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1,3,5-TRICHLOROBENZENE
PROGRESS REPORT

Z. L. Estes

DEVELOPMENT DIVISION

SEPTEMBER 1976
(SANL NO. 458-067)

Normal Process Development
Endeavor No. 106

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For
Lawrence Livermore Laboratory
Livermore, California

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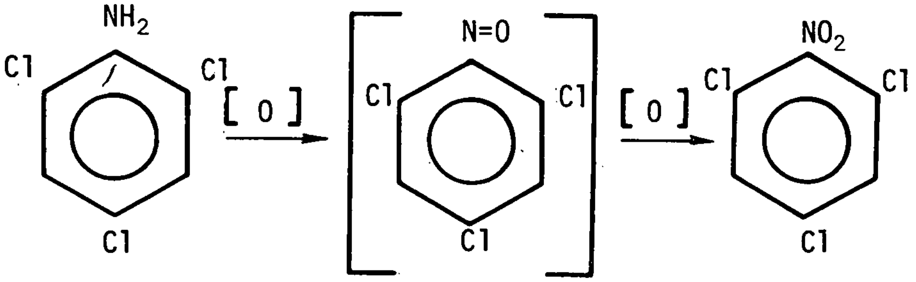
SANL No. 458-067 provides for 1,3,5-trichlorobenzene research and development in the areas listed below:

A. Conduct a literature search to determine what closely related chemistry has been done.

In continuing this literature search, the primary emphasis has been directed toward obtaining information related to 2,4,6-trichloroaniline (TCA)(*1, 2, 3*), its conversion to 2,4,6-trichloronitrobenzene (TCNB)(*4, 5*) and the synthesis, nitration and analysis of 1,2,4-trichlorobenzene.

The conversion of TCA to TCNB:

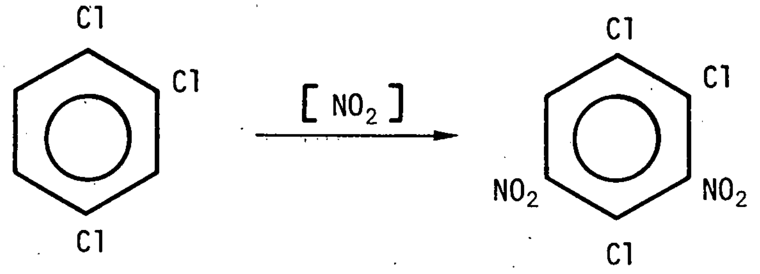


is reported to be accomplished by at least three different methods. Conversion using the expensive compound pertrifluoroacetic anhydride is reported to provide a 98% yield. Conversion using permaleic anhydride with 90% hydrogen peroxide is also reported to provide excellent yields of the nitro compound. Probably the most practical method, however, and the one evaluated in our laboratory, is reported in U.S. Patent 3,396,200(*6*). Conversion of TCA to the intermediate nitroso compound using 30% hydrogen peroxide, and oxidation to the nitro compound using dilute nitric acid, gives an over-all yield of approximately 60%.

B. Determine if 99% 1,3,5-TCB is necessary by evaluating aminations and purifications with mixtures of 1,2,4- and 1,3,5-TCB.

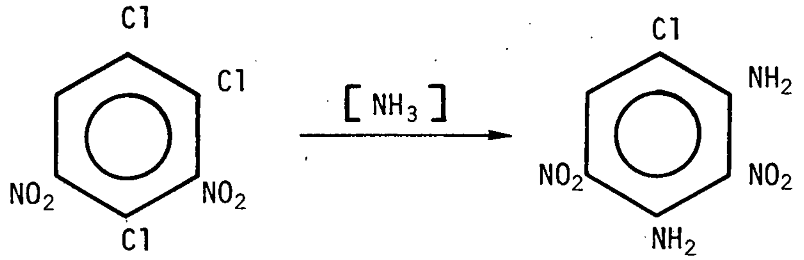
Nitration of TCB

In a continuation of the study of the possibly harmful presence of 1,2,4-TCB in 1,3,5-TCB, three mixtures containing 5%, 10% and 15% 1,2,4-TCB were nitrated and subsequently aminated to TATB. Under the vigorous nitration conditions normally used in TCTNB production ($NaNO_3$, 30% Oleum, 150 C), it was found that although a considerable amount of the 1,2,4-TCB is destroyed by oxidation, most of the 1,2,4-TCB is dinitrated to the 1,2,4-trichloro-3,5-dinitrobenzene:



The increasing amounts of the 3,5-dinitro compound are illustrated in the gas chromatograms (Figs. 1 through 3). Identification of the 1,2,4-trichloro-3,5-dinitrobenzene was made by nitrating pure 1,2,4-TCB and comparing the infrared spectra (Fig. 4) and gas chromatography elution time with a known sample of 1,2,4-trichloro-3,5-dinitrobenzene.

Considering the chemistry of the 1,2,4-trichloro-3,5 dinitrobenzene, the chlorine atoms in the 2 and 4 positions should be easily replaceable,



and the resulting 1-chloro-2,4-diamino-3,5-dinitrobenzene should be soluble in toluene; however, entrapment of this compound within the TATB crystal can be expected. To check this possibility, the 5%, 10% and 15% nitration mixtures from above were aminated with ammonia at atmospheric pressure in refluxing toluene. The total elemental chlorine contents of the resulting TATB samples were 0.68%, 0.68% and 1.37% respectively, and the DTA of the samples indicates a slightly decreasing thermal stability with increasing 1,2,4-trichloro-3,5-dinitrobenzene content (Figs. 5 through 7).

From the information obtained thus far it appears that the presence of 1,2,4-trichlorobenzene in TCB would have an effect on the resulting TATB very similar to that of the 1,2,4,6-tetrachloro-3,5-dinitrobenzene produced in the nitration reaction. It is therefore believed that small amounts ($\sim$ 5%) of the 1,2,4-TCB can be tolerated, however, we plan to evaluate this by a pilot plant production run.

C. Begin exploration of the proposed route to TCB via aniline.

This project has been discontinued due to the large number of companies proposing to use this TCB route. Previous work has shown that this is a feasible route and thus process optimization is left to the individual companies. The following samples of TCB have been received and analyzed:

Pacific Chemical Corp.
    Form: White Solid
    Melting Point: 63 C
    Infrared Spectra: 1,3,5-TCB
    Gas Chromatography: No detectable impurity

United Technologies Corp. (CSD process)
    Form: Tan Solid
    Melting Point: 62.5 - 63.5 C
    Infrared Spectra: 1,3,5-TCB
    Gas Chromatography: No significant impurities

Ashland Chemical Co. (3/26/76)
    Form: Tan solid
    Melting Point: 62.5 - 63.5
    Infrared Spectra: 1,3,5-TCB
    Gas Chromatography: Contains ∿ 1% high boiling impurity

    (5/28/76)
    Form: White solid
    Melting Point: 62 - 63 C
    Infrared Spectra: 1,3,5-TCB
    Gas Chromatography: No detectable impurities

Arapahoe Chemical Co. (Lot 250-119A)
    Form: White solid
    Melting Point: 62 - 63 C
    Infrared Spectra: 1,3,5-TCB
    Gas Chromatography: 97.1% TCB; 0.6% low boiling impurity; 2.3% high boiling impurities (3)

    Lot 250-120
    Form: White solid
    Melting Point: 62 - 63 C
    Infrared Spectra: 1,3,5-TCB
    Gas Chromatography: 94.6% TCB; 2.66% low boiling impurities (2); 2.73% high boiling impurities (4)

Fike Chemical Company
    Form: Tan solid
    Melting Point: 61.5 - 62.5 C
    Infrared Spectra: 1,3,5-TCB, impurity peak at 7.15 microns
    Gas Chromatography: ∿ 0.5% low boiling impurity, ∿ 0.5% high boiling impurity.

