



An Application of Thin Layer Chromatography Combined with Optical Densitometry to Quantitative Analysis of Diphenylamine and Its Initial Daughter Reaction Products in Single-Base Propellants Aged under Natural Conditions

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Abstract: Thin Layer Chromatography (TLC) was used for the quantitative measurement of the composition of stabilizers used to retard chemical decomposition of single-base (SB) propellants i.e. diphenylamine (DPA), and its initial reaction products due to natural ageing of these propellants under natural (ambient) conditions with test results and certain observations in this matter, are presented. The quantitative determination of DPA and its reaction products was possible by a combination of TLC with the densitometric spectrophotometry technique in the UV detection region. The crucial stage of TLC analytical quantitations was complete extraction of the substances to be analysed from SB propellants nitrocellulose (NC), which was done by rapid dissolution of the SB propellant samples followed by dilution of the solutions obtained to such degree as to make possible TLC separation of the substances to be analysed from the NC “matrix” in which they are “trapped” when the solution is too viscous. Initial chemical changes of DPA in SB propellants resulting in the appearance of DPA initial daughter reaction products such as N-nitroso-DPA, 2-nitro-DPA and 4-nitro-DPA, gave important information on the natural ageing of these homogeneous propellants starting from their very short storage period (some days, weeks or months just after their manufacture) up to long storage lasting even 50 years.

Key words: TLC, optical densitometry, SB propellants, DPA, natural ageing

Introduction

In order to introduce new method(s) on chemical stability assessment of the SB propellants being in service with Polish Military Forces, some analytical techniques were developed in the Military Institute of Armament Technology related to the quantitative determination of DPA and its initial daughter reaction products in SB propellants, i.e. N-nitroso-DPA, 2-nitro-DPA and 4-nitro-DPA. The analytical techniques most commonly applied to this aim, are High Performance Liquid Chromatography (HPLC) and Thin Layer Chromatography (TLC) [1-8]. The investigations of SB propellants stability through observation of the chemical reactions of their stabilizers, were very promising because DPA is one the most sensitive chemical indicators of propellant decomposition even in the very early stage of its progress. Because the HPLC technique is much more well known and used in common practice as a quantitative analytical method than TLC, it seems worthwhile to underline the suitability of TLC as a reliable and efficient method for quantitative measurements. Taking the above into consideration, the main issues presented and discussed in this paper, are as follows:

- 1) The TLC technique combined with optical densitometry as an efficient tool for quantitative analysis of DPA and its daughter reaction products in SB propellants;
- 2) Certain, important, practical observations and aspects dealing with the natural ageing of SB propellants on the basis of the initial chemical changes of DPA determined quantitatively by the TLC method.

An analytical procedure using the TLC technique combined with optical densitometry (UV) for quantitation of DPA and its main initial reaction products i.e. N-NO-DPA, 2-NO₂-DPA and 4-NO₂-DPA consists of the following steps:

- 1) Test sample preparation incl. their dissolution and dilution;
- 2) Application (dosing) of the solutions to be analysed on TLC plates;
- 3) TLC development/separation of the analysed substances;
- 4) Optical visualization of the separated components (in the form of spots/bands) on the TLC plate by UV light for positioning and setting of the scanning parameters and scanning procedure of TLC chromatograms by the optical densitometric system;
- 5) Quantitation of the densitometric peaks (scans) of the resolved substances corresponding to appropriate TLC spots (bands) by the optical densitometric system;
- 6) Calculation of the concentration of the analysed substances in the tested propellant samples on the basis of the densitometric peaks obtained and calibration curves of standards of the analysed substances.

