

CHROM. 4481

APPLICATION OF THIN-LAYER CHROMATOGRAPHY FOR IMPROVING THE CONTINUOUS TNT PROCESS

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(Received October 23rd, 1969)

SUMMARY

Thin-layer chromatographic separations were performed on TNT samples removed throughout the process in order to study and improve the continuous TNT process. Nitrator samples were chromatographed to examine the effects of changes in nitrating conditions on reaction products. Separation of the product TNT showed that two impurities were formed during the purification, and TLC was used to relate the amounts of these impurities produced under different operating conditions and thus to establish which conditions were required to eliminate their formation.

INTRODUCTION

The use of thin-layer chromatography (TLC) for the analysis of TNT has been reported by YASUDA¹. In his paper, YASUDA describes the separation techniques and results of the analysis of purified TNT obtained using the three-stage nitration (batch) process. Recently, a continuous-process TNT plant was constructed at the Radford Army Ammunition Plant (RAAP). In this continuous process², toluene is fed to the first nitrator and concentrated nitrating acids to the higher nitrators. The organic phase proceeds through the process in which the toluene is successively nitrated to mono-, di-, and trinitrotoluene. The acid flows countercurrent to the nitrotoluenes and becomes weaker as a result of nitration. Thus, the rate of nitration in the lower nitrators is controlled by using progressively weaker acids.

The impure TNT from the last nitrator is washed with water to remove entrained acids and then is treated with sodium sulfite (Sellite), a process called Selliting, in two successive washers to remove the asymmetrical β - and γ -isomers. The process was originally designed to carry out Selliting at a pH of about 8.5, using soda ash for pH adjustment and control. After the Sellite treatment, the purified TNT is again washed with water and then dried and flaked.

When the continuous plant at RAAP was begun, TLC techniques were investigated to aid studies on process and product control and to increase understanding of the reactions occurring at each step in the process. TLC analyses were performed on samples taken at various stages of nitration and purification. The separation tech-

niques used were considerably different from those previously reported. The support used in the present study was silica gel with a starch binder; it was easily prepared and had an excellent adhesion to glass plates. The spray reagent found most suitable for visualizing the TLC fractions was ethylenediamine. This reagent has also been used for the spectrophotometric determination of polynitroaromatic compounds³.

MATERIALS AND METHODS

Apparatus and reagents

Silica gel with a starch binder and a fluorescent indicator was purchased from Brinkmann Instruments, Inc.; applicator and glass plates (200 × 200 mm) were purchased from Kensington Scientific Co. All solvents were reagent grade, and no further purification was necessary; ethylenediamine was reagent grade. A 25- μ l syringe was used to deliver aliquots of the sample to the support.

Experimental

Preparation of thin-layer plates. Thirty grams of support were added to 75 ml of warm water which was constantly agitated. The water temperature was then raised to near boiling to assure that the starch binder was well mixed. A 275- μ gate was used to control plate thickness, and the plates were oven dried at 110° for 2 h before use.

Separation procedure. Best separation results on finished TNT and nitrator samples were obtained with a benzene-cyclohexane-ethyl acetate mixture (50:45:5). A more polar solvent system of benzene-ether-ethanol (50:30:20) was used to separate oxidation products from the nitrator vessels. A few drops of ammonium hydroxide were added to the latter solvent system to prevent tailing.

No single solvent system was found which could separate all nitration products in one separation. However, a two-dimensional separation using benzene-cyclohexane (75:25) as a second solvent at 90° after an initial development with benzene-cyclohexane-ethyl acetate (50:45:5) gave satisfactory results. A two-dimensional separation of an extremely impure TNT sample is shown in Fig. 1.

Nitration studies. Sampling and sample preparation. Approximately 1 ml of the organic phase was pipetted from the nitration separator vessels into a preweighed 25-ml volumetric flask containing 3-5 ml of water. The flask was reweighed, and the sample was diluted to volume with acetone. A 15- μ l aliquot of the sample was placed about 1.5 in. from the bottom of the plate. If a two-dimensional separation was to be made, the aliquot was placed in the lower left-hand corner. Care was taken to prevent broadening of the aliquot spot. Development was made in a saturated chromatographic tank containing 100 ml of the solvent system. Approximately 1.5 h were required for the front to travel 15 cm.

The developed chromatogram was viewed first using short-wavelength UV light to determine if the separation was adequate. The plate was next sprayed with ethylenediamine; and red, brown, yellow and blue spots developed showing the locations of the various fractions.