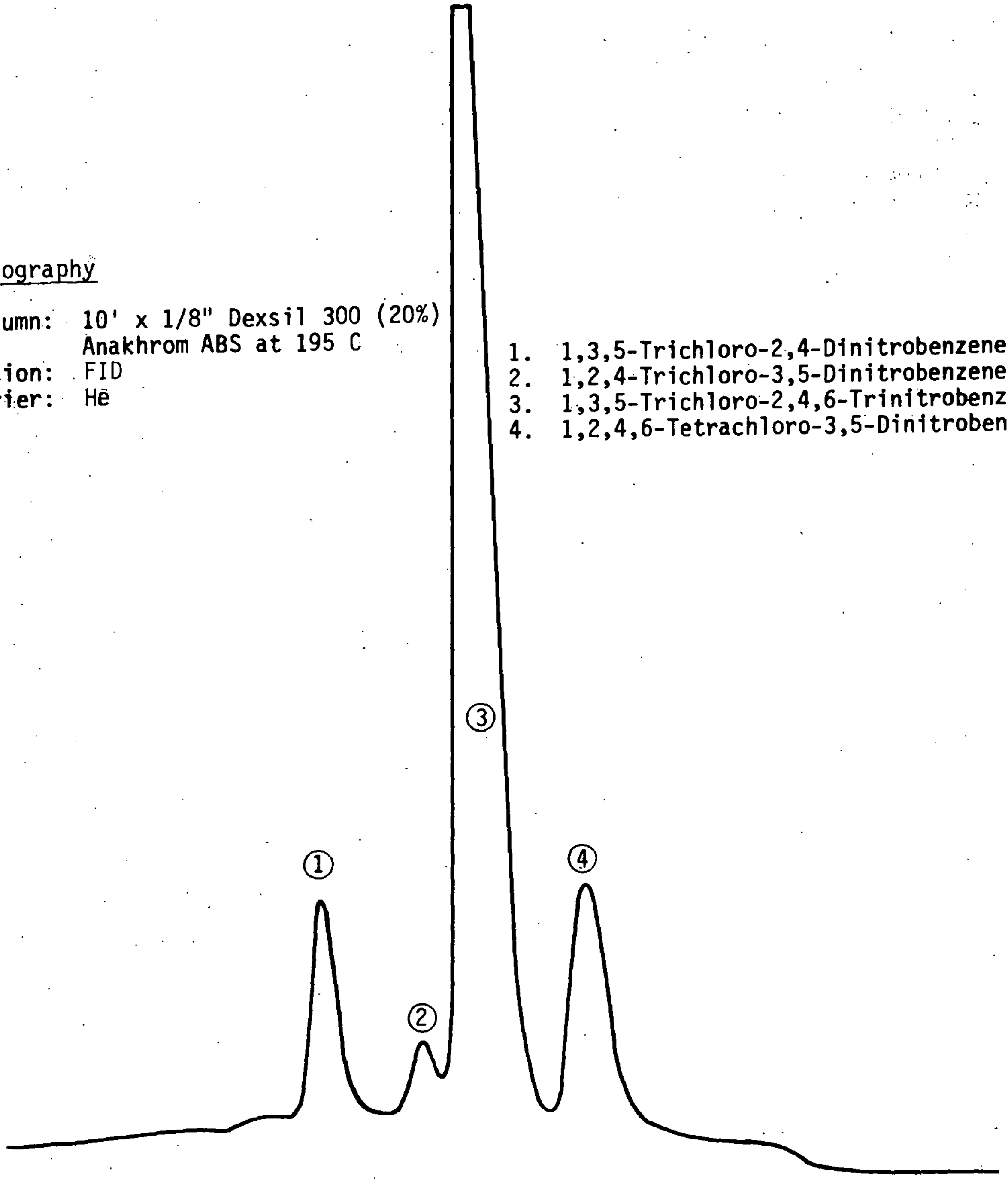
D. Explore the direct nitration of trichloroaniline.

Laboratory trials of the procedure for the conversion of TCA to trichloronitrosobenzene (TCNB) by U.S. Patent 3396200 indicate this may offer a route competitive with TCB. Although TCNB offers no advantage over TCB in the synthesis of TCTNB, it can be used equally well. The major disadvantage in converting TCA to TCNB rather than TCB is the long time period required for the conversion.

The chromatograms(7) in Figs. 8, 9 and 10 show the oxidation of TCA to the trichloronitrosobenzene with 30% hydrogen peroxide at 24 C to be incomplete after 22 hours, although most ($\sim$ 80%) of the TCA has been converted within three hours. The chromatogram in Fig. 11 illustrates the final product after the oxidation step with dilute nitric acid for 8 hours at 88 C. The chromatogram indicate approximately 5% of the nitroso compound remained unoxidized and the presence of some unknown oxidation products.

Chromatography

Column: 10' x 1/8" Dexsil 300 (20%)
Anakhrom ABS at 195 C
Detonation: FID
Carrier: He



1. 1,3,5-Trichloro-2,4-Dinitrobenzene (9.3%)
2. 1,2,4-Trichloro-3,5-Dinitrobenzene (2.9%)
3. 1,3,5-Trichloro-2,4,6-Trinitrobenzene (75.2%)
4. 1,2,4,6-Tetrachloro-3,5-Dinitrobenzene (12.6%)

Fig. 1. Nitration Products from 5% 1,2,4-TCB/95% 1,3,5-TCB

Chromatography

Column: 10' x 1/8" Dexsil 300 (20%)
Anakhrom ABS at 195 C
Detonation: FID
Carrier: He

1. 1,3,5-Trichloro-2,4-Dinitrobenzene (9.0%)
2. 1,2,4-Trichloro-3,5-Dinitrobenzene (6.5%)
3. 1,3,5-Trichloro-2,4,6-Trinitrobenzene (71.9%)
4. 1,2,4,6-Tetrachloro-3,5-Dinitrobenzene (12.6%)

