

IDENTIFICATION OF IMPURITIES IN α -TRINITROTOLUENE BY THIN-LAYER CHROMATOGRAPHY

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INTRODUCTION

2,4,6-Trinitrotoluene (α -TNT) is a common military explosive, prepared commercially by the three-stage nitration of toluene, and purified by the sellite process¹. The final product is relatively pure; however, various by-products do remain in the purified TNT to alter its physical properties. In this laboratory we have sought for a qualitative scheme to separate and identify the impurities present in production grade TNT.

A review of the literature reveals that very few, if any, identification methods for α -TNT impurities are reported. Although quantitative methods utilizing infrared² and gas chromatography³ are cited in the literature, application of these methods for identification work leaves something to be desired. Infrared lacks sensitivity unless some preliminary concentration step such as column chromatography is used⁴. Only the mono- and di-nitrotoluene isomers have been successfully separated and determined by gas chromatography. Paper chromatography, as reported by ETTTEL *et al.*⁵, can be used for separating some of the nitroaromatic compounds. With the advent of thin-layer chromatography (TLC) according to KIRCHNER^{6,7} and STAHL⁸, a simple, efficient method of separation has been presented. TLC is often effective for the separation of materials that cannot be resolved by other techniques.

This article describes a two-dimensional TLC method for the separation and identification of α -TNT impurities, including some oxidation-reduction products of decomposition as well as common production grade impurities. In addition, a unique detection method is described in which the reductor of the developing reagent is directly incorporated in the thin layer.

APPARATUS AND REAGENTS

Applicator, chromatoplar, silica gel G, and glass plates (200 × 200 mm), purchased from Brinkmann Instruments, Inc.

Zn metal dust, AR grade, from Mallinckrodt Chemical Works.

All solvents were reagent grade, and further purification was not necessary. Petroleum ether with a boiling range of 30–60° was used.

The spray reagent consisted of 0.25% *p*-diethylaminobenzaldehyde (*p*-DEAB), 0.25 N HCl in absolute ethanol. Concentrated HCl was used to prepare the reagent.

An Agla micrometer syringe was used to deliver aliquots of sample.

EXPERIMENTAL

Preparation of thin layer

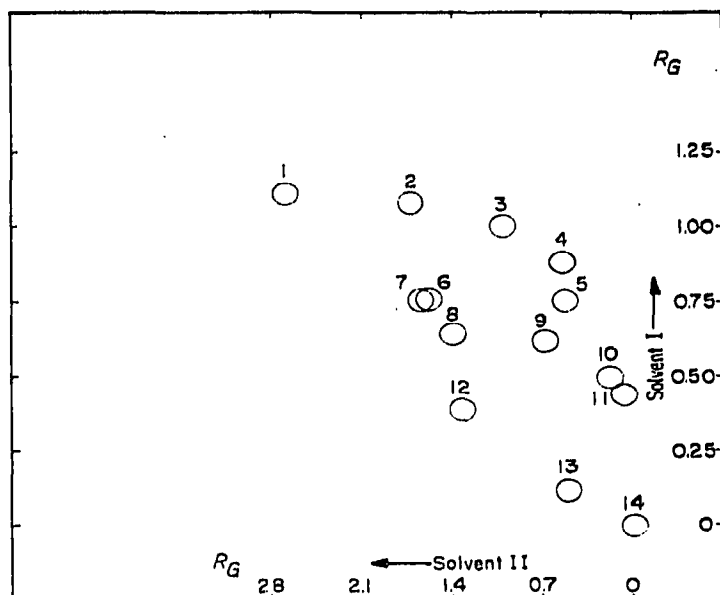
STAHL's procedure for preparation of thin layers was modified in order to incorporate zinc dust as reductor for the developing reagent. The proportions were 30 g of silica gel G and 3 g of zinc dust added to 65 cc of rapidly stirred distilled water. Glass plates (200 \times 200 mm) were coated by pulling the applicator at a constant speed with a Bodine speed reducer motor. Silica gel G/Zn plates were activated at 110° for 1–2 h before use.

R_G measurements

Approximately fifteen solvent systems were tested on activated silica gel G/Zn plates, using a three component mixture of nitro-, 2,4-dinitro-, and 2,4,6-trinitrotoluenes as the sample. Based on the separation efficiency, two solvent systems were selected: (1) a 15:85 ethyl acetate–petroleum ether mixture (solvent I), and (2) a 25:75 1,2-dichlorethane–petroleum ether mixture (solvent II). When more complex mixtures were studied, solvent I proved to be superior to solvent II. It also became evident that no single solvent or mixed solvent system could resolve all of the fourteen impurities sought; therefore, it was decided to utilize the two best solvents in a two-dimensional method to gain full advantage of each.

To evaluate the efficiency of the two selected solvent systems, R_G values were measured for each of the fourteen components, using α -TNT as the reference compound. Chromatographic conditions and the graphic plot of R_G values in solvents I and II are presented in Fig. 1.

