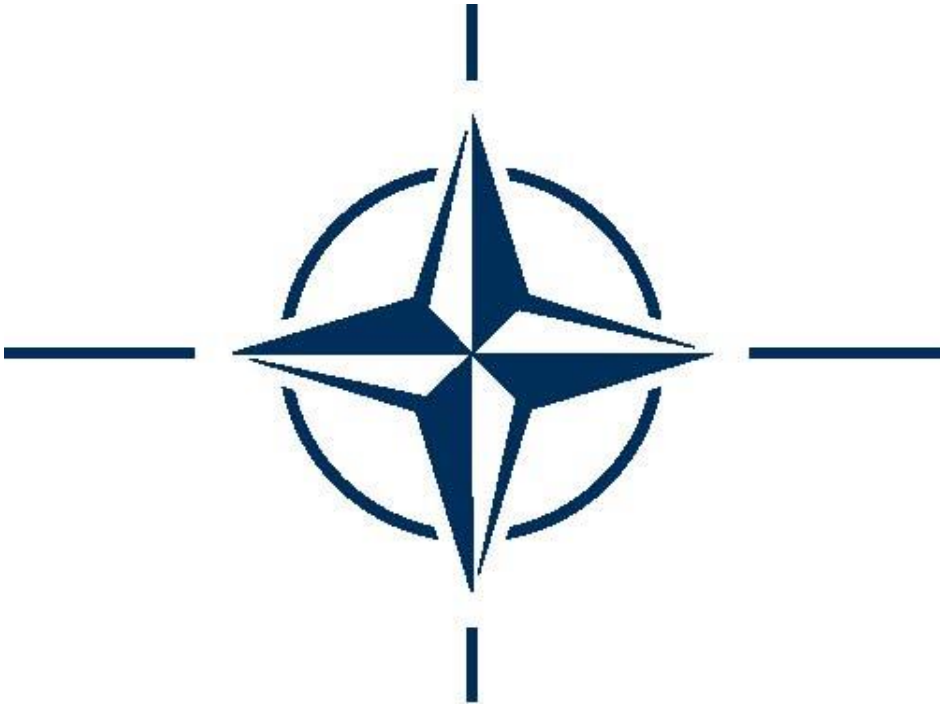
NATO STANDARD

AOP-4566

ENERGETIC MATERIALS, SPECIFICATION FOR HEXANITROHEXAAZAISOWURTZITANE (HNIW/CL-20)

Edition A, version 1

SEPTEMBER 2021



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NATO LETTER OF PROMULGATION

21 September 2021

1. The enclosed Allied Ordnance Publication AOP-4566, Edition A, version 1, ENERGETIC MATERIALS, SPECIFICATION FOR HEXANITROHEXAAZAISOWURTZITANE (HNIW/CL-20), which has been approved by the nations in the CNAD AMMUNITION SAFETY GROUP (CASG – AC/326), is promulgated herewith. The agreement of nations to use this publication is recorded in STANAG 4566.

2. AOP-4566, Edition A, version 1, is effective upon receipt.

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4. This publication shall be handled in accordance with C-M(2002)60.

Dimitrios SIGOULAKIS
Major General, GRC (A)
Director, NATO Standardization Office

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RECORD OF RESERVATIONS

CHAPTER	RECORD OF RESERVATION BY NATIONS

Note: The reservations listed on this page include only those that were recorded at time of promulgation and may not be complete. Refer to the NATO Standardization Document Database for the complete list of existing reservations.

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RECORD OF SPECIFIC RESERVATIONS

[nation]	[detail of reservation]

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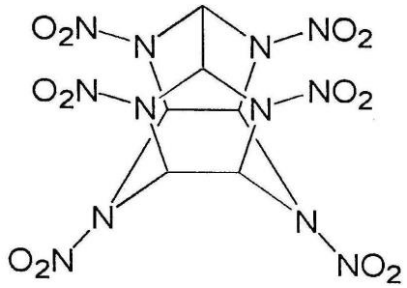
CHAPTER 1 INTRODUCTION

1.1. Aim

The aim of this agreement is to ensure that Hexanitrohexaazaisowurtzitane (CL-20) shall possess properties which make it suitable for military use and to provide, within NATO, an acceptable basis for the procurement and certification of CL-20. Epsilon is the preferred polymorph for CL-20.

1.2. Agreement

Participating nations agree that CL-20, proposed for military use, shall meet all the physical and chemical requirements of Annex A Table 1 of this document. The test procedures used to verify the requirements of Annex A Table 1 are described in Annex C and the rejection criteria shall be in accordance with Annex B, paragraph 2 of this document.



CL-20 (HEXANITROHEXAAZAISOWURTZITANE)

1.3. Use

CL-20 is intended for use in rocket and gun main propellant formulations and in explosive charges mainly of the metal accelerating type.

WARNING. This standard calls for the use of substances and test procedures that may be injurious to health if adequate precautions are not taken. It refers only to technical suitability and in no way absolves the user from the statutory obligations relating to health and safety at any stage during use.

1.4. Implementation

This standard is considered implemented when a nation has issued the necessary orders and instructions putting the contents of this agreement into effect.

ANNEX A TO AOP-4566

ANNEX A PHYSICAL and CHEMICAL PROPERTIES

A.1. Physical and Chemical Properties

The requirements for the physical and chemical properties for CL-20 shall be as specified in Table A-1. Testing Methods are given as ANNEX C of this document. CL20 in all forms should be stored below 60 °C at all times. It has been demonstrated that at temperatures near or above this polymorph conversion occurs slowly over time. Any previously tested lot that has been exposed to a temperature of 60 °C for 2 days or more or a higher temperature for the threshold time (for a higher temperature the threshold time can be determined by dividing 48 by 2n, where n is equal to the number of degrees above 60 °C divided by 10) should be reanalyzed using Procedure 8 (FTIR) to verify polymorph integrity.

Table A-1. Physical and Chemical Requirements

Property	Requirement	Procedure
A. Chemical Analysis: (1) CL-20 content (% by weight) (2) Conversion to nitramine (% by weight) (Note 1) (3) (3) other impurities (% by weight)	 98.0 (min) 99.0 (min) 1.0 (max)	 7
B. Polymorph purity - percent epsilon (%)	95 (min)	8
C. Particle density (g/cc) (one method only is required) (1) by gas pycnometer or (2) by flotation or (3) by liquid pycnometry	 2.02 (min) (Note 2) 2.02 (min) 2.02 (min)	 9 10 11
D. Insoluble in acetone (%)	0.5 (max)	12
E. Acidity (meq/100g)	0.2 (max)	13
F. Thermal Stability (1) Decomposition Temperature by DSC - peak exotherm temperature (°C) (2) Vacuum Stability ($cm^3/g/48$ hrs)	 Manufacturer will provide the DSC trace 0.2 (max)	 14 15

G. Particle Size Distribution	Manufacturer will provide data and documentation of method used (Note 3)	
H. Impact Sensitivity	Manufacturer will provide data (Note 4)	

Note 1: CL-20 may have as impurities oxa compounds and other under-nitrated derivatives. Some examples that arise from current synthesis routes are:

1. Oxa compounds:
    a. 2-oxa-4,6,8,10,12-pentanitro-4,6,8,10,12-pentaazaisowurtzitane [monooxa]
    b. 4,6,8,10-tetranitro-2,12-dioxa-4,6,8,10-tetraazaisowurtzitane
    c. 2,6 and 2,8 dioxa isomers [collectively the dioxa]

2. Impurities that have the isowurtzitane skeleton
    a. 4-formyl-2,6,8,10,12-pentanitro-2,4,6,8,10,12-hexaazaisowurtzitane [monoformyl]
    b. 2-acetyl-4,6,8,10,12-pentanitro-2,4,6,8,10,12-hexaazaisowurtzitane [monoacetyl]

The “conversion to nitramine” measure reflects the fact that these impurities have lower energy content than CL-20, and weights them according to the number of nitro groups they have relative to the number in CL-20 (viz., six). For example, each mole of the mono-oxa will be counted as five-sixths of a mole of CL-20-equivalent, since it has five nitro groups, compared to the six that are present in CL-20.

