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# ANALYSIS OF IMPURITIES IN COMPOSITION B BY THIN LAYER CHROMATOGRAPHY

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| TNT | Identification | Malfunction |
| RDX | Thin layer chromatography | M110E2-XM201 Cannon |
| Impurities | Ethylenediamine | m-nitrotoluene |

ALPHA

20. ABSTRACT (Continue on reverse side if necessary and identify by block number)


A thin layer chromatographic procedure was developed to identify α-TNT associated impurities in Composition B. The method involved reducing RDX and α-TNT levels in the solubilized Composition B sample before two-dimensional chromatographic developing. Impurities were identified after applying ethylenediamine reagent. Color development, fluorescence quenching, and $R_f$ values were compared to those established for a variety of impurities known to be R sub f


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20. ABSTRACT (Continued) ALPHA

present in Military Grade α-TNT. Six fragments from a Composition B warhead (which did not premature but was taken from the same lot as those suspected of premature functioning) and a control sample of Composition B obtained from the Holston Army Ammunition Plant were analyzed and compared. The analyses revealed the presence of m-nitrotoluene impurity in only the fragment samples suspected of premature initiation.

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## INTRODUCTION

An investigation was conducted to determine causes of malfunctions which took place during the test firing of a particular group of XM650 RAP rounds (ref. 1). The warheads initiated prematurely, one possible cause of which could be the presence of impurities in the Composition B warhead charges. The time available for identifying such impurities and determining their levels of concentration was limited to approximately five weeks. One approach was to analyze suspect samples of Composition B using thin layer chromatography (TLC) procedures and to confine the analysis to $\alpha$-TNT associated impurities. Work has appeared (ref. 2, 3, and 4) in which TLC procedures were used to identify impurities in production samples of $\alpha$-TNT. In the work reported here, RDX is a main constituent of the samples to be analyzed since the nominal formulation of Composition B is 60 parts RDX, 40 parts $\alpha$-TNT and 1 part wax. The presence of RDX and $\alpha$-TNT at such high levels interfered with the separation and visualization of the compounds to be identified. A method was developed to remove RDX and $\alpha$-TNT. An important aspect of this method involved dissolving RDX and $\alpha$-TNT in acetone and then displacing acetone with ethanol. This resulted in an alcoholic solution of impurities with RDX and $\alpha$-TNT levels greatly reduced.

Six samples of Composition B from fragments of a suspect warhead charge were received for analysis. A control sample of Composition B, from a lot manufactured at the Holston Army Ammunition Plant, was used for comparison.

## EXPERIMENTAL

### Apparatus and Reagents

Baker-Flex silica gel 1B-F (with fluorescence [illegible]ator) flexible sheets (20 x 20 cm; J. T. Baker Chemical Co.) were activated at $115 \pm 3$°C for at least 6 hours and kept in an oven at this temperature until needed.

Standard substances for identification purposes were practical grade. Other reagents and solvents were reagent grade except in later experiments where industrial grade absolute ethyl alcohol was used

The spray reagent was a 10 M ethylenediamine solution in dimethylsulfoxide, 65:35 by volume (ref. 5). A 100 µl Hamilton syringe was used to deliver 15 µl aliquots of preconcentrated solution of impurities to the TLC sheets.

A Perkin-Elmer 202 Ultraviolet-Visible Spectrophotometer was used to record visible spectra of the extracted impurities in absolute ethyl alcohol.