Fig. 1. Graphic plot of R_G values. Chromatographic conditions: Silica gel G/Zn plate, $T = 25^\circ$. Reference compound: α -TNT. Length of chromatographing (a) Solvent I = 1.1 h (b) Solvent II = 1.0 h. Spray reagent: *p*-diethylaminobenzaldehyde. Compounds: (1) *m*-Nitrotoluene (MNT), (2) 2,5-Dinitrotoluene (2,5-DNT), (3) 2,4,6-Trinitrotoluene (α -TNT), (4) 1,3,5-Trinitrobenzene (TNB), (5) 4,6-Dinitroanthranil (4,6-DNA), (6) 3,5-Dinitrotoluene (3,5-DNT), (7) 2,6-Dinitrotoluene (2,6-DNT), (8) 2,4-Dinitrotoluene (2,4-DNT), (9) 2,4,5-Trinitrotoluene (γ -TNT), (10) 2,4,6-Trinitrobenzaldehyde (TNB_{al}), (11) 2,4,6-Trinitrobenzylalcohol (TNB_{OH}), (12) 3,4-Dinitrotoluene (3,4-DNT), (13) 2,3,4-Trinitrotoluene (β -TNT), (14) 2,4,6-Trinitrobenzoic acid (TNB_{acid}).

*Procedure*

An aliquot containing 0.5 to 1.0 mg of α -TNT in chloroform is placed about 1.5 in. from the lower right hand corner of an activated silica gel G/Zn plate. The diameter of the spot is kept at about 0.5 in. to minimize broadening of the spot as the sample is chromatographed. The plate is placed in a chromatobar containing 200 cc of solvent I.

Using an ascending technique, the sample is chromatographed for 1.1 h. The plate is exposed to the atmosphere for 3 min. Solvent I is replaced with an equal amount of solvent II, and the sample is rechromatographed at an angle of 90° to the direction of flow of solvent I for an additional hour. The separated impurities are located by spraying *p*-DEAB reagent on the plate. Yellow, brown and red spots develop immediately.

RESULTS AND DISCUSSION

From the graphic plot of R_G measurements, it can be seen that: (1) solvent I will partially or completely separate about nine of the fourteen components, (2) solvent II will tend to group the components according to the degree of nitration, and (3) the combined properties of both solvents will resolve twelve components.

To test the validity of the R_G data (Fig. 1) a synthetic sample containing isomers of nitro-, dinitro-, and trinitrotoluenes and several oxidation-reduction products of α -TNT was chromatographed by the described procedure. Fig. 2 shows the locations of

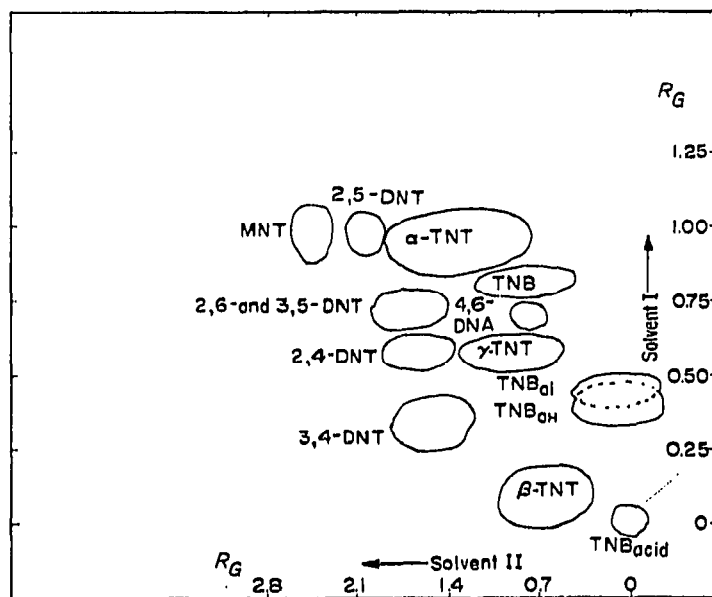


Fig. 2. Two-dimensional separation of TNT impurities.

developed spots on the two-dimensional TLC plate. Only the 2,6- and 3,5-DNT spots are not resolved, as predicted in Fig. 1. Partial separation of trinitrobenzyl alcohol and trinitrobenzaldehyde is obtained; however, the difference in color of the spots helps distinguish the two compounds. Both spot location and color provide evidence to be used to identify components.

Since it is unlikely that all fourteen impurities will be present together in TNT samples, several production grade TNT samples were examined by the TLC procedure. Table I lists the impurities found in different lots of TNT.

From Table I it can be seen that the common impurities found in α -TNT are dinitro- and trinitrotoluenes of which 2,4-DNT is the predominant impurity.