Note 2: The manufacturer will identify the apparatus used to determine the density.

Note 3: The particle size should be determined using an industry standard particle size analyzer.

Note 4: The manufacturer will provide data on the CL-20 and on a PETN standard tested on the same instrument along with a description of the apparatus and test. Buyer will determine acceptability.

ANNEX B TO
AOP-4566

ANNEX B SAMPLING and REJECTION CRITERIA

B.1. Sampling and Rejection Criteria

B.1.1. Sampling

The specified number (as in Table B-1) of one hundred gram samples of CL-20 should be taken at random at different locations from each inspection lot using a sampling thief. Each sample shall be placed in a clean dry conductive container labeled to identify the lot number. For the purposes of this standard a lot is defined as an individual recrystallization batch of CL-20.

Table B-1. Sampling Criteria

INSPECTION LOT SIZE (KG)		NUMBER OF SAMPLES
From:	To and including:	
0.0	100	1
100.1	250	2
greater than 250.1		3

B.1.2. Rejection Criteria

Failure of any sample of CL-20 to meet the requirements specified herein shall cause rejection of the lot of CL-20 from which it was taken.

ANNEX B TO
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ANNEX C TO AOP-4566

ANNEX C TESTING METHODS

WARNING: Adequate safety precautions shall be taken during the processing, testing, and handling of the CL-20 to protect personnel from accidents, fires, or explosions, and to limit damage to equipment and processing areas.

C.1. High Performance Liquid Chromatography

C.1.1. Test Description

The chemical purity shall be determined by HPLC using a standard instrument. Parameters very similar to those used for HMX or RDX are directly applicable to CL-20

C.1.2. Apparatus and Reagents

Apparatus: A high performance liquid chromatograph (HPLC) equipped with a 226 nm UV detector and an integrator or computer link up to a data acquisition system.

Materials: Analytical column (such as Microsorb C-8 or C-18 or a Supelcosil LC-8), Acetonitrile (HPLC grade), distilled water.

Conditions:

Eluent:	50/50 acetonitrile/water
Flow rate:	1.2 ml per minute
Injection volume:	100 microliters
UV Detector wavelength:	226 nm
UV Detector bandwidth:	8 nm
Temperature:	30-40 ^{o}C

Note: These parameters and sample size are given for information only since each instrument and column will require conditions specific to the instrument used and the nature of any impurities present.

C.1.3. Sample and Standard Preparation

1. Approximately 200 mg of dry CL-20 are added to a 25-ml volumetric flask.
2. Acetonitrile is added to dissolve the CL-20.
3. Further acetonitrile is added to fill the volumetric flask.

4. From this solution, 0.5 ml is removed and diluted to 25 ml with the eluent solution.
5. This solution is used for injection on the column.

Note: These weights and volumes are suggested weights and volumes - they may be modified depending on the specific conditions used.

C.1.4. Procedure

The CL-20 solution is injected into the HPLC using a syringe and sampling loop of the appropriate volume as required for the conditions being used. A standard CL-20 sample can be prepared using the procedure in Annex C-1. Standard samples of the impurities which may be present based on the synthesis route used will be used to determine their retention times and response factors under the conditions used. The analysis is run on the standard CL-20.

C.1.5. Calculation of the Response Factor

The response factor RF is calculated as the weight of the standard CL-20 used divided by the area of the standard CL-20 peak. The %CL-20 in the sample being analyzed is calculated as follows:

$$\%CL-20 = \frac{(area\ of\ CL{-}20\ peak)\ x\ RF}{wt\ sample} \text{ x } 100$$

The response factors and %s for the various impurities are determined analogously. Alternatively, for the CL-20 analog type impurities which cannot be isolated in the pure state, their amount can be calculated using response factors based on the number of nitramino groups present - the response factor of an impurity with 5 nitramino groups is assumed to be 1.2 times the response factor of CL-20 and that of one with 4 nitramino groups is assumed to be 1.5 times that of CL-20. (These general response factors hold for wavelengths around 226 nm. If a significantly different wavelength is used [for example 254 nm] response factors must be determined.) See Annex C-2 for sample HPLC traces. Three injections per CL-20 sample will be made. The results of the three injections are averaged. If the average for any of the samples does not meet the requirement, the CL-20 is rejected.

C.2. Fourier Transform Infrared

C.2.1. Test Description

The polymorph of the CL-20 sample shall be determined by FTIR and comparison with standard spectra. A visual comparison of the spectrum with reference standards such as the diffuse reflectance spectra of alpha, beta, gamma and epsilon CL-20 in Figures 1 through 3 will allow a qualitative determination of the presence of other polymorphs. In the 3080 - 3000 cm-1 region epsilon has the lowest frequency peak at 3018 cm-1 and no peak above 3046 cm-1, while gamma has a peak at 3059 cm-1 and both alpha and beta have a peak at 3053 cm-1. Alpha-CL-20 has clathrate water peaks at 3695 and 3607 cm-1. Figure 3 shows several other regions that can be used to distinguish epsilon from the other three polymorphs. Quantitative analysis of polymorph mixtures requires a least square or partial least square (PLS) program and a reference set of pure and mixed CL-20 polymorph spectra. The unknown CL-20 spectrum must be obtained using the same FTIR sampling method as the reference spectra. Three FTIR sampling methods can be used to obtain good quality FTIR spectra of CL-20, diffuse reflectance spectroscopy (DRS), transmittance and attenuated total reflectance (ATR).

C.2.2. Apparatus and Reagents

Apparatus: A standard Fourier Transform Infrared spectrometer.

C.2.3. Data Acquisition

Neat CL-20 is best analyzed using DRS or transmittance.

Qualitative Analysis: about 1 - 2 mg is mixed with 100 mg of spectral grade potassium bromide (KBr) and pressed into a pellet for transmittance sampling or packed into a sample cup for DRS. The FTIR spectrum must be acquired at 2 cm-1 resolution with sufficient scans to obtain good signal-to-noise. Quantitative CL-20 polymorph analysis requires a reference set of known polymorph mixtures (made in the composition region of interest) and pure polymorphs with their FTIR spectra collected using the same sampling method to be used for the unknown CL-20 sample.