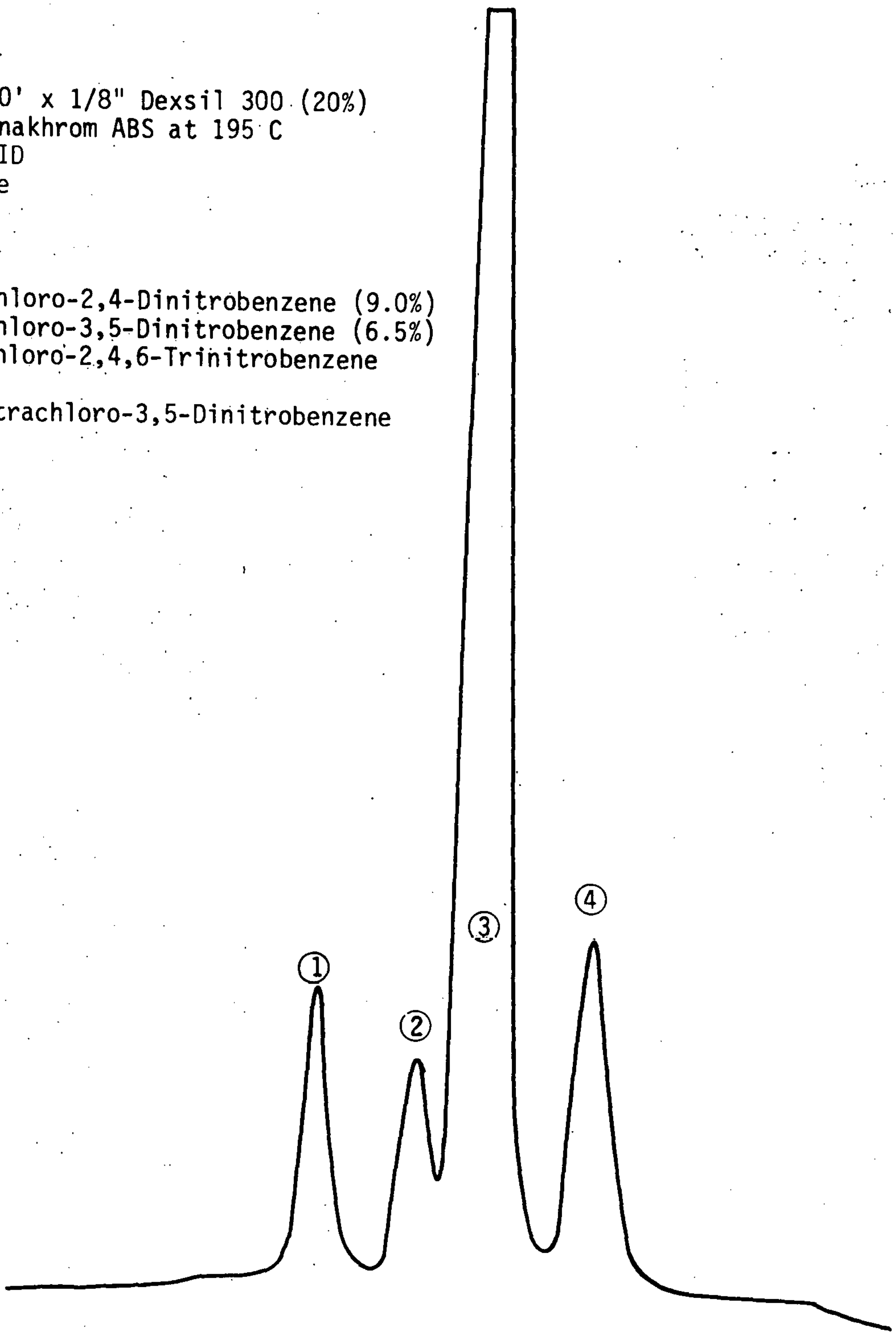


Fig. 2. Nitration Products from 10% 1,2,4-TCB/90% 1,3,5-TCB

Chromatography

Column: 10' x 1/8" Dexsil 300 (20%)
Anakhrom ABS at 195 C
Detonation: FID
Carrier: He

1. 1,3,5-Trichloro-2,4-Dinitrobenzene (4.8%)
2. 1,2,4-Trichloro-3,5-Dinitrobenzene (9.9%)
3. 1,3,5-Trichloro-2,4,6-Trinitrobenzene (64.7%)
4. 1,2,4,6-Tetrachloro-3,5-Dinitrobenzene (20.4%)