Purification. Sampling and sample preparation. A clean metal rod was used to remove TNT at various purification stages. The metal rod was dipped into the decanter vessels and, upon withdrawal, the TNT solidified and was removed from the rod. One

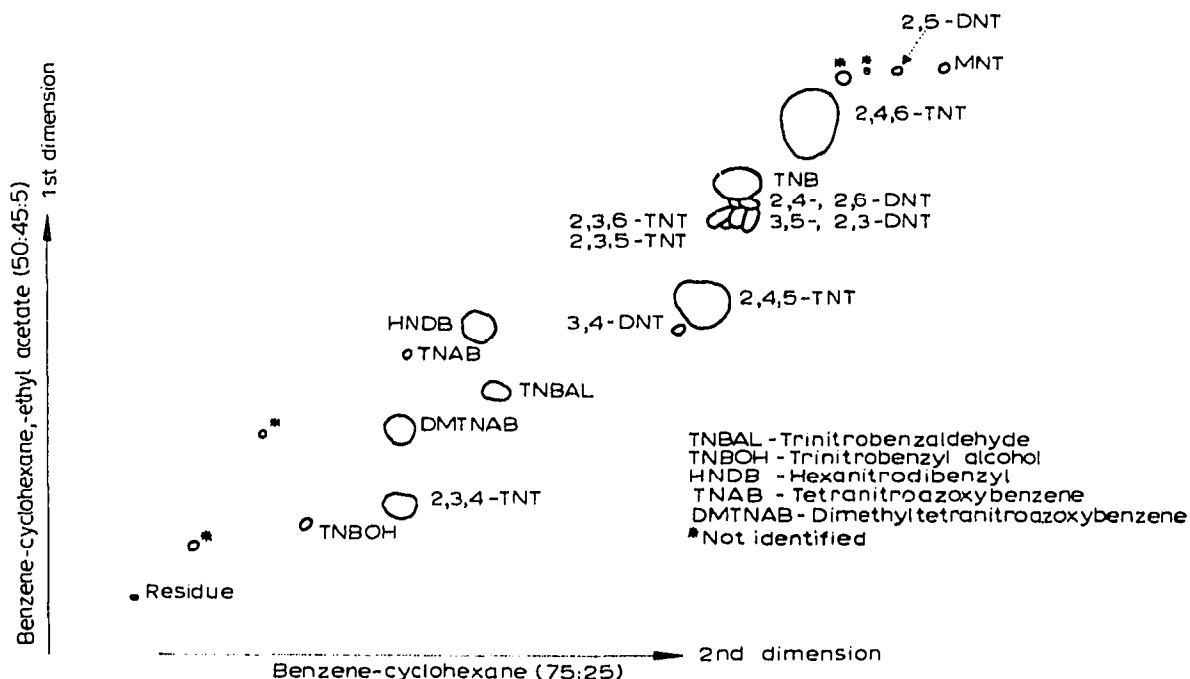


Fig. 1. A two-dimensional separation of an impure TNT sample.

gram of the solidified TNT was placed in a 25-ml volumetric flask, dissolved in acetone and diluted to volume.

Investigation of Sellite variables. The process variables, pH and solution density were studied in a complete 2^n factorial experiment to relate these variables to complete isomer removal and by-product formation. The effects of the different pH and density levels were determined by TLC analyses of TNT samples taken during the investigation.

RESULTS AND DISCUSSION

Nitrator studies

Samples from all nitrators were analyzed by TLC to identify the various nitration and oxidation products formed and to determine the nature of the reactions occurring at each step of the process.

Nitration products. The progression of nitration through mono-, di-, and tri-stages can be seen in Fig. 2. The mononitrotoluenes from separators 1 and 2 were not separated into *ortho*-, *meta*-, and *para*-isomers under the conditions used. All the other major nitration products were identified, as well as some of the minor fractions. The small amounts of TNT in nitrators 1 and 2 result from the addition of the acidic wash water from the purification to nitrator 2. This is done both to recover the TNT in the wash water and to dilute further the nitrating acids in these nitrators to control the rate of nitration.