DRS Spectrum for Quantitative Analysis:

1. Mix 1 mg of CL-20 with 100 mg of spectral grade KBr
2. Mix in a sample homogenizer for a constant time (about 15 - 30 seconds)
3. Pack a constant weight of the CL-20 in KBr into a DRS sample cup and level the top surface
4. Take about 100 scans at 2 cm-1 resolution and convert the spectrum to Kubelka-Munk units.

The PLS analysis program is then used to set up a calibration matrix in specific spectral regions where spectral data occurs and no spectral interferences from impurities are present. The PLS program is then used to determine the polymorph composition of the unknown CL-20 sample using the calibration matrix.

Transmittance Spectra for Quantitative CL-20 Polymorph Analysis: mix a constant 1 - 2 mg of CL-20 in 100 mg of KBr, pressing at a constant pressure for the same time and obtaining the spectrum at 2 cm-1 resolution. The PLS program is then used to analyze the data.

C.3. Gas Pycnometer Density

C.3.1. Test Description

The density of the CL-20 is determined by comparing the density of the CL-20 with the density of a gas using a pycnometer.

C.3.2. Apparatus and Reagents

Apparatus: A commercial gas pycnometer and solid objects of known volume for calibration of the pycnometer.

C.3.3. Sample & Standard Preparation

Weigh accurately a 25 g sample of CL-20 (or the amount appropriate for the pycnometer being used) to the nearest 0.01 g (w1). Determine the volume of the weighed specimen as directed by the operating instructions supplied with the pycnometer (v). Calculate the density of the sample with the following equation:

$$\text{Density} = w1/v \text{ (where v is in ml)}$$

C.4. Floatation Density

C.4.1. Test Description

The density of the CL-20 is determined by matching its density with a mixture of toluene and dibromomethane across the range needed to separate all the CL-20 in a sample. This method has the advantage of giving a distribution rather than a single value but is labor intensive.

C.4.2. Apparatus and Reagents

Apparatus:

1. A Mettler DA-110M density/specific gravity meter or equivalent.
2. Several 125 ml Teflon separatory funnels (normally 8).
3. A matching number of 30 ml medium fritted crucibles.

C.4.3. Sample & Standard Preparation

1. A stock solution with a theoretical density of 2.0600 g/ml is prepared by adding 260 ml of toluene with 740 ml of dibromomethane in a large beaker (the density of toluene is 0.866 g/ml and the density of dibromomethane is 2.477 g/ml).
2. Remove a 40 ml aliquot of the prepared flotation mixture and add it to the separatory funnel.
3. Weigh accurately a 5 g sample (w1) of the CL-20 sample into the funnel.
4. Shake well to wet the CL-20. Allow the mixture to separate and settle for approximately 2 hours.
5. Prepare a second 40 ml sample with a density reduced by approximately 0.005 g/ml by adding 0.5 to 1.0 ml of toluene to the original sample.
6. Verify the density with the specific gravity meter.
7. Prepare another 5 g CL-20 sample and shake in a separatory funnel and allow to settle.
8. Continue until all the CL-20 is denser than the solution.
9. The typical range required is 2.05 to 2.02 g/ml.
10. Allow all the CL-20 samples to fully reach equilibrium.
11. Filter the CL-20 that has settled out through the clean tared medium fritted crucible (w2).
12. Place the crucible in a 100 °C oven for 2 hours.
13. Cool in a desiccator to room temperature.
14. Reweigh the crucible (w3).

Note: The CL-20 should be removed from the fritted crucible using a solvent to dissolve it. It should not be scraped off the frit due to the sensitivity of CL-20.

From this, calculate the amount of CL20 recovered (with density higher than the solvent density) for each solvent density according to the following equation:

$$\% \text{ Recovered} = (w3-w2) * 100/w1$$

The average density of the sample is reported as the density of the solvent at which 50% of the CL-20 is recovered. Since the 50% value will normally not fall exactly on a

solvent density point selected, the 50% number will be determined by a linear interpolation from the nearest two points.

C.5. Liquid Pycnometry

C.5.1. Test Description

The density of a solid is measured by filling a tared, calibrated volumetric container (pycnometer) with the solid and back filling with distilled water containing surfactant. Results are reported as g/ml at the conditioned temperature.

C.5.2. Apparatus and Reagents

Apparatus:

1. A specific gravity bottle, pycnometer or equivalent.
2. A constant temperature bath controlled to 0.1 oC.
3. An analytical balance accurate to 0.0002 g.
4. A desiccator.
5. Distilled water containing 1% Aerosol OT or other suitable surfactant.

C.5.3. Pyncometer Calibration

Weigh the clean dry pycnometer on the analytical balance (w1). Fill the pycnometer with freshly distilled water cooled to room temperature. Replace the top on the pycnometer. Place the pycnometer in the constant temperature bath at near 25 °C for at least 30 minutes to reach equilibrium temperature. During conditioning the pycnometer top should always have a small bead of distilled water covering the capillary to prevent loss of water by evaporation through the capillary. Remove the pycnometer from the bath, push the top down tight and immediately wipe the top with a non-absorbent material so that the liquid level in the pycnometer is absolutely flush with the top of the lid. Wet the outside of the pycnometer, except the lid, with acetone and evaporate the acetone by blowing oil-free air or nitrogen on the pycnometer. Repeat until dry and cool. Wipe finally with a dry, clean, lint-free cloth being careful not to warm with the hands. Weigh the filled pycnometer on an analytical balance (w2).

Determine the exact volume of the pycnometer with the following calculation:

Volume of pycnometer (ml) = (w2 - w1)/d1
(where d1 is the density of distilled water at the bath temperature)

C.5.4. Procedure for Solid Sample Density

1. Accurately weigh a clean dry calibrated pycnometer to the nearest 0.0002 g.
2. Calculate the weight of this pycnometer when filled with the surfactant solution at the bath temperature (w3).
3. Weigh to the nearest 0.0002 g a sufficient amount of CL-20 into the pycnometer to fill it about one third full (w4).
4. Fill the pycnometer the rest of the way with the surfactant solution.
5. Place the pycnometer under light vacuum to remove any bubbles adhering to the surface of the CL-20 particles.
6. Lightly place the top on the pycnometer and immerse it in a bath of distilled water in a small beaker.
7. Place the beaker with the pycnometer in the temperature controlled bath and allow it to equilibrate at least 30 minutes.
8. Dry the pycnometer as in the calibration procedure.
9. Weigh the dry pycnometer (w5).

Determine the material density using the following equation:

Density of material (g/ml) = w4*d2/(w4+w3-w5)
(where d2 is the density of the surfactant solution at the bath temperature)

The density of the surfactant solution at the bath temperature can be determined by filling an accurately weighed (w6) clean dry pycnometer with the solution and conditioning it at the test temperature as in Section 6.b. After conditioning, the weight (w7) of the filled pycnometer is determined accurately. The density of the solution is calculated using the following equation:

Density of the surfactant solution (g/ml) d2 = (w7 -w6)/V
(where V is the volume of the pycnometer (ml))

C.6. Acetone Insoluble

C.6.1. Test Description

To determine the amount of acetone insoluble material present in the sample.

