A Novel Method for Testing Propellant Stabilizers

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Abstract: In many laboratories, investigations aimed at replacing diphenylamine (DPA, propellant stabilizer) with other, less harmful substances are being carried out. For instance, good effects have been obtained in experiments with triphenylamine (TPA), which cannot produce – due to its structure – carcinogenic nitroso derivatives. In this work, a new, cheap and fast method for testing stabilizing properties of propellant stabilizers that have been used or being developed is presented. It consists in dispersing a stabilizer within silica gel followed by the measurement of the stabilizer transformation kinetics during its nitration with nitrogen oxides. The method combined with thin layer chromatography (TLC) provides a fast evaluation of stabilizing effectiveness.

Keywords: propellant stability, TPA, DPA, C-I, TLC analysis

Introduction

The kinetics of the changes occurring in the currently used stabilizers under influence of nitrogen oxides emitted in the process of ageing of smokeless propellants is well known [1]. For example, diphenylamine (DPA) – the basic stabilizer of single-base propellants – is initially transformed into N-nitrosodiphenylamine (N-NO-DPA) and next, as the propellant ageing process advances, N-nitroso-mononitro-DPA as well as 2-nitro-, 4-nitro- and higher nitrated derivatives of DPA are formed [2]. Since carcinogenic properties of N-NO-DPA have been confirmed, its generation is a drawback of DPA. It should also be mentioned that

nitrosamines are formed during the ageing process of the propellants containing other stabilizers, like centralite, akardite [3] or 4-nitro-N-methyl aniline, thus they are all suspected of being carcinogenic. This means that stabilizers which are nowadays used in propellants produce very toxic products. Taking this into consideration, S. Wilker and coworkers [4] proposed the application of the new propellant stabilizer – triphenylamine (TPA). This compound does not include N–H bonds, so that N-nitroso-compounds cannot be created. The authors have shown that TPA is an effective stabilizer for nitrocellulose based propellants.

Taking into account that other compounds may be considered as possible stabilizers, we undertook an attempt to develop a simple and cheap method for measurements of the reaction kinetics of various stabilizers. It is a quite important problem as the currently used test methods for the evaluation of propellant stability are expensive and time consuming. The proposed method consists a direct nitration of a stabilizer adsorbed on a silica gel (so that the stabilizer is dispersed like in a propellant sample) with nitrogen oxides followed by the qualitative and quantitative analyses of the formed nitration products.

Experimental

All the analyses were performed by the means of instrumental thin layer chromatography (TLC). Triphenylamine (TPA), 2-nitro-TPA, 4-nitro-TPA, 2,4'-dinitro-TPA, 4,4'-dinitro-TPA, diphenylamine (DPA), N-nitrosodiphenylamine (N-NO-DPA), 2-nitrodiphenylamine (2-nitro-DPA), 4-nitrodiphenylamine (4-nitro-DPA), centralite (C-I), 4-nitrocentralite (4-nitro-C-I) and 4,4'-dinitrocentralite (4.4'-dinitro-C-I) were selected for testing.

The used equipment, chemicals and solvents: applicator Linomat IV (Camag); horizontal chromatographic chamber DS (Chromdes); densitometer CS-9000 (Shimadzu); chromatoplates with silica gel 60 F_{254} HPLC (Merck, No. 1.05548) or silica gel with chemically bounded octadecyl groups (Merck, No. 1.05559); solid phase extraction set (J.T. Baker), stabilizer standards (WIWEB ASt Heimerzheim and Merck), organic solvents (J.T. Backer and Merck).

Selection of the chromatographic systems

The first step of investigations included a search for a chromatographic system making the separation of the analytes, their identification, quantification and determination of the analytical parameters possible. The experiments were conducted using methylene chloride solutions of the standards (TPA, DPA, C-I and their nitro- and nitroso derivatives) with concentration of 10 ng/µL. Samples

of the solutions of 10 μL in volume were applied (spraying technique, band width 4 mm) on the start lines of chromatoplates. The chromatograms were developed to a length of 5÷10 cm in the horizontal chamber DS. The spots originating from the nitro-derivatives of TPA, DPA and C-I were seen in the visible light and TPA, DPA, N-NO-DPA and C-I were visualized by observation of the fluorescence quenching. The best separation conditions of the individual groups of analytes (Figures 1a-c) were obtained in the following chromatographic system:

- TPA (isocratic two-steps elution): stationary phase – high-performance silica gel (Merck, No. 1.05548); mobile phase – diethyl ether:hexane 2:1; v/v (first step: distance of elution – 4 cm), chloroform:hexane 1:2 (v/v) (second step: distance of elution – 8 cm).
- DPA (isocratic one-step elution): stationary phase – high-performance silica gel (Merck, No. 1.05548); mobile phase – hexane:methylene chloride 7:5 (v/v).
- C-I (isocratic two-steps elution): stationary phase – silica gel with chemically bounded octadecyl groups (Merck, No. 1.05559); mobile phase – acetonitrile (first step: distance of elution – 4 cm), methylene chloride:tetrachloromethane 1:2 (v/v) (second step: distance of elution – 5 cm).
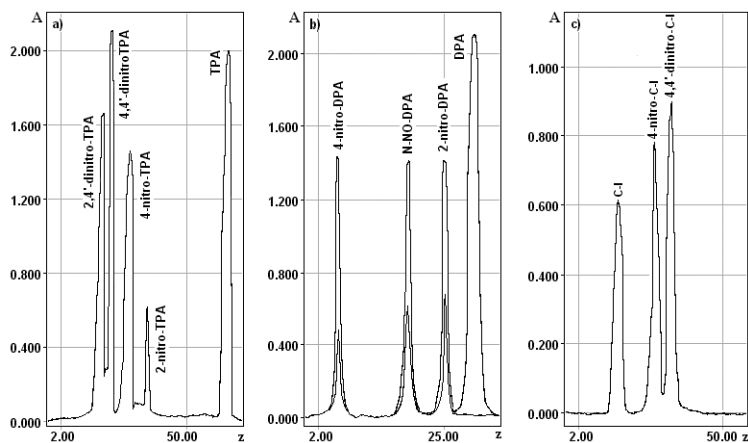

Figure 1. Separation of the TPA (a), DPA (b), and C-I (c) derivatives A – absorbance in relative units of the apparatus; z – range of the chromatographic band [mm].

Quantification

To establish the quantitative relations $A = f(m)$ (where: A – an area of a densitometric peak in relative units of the apparatus, m – a mass of an

analyte in a chromatographic band [ng]), variable volumes (5÷500 μL) of the solutions of standards were applied on the start line of the chromatoplates and the chromatograms were developed in the described above systems. Next the absorption spectra of the analytes were measured *in situ* to get information on the wavelengths λ_{max} corresponding to an absorbance maximum. Finally, the absorption measurements were performed and the obtained results were used to determine the dependence of $A = f(m)$, as well as to evaluate the limit of detection, and the maximum range of linearity of the detector indications (Tables 1a-c).

Table 1a.　Analytical parameters of the TPA derivatives

Analyte	λ_{max} [nm]	Calibration curve			Detection limit [ng]
		$A* = f(m)$	Correlation coefficient	Range of linearity [μg]	
TPA	285	$A=50.2 \cdot m - 4925$	0.964	3.0	200
2-nitro-TPA	275	$A=56.4 \cdot m - 2958$	0.989	2.8	100
4-nitro-TPA	410	$A=74.1 \cdot m - 658$	0.994	2.5	100
2,4'-dinitro-TPA	390	$A=56.1 \cdot m + 1555$	0.995	2.5	100
4,4'dinitro-TPA	415	$A=73.4 \cdot m + 5633$	0.980	2.7	100

*A – absorbance, m – the mass of an analyte in the chromatographic band [ng].

Table 1b.　Analytical parameters of the DPA derivatives

Analyte	λ_{max} [nm]	Calibration curve			Detection limit [ng]
		$A* = f(m)$	Correlation coefficient	Range of linearity [μg]	
DPA	265	$47.7 \cdot m - 2422$	0.990	2.5	150
N-NO-DPA	282	$32.7 \cdot m + 1564$	0.988	1.8	120
2-NO$_2$-DPA	430	$51.3 \cdot m + 2047$	0.999	2.0	90
4-NO$_2$-DPA	380	$67.5 \cdot m + 3973$	0.999	2.1	80

*A – absorbance, m – the mass of an analyte in the chromatographic band [ng].

Table 1c.　Analytical parameters of the C-I derivatives

Analyte	λ_{max} [nm]	Calibration curve			Detection limit [ng]
		$A* = f(m)$	Correlation coefficient	Range of linearity [μg]	
C-I	235	$19.1 \cdot m - 3919$	0.978	2.5	200
4-NO$_2$-C-I	315	$60.7 \cdot m - 2693$	0.972	1.5	100
4,4'-dinitro-C-I	310	$83.2 \cdot m + 2588$	0.996	1.6	100

*A – absorbance, m – the mass of an analyte in the chromatographic band [ng].

Transformations of stabilizers exposed to nitrogen oxides

Having developed an analytical tool which could be used for the qualitative and quantitative analyses of stabilizers and their nitration products, we made an attempt to assess the rate of the changes of the TPA, DPA and C-I exposed to nitrogen oxides. To this end a 0.1% (wt.) solution of each stabilizer in methylene chloride was prepared and then it was mixed with silica gel. The mixture was kept for half an hour at room temperature to reach the adsorption-desorption equilibrium and retention of the TPA, DPA or C-