## Procedure

### Preconcentration of Impurities and RDX Removal

A sample of Composition B (5 to 7 gram piece) was crushed remotely into small granular pieces. A 300 mg portion of the sample was weighed into a 2 ml test tube and approximately 1.3 ml of acetone were added. The mixture was placed in a dibutylphthalate bath and the bath temperature was raised slowly to 60°C to prevent excessive loss of solvent. The sample was mixed frequently to completely dissolve it. More acetone was added as needed. The solution was then evaporated to apparent dryness. During the evaporation, the solid RDX which had accumulated on the inner wall of the test tube was scraped to the bottom of the test tube with a stirring rod to minimize the entrapment of impurities in the solid mass. The mixture was centrifuged for 3 to 4 minutes to separate the mother liquor (about 0.1 ml) from RDX. The mother liquor was decanted to a second 2-ml test tube. About 0.3 ml absolute ethanol was added drop-by-drop to the first test tube to wet the RDX and the combination was mixed thoroughly. This solution was centrifuged and decanted into the second test tube. Three alcohol washings were conducted. The combined solution of impurities (about 1 ml) was heated slowly to 78°C to prevent bumping and again evaporated to apparent dryness. The mixture was centrifuged and the concentrated alcohol solution (about 0.1 ml) was used to spot the TLC sheet.

### Preparation of Impurity Solution for Recording Visible Spectrum

After sampling for spotting the TLC sheet, the concentrated supernatant alcohol solution was used to record the visible spectrum. About 1 ml ethanol was added to the remaining supernatant solution and the combination was thoroughly mixed. The mixture was centrifuged and the supernatant solution carefully withdrawn with a dropping pipette and transferred to a 10 ml volumetric flask. The washing was repeated twice. To prevent scattering in the spectrophotometric recording, care was exercised to assure that no solid material was transferred. Additional alcohol was added as needed and the solution was then used to record the absorption spectrum in the visible region in a 1 cm silica cell.

## Separation Procedure

A 15 μl aliquot of the preconcentrated alcohol solution of impurities was placed at a spot on the lower left corner of the TLC sheet 3.3 cm from each edge. Care was taken to avoid sampling of solid residue into the syringe. The syringe was clamped on a stand and the needle tip adjusted to 1.5 mm above the TLC sheet for reproducing spotting without unnecessarily broadening the spot.

After the alcohol evaporated, the sheet was placed in the first chromatographic tank (24.2 cm H x 27.3 cm L x 7.4 cm W) which contained 100 ml benzene-cyclohexane-ethylacetate (50: 45: 5 by volume). To get a solvent vapor-saturated atmosphere, the solvent mixture was used to completely wet two solvent saturation pads,[1] each of which had been positioned against a narrow side of the tank. The pads were cut to the approximate dimensions of the tank sides. The tank atmosphere equilibrated for at least one hour. The sample was chromatographed for 55 ± 5 minutes at 23 ± 4°C by the ascending technique and the solvent front was allowed to travel to approximately 4 mm from the upper edge of the sheet. The sheet was removed from the tank and exposed to the atmosphere for about 15 minutes. The sheet was turned 90° to the direction of the previous development and chromatographed again in a tank (22.6 cm H x 22.0 cm L x 6.3 cm W) containing an equilibrated benzene-cyclohexane (75: 25 by volume) atmosphere. The sheet was removed when the sample had traveled to approximately 4 mm from the upper edge of the sheet (50 ± 5 minutes).

The separated impurities were located by spraying the TLC sheet with ethylenediamine reagent and viewing it under short wavelength ultraviolet illumination. Fluorescence quenching revealed colorless or faintly colored spots. The colored spots faded with time, especially in the presence of light so the developed colors were noted within 15 minutes of spraying. The rates of color development and fading varied considerably among the impurities.

[1]Gelman Instrument Company, Catalog Number 51334.

## RESULTS AND DISCUSSION

The preliminary experiments, using preconcentrated acetone solution of impurities in Composition B samples, established that RDX in the saturated acetone solution, 7.3 g RDX/100 g acetone at 20°C (ref. 6), caused extensive streaking and interfered with the separation and identification of various components. This problem was solved by displacing acetone with absolute ethanol, which reduced the RDX solubility by seventy fold, 0.105 g RDX/100 g ethanol at 20°C (ref. 6). This procedure removed 99.9 and 99 percent of the RDX and α-TNT, respectively, from the 300 mg sample of Composition B. The 1 percent wax in the Composition B did not interfere with the separation of the various components.