C.6.2. Apparatus and Reagents

Apparatus:

1. ACS Reagent Grade acetone
2. Erlenmeyer flask(s)
3. Vacuum filter apparatus
4. Fritted crucible

C.6.3. Sample & Standard Preparation

The acetone insoluble material content shall be determined by dissolving a 10+/-0.5 g (s1) sample of CL-20 in 100 ml of ACS Reagent Grade acetone in a 250 ml Erlenmeyer flask. The mixture is stirred for 15 minutes. The acetone solution is vacuum filtered through a pre-weighed 30 ml medium fritted crucible (w1). The material in the crucible is washed twice with 5 ml acetone. The crucible is dried in an oven at 60 °C for 1 hour and weighed (w2).

The percent insoluble is calculated according to the following equation:

$$\% \text{ insoluble} = (w2 - w1)*100/s1$$

A second analysis is conducted if the two analyses do not agree within 0.2 percent absolute, then an additional two analyses will be done. The average of the two analyses is reported. If an additional two analyses are done, the average of the four values is reported.

C.7. Acid Number

C.7.1. Test Description

To determine the total acid amount in the sample. The dry material is dissolved in tetrahydrofuran (THF) and titrated in a non-aqueous system using tetra-butylammonium hydroxide (TBAH) to determine the total acid in the sample. This method has shown excellent reproducibility for CL-20. Since the CL-20 completely dissolves in the THF, acid both on the surface and in the interior of the CL-20 can be measured. This gives an accurate measure of all the acid that could deleteriously effect the properties of the CL-20.

C.7.2. Apparatus and Reagents

C.7.3. Sample & Standard Preparation

1. In a 150 ml beaker are added 5.0+/-0.1 g (s1) of dry CL-20 and 100 ml of THF.
2. The mixture is stirred until the CL-20 dissolves.
3. The solution is titrated (t1) using a potentiometric titrator with a 0.050+/-0.005 Normal TBAH solution in THF (c1).
4. The TBAH solution is standardized using a primary standard acid (e.g. potassium biphthalate) of a known quantity in this same apparatus.
5. A combination glass electrode or equivalent is used for measuring.
6. A blank is also done using the same procedure but omitting the sample (t2).

The acidity is calculated as follows:

$$\text{Acid (meq/100g)} = (t1 - t2)*c1*100/s1$$

The titration is repeated on a second 5 gram sample. The average of the two titrations is reported.

C.8. Determination of Decomposition Temperature

***WARNING**: Explosions were observed when using heating rates of 2°C/min and above and sample sizes of 2 mg and above.

C.8.1. Test Description

The temperature at which the exothermal decomposition of a material reaches its thermal maximum is determined by differential scanning calorimetry (DSC).

C.8.2. Apparatus and Reagents

Apparatus: A commercial differential scanning calorimeter.

C.8.3. Sample & Standard Preparation

Sample Preparation: A sample weight of between 1.0 and 2.0 milligrams shall be used. The sample shall be prepared in accordance with the procedures detailed in the instruction manual of the specific DSC instrument used.

Test Procedure and Results: The sample shall be contained in an unsealed covered aluminum pan with a pinhole in the lid. The sample shall be run in a nitrogen atmosphere. The temperature is ramped to 140 °C using a heating rate of 10 °C/min. It is then raised to 240 °C using a heating rate of 2 °C/min*. The operation, analysis, and calculation procedures of the DSC instrument used shall be followed for maximum accuracy and precise measurement of the DSC curve. The peak exotherm temperature shall be reported and the DSC trace provided.

C.9. Determination of Vacuum Thermal Stability (VTS)

C.9.1. Test Description

The vacuum thermal stability (VTS) of an explosive is the volume of gas, at standard conditions, produced by the constant temperature, constant volume thermal decomposition of the explosive using a specified apparatus, heating period, explosive weight, and an initial pressure of 2 mm Hg (266 Pa) or less.

C.9.2. Apparatus and Reagents

Apparatus: Reference STANAG/AOP-4556

C.9.3. Sample & Standard Preparation

Sample Preparation: Prior to taking the sample for the test, the CL-20 must be dried for 8 hours at a pressure of 2 mm Hg (266 Pa) or less at 55 °C. A representative portion of the dried explosive (1.0 gram) shall be transferred to the bottom of the test chamber using a powder funnel.

Test Procedure: The test should be done in accordance with NATO STANAG 4556 for Explosives: Vacuum Stability Test. For CL-20, the weight of explosive used is 1.0 g; the test temperature is 100+/-0.5 °C; the test time is 48 hrs.