TABLE I
IMPURITIES IN PRODUCTION GRADE α -TNT

Sample	Impurities found
A	2,4-DNT, γ -TNT
B	2,4-DNT, γ -TNT
C	2,4-DNT, γ -TNT, β -TNT
D	2,4-DNT, 2,6- or 3,5-DNT, γ -TNT, β -TNT
E	2,4-DNT, 2,6- or 3,5-DNT, 2,5-DNT, γ -TNT

Zone refined α -TNT samples were also analyzed by this chromatographic procedure. Two samples were obtained: (1) the "purified" TNT, and (2) the red-brown zone of accumulated impurities. The latter sample was found to contain three additional impurities not observed in the original sample: traces of 2,5-DNT, trinitrobenzene, and an appreciable amount of an immobile impurity. The zone of "pure" TNT showed traces of 2,4-DNT, γ -TNT, and an immobile impurity.

In making a tentative identification of the immobile impurity it was noted that, although trinitrobenzoic acid (TNB-acid) does not migrate, the color and behavior of the immobile spot does not resemble that of TNB-acid. TNB-acid placed on a silica gel G/Zn plate apparently reacts with the zinc dust in the thin layer and becomes fixed in a concentrated spot.

The immobile impurity from the zone refined TNT sample was isolated from TLC plates in sufficient quantity to obtain an infrared spectrum. Very few characteristic bands could be identified; however, the very low intensity of the carbonyl band would suggest that TNB-acid was not a major component.

The possibility that the immobile impurity was α -nitroTNT was investigated. A solution of α -nitroTNT in toluene, of uncertain age and doubtful purity, was the only authentic sample available. Chromatography of the solution indicated two major components. One of the components was identified as trinitrobenzyl alcohol. The other component, an immobile material, was assumed to be α -nitroTNT. It was found that the infrared spectrum of the immobile component and the original immobile component of α -TNT were identical. It was, therefore, concluded that the immobile impurity observed in various TNT samples must be α -nitroTNT.

The possibility of generating additional impurities in TNT by heating near the melting point for 1 to 5 days, or during zone refining, was investigated. For this reason, some of the likely oxidation-reduction products of α -TNT were included in this work, e.g., trinitrobenzene, 4,6-dinitroanthranil, 2,4,6-trinitrobenzyl alcohol, 2,4,6-trinitrobenzaldehyde, and 2,4,6-trinitrobenzoic acid. It was found that two different grades of TNT showed no appreciable change; however, there may be a gradual increase in the component tentatively identified as α -nitroTNT.

The chemistry of the condensation reaction between nitroaromatics and *p*-DEAB was studied. It was found that one or more nitro groups are reduced to the amine, followed by the condensation of the amine with *p*-DEAB to form a Schiff's base. Although the position and/or number of the nitro groups involved in the reaction is not known conclusively, it is our belief that one nitro group is reduced and involved in the final condensation product. Supporting evidence is as follows: (1) C, H and N analyses of the condensation product with α -TNT extracted from TLC plates are very

close to being correct for a 1:1 ratio of α -TNT to *p*-DEAB; and, (2) direct condensation products formed between *m*- and *p*-nitroaniline and *p*-DEAB are yellow-orange and red, respectively, as are the products formed with 3,5- and 2,5-DNT on TLC plates.

The developing reagent, *p*-DEAB, is similar to the Ehrlich's reagent, *p*-dimethylaminobenzaldehyde (*p*-DMAB); however, with aromatic nitro compounds the nitro group must be reduced to the amine before condensation can occur. Stannous chloride is commonly used as the reductor with *p*-DMAB⁵. It has been our experience that zinc dust can be incorporated directly in the thin layer, giving an efficient, uniform reducing medium. Nitroaromatic compounds recovered from silica gel G/Zn plates without use of the spray reagent showed no change in physical properties as compared with the authentic sample.

The *p*-DEAB/zinc detection system is quite sensitive. One microgram of nitro-, dinitro- and trinitrotoluenes can readily be detected. Approximately 5 μ g of the oxidation-reduction products is required to obtain positive test.

Several authentic samples were synthesized for this work, since they were not available commercially or were too expensive to be purchased. The 2,5-DNT and α -TNT were isolated from nitration products. The trinitrobenzyl alcohol was obtained through the hydrolysis of its corresponding trinitrobenzyl bromide. The 4,6-DNA was prepared according to the procedure of SPLITTER AND CALVIN⁹. In all cases, melting point, infrared, and/or C, H and N data were used to confirm the identity of the product.

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SUMMARY

A two-dimensional thin-layer chromatography method, capable of separating and identifying the impurities in α -trinitrotoluene (α -TNT), is described. A unique developing method is used in which a zinc reductor is incorporated directly in the thin layer. *p*-Diethylaminobenzaldehyde is condensed with the reduced product to obtain the color-developed spot. The impurities commonly occurring in TNT are readily identified by means of this procedure and are found to be the dinitro- and trinitrotoluenes. In addition, an unexpected impurity, α -nitroTNT, was found in one sample of TNT.

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