Experimental

Materials and Apparatus

For analytical TLC quantitative determinations, the following materials were used:

- 1) SB propellants composed of ca. 96-99% (by mass) of NC, 1-2% of DPA and other technological ingredients;
- 2) Standards of the analysed substances: DPA, N-NO-DPA, 2-NO₂-DPA, 4-NO₂-DPA pure for chromatographic analysis (SIGMA ALDRICH, Germany), NC – pure for technological process (ZPS-Pionki (Chemical Works for Special Production, Poland));
- 3) Solvents: methanol, acetone, methylene chloride, n-hexane – pure for chemical analysis (MERCK, JT BAKER);
- 4) TLC (20mm x 20 mm) plates coated with silicagel Si 60 with fluorescent agent F-254 (MERCK, Catalogue No. 5548).

For TLC analytical procedures, the following apparatus were applied:

- 1) Optical scanning densitometric system CS-9000 (SHIMADZU, Japan) for visualization of the chromatographic bands (spots) of TLC chromatograms in the form of densitometric (optical absorbance) peaks - densitograms;
- 2) TLC autosampler LINOMAT IV-Y (CAMAG, Switzerland) for sampling of the analysed solution onto the start line of TLC plate by the spray on technique with simultaneous evaporation of solvent in order to obtain very narrow bands of the mixtures;
- 3) TLC saturated, vertical chambers (CAMAG) for chromatographic developments;
- 4) UV- light (254/366 nm) chamber (CAMAG) for positioning (position visualization) of the analysed solutions and separated components on the TLC plate.

SB Propellant Samples Preparation and Their Dissolution Procedure

Single-base propellants used for small caliber ammunition do not need to be ground, but larger gun propellant grains need to be disintegrated to accelerate their dissolution in the next step of sample preparation. Accurately weighed 1 gram of propellant from each tested propellant batch is dissolved in 100 cm³ of appropriate solvent (preferably acetone). The total dissolution of single-base propellants to achieve a relatively homogenous colloidal mixture is very rapid. It usually takes from 10 to 60 minutes, mainly depending upon the size of the propellant grains and solution temperature.

SB Propellant Samples TLC Separation

The type of TLC adsorbent, elution strength, polarity and composition of the developing (mobile) phases were varied in order to isolate the NC 'matrix' and to separate the rest of the components i.e. DPA, N-NO-DPA, 2-NO₂-DPA and 4-NO₂-DPA in the shortest possible distance of chromatographic development.

A test propellant sample solution volume of 100 µl was sprayed onto the chromatographic development start line of the TLC plate (preferably prewashed with methanol and activated at 100 °C for 1 h) by means of the autosampler LINOMAT IV-Y (or optionally by chromatographic syringe dosing eg. 5 µl of analyte). Autosampler use is preferred to use than a syringe because the applied analytes on the start line of the TLC plate by the autosampler are much narrower in comparison with the 'round/oval' spots applied on the start line of the TLC plate by a syringe. The narrow shape of bands (spots) of the applied analytes is very beneficial because during chromatographic development, the moving bands (spots) progressively broaden mainly due to diffusion in the layer of the TLC plate adsorber and since it is known that the wider the bands (spots) are, the distances between them are less, and substances located in the bands (spots) have lower concentration, so the densitometric peaks corresponding to the given bands (spots) are relatively low (more difficult to be detected), wide and the distances between them are less resulting in poor chromatographic separation. The length of each solution band applied onto the start line of the TLC plate was 5 mm, the distance between adjacent bands was 8 mm. Satisfactory results for the separation of the analysed substances (DPA and its daughter reaction products) were achieved using TLC development to a distance of 80 mm in the saturated, vertical TLC chambers by means of a mobile phase which was a binary mixture of n-hexane and methylene chloride (7:5) (v/v). In this step of the analysis, the positions of the separated components on the TLC chromatograms were visualised through fluorescence quenching observed in UV-light at 254 nm. The time of chromatographic development under the above experimental conditions was ca. 20 minutes. Values of the retardation factor (R_F) for the components – DPA, N-NO-DPA, 2-NO₂-DPA and 4-NO₂-DPA were 0.75, 0.35, 0.49 and 0.16 respectively.