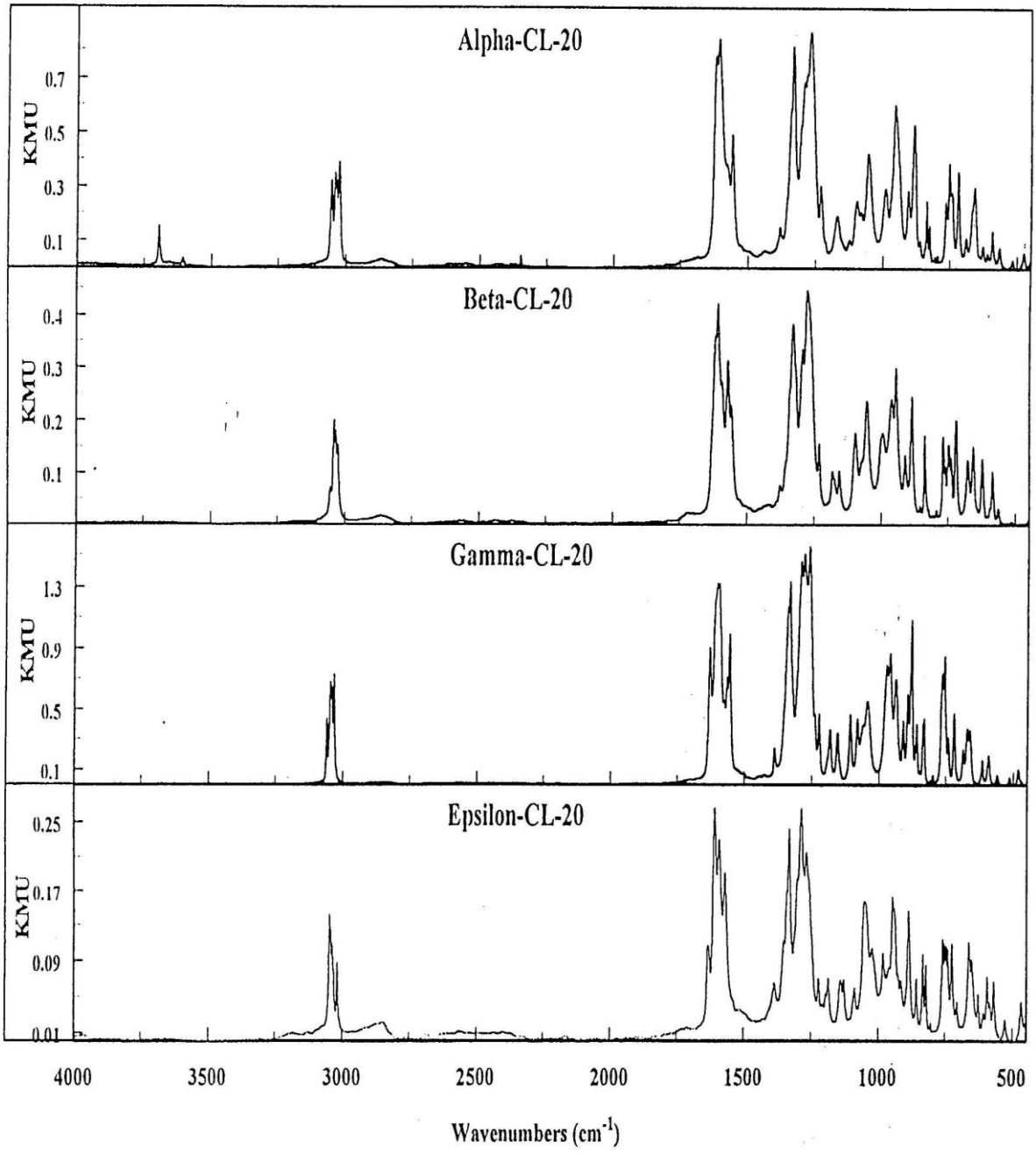

FIGURE C-1. FTIR SPECTRA OF CL-20 POLYMORPHS

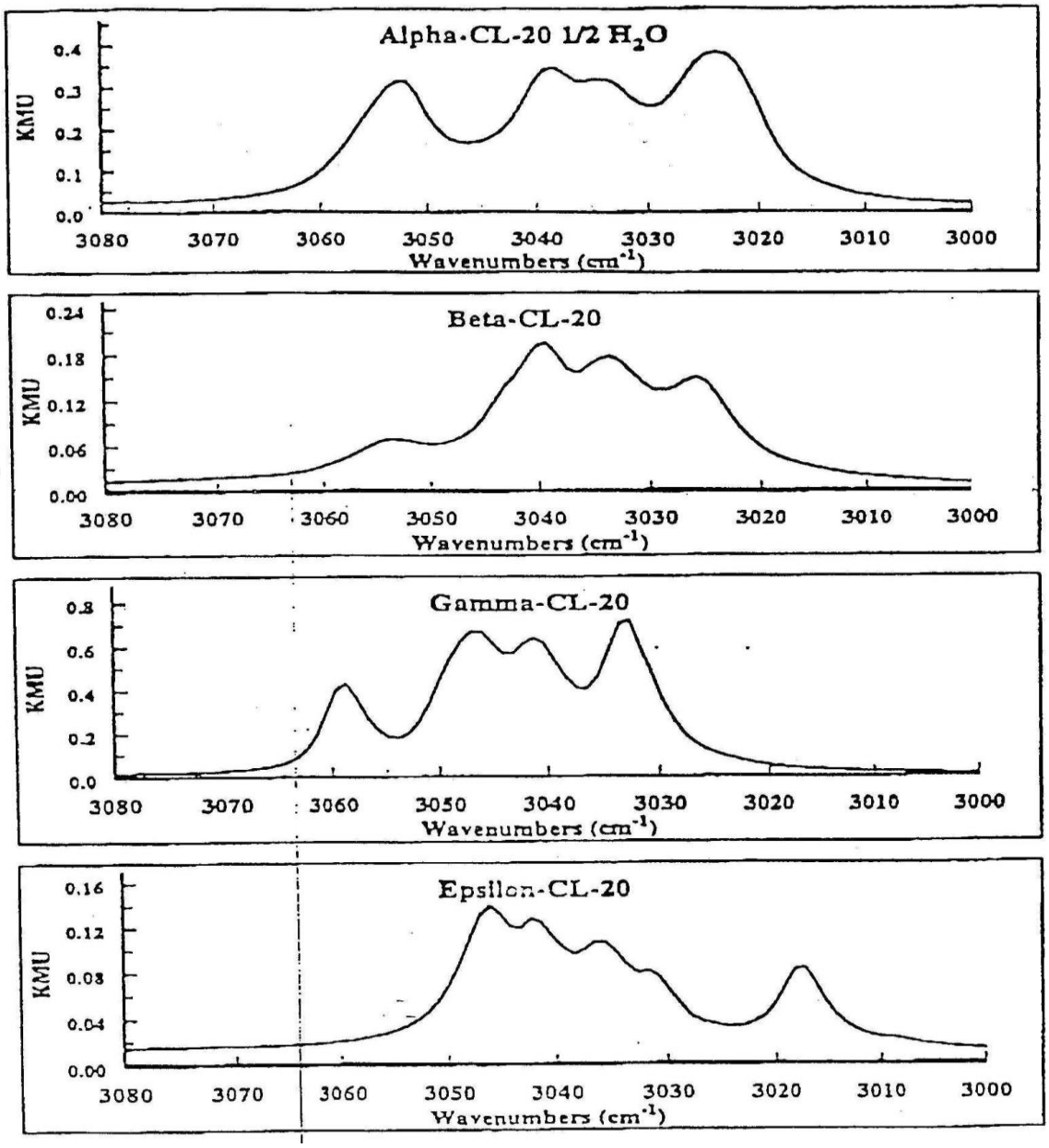

FIGURE C-2. EXPANDED FTIR SPECTRA OF CL-20 POLYMORPHS SHOWING THE 3000-3080 cm-1 REGION

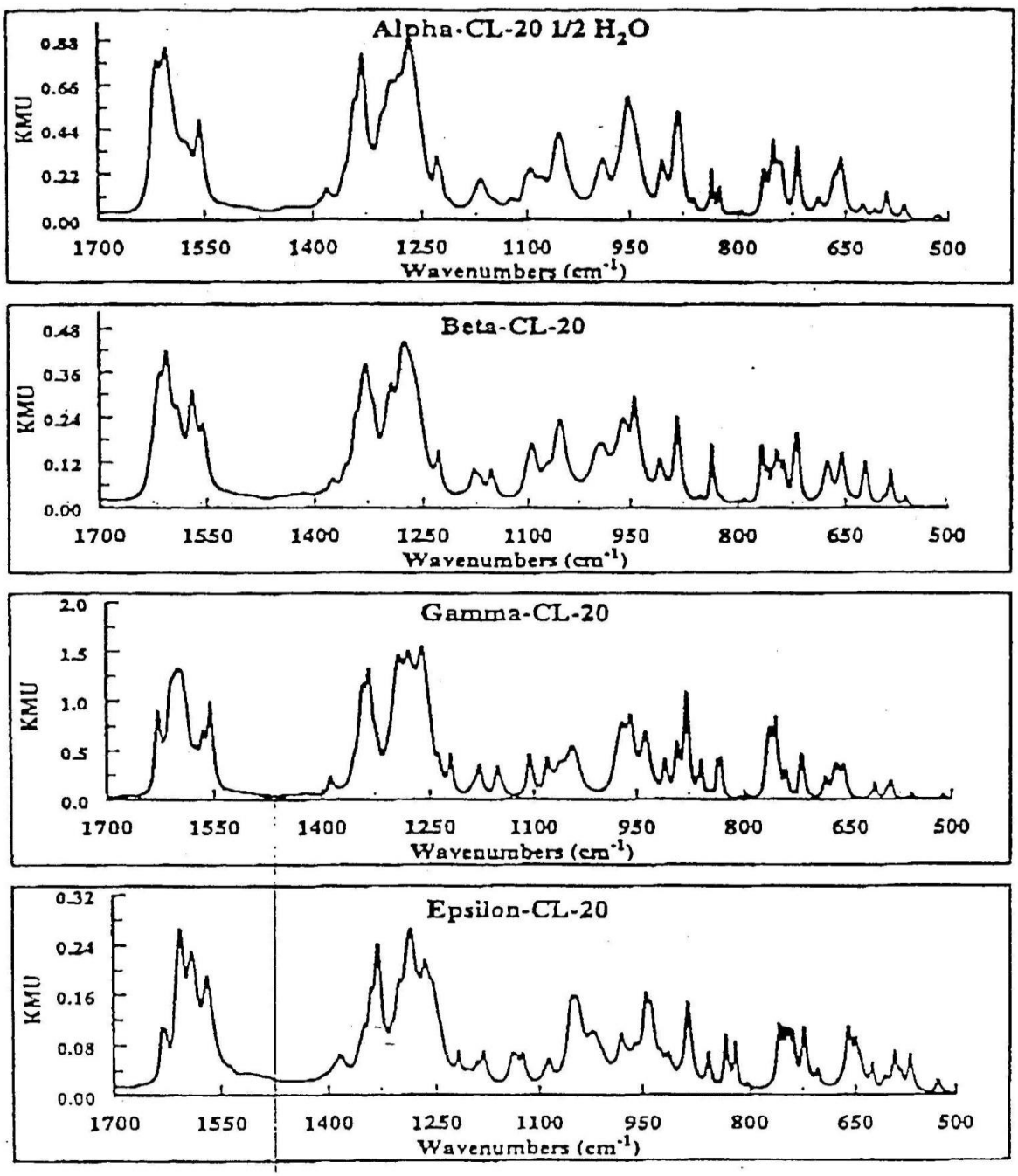

FIGURE C-3. EXPANDED FTIR SPECTRA OF CL-20 POLYMORPHS SHOWING THE 500-1700 cm-1 REGION

C.10. Appendix 1 – Procedure for Preparation of Standard CL-20

C.10.1. General Purification of CL-20 by Column Chromatography

CL-20 can be purified by column chromatography on a column loaded with a silica gel slurry in hexanes, eluting with an 80/20 mixture by volume of hexanes/ethyl acetate. The CL-20 (containing oxa impurities) elutes first, followed by some transition fractions of CL-20 mixed with the monoacetyl and/or monoformyl impurities. This method will usually be effective for removal of other partially nitrated impurities because they are more polar than CL-20.

Purification of CL-20 from the TADF route: In a typical column separation, a solution of 15 g of CL-20 from the TADF route in 28 ml of acetone is loaded onto a column of 300 g of Silica gel 60 (70-230 mesh) wet with hexanes. The dimensions of the column of silica gel are typically 1.75 inches in diameter and 18 inches long. The acetone solution of CL-20 is washed onto the column with a very small amount of acetone and then with a small amount of 80/20 hexanes/ethyl acetate. The elution is done with the 80/20 hexanes/ethyl acetate solvent mixture to give 10 g of CL-20 