All six samples of suspected Composition B (SCB) and that of controlled Composition B (CCB) were analyzed by two-dimensional TLC to separate and tentatively identify the impurities. The CCB and SCB samples were separated into twelve and thirteen components respectively, the only difference being the presence in the SCB of a relatively non-polar component identified as m-nitrotoluene.

A typical chromatogram of the SCB samples is shown in figure 1. It should be emphasized that the identifications of the various components were based on the comparison of Rf values, colors developed by ethylenediamine reagent, and fluorescence quenching of standard substances (table 1) and unknowns (table 2). No further identifications were made. The identities of ten of the thirteen components in Composition B are listed in the last column of table 2.

The relative amounts of impurities in SCB and CCB samples could not be determined from the TLC results. However, as shown in figure 2, the SCB samples contained more colored impurities than samples of CCB. The concentrated alcohol solution of impurities absorbs intensely below 370 nm but absorbs weakly above 400 nm. The major difference between SCB and CCB samples is the slightly greater absorption of the SCB in the 400-510 nm region.

The TLC results pertain primarily to α-TNT impurities since the solvent systems used for chromatographic developments were originally intended for α-TNT analysis (ref. 4). Moreover, the limited time available for the present work did not permit further refinements of the procedures used or the development of procedures for analyzing RDX impurities in Composition B.

## CONCLUSIONS

An analytical method employing thin layer chromatography was developed to identify impurities associated with α-TNT in Composition B. It was essential that the RDX and α-TNT levels in the solution to be applied to the TLC plate be reduced using ethanol to displace the acetone initially used to dissolve the Composition B sample. 99.9 percent of the RDX and 99 percent of the α-TNT originally present in the Composition B sample were removed, leaving α-TNT associated impurities in the mother liquor. The procedure involved a two-dimensional development of mother liquor spotted on fluorescent silica gel plates. Impurities were identified after the plates were sprayed with 10 M ethylenediamine in dimethylsulfoxide. Color development, fluorescence quenching, and Rf values were compared to established values for twenty-one compounds known present in α-TNT as it is conventionally manufactured for military use. The analyses of Composition B samples revealed the presence of m-nitrotoluene impurity in the suspected samples but not in the controlled sample.

## RECOMMENDATIONS

Additional work in this area would relate to developing procedures by which RDX associated impurities could be identified, making it possible to conduct a complete qualitative and possibly semi-quantitative analysis of Composition B samples. Further work is also indicated to identify α-TNT associated impurities so that greater resolution of separation for the various compounds could be effected. The entire effort would be extensive and would involve choosing appropriate solvent systems and plate materials for chromatographic development and using the appropriate visualization agents to study the color forming reactions of aromatic nitramines.

## REFERENCES


1. "Preliminary Malfunction Investigation Report. M110E2-XM201 Cannon Firing XM650E4 HE RAP with XM188 Zone 9 Propelling Charge," (Fred Menke Chief Investigator, 1976).

2. C. D. Chandler, J. A. Kohlbeck and W. T. Bolleter, "Continuous TNT Process Studies, III. Thin layer Chromatographic Analysis of Oxidation Products from Nitration," J. Chromatog., 64, 123 (1972).

3. S. K. Yasuda, "Identification of Impurities in α-Trinitrotoluene by Thin-layer Chromatography," J. Chromatog., 13, 78 (1964).

4. J. A. Kohlbeck, C. D. Chandler, and W. T. Bolleter, "Application of Thin-layer Chromatography for Improving the Continuous TNT Process," J. Chromatog., 46, 173 (1970).

5. D. J. Glover and E. G. Kayser, "Quantitative Spectrophotometric Analysis of Polynitroaromatic Compounds by Reaction with Ethylenediamine," Anal. Chem., 40, 2055 (1968).

6. AMCP 706-177, "Engineering Design Handbook, Explosives Series, Properties of Explosives of Military Interest," Headquarters, U.S. Army Materiel Command, 22 March 1967, pp 72, 354-355.