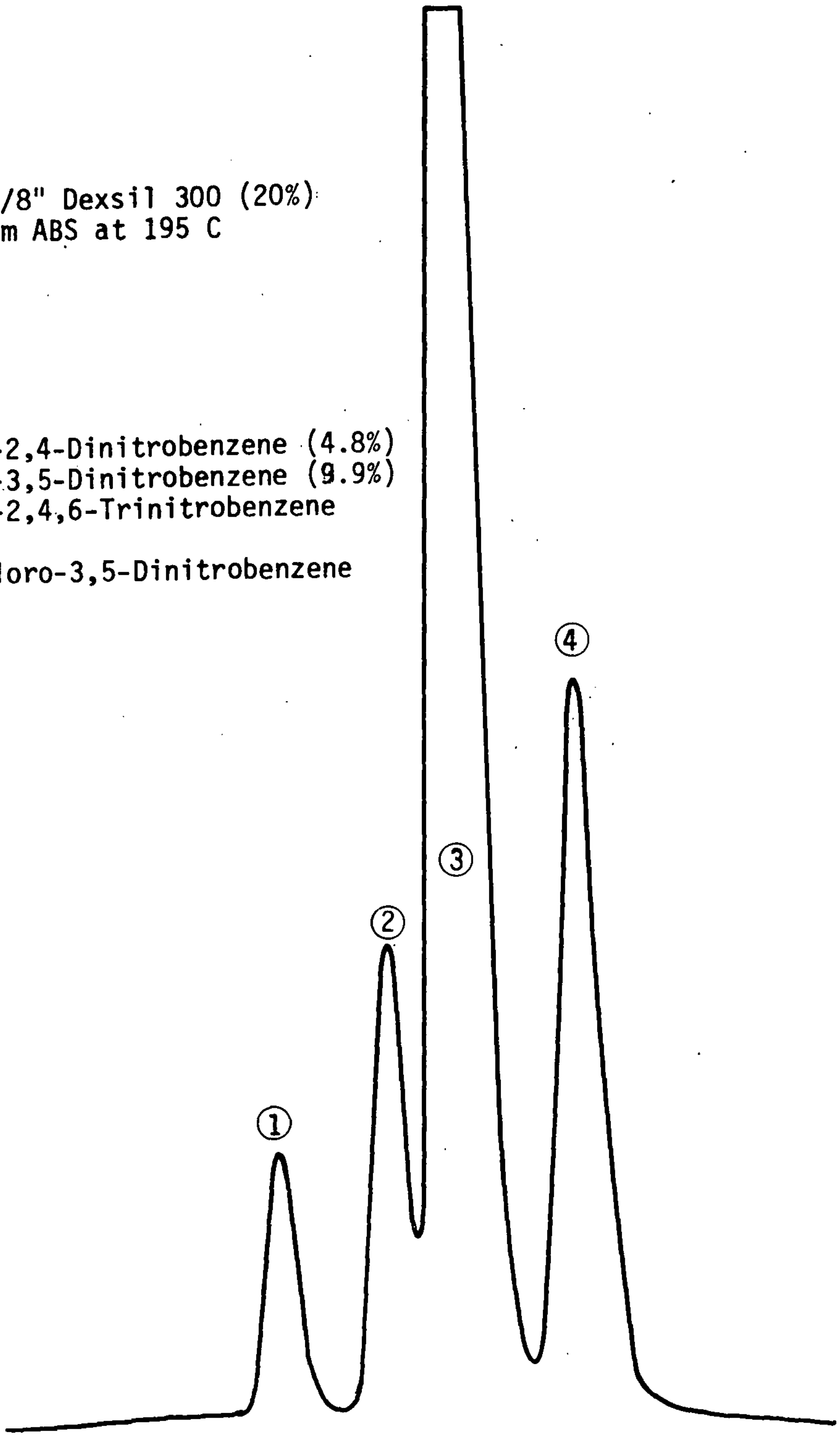
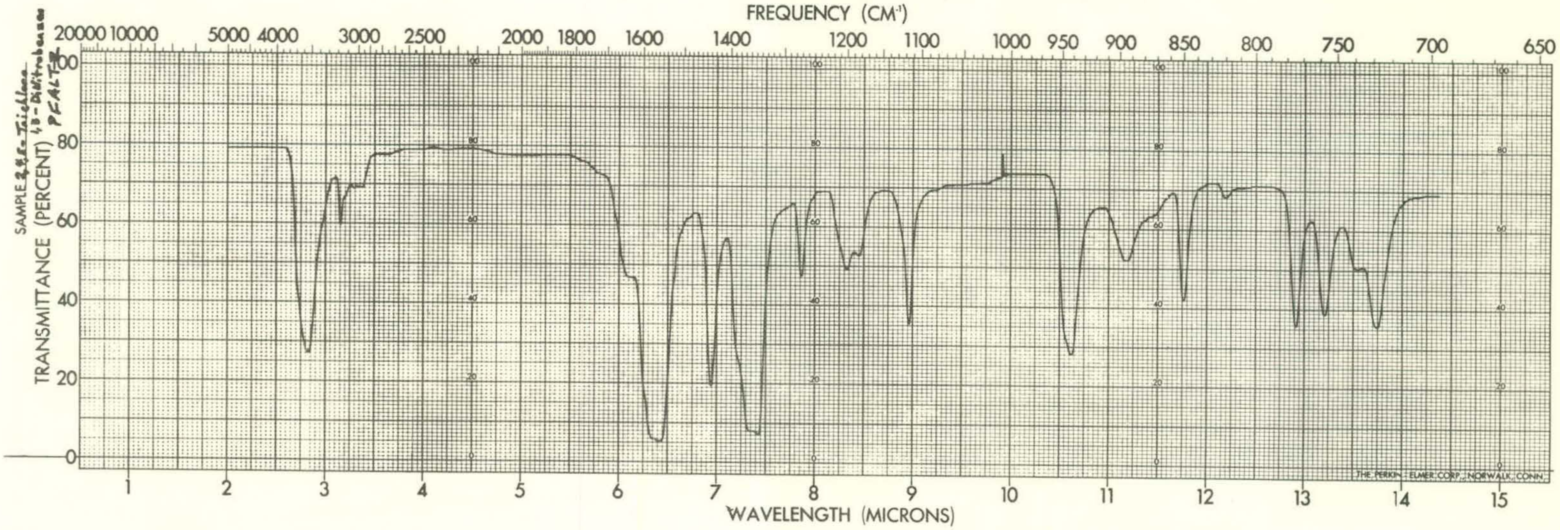
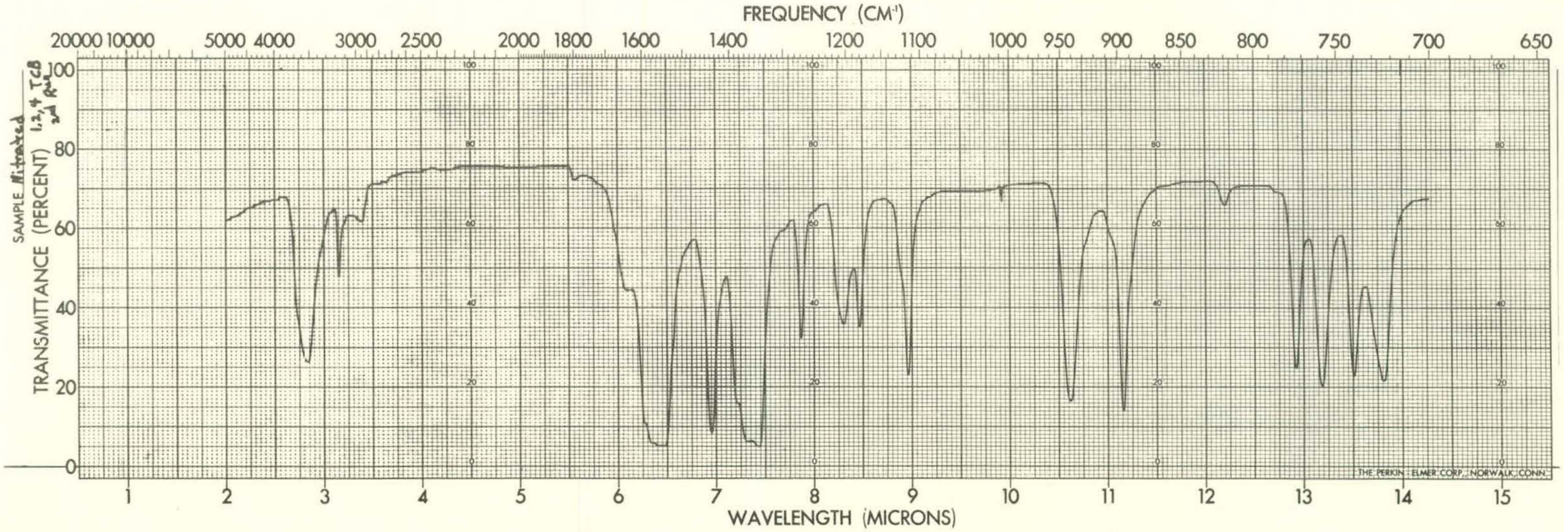


Fig. 3. Nitration Products from 15% 1,2,4-TCB/85% 1,3,5-TCB



2,4,5-Trichloro-1,3-Dinitrobenzene (Pfaltz)



Nitrated 1,2,4-TCB (2nd Run)