The predominant fractions in nitrator 1 are the mononitrotoluenes, while nitrators 2 and 3 contain large quantities of 2,6- and 2,4-DNT. The DNT decreases as nitration continues through nitrators 4 and 5 and usually cannot be seen by TLC at nitrator 6. Corresponding to the decrease in DNT, the 2,4,6-TNT increases as do the 2,3,4 (β -) and 2,4,5 (γ -) isomers of TNT. In nitrator 6, the major fraction is

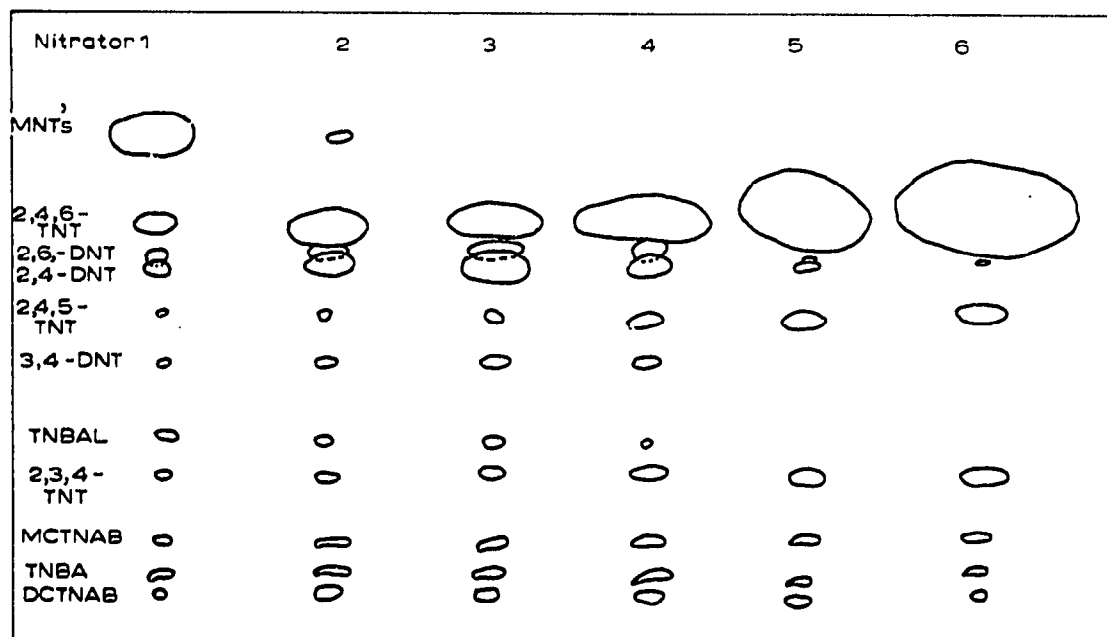


Fig. 2. A separation of the products in the organic phase of nitration.

2,4,6-TNT and about 3.5 % of the β - and γ - isomers. The DNT content is generally less than 0.2 %.

Oxidation products. The second part of the nitration study was designed to identify the type and quantity of oxidation products produced in nitration. Fig. 2 also shows a separation of the oxidation products present in the organic phase. The major oxidation products were found to be 2,2'-dicarboxy-3,3',5,5'-tetranitroazoxy benzene (DCTNAB) known as "white compound", a monocarboxy tetranitroazoxy benzene (MCTNAB), and trinitrobenzoic acid (TNBA). These fractions were identified from their IR spectra and R_F values on thin-layer plates. Quantitative methods have been developed for these fractions and will be described in a later paper. Several minor oxidation products were also separated and are believed to be nitrocresols⁴⁻⁷.

Purification studies

As indicated above, the crude TNT entering the purification process is primarily 2,4,6-TNT with small amounts of the β - and γ -TNT isomers and lesser amounts of DNT. Some TNBA and DCTNAB are also present in the crude TNT. The amount of these oxidation products varies with nitrating conditions. In the first step of purification (water wash), TNBA readily decarboxylates to trinitrobenzene (TNB) which remains with the TNT throughout purification.

Removal of the β - and γ -isomers of TNT is accomplished by treating the water-washed TNT with an aqueous solution of sodium sulfite. Separation of samples following Selliting showed that two products were formed as the β - and γ -isomers were removed. These products are not normally found in TNT manufactured by the batch process. The presence of these new products was undesirable, since they lowered the freezing point of the product TNT, and occasionally they were produced in sufficient amounts to cause the TNT to be rejected. Therefore, it was necessary to identify these products in an effort to reduce or eliminate their formation. Using IR and

NMR analysis of these products from TLC separations, one was identified as hexanitrodibenzyl (HNDB). The second has not yet been positively identified but is believed to be 2,2'-dimethyl-3,3',5,5'-tetranitroazoxy benzene (DMTNAB). The formation of at least one of these compounds, HNDB, would be expected to be pH dependent; therefore, the pH was considered to be an important variable in the Selliting process.

Although a quantitative method was neither developed for HNDB nor for DMTNAB, TLC was an excellent and rapid semi-quantitative analytical method. Best estimates from standards on thin-layer plates showed that HNDB was present at 0.5 % or higher in TNT initially produced at RAAP. No measurements were made for DMTNAB.

