

IDENTIFICATION OF N-NITROSO- AND NITRODIPHENYLAMINES  
BY TWO-DIMENSIONAL THIN-LAYER CHROMATOGRAPHY\*

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## INTRODUCTION

Diphenylamine (DPA) has been used extensively as a stabilizer in nitrocellulose (NC) containing explosives and propellants. Its primary function is to react with the oxides of nitrogen formed by the slow decomposition of the NC, thereby being converted into the corresponding N-nitroso- and nitro- derivatives.

The complexity of diphenylamine products is well known<sup>1</sup>, and very few identification methods are reported in the literature. HANSSON AND ALM<sup>2</sup> describe a one-dimensional thin layer chromatographic (TLC) method for the identification of eight derivatives of diphenylamine; however, several important derivatives, *e.g.*, N-nitrosodinitro- and trinitrodiphenylamine, are not included in the study. This is understandable, since authentic DPA derivative samples are difficult to obtain.

The excellent work of SCHROEDER *et al.*<sup>3</sup> utilized column chromatography to identify and estimate N-nitroso- and nitrodiphenylamine products in smokeless powder; however, the efficiency of separation and method of locating the products proved unsatisfactory for our use. Other quantitative methods were not applicable for identification work, and were eliminated from further consideration.

This article presents a two-dimensional TLC method to separate and identify nineteen N-nitroso- and nitrodiphenylamines. A spray reagent capable of detecting a 0.5 to 1  $\mu$ g quantity of each product is described. Samples of PBX-9404, a plastic bonded explosive, and reaction products of DPA and 2-nitrodiphenylamine with nitrogen tetroxide were examined by the method developed.

## REAGENTS AND EQUIPMENT

Applicator, chromatjar, silica gel G, and glass plates (200  $\times$  200 mm), purchased from Brinkmann Instruments, Inc.

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

All solvents were reagent grade. Petroleum ether from Merck and Co., Inc., with a boiling range of 30–60° was used.

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

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An Agla micrometer syringe or capillary melting point tube was used as an applicator.

#### EXPERIMENTAL

##### *Preparation of thin layer*

Modification of STAHL's technique for thin layer preparation was necessary to incorporate zinc dust directly into the silica gel G, a procedure previously described<sup>4</sup>. A slurry mixture of 30 g of silica gel G and 3 g of zinc dust in 65 ml of rapidly stirred water was prepared. Coating was accomplished by pulling the applicator with a Bodine speed reductor motor at a constant speed over five glass plates. The silica gel G/Zn plates were activated at 110° for 1 to 2 before use.

##### *R<sub>G</sub> measurements*

Since nineteen N-nitroso- and nitrodiphenylamines were included in this work, it was apparent that complete separation could not be accomplished by a one-dimensional technique; therefore, solvents were screened, using a simple DPA-derivative mixture as the sample on activated silica gel G/Zn plates. Based upon separation efficiency, several solvents were selected and tested with more complex mixtures. The two most promising solvents were, (1) 2:99:99 acetone-benzene-petroleum ether (solvent I), and (2) 20:80 ethyl acetate-petroleum ether (solvent II). Each authentic sample of N-nitroso- and nitrodiphenylamine was tested in solvents I and II. The measured *R<sub>G</sub>* values are plotted graphically in Fig. 1, using DPA as the reference compound.

##### *Procedure*

Finely powdered explosives samples, e.g., PBX-9404 (HMX/NC/tris(2-chloroethyl)-phosphate/DPA), were extracted for 2 h at room temperature, using 25 ml of methylene chloride per 0.4 g of sample. Use of a wrist-action shaker is suggested. The solvent was decanted and filtered, an additional 25 ml of solvent was added, and the extraction repeated for 1.5 h. The combined extract was placed under mild vacuum to strip off the solvent. About 0.2 ml of acetone was used to dissolve the residue.

Samples of the DPA/N<sub>2</sub>O<sub>4</sub> and 2-nitroDPA/N<sub>2</sub>O<sub>4</sub> reaction products were dissolved directly in acetone.