Fig. 4. IR Spectra Identification of 2,4,5-Trichloro-1,3-Dinitrobenzene

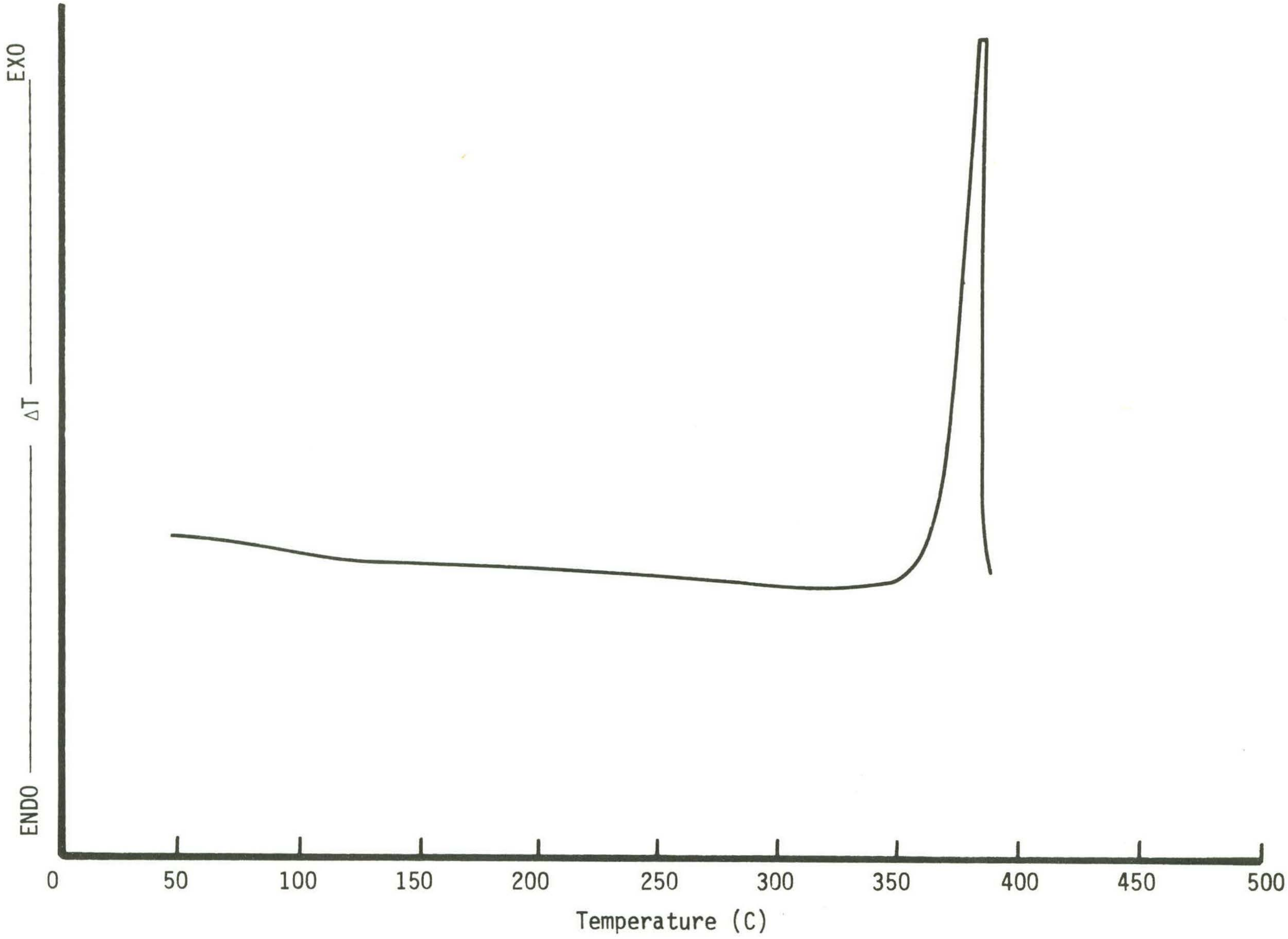


Fig. 5. DTA Scan of TATB (5% 1,2,4-TCB Starting Material)

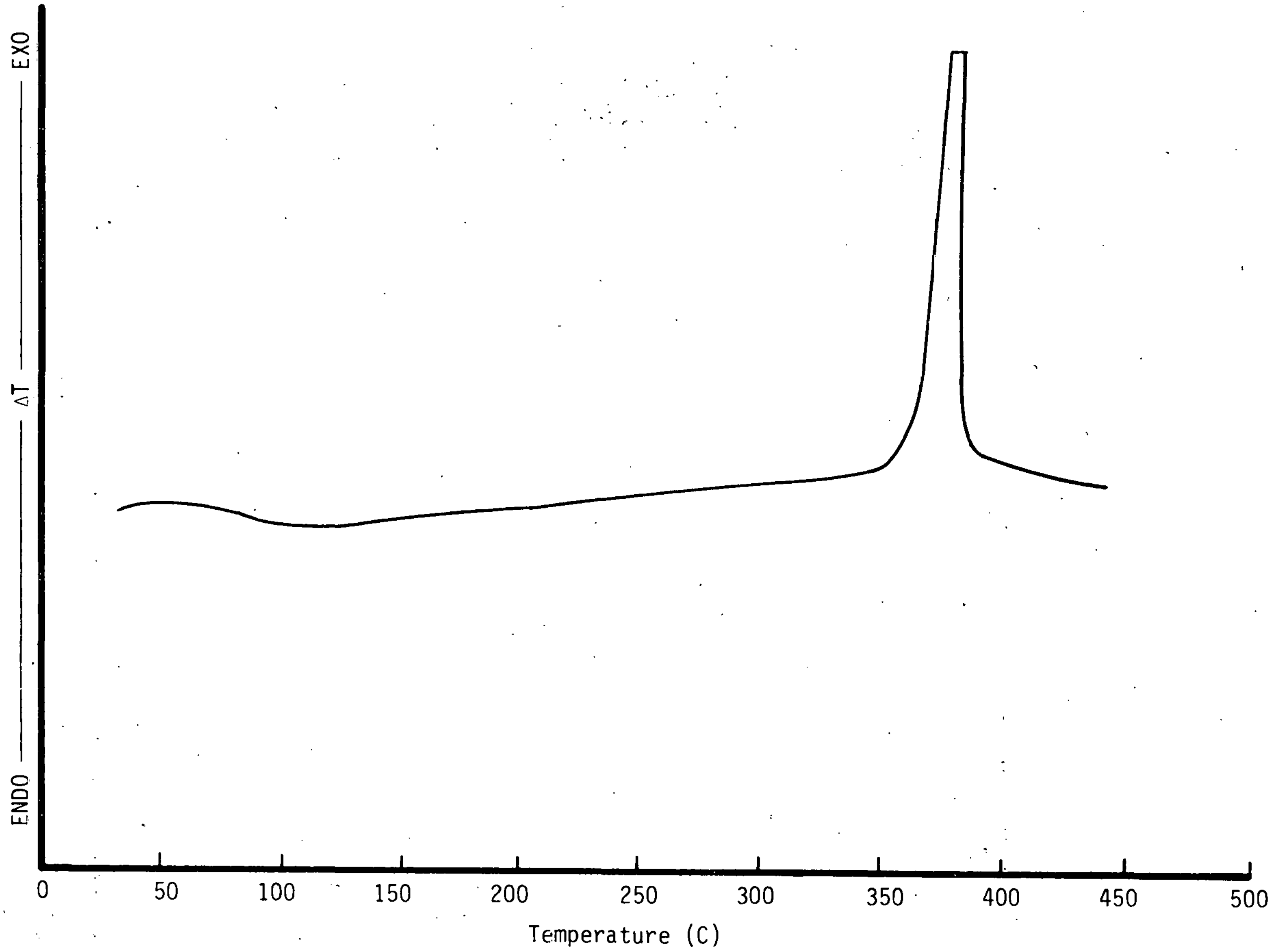


Fig. 6. DTA Scan of TATB (10% 1,2,4-TCB Starting Material)