The experiment designed was carried out on one of the operating TNT lines on four successive days with two levels of operational conditions being run each day (one in the morning and one in the afternoon). Fig. 3 shows a separation of samples of equal weight obtained under the two extreme experimental conditions in the study. It can be readily seen that at low levels, little HNDB and DMTNAB were produced. There was also a corresponding increase in the freezing point of the product TNT made

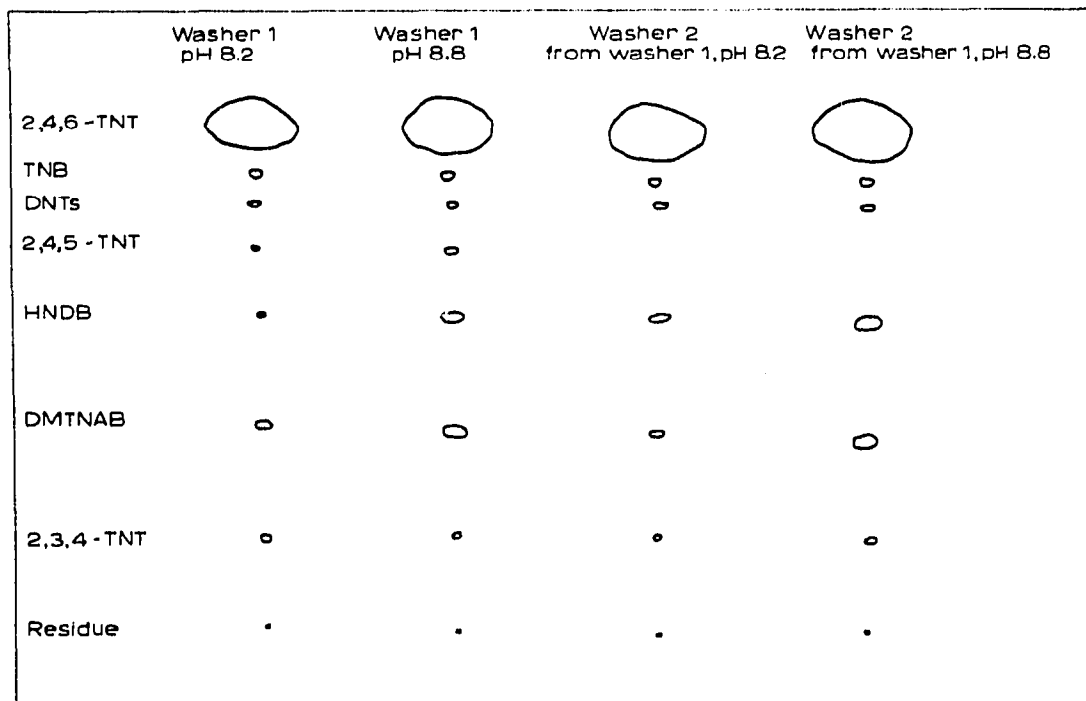


Fig. 3. A separation of samples under extreme conditions in the Selliting study.

under these conditions. The effect of the density of Sellite (concentration) over the range investigated was small. Therefore, pH was the primary parameter of the process affecting formation of HNDB and DMTNAB.

Since lowering the pH from 8.8 to 8.2 considerably reduced the amount of HNDB and DMTNAB, lowering the pH even further should eliminate their formation. However, attempts to do this on an operating line led to incomplete separation of the TNT and the aqueous phases which resulted in improper operation of Sellite

washers and separators. The cause of this poor separation was attributed to the release of CO_2 from the soda ash used for pH control as the pH in washer 1 was allowed to go below about 8.0.

Sellite studies in the laboratory

In an effort to overcome some of the problems encountered with the soda ash-Sellite system, a study of Selliting was begun in the laboratory. A sodium *meta*-bisulfite-Selite mixture was used to determine the effects of Selliting at pH 5. Although no HNDB or DMTNAB were produced under these conditions, removal of the isomers was not adequate for production of high quality TNT. Therefore, Selliting at higher pH values was tried.

The use of soda ash with *meta*-bisulfite to maintain a pH of 7 was attempted. Under these conditions, some HNDB and DMTNAB were formed and gassing occurred. Thus, this system could not be used. The purification system which held the most promise of success was a Sellite-*meta*-bisulfite mixture at near neutral pH. In laboratory studies, this system worked extremely well, with good isomer removal and no HNDB or DMTNAB formation. Separations for the conditions described above are shown in Fig. 4.