with <0.2% of the monoformyl impurity. The progress of the separation can be monitored by TLC on silica gel plates (fluorescent binder) with a solvent of 75/25 hexanes/ethyl acetate (RF = 0.57 for CL-20 and 0.22 for the monoformyl impurity). The oxa impurities can be seen just below the CL-20 spot.

C.11. Appendix 2 – HPLC Analysis of CL-20 Produced by Different Routes

C.11.1. Sample Analysis of CL-20 From the TAIW Route

Apparatus: Waters HPLC model 510 with Waters 490 detector set to 226 nm, Supelcosil LC-8 column, Acetonitrile (Baker, PA), Reagent grade water (Modulab type II).

Conditions:

Eluent	50/50 acetonitrile/water
Flow rate:	1.2 ml per minute
Injection Volume	100 microliters
UV Detector wavelength	226 nm
UV Detector bandwidth	8 nm
Temperature	Ambient

Procedure: 100 microliters of a solution prepared as in 7.4 are injected into the HPLC system. The elution time for CL-20 using the mentioned conditions is 5.82 minutes. The monoacetylpentanitroisowurtzitane (MAPNIW) has a nominal retention time of 4.12 minutes. The other impurities are unidentified. The one at 0.94 minutes could be meta-nitrobenzoic acid. Representative chromatograms are shown below.

Peak table for CL-20 from TAIW under the above conditions.

Retention Time	Area	%Area	Impurity
0.593	17730	0.07	
0.941	20481	0.08	possibly meta-nitrobenzoic acid
1.441	25517	0.01	
1.738	266044	1.00	probable solvent related
2.252	3105	0.01	
4.123	91310	0.34	MAPNIW
4.592	4007	0.02	
5.077	52704	0.20	
5.829	26076079	98.19	CL-20