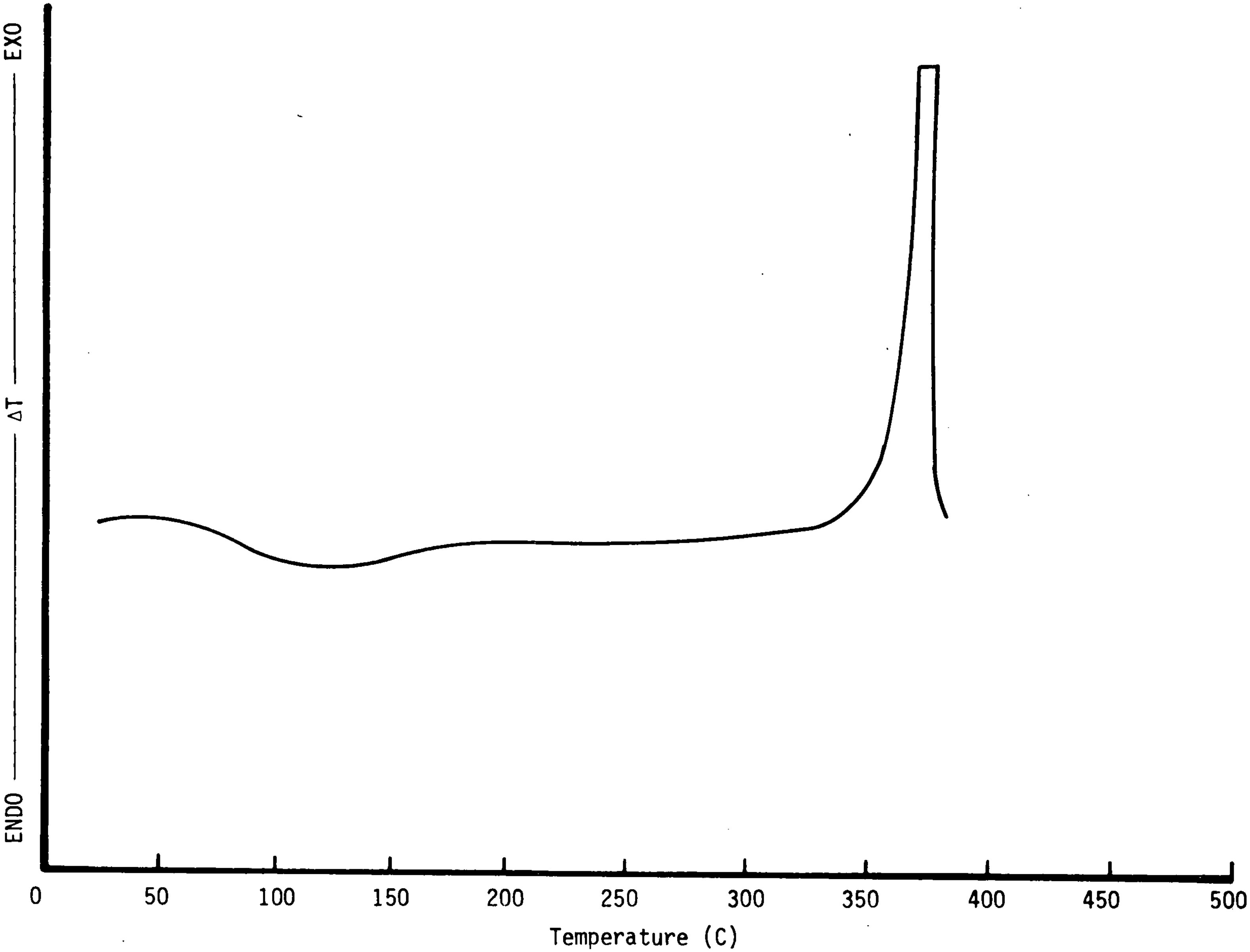


Fig. 7. DTA Scan of TATB (15% 1,2,4-TCB Starting Material)

