	0.52
Equivalent Circular Diameter (μm)	17	52
Powder Uniformity	4.91	3.02

Surface Areas (cm^2/g)

B.E.T. 29,900

PANTEX SYNTHESIZED HNS

Density 1.7400 Mg/m^3

PX-08 Hot DMF Slurried

Zeiss Arithmetic Means

	Frequency	Weight
Length (μm)	22	57
Width (μm)	11	35
Length/Width Ratio	1.97	1.87
Cross-Sectional Area (μm^2)	335	2500
Volume (μm^3)	1500	28000
Equivalent Spherical Diameter (μm)	10	29
Surface Area (μm^2)	875	6700
Degree of Sphericity	0.51	0.52
Equivalent Circular Diameter (μm)	18	50
Powder Uniformity	4.81	3.23

Surface Areas (cm^2/g)

B.E.T. 26,200

PANTEX SYNTHESIZED HNS

Density 1.7400 Mg/m^3

PX-09 Hot DMF Slurried

Zeiss Arithmetic Means

	Frequency	Weight
Length (μm)	20	67
Width (μm)	11	39
Length/Width Ratio	1.93	1.85
Cross-Sectional Area (μm^2)	310	3200
Volume (μm^3)	1500	34000
Equivalent Spherical Diameter (μm)	10	34
Surface Area (μm^2)	800	8400
Degree of Sphericity	0.52	0.52
Equivalent Circular Diameter (μm)	17	57
Powder Uniformity	4.72	3.44

Surface Areas (cm^2/g)

B.E.T. 27,400

PANTEX SYNTHESIZED HNS

Density 1.7400 Mg/m^3

PX-10 Hot DMF Slurried

Zeiss Arithmetic Means

	Frequency	Weight
Length (μm)	22	56
Width (μm)	11	33
Length/Width Ratio	1.99	1.92
Cross-Sectional Area (μm^2)	320	2200
Volume (μm^3)	1400	22000
Equivalent Spherical Diameter (μm)	10	28
Surface Area (μm^2)	830	5900
Degree of Sphericity	0.51	0.52
Equivalent Circular Diameter (μm)	17	48
Powder Uniformity	4.73	3.53

Surface Areas (cm^2/g)

B.E.T. 26,500

PANTEX SYNTHESIZED HNS

Density 1.7400 Mg/m^3

PX-11 Hot DMF Slurried

Zeiss Arithmetic Means

	Frequency	Weight
Length (μm)	26	62
Width (μm)	16	44
Length/Width Ratio	1.62	1.64
Cross-Sectional Area (μm^2)	500	2800
Volume (μm^3)	8100	112000
Equivalent Spherical Diameter (μm)	18	48
Surface Area (μm^2)	1800	10800
Degree of Sphericity	0.83	0.81
Equivalent Circular Diameter (μm)	21	55
Powder Uniformity	4.56	3.22

Surface Areas (cm^2/g)

B.E.T. 25,000

APPENDIX 3

APPENDIX 3

HNS ANALYSIS

C. L. *Schaffer*

DEVELOPMENT DIVISION

The objective of this project is to develop a method for the assay of hexanitrostilbene (HNS).

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Endeavor No. 223

ABSTRACT

Future programmatic uses of HNS will require specifications for material acceptance. A purity assay of the HNS should be a significant part of the specifications; therefore a rapid accurate liquid chromatographic method was developed. This report contains the details of the method which is applicable to crude samples, normal production lots and highly purified special batches.

DISCUSSION

Hexanitrostilbene (HNS) assays were made using a liquid chromatograph[a] with a 254 mm precision photometer detector and an integrator[b]. The liquid chromatograph employed three columns (2.1 mm inside diameter x 1 m length) packed with Corasil II[c]. The liquid pressure at the head of the chromatographic column was 1.03 MPa. The flow rate was 3.5 mℓ per minute. Samples were prepared using 2.5 mg of sample per 15 mℓ of p-dioxane with 5 μℓ injections. Fig. 1 is a chromatogram of a mixture containing 75% HNS and 25% sym-hexanitrobibenzyl, the major impurity found in HNS. The chromatogram has three major peaks, the first being the solvent p-dioxane, the second hexanitrobibenzyl and the third HNS. For purified samples of HNS where hexanitrobibenzyl is the only major impurity present, the peak areas found using the 20% p-dioxane/n-heptane eluent are sufficient for quantitation.