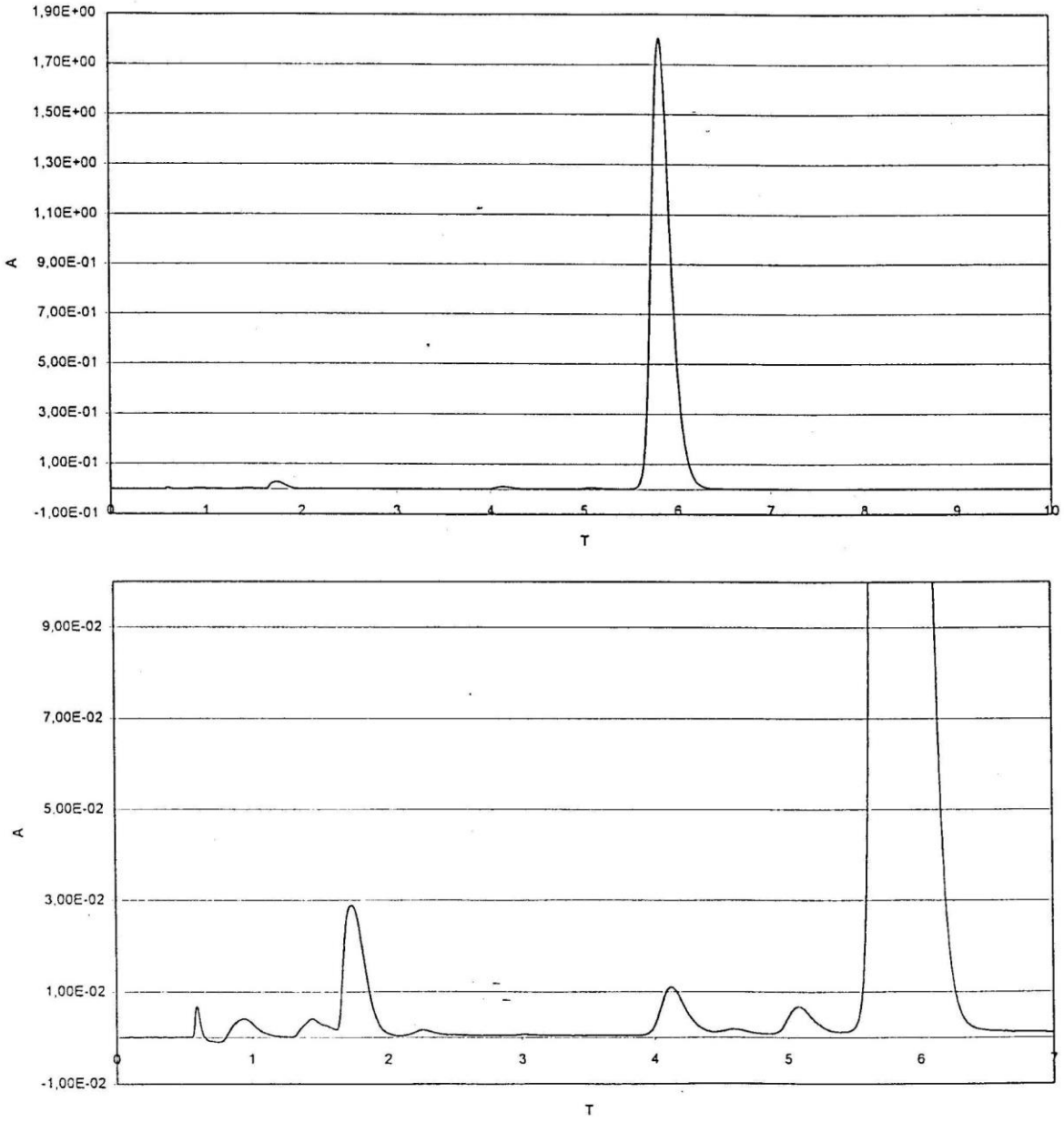

FIGURE C-2.1-1. HPLC TRACES OF CL-20 FROM TAIW ROUTE

C.11.2. Sample Analysis of CL-20 From the TAIW Route Using Different Conditions

Apparatus: Silica C 18 column - 5 micron particles, 15 cm long

Conditions:

Eluent	40/60 water/acetonitrile + 0.1% H3PO4
Flow rate:	1.0 ml per minute
Injection Volume	20 microliters
UV Detector wavelength	230 nm
Temperature	Ambient

Procedure: CL-20 (50 mg) was dissolved in 25 ml of acetonitrile. A 5 ml portion of this solution was dissolved in 20 ml of the eluent solution. 20 microliters are injected into the HPLC system.

Representative chromatograms are shown below.