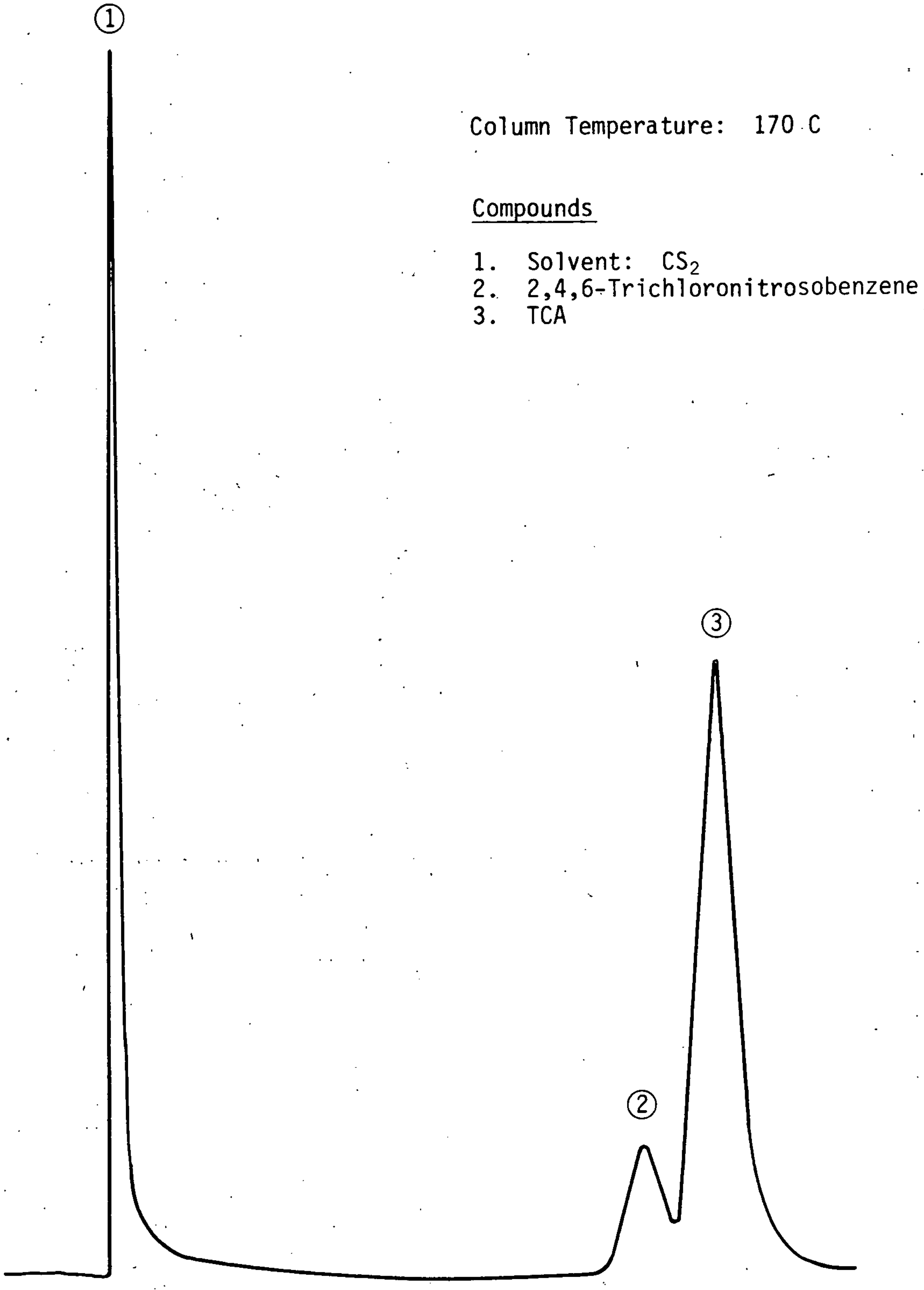
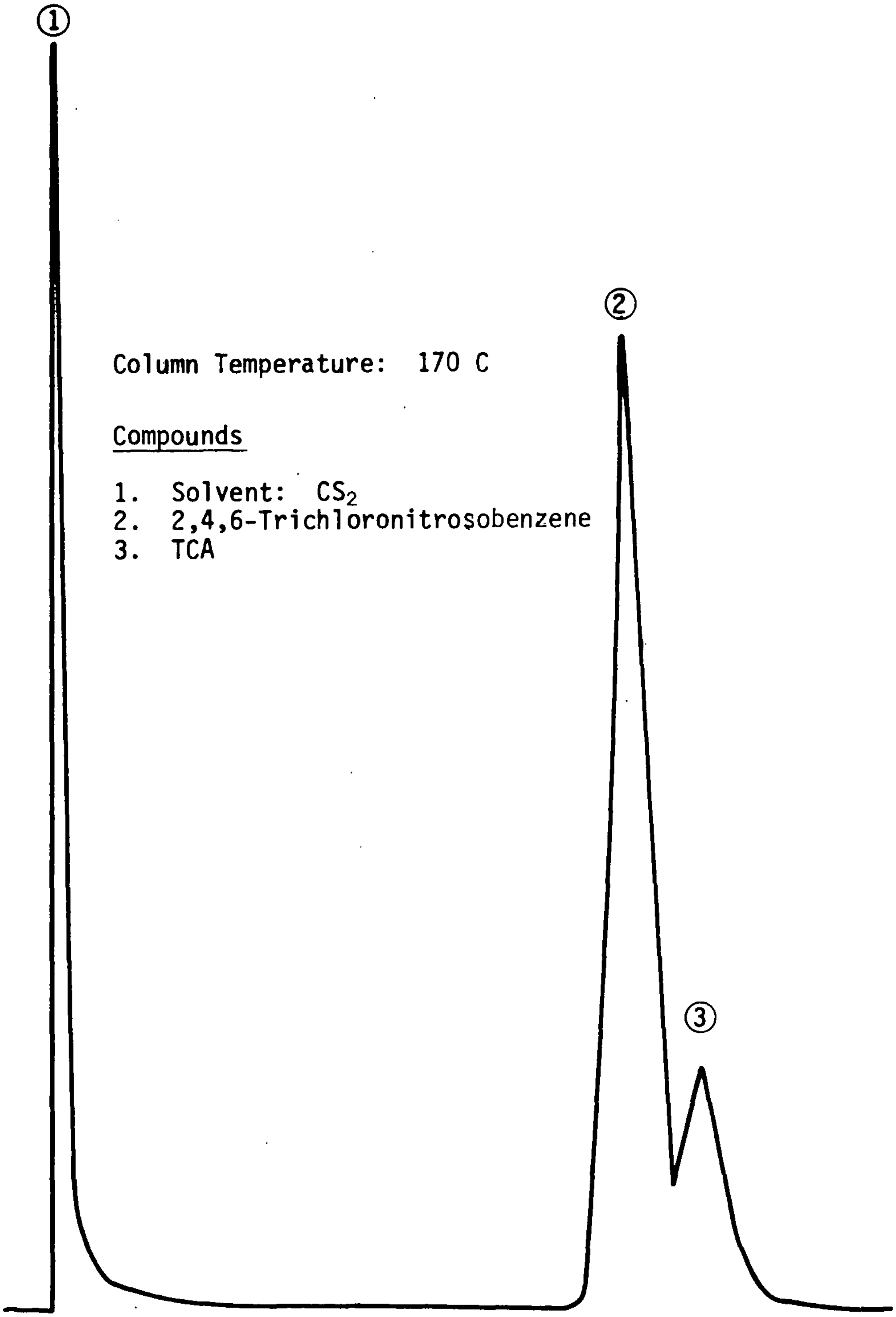