Table 1

$R_f$ values and colors developed by ethylenediamine reagent of standard substances

Solvent: benzene-cyclohexane-ethyl acetate (50:45:5 by volume)
Concentration: 10 mg/ml or saturated solution in ethanol
Sample size for TLC: 15 µl

| No. | $R_f$ | Rel. $R_f$ Ref. α-TNT | Color | Substance[1] |
|---|---|---|---|---|
| 1 | 0.57-0.61 | 1.02-1.12 | Faint Pink-Violet | 3-MNT |
| 2 | 0.58-0.60 | 1.03-1.10 | Colorless | 2-MNT |
| 3 | 0.58-0.60 | 1.05-1.09 | Faint Orange-Pink | 4-MNT |
| 4 | 0.59 | 1.09 | Yellow | 2,5-DNT |
| 5 | 0.53-0.56 | 1.00 | Dark Reddish Brown | 2,4,6-TNT |
| 6 | 0.54 | 0.95-0.98 | Orange-Yellow | 1,4-DNB |
| 7 | 0.50-0.53 | 0.93-0.98 | Colorless | 2,6-DNT |
| 8 | 0.43-0.52 | 0.81-0.96 | Colorless | 3,5-DNT |
| 9 | 0.51 | 0.93 | Reddish Brown | 2,4,6-TNB |
| 10 | 0.44-0.49 | 0.82-0.91 | Pale Violet | 2,4-DNT |
| 11 | 0.43-0.48 | 0.81-0.86 | Light Orange-Yellow | 2,3,5-TNT |
| 12 | 0.44-0.47 | 0.83-0.87 | Orange | 2,3,6-TNT |
| 13 | 0.40-0.45 | 0.74-0.83 | Orange | 2,4,5-TNT |
| 14 | 0.45-0.47 | 0.82-0.84 | Colorless | 1,3-DNB |
| 15 | 0.34-0.42 | 0.64-0.77 | Yellow | 3,4-DNT |
| 16 | 0.34-0.41 | 0.64-0.75 | Yellow | 2,3-DNT |
| 17 | 0.30-0.37 | 0.55-0.65 | Pink | Hexanitrobibenzyl |

[1] MNT, DNT, and TNT designate mono-, di-, and trinitrotoluene, respectively. DNB and TNB designate dinitro- and trinitrobenzene, respectively.

Table 1 (Continued)

| No. | $R_f$ | Rel. $R_f$ Ref. α-TNT | Color | Substance |
|---|---|---|---|---|
| 18 | 0.33-0.36 | 0.59-0.65 | Orange-Yellow | 1,2-DNB |
| 19 | 0.30-0.32 | 0.57 | Reddish Orange | 2,4,6-Trinitrobenzaldehyde |
| 20 | 0.23-0.27 | 0.42-0.47 | Yellow (slightly orange) | 3,4,5-TNT |
| 21 | 0.21-0.24 | 0.39-0.43 | Yellow | 2,3,4-TNT |
| 22 | 0.065-0.087 | 0.12-0.16 | Brown | 2,4,6-Trinitrobenzoic acid |
| 23 | 0.039-0.055 | 0.071-0.10 | Colorless | RDX |