Crude samples of HNS contain at least five other impurities which are not separated from either the p-dioxane or from the hexanitrobibenzyl peaks when the 20% eluent is used. It is found, as shown in Fig. 2, that if the polarity of the eluent is lowered by using 12.5% p-dioxane/87.5% n-heptane these impurities are at least partially separated and a semi-quantitative analysis can be performed.

The major impurity found in crude HNS products was isolated using a gravity column chromatograph 1 m in length x 25 mm diameter packed with silica gel. The eluent used was 30% p-dioxane in n-heptane. This impurity was identified as hexanitrobibenzyl by IR and NMR spectrograms. An HNS sample was recrystallized with p-dioxane until no impurities were detectable by thin layer chromatography. These isolated hexanitrobibenzyl and recrystallized HNS samples were used to make a liquid chromatograph standard. Trinitrotoluene (TNT) and trinitrobenzene (TNB) were injected into the liquid chromatograph and peaks were identified as two of the minor impurities found in the HNS chromatograms.

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[a] *Liquid Chromatograph 820, DuPont Instrument Product Division, Wilmington, DE.*

[b] *Infotronics Model CRS 100, Infotronics Corporation, 7800 Westglen, Houston, TX.*

[c] *Waters Assoc. Inc., Framingham, MA.*

CONCLUSIONS

Liquid chromatography is a fast accurate method for analyzing purified HNS samples, and will function adequately for a semi-quantitative analytical method for crude HNS samples. A chromatographic system using 3 m of column packed with Corasil II and from 12.5 to 20% p-dioxane/n-heptane eluent system is capable of separating at least five common impurities normally found in crude HNS synthesized from TNT.

FUTURE WORK

Future work is planned to identify the unknown impurity peaks in the chromatogram. As these impurities are isolated and identified more accurate quantitative analysis of HNS will be obtained.

CONDITIONS

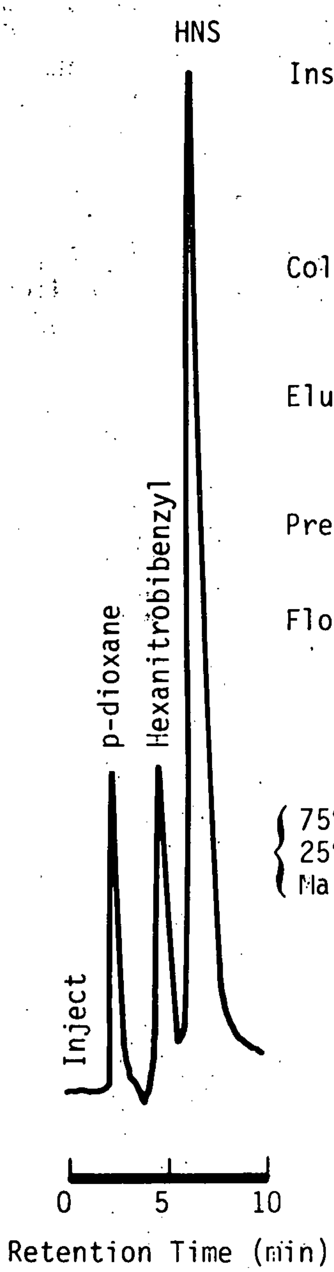
Instrument: DuPont 820 Liquid Chromatograph 254 UV - Photometer Detector

Column: Corasil II - 3 ea 1 m x 2.1 mm

Eluent: 20% p-dioxane, 80% n-heptane

Pressure: 1.03 MPa

Flow: 3.5 mℓ/min



75% HNS
25% Hexanitrobibenzyl
Master

Fig. 1