Fig. 8. Oxidation of TCA to Trichloronitrosobenzene After 1 Hour

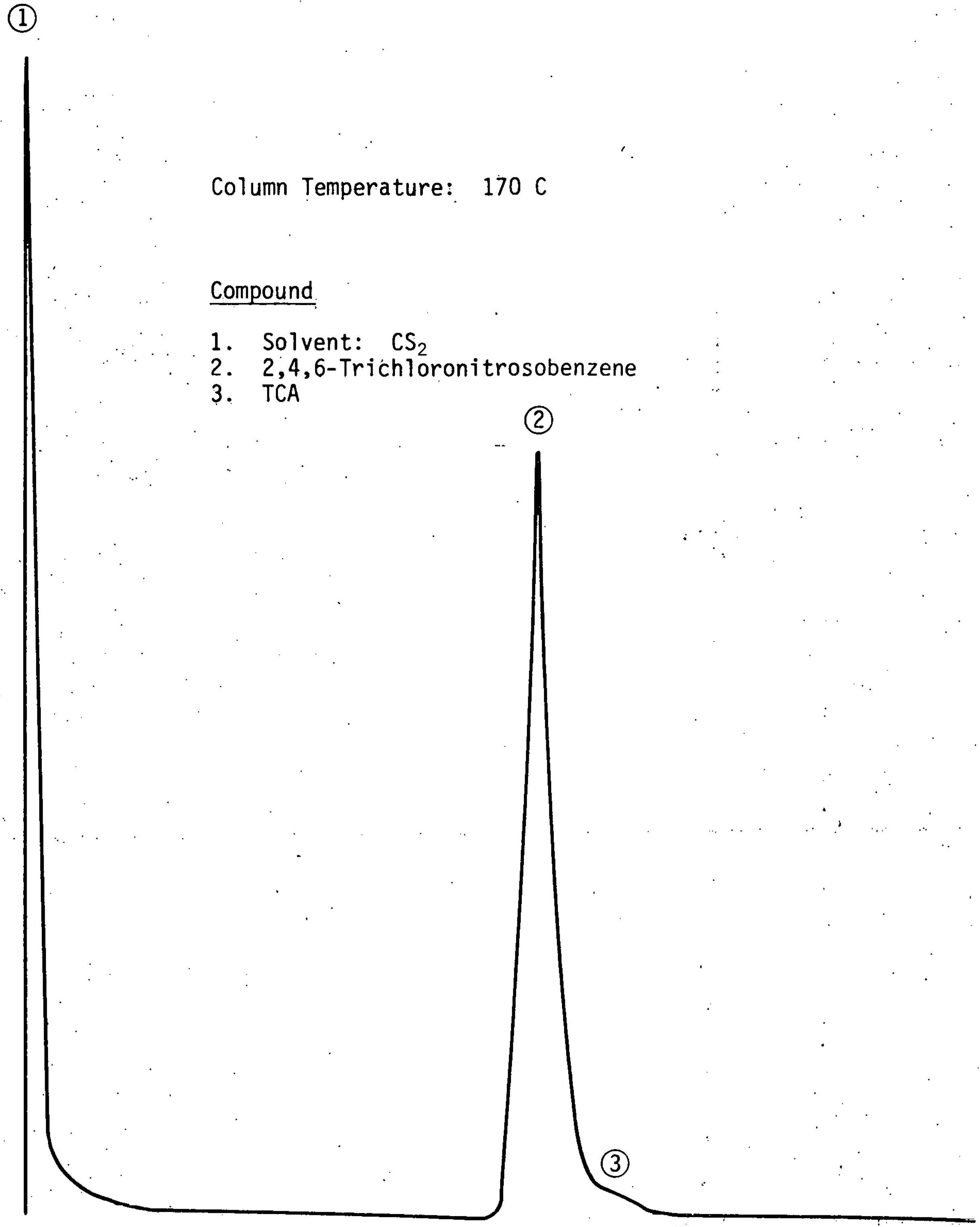


Column Temperature: 170 C

Compounds

1. Solvent: CS_2
2. 2,4,6-Trichloronitrosobenzene
3. TCA

Fig. 9. Oxidation of TCA to Trichloronitrosobenzene After 3 Hours

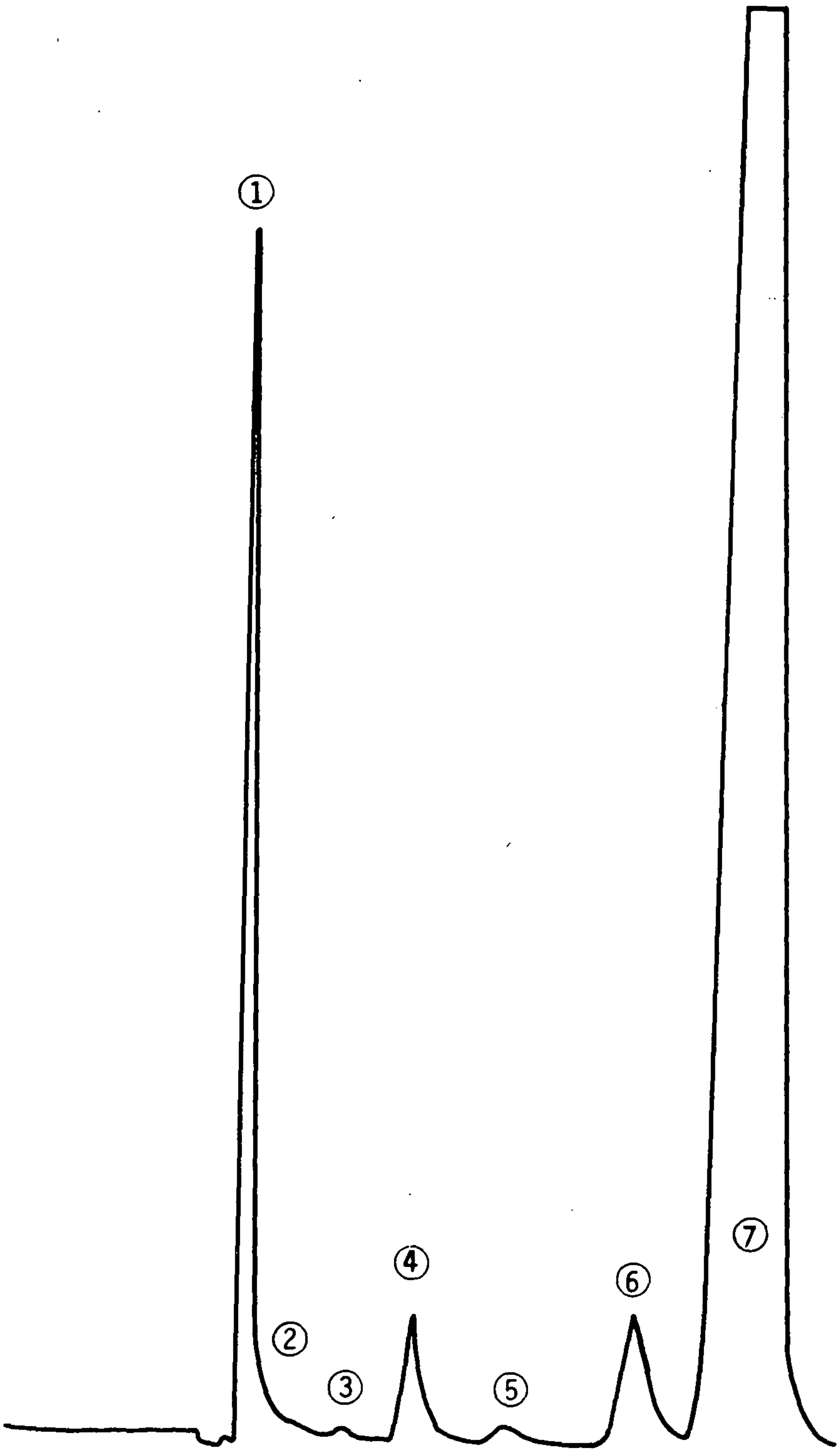


Column Temperature: 170 C

Compound

1. Solvent: CS_2
2. 2,4,6-Trichloronitrosobenzene
3. TCA

Fig. 10. Oxidation of TCA to Trichloronitrosobenzene After 22 Hours



Column Temperature: 170 C

Compound

1. Solvent: CS_2
2. Acetic Acid
3. Unknown
4. Unknown
5. Unknown
6. Trichloronitrosobenzene
7. TCNB

Fig. 11. Oxidation of Trichloronitrosobenzene to TCNB After 8 hours

REFERENCES

1. F. D. Chattaway and H. Irving, J. Chem. Soc., 1933, 142.
2. A. W. Hoffman, Ann., 53, 8, 29, 35.
3. E. Kleman, Bes., 55, 217.
4. W. D. Emmons, J.A.C.S., 1954.
5. L. F. Fieser and M. Fieser, Advanced Organic Chemistry, 1961, 160.
6. R. S. George and R. K. Rohwer, U.S. Patent 3,396,200, Preparation of 2,4,6-Trichloronitrosobenzene.
7. S. K. Yasuda, J. of Chrom., 76, 1973, 331.