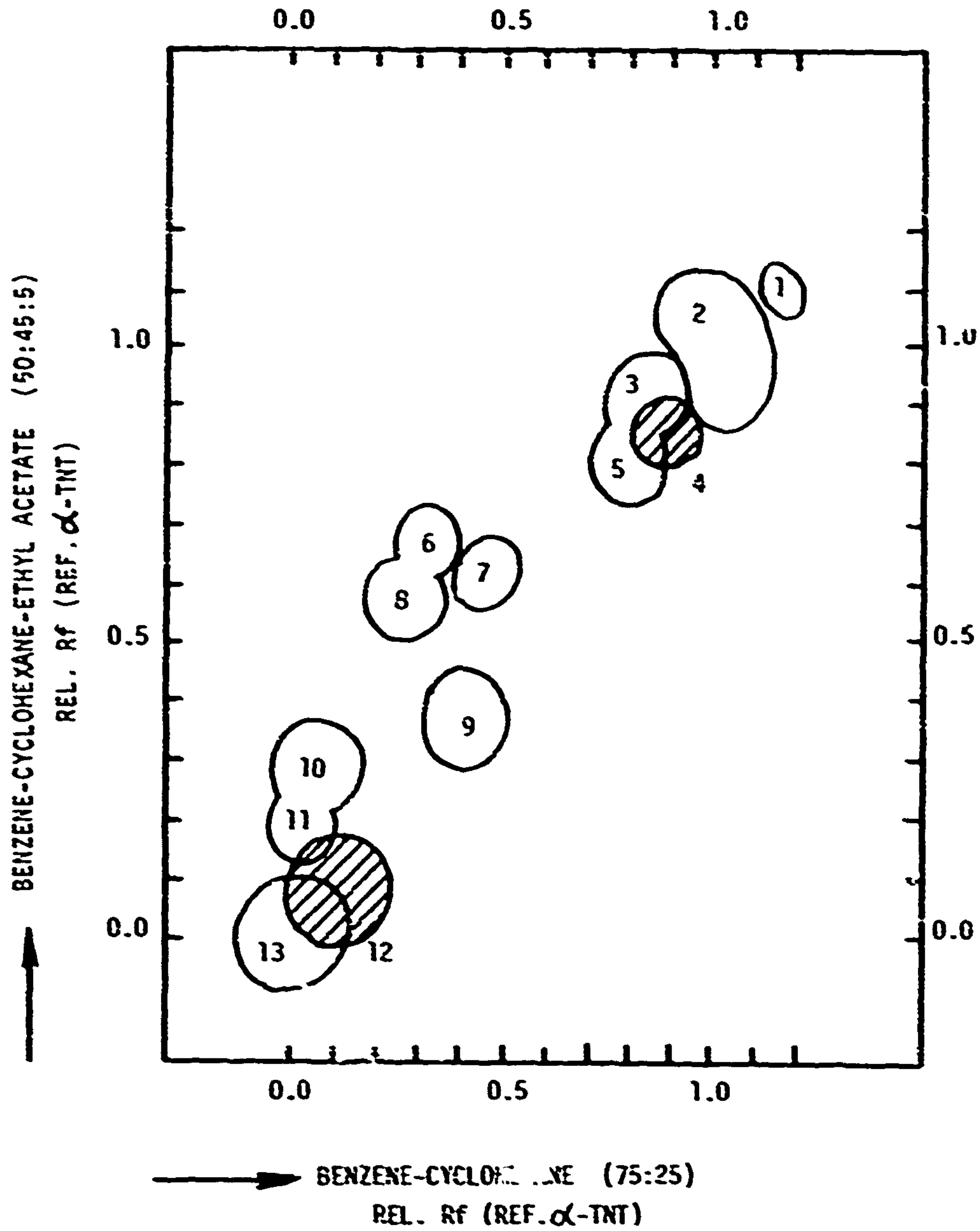
Table 2

$R_f$ values and colors developed by ethylenediamine reagent of components in Composition B

Solvents: benzene-cyclohexane-ethyl acetate (50:45:5 by volume)
Sample size for TLC: 15 µl