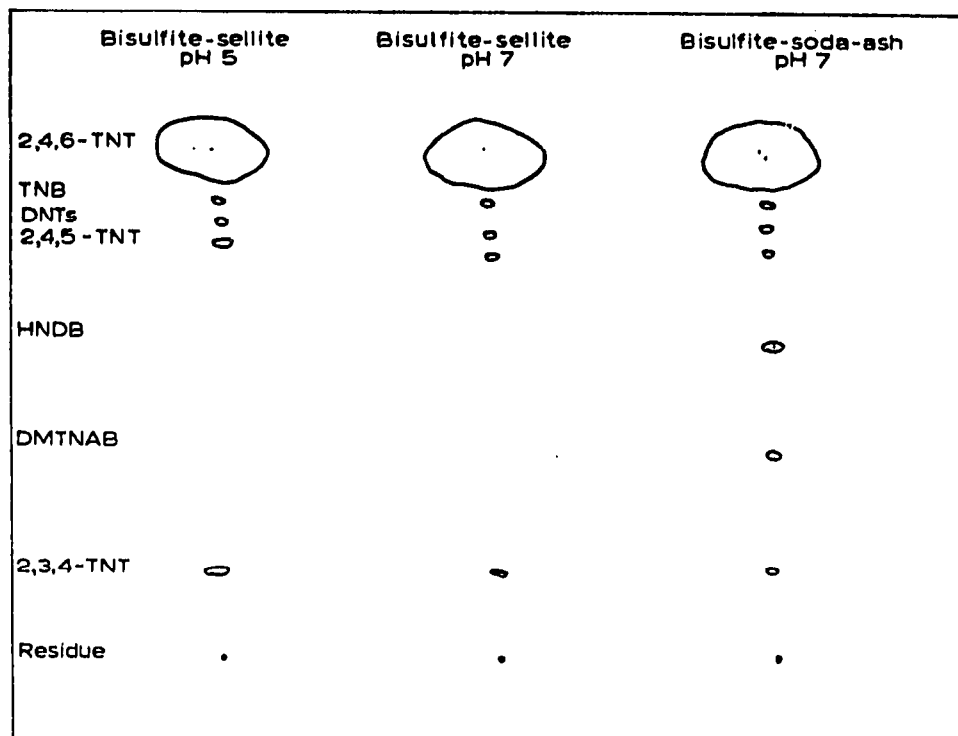


Fig. 4. A separation of samples under laboratory conditions in the Selliting study.

*Sellite-*meta*-bisulfite studies*

Following the successful demonstration of the Sellite-*meta*-bisulfite system in the laboratory, an evaluation of the system was made on one of the operating lines. A solution of Sellite, rather than soda ash, was fed to the first Sellite washer to control the pH. By using Sellite, the pH of the washer could be controlled over the range of 6.5 to 9.0 with proper physical operation of the washer and separator. A solution of

Sellite only, or a mixture of Sellite and *meta*-bisulfite, was fed to Sellite washer 2 and, in turn, to washer 1. In this manner, the pH of washer 2 could be controlled at any level between 7 and 9, the range to be investigated. It was found that controlling the pH of washer 1 at about 7.5 and washer 2 at about 8.0 was optimum in terms of completeness of removal of β - and γ -isomers and minimization of the formation of HNDB and DMTNAB.

By using only a solution of Sellite in washer 2, the pH of this washer was consistently maintained at 9.0. Under these conditions and controlling washer 1 at pH 7.5 with Sellite, isomer removal was essentially complete and only a small amount of HNDB (< 0.20 %) and DMTNAB were produced. Thus, with the aid of TLC techniques, a marked improvement was made in both purification operations and quality of product TNT as a result of eliminating the use of soda ash and lowering the pH at which Selliting occurred.

REFERENCES

- 1 S. K. YASUDA, *J. Chromatog.*, 13 (1964) 78.
- 2 H. C. PRIME, *Chem. Eng.*, 71 (1964) 126.
- 3 D. J. GLOVER AND E. G. KAYSER, *Anal. Chem.*, 40 (1968) 2055.
- 4 V. DADÁK, J. SEITL AND K. ŠMEJKAL, *Chem. Průmysl*, 12 (1962) 69.
- 5 V. DADÁK AND J. SEITL, *Chem. Průmysl*, 12 (1962) 352.
- 6 V. DADÁK, K. ŠMEJKAL AND E. BALÁŠOVÁ, *Chem. Průmysl*, 13 (1963) 241.
- 7 V. DADÁK, E. HROMADKOVÁ AND K. ŠMEJKAL, *Chem. Průmysl*, 13 (1963) 629.

J. Chromatog., 46 (1970) 173-179