Before densitometric scanning of TLC chromatograms, the UV absorption spectrum of each component was obtained by scanning the applied band (spot) of each pure component on the TLC plate under conditions that were as close as possible to the conditions of the final quantitative, densitometric measurements. After application of each component in the form of a spot (band) on the TLC adsorbant, it was scanned by the UV light beam and the reflected UV light was measured. An example of such a UV spectrum for DPA is shown in Figure 1,

from which the DPA absorbance maximum at 265 nm is revealed. Because of the structure – the presence of double bonds in the phenyl rings of DPA, N-NO-DPA, 2-NO₂-DPA and 4-NO₂-DPA, they all have local maxima in the UV spectra, located relatively close each other. Because all of the analysed substances possess satisfactory, relatively high absorbance at 265 nm, it was decided to use this wavelength for scanning.

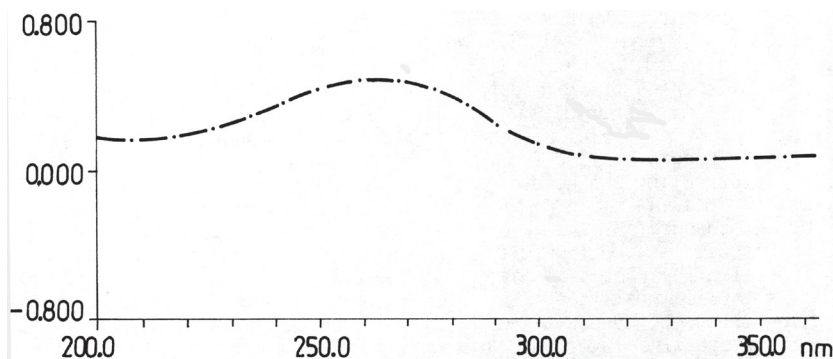


Figure 1. UV absorption spectrum of DPA obtained by scanning its spot (band) on the TLC plate by optical densitometric system CS-9000 (local UV maximum at 265 nm).

Quantitative Analysis of DPA and Its Daughter Reaction Products in SB Propellant Solutions Developed as TLC Chromatograms

The amounts of DPA, N-NO-DPA, 2-NO₂-DPA and 4-NO₂-DPA located in the separated bands (spots) were determined through densitometric scanning of the developed TLC chromatograms at 265 nm. The densitometer was run in UV reflection-absorbance and a zig-zag scan mode. As a result of such densitometric measurement conditions, separated bands (spots) areas were scanned in a zig-zag pattern. Regarding the width of the applied bands (spots) on the TLC plates, the start line and the distances between them, the width of the scan path was 13 mm to cover all areas of the analysed bands (spots) and simultaneously to avoid scanning of adjacent TLC chromatograms. The measured densitometric signals in the form of densitometric absorbance areas of peaks corresponding to the position of a given band (spot) of an analysed substance (Figure 2), were proportional to the mass of the analysed substance covering the separated band (spot) on the TLC chromatogram.

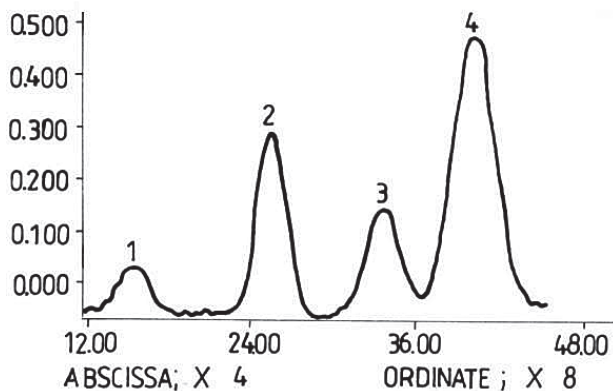


Figure 2. Densitogram of a mixture of DPA and its daughter reaction products obtained through scanning of the TLC chromatogram by means of optical densitometric system CS-9000 (UV beam wavelength 265 nm). Peak point positions of bands (spots) on the TLC chromatogram: (1) 4-NO₂-DPA, (2) N-NO-DPA, (3) 2-NO₂-DPA, (4) DPA. Vertical coordinates are given in Absorbance Units of Full Scale (AUFS).