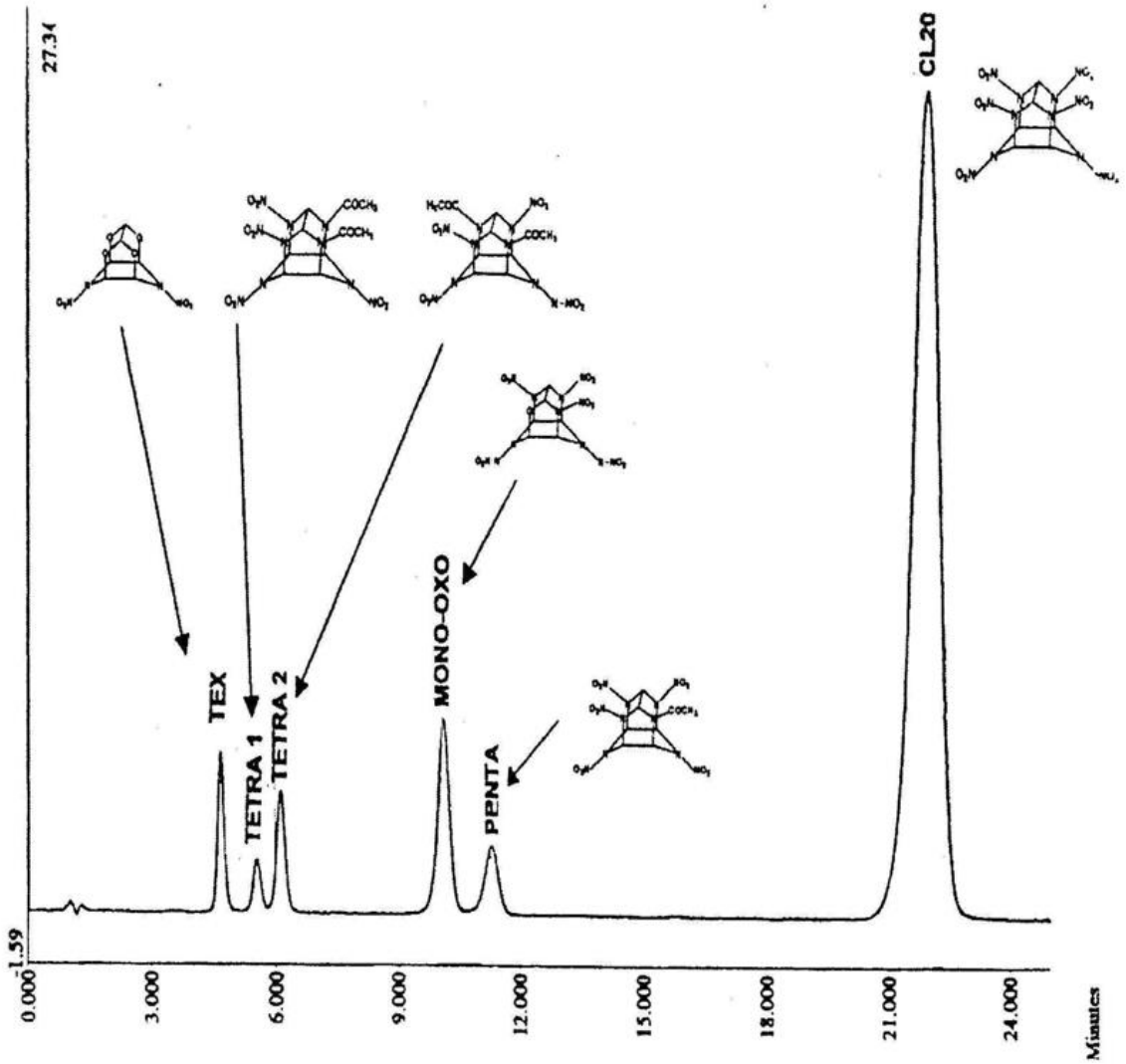

FIGURE C-2-2-1. HPLC TRACE FROM TAIW ROUTE SHOWING POSSIBLE IMPURITIES

ANNEX C TO
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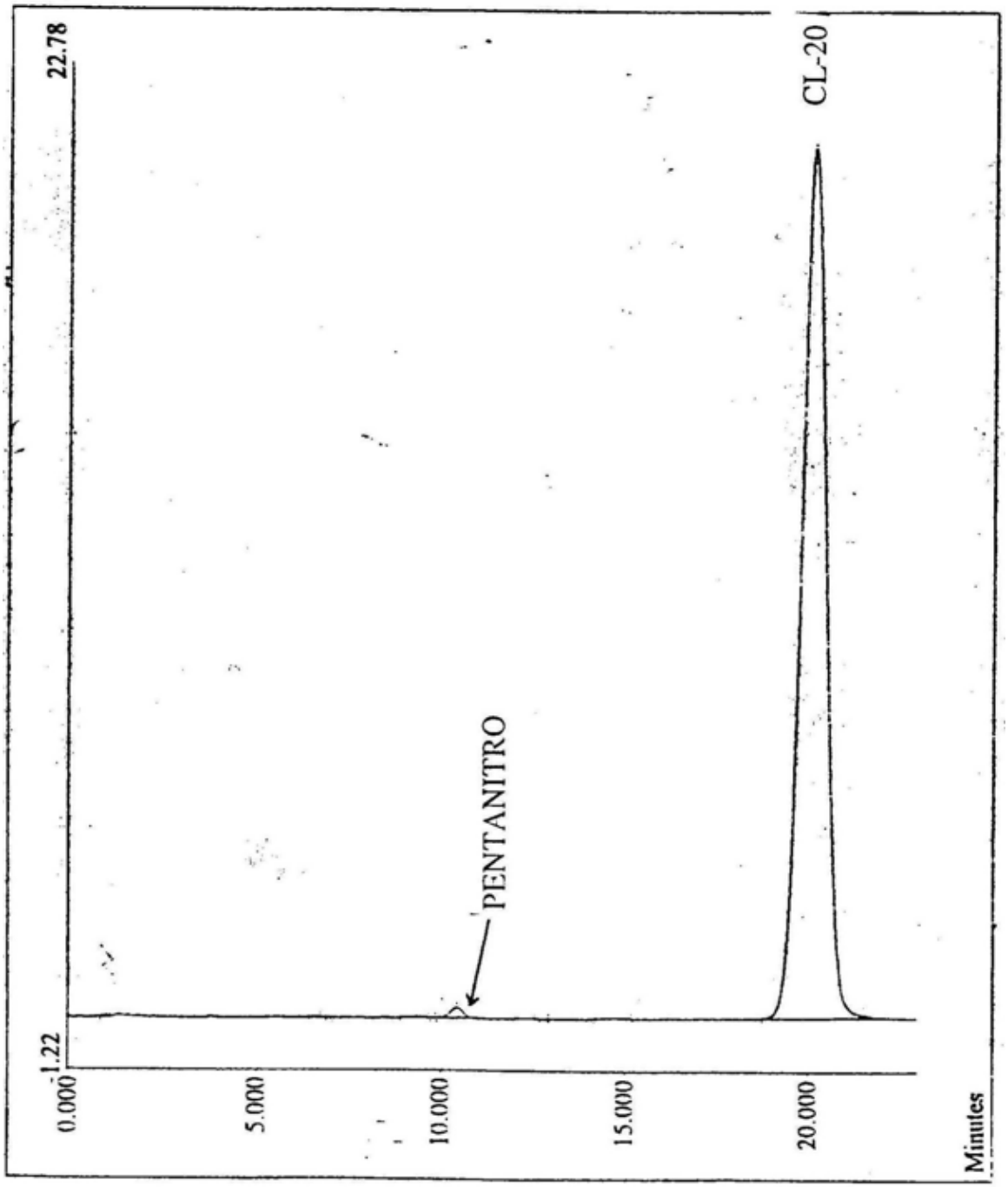

FIGURE C-2.2-2. HPLC TRACE OF CL-20 FROM TAIW ROUTE

C.11.3. Sample Analysis of CL-20 From the TADF Route

Apparatus: 250 x 4.6 mm Rainin Microsorb MV C-18 5 micron column

Conditions:

Eluent	50/50 water/acetonitrile
Flow rate:	1.5 ml per minute
Injection Volume	20 microliters
UV Detector wavelength	230 nm
Temperature	40 °C

Procedure: CL-20 (10-20 mg) was dissolved in acetonitrile to give a concentration of 1.00 mg/ml. A 200 microliter portion of this solution was added to 800 microliters of mobile phase.

Representative chromatograms are shown below.

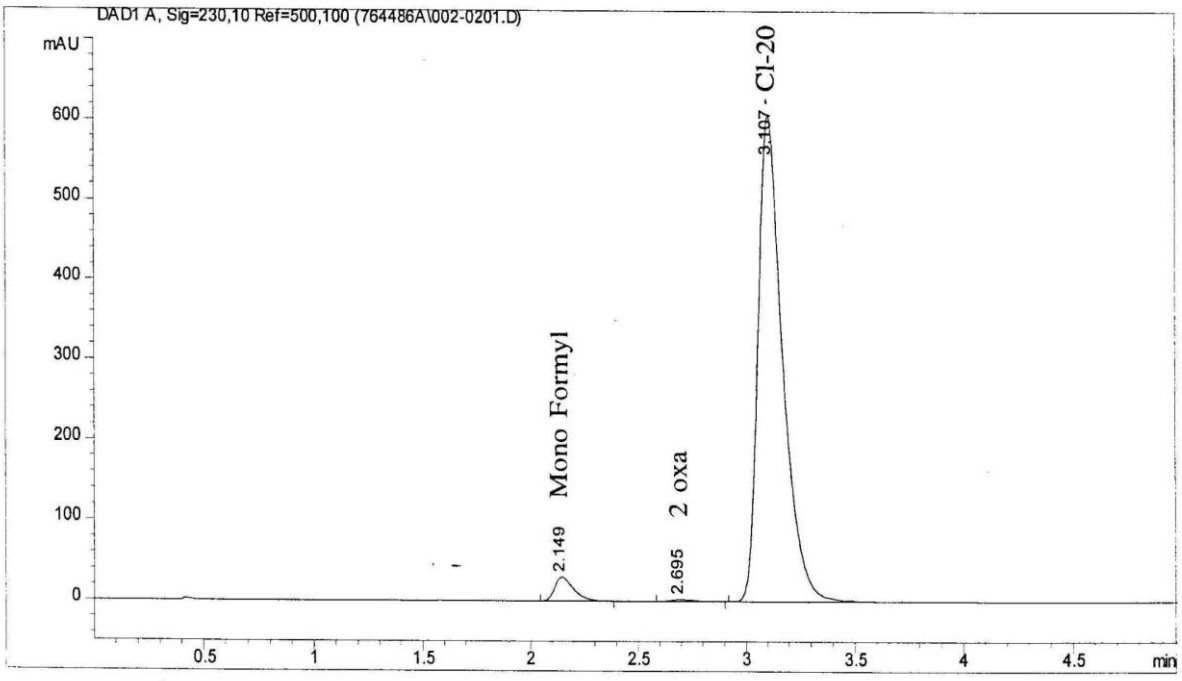

FIGURE C-3.3-1 HPLC TRACE OF CL-20 FROM THE TADF ROUTE

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AOP-4566(A)(1)