The acetone solution, containing about 100-400 mg of DPA derivatives, was transferred to a point approximately 1.5 in. from the lower right-hand corner of an activated silica gel G/Zn plate. Transfer was accomplished by using an Agla micrometer syringe or melting point capillary. The diameter of the applied spot was kept at or below 0.5 in.

The plate was chromatographed in 200-250 ml of solvent I for 1 h, exposed to the atmosphere for several minutes to evaporate the solvent, and rechromatographed at 90° to the original solvent flow direction in an equal volume of solvent II for an additional hour.

The separated N-nitroso- and nitrodiphenylamine products were located by spraying the plate uniformly with *p*-DEAB reagent. The plate was heated with a hair dryer, particularly in the DPA/2-nitroDPA region, to intensify the colored spots.

#### RESULTS AND DISCUSSION

Fig. 1 indicates that nineteen of the twenty N-nitroso- and nitrodiphenylamines

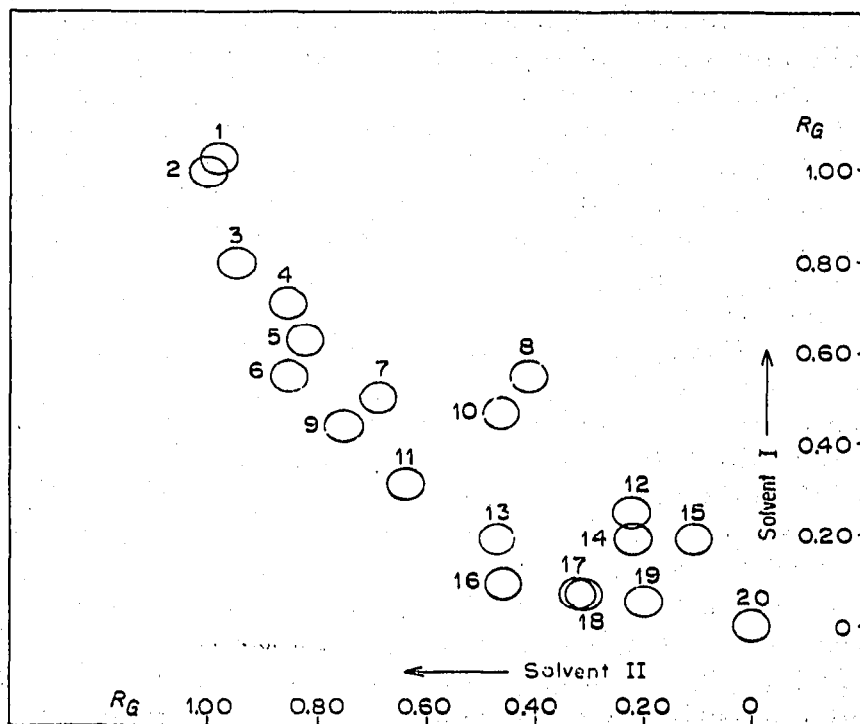


Fig. 1.  $R_G$  measurements of N-nitroso- and nitrodiphenylamines. (1) 2-nitroDPA; (2) DPA; (3) N-nitrosoDPA; (4) N-nitroso-4-nitroDPA; (5) 2,4-dinitroDPA; (6) 2,4,6-trinitroDPA; (7) 2,4'-dinitroDPA; (8) 2,2'-dinitroDPA; (9) N-nitroso-4,4'-dinitroDPA; (10) N-nitroso-2-nitroDPA; (11) 4-nitroDPA; (12) N-nitroso-2,4'-dinitroDPA; (13) 2,4,4'-trinitroDPA; (14) 2,2',4-trinitroDPA; (15) N-nitroso-2,2'-dinitroDPA; (16) 4-nitrosoDPA; (17) 2,2',4,4'-tetranitroDPA; (18) 2,2',4,4',6-pentanitroDPA; (19) 4,4'-dinitroDPA; (20) 2,2',4,4',6,6'-hexanitroDPA.