For each standard component a linear relation between the areas of the densitometric peaks and the concentrations of the analysed substance in the tested sample was obtained. This relation permitted standard curves for DPA, N-NO-DPA, 2-NO₂-DPA and 4-NO₂-DPA to be constructed. As an example of such a relation, the calibration curve for DPA is presented in Figure 3.

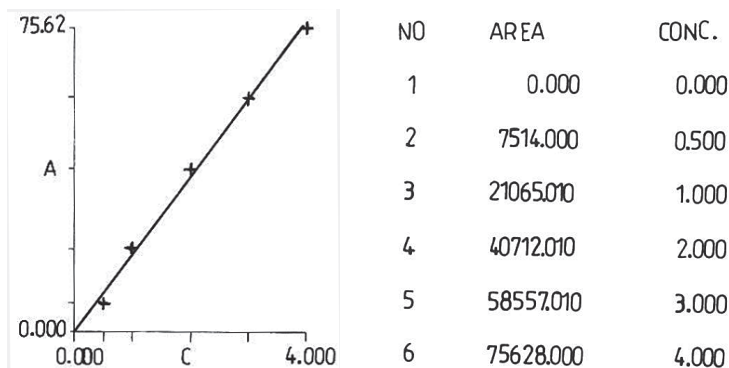


Figure 3. Standard curve for DPA quantitative UV densitometric determinations (265 nm), describing the dependence of its densitometric peak areas as a function of DPA mass concentration in the SB propellant sample.

Chemical Stability Investigations of SB Propellants on the Basis of DPA Chemical Reactions under Natural Ageing Conditions

Multi-cycle Vieille tests at 106.5 °C [9] – traditionally used for several dozen years in Poland as the main tests of chemical stability determination of SB propellants, showed that their chemical stability practically does not depend on their age, taken as a period of natural ageing (storage under ambient conditions) from the date of their manufacture to the date of their chemical stability determination. Moreover these results indicated that older propellants i.e. manufactured in the fifties and sixties years, in many cases had better chemical stability than propellants produced later. To check this observation, further tests on the chemical stability of SB propellants by stabilizer contents determination were focused on initial DPA chemical reactions. Typically, quantitation results obtained by TLC combined with optical densitometric measurement for DPA chemical reactions in SB artillery propellants aged (stored) for a long time in Poland under ambient conditions at mean annual environmental temperatures i.e. at ca. 10 °C, are presented below in the Table.

Table. Test results obtained by quantitative TLC on DPA and N-NO-DPA contents in artillery SB propellants aged (stored) under ambient conditions

Manufacture period of the SB propellants [years of former age]	Range of contents of DPA and N-NO-DPA in SB propellants	
	DPA [% (by weight)]	N-NO-DPA [% (by weight)]
1950-1969	1.20 - 1.50	0.05 - 0.10
1970-1989	1.20 - 1.50	0.20 - 0.30
1990-2000	1.20 - 1.50	0.05 - 0.20

From the test results given in the Table, it appears that SB propellants manufactured between 1970 and 1989 indicate more advanced – larger range of DPA chemical conversion into N-NO-DPA in comparison with older or younger SB propellants respectively, i.e. produced in 1950-1969 and 1990-2000, under the assumption that the purity of the DPA initially introduced into the propellants during their processing was essentially the same (very similar) for all tested propellants. The mono-nitroderivatives of DPA i.e. 2- and 4-nitro-DPA, appeared in SB propellants only in very small concentrations (most often in trace quantities). These results seem to confirm to some extent the Vieille test results that SB propellants produced in the 70s and 80s exhibited a tendency towards lower stability than “younger” and “older” ones.