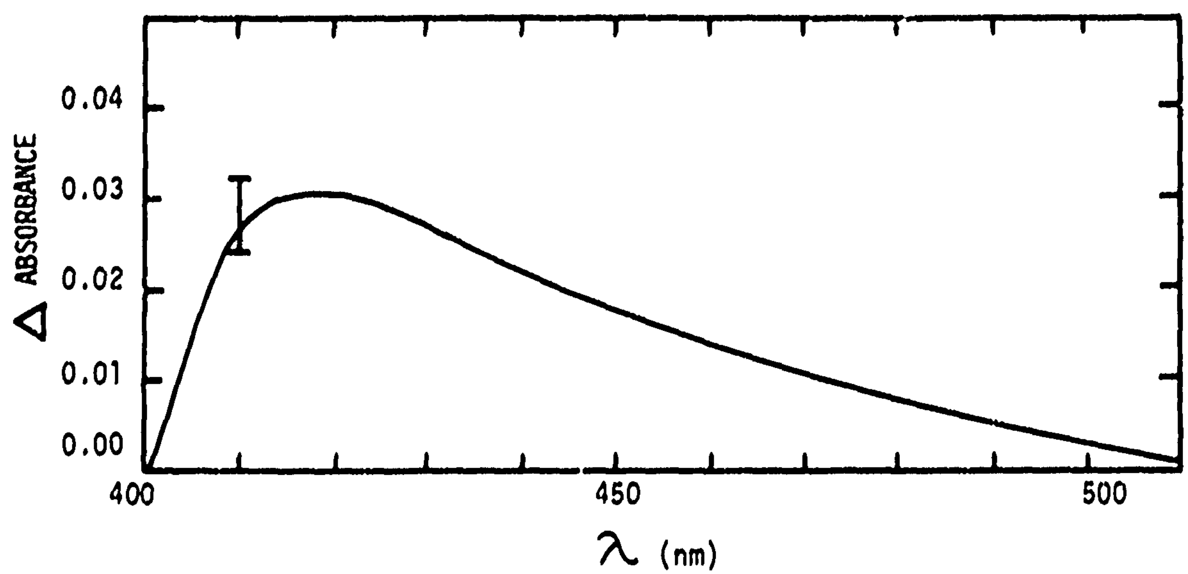
| No. | $R_f$ | Rel. $R_f$ Ref. α-TNT | Color | Identification |
|---|---|---|---|---|
| 1 | 0.58-0.64 | 1.10-1.14 | Violet | 3-MNT |
| 2 | 0.50-0.58 | 1.00 | Dark Reddish Brown | 2,4,6-TNT |
| 3 | 0.42-0.53 | 0.83-0.91 | Faint Violet | 2,4-DNT |
| 4 | 0.43-0.50 | 0.83-0.89 | Colorless | 3,5-DNT |
| 5 | 0.38-0.47 | 0.76-0.82 | Yellow (slightly orange) | 2,3,5-TNT alone; or 2,3,5-TNT mixed with either 2,4,5-TNT or 2,3,6-TNT or both[1] |
| 6 | 0.30-0.38 | 0.57-0.69 | Pink | Hexanitrobibenzyl |
| 7 | 0.28-0.36 | 0.53-0.61 | Faint Tan | 2,4,6-Trinitrobenzaldehyde |
| 8 | 0.23-0.33 | 0.43-0.58 | Purple | Unidentified |
| 9 | 0.16-0.22 | 0.31-0.40 | Yellow | 2,3,4-TNT |
| 10 | 0.11-0.16 | 0.19-0.28 | Tan | Unidentified |
| 11 | 0.067-0.11 | 0.12-0.19 | Tan | 2,4,6-Trinitrobenzoic acid |
| 12 | 0.032-0.050 | 0.058-0.095 | Colorless | RDX |
| 13 | 0.00 | 0.00 | Light Brown | Residue unidentified |

[1] This identification is uncertain. On the basis of the color developed, it appears to be 2,3,5-TNT or 2,3,5-TNT mixed with 2,3,6-TNT. On the basis of relative $R_f$ value, it appears to be 2,4,5-TNT.




Identification: see table 2
Sample: 300 mg "C" Seg. DP; 15 µl ethanol solution for spotting
Location of Components: by the color developed with
10 M ethylenediamine solution in dimethylsulfoxide (all except 4 and 12) and by fluorescence quenching (4 and 12)

Figure 1. Two dimensional separation of components in the concentrated mother liquor of a suspected Composition B sample




Samples: Suspected, 300 mg FC "D" segment
Controlled, 300 mg HOL 050-11

Figure 2. Differential visible absorption spectrum of Composition B samples (suspected - controlled) in ethanol

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