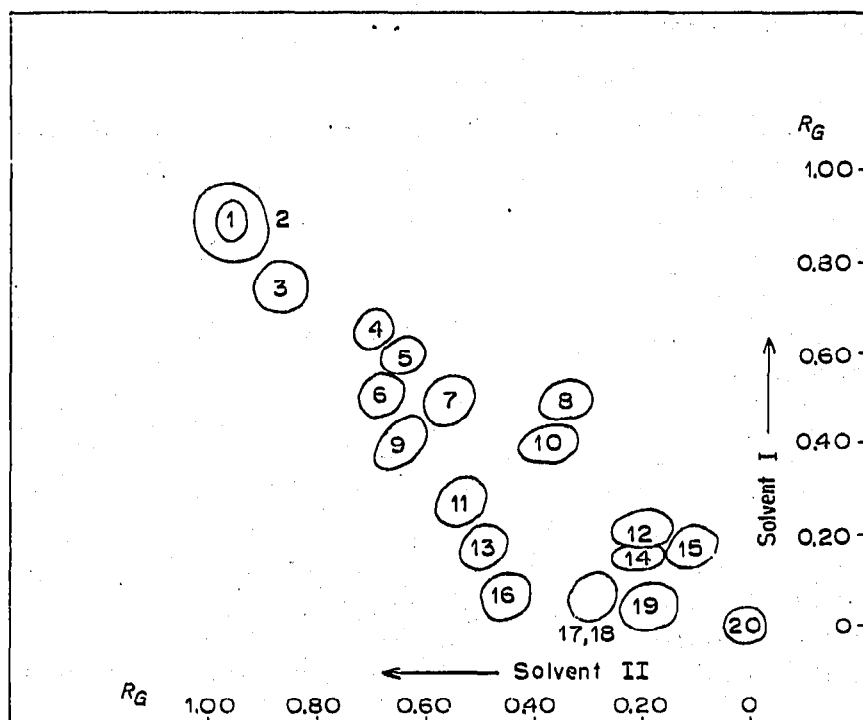


Fig. 2. Two-dimensional separation of synthetic mixture of diphenylamine derivatives.

could be partially or completely separated for identification. Only the tetranitro- and pentanitrodiphenylamines are not separable. Attempts to resolve these spots caused poor separation of the other diphenylamines.

To verify the  $R_G$  measurements, a synthetic mixture of twenty components was chromatographed. Figure 2 is a tracing of the developed plate. Close resemblance between Figs. 1 and 2 is noted, although in general the spots in Fig. 2 are displaced. The tracing is, however, adequate for identification work. It is likely that the spot displacement observed in Fig. 2 is due to the influence of each component on the migration rate of the others.

From Fig. 2 it can also be seen that DPA and 2-nitroDPA overlap more than predicted by Fig. 1; however, 2-nitroDPA is a self indicator and can be detected on the unsprayed plate. Furthermore, after spraying and heating, the color intensity of the 2-nitroDPA spot diminishes; an intense yellow to green spot (depending upon the concentration of DPA) develops at the location of the DPA fraction. By using all of the properties of the system,  $R_G$  measurement, color, and developed color, it is possible to identify all of the DPA derivatives.

As part of a study on the capacity of various stabilizers for reaction with  $N_2O_4$ , samples of the reaction products of DPA and 2-nitroDPA with  $N_2O_4$  and extracts from samples of PBX-9404 were analyzed by the described procedure. Based upon the relative sizes and intensities of the developed spots, N-nitroso- and nitrodiphenylamines found in the samples are listed in Table I in the approximate order of decreasing concentration.

The complexity of the DPA derivatives is evident. Differences between the present results and those reported by HANSSON AND ALM<sup>2</sup> can probably be attributed to the composition of the original sample. For example, the tris(2-chloroethyl)phosphate in the PBX-9404 increases the rate of formation of N-nitroso- and nitrodiphenylamine products as compared with aged DPA/NC mixtures.