So, the question arises, what are the reason(s) for the clear differences in N-NO-DPA content in the propellants of the same type, esp. taking into consideration the heightened range of DPA changes for the propellants produced in the 70s and 80s (Table). To try to answer this question, the following procedures were undertaken

- examination of the purity of DPA synthesised for introduction into the initial composition (cake) of the SB propellants during their solvent extrusion process;
- determination of DPA and N-NO-DPA contents in SB propellants just after their manufacture and after short periods i.e. after several weeks or months.

Batches of DPA prepared for incorporation into the propellant during manufacture, analysed by the above TLC method, contained the following impurities given in mass percentage of DPA: N-NO-DPA in the range of (0.91-3.66)%, traces of 4-NO₂-DPA, and aniline (impurity from DPA synthesis) appearing in DPA in the range of (0.03-0.33)%. Before the introduction of chromatographic methods to SB propellant analysis, the purity of DPA batches was examined only by a titration technique which indicated DPA of higher purity than the chromatographic methods because analysis by titration was not able to distinguish between DPA and its daughter reaction products, the latter being present in the mixture.

Differences between measured ranges of DPA and N-NO-DPA in SB propellants stored for relatively long periods after their production, presented in the Table, as well as N-NO-DPA concentrations in DPA batches prepared for introduction into propellant premixes during manufacture, point to a very strong, decisive influence of the SB propellant manufacturing process on the DPA and N-NO-DPA contents in these propellants. DPA and N-NO-DPA contents in SB propellants were held at a practically constant level for many (several tens) years under conditions of natural ageing.

Conclusions

On the basis of the conducted analysis and discussion on methodology of analytical determination of DPA and its daughter reaction products in SB propellants, and on the basis of test results concerning DPA chemical changes in these propellants aged under natural conditions, it is possible to withdraw the following conclusions.

- The TLC technique combined with densitometric measurements of TLC chromatograms, is an efficient (relatively fast) and reliable method for

the determination of stabilizers and their daughter reaction products in SB propellants.

- N-NO-DPA is the main substance which indicates the first symptoms of the natural ageing progress in SB propellants.
- DPA purity determination by chromatographic methods, just before its introduction into the SB propellant premixes, gives important information concerning the quality of the technological process of SB propellant manufacture.
- The early stage of the SB propellants life i.e. covering their manufacture period and some weeks or months directly after their production, has an important influence on the range of chemical reactions of DPA. During this period the majority of chemical changes governing chemical stability take place. After this period, chemical changes of DPA are practically “frozen” for a long time, even several tens of years if the SB propellants are stored properly under ambient (natural) conditions, preferably in hermetically sealed boxes located in appropriate depots, magazines, stockpiles, not exposed to harmful environmental factors like air pollutions (particularly sulphur-oxides and nitro-oxides), to elevated temperature and/or humidity.
- The N-NO-DPA (possibly together with DPA mono-nitro-derivatives) concentration increase in the propellant parallel with a corresponding decrease in DPA concentration in the propellant, initiated by the SB propellant manufacture process, gives valuable knowledge about the overall quality of this technological process incl. conditions of propellants production and components purity used in the technological processing, especially – knowledge about the quality of the NC stabilisation process and about the influence of each production stage of SB propellant on their quality, for example – the influence of temperature of propellant processing particularly in the stage of their final drying at ca. 50 °C for relatively long time. These observations seem to be confirmed by literature reports and data on the decomposition processes of NC [10] and by comparative tests conducted in MIAT on the chemical stability of SB propellants for military and civil usage (hunting and sport ammunition). On the basis of these tests, it was observed that in some cases of “civilian” propellant processing, when possibly poorer quality cellulose was used for production of NC and/or used NC pulp that was less stabilised i.e. containing for example acid impurities (HNO_2 , HNO_3) and/or the NC pulp was stored under direct access of light and/or environmental air and/or moisture (inappropriate storage conditions), the range of DPA chemical conversion into N-NO-DPA, was 1.5-2 times larger in comparison to a range of DPA chemical conversion measured in

military SB propellants of similar compositions and manufactured by an analogous technological process.

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