TABLE I  
IDENTIFIED DIPHENYLAMINE PRODUCTS IN VARIOUS SAMPLES

<i>Sample</i>	<i>Derivatives found</i>
PBX-9404-03	N-nitrosoDPA $\gg$ DPA = 2-nitroDPA > 4-nitroDPA > N-nitroso-4-nitroDPA
PBX-9404-03, heated at 60° for 15 weeks	2,4'-dinitroDPA $\geq$ N-nitrosoDPA > N-nitroso-4-nitroDPA = 4-nitroDPA = 2,4,4'-trinitroDPA = 4,4'-dinitroDPA > 2,2'-dinitroDPA > N-nitroso-4,4'-dinitroDPA > N-nitroso-2,2'-dinitroDPA = 2,2',4-trinitroDPA > 2-nitroDPA $\geq$ tetranitro- or pentanitroDPA $\geq$ 2,4-dinitroDPA

(continued on p. 69)

TABLE I (continued)

Sample	Derivatives found
PBX-9404, heated at 60° for 24 weeks	2,4'-dinitroDPA > 2,2'-dinitroDPA = 2,4,4'-trinitroDPA > N-nitroso-4-nitroDPA = N-nitrosoDPA ≥ N-nitroso-4,4'-dinitroDPA = 4-nitroDPA = 1,4'-dinitroDPA > 1-nitroso-2,2'-dinitroDPA > 2,2-trinitroDPA > 2,4-dinitroDPA = 2-nitroDPA ≥ tetranitro- or pentanitroDPA
DPA/N <sub>2</sub> O <sub>4</sub> reaction product	N-nitroso-4,4'-dinitroDPA > 4,4'-dinitroDPA = N-nitroso-2,4'-dinitroDPA > 2,4,4'-trinitroDPA > 2,2'-dinitroDPA > 2,2',4-trinitroDPA > 2,4'-dinitroDPA = hexanitroDPA > N-nitroso-4-nitroDPA ≥ 2,4-dinitroDPA > N-nitroso-2,2'-dinitroDPA > traces of N-nitrosoDPA, 2-nitroDPA, DPA, tetra- or pentanitroDPA, and two unknowns.
2-nitroDPA/N <sub>2</sub> O <sub>4</sub> reaction product*	N-nitroso-2,4'-dinitroDPA ≫ N-nitroso-2,2'-dinitroDPA ≫ 2,4'-dinitroDPA = N-nitroso-2-nitroDPA = 2,2',4-trinitroDPA = 2,4,4'-trinitroDPA > 2,2'-dinitroDPA = 2,4-dinitroDPA = hexanitroDPA > traces of tetra- or pentanitroDPA, 4,4'-dinitroDPA, N-nitroso-4-nitroDPA, 4-nitroDPA, and two unknowns.

\* 4-nitroDPA was present in the 2-nitroDPA as an impurity.

Reaction conditions used in testing the pure stabilizers, DPA and 2-nitroDPA, were designed to drive the reactions to their practical completion. Note, however, the complexity of the products after the stabilizer capacity of the compounds has been exceeded.

The extraction of DPA and its derivatives from explosives is carried out at ambient temperature to minimize the decomposition of the less stable DPA derivatives. For example, it was found that N-nitroso-4,4'-dinitrodiphenylamine tends to denitrosate and revert to 4,4'-dinitrodiphenylamine. Extractions requiring heating should be avoided.

Authentic samples of N-nitroso- and nitrodiphenylamines were difficult or

extremely expensive to purchase; therefore, most of the compounds tested were prepared in this laboratory. The trinitro-, tetranitro-, and pentanitro-diphenylamines were isolated from nitration products. The nitroso-nitrodiphenylamines were prepared by nitrosating the corresponding nitro- compounds. In all cases, purification was carried out on TLC plates. The purified product was characterized by its melting point, infrared spectrum, and elemental analysis.

The spray reagent, *p*-DEAB, can detect minute quantities of diphenylamine derivatives. For each compound included in this work, 1  $\mu$ g or less could easily be detected.

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#### SUMMARY

A two-dimensional thin-layer chromatographic method, capable of separating and identifying nineteen N-nitroso- and nitrodiphenylamines, is described. The method is applied to the analysis of diphenylamine/ $N_2O_4$  and 2-nitroDPA/ $N_2O_4$  reaction products and the stabilizer fraction of a plastic bonded explosive. A spray reagent, *p*-diethylaminobenzaldehyde, used in conjunction with silica gel G/Zn plates, offers a sensitive detection method for each diphenylamine derivative.

#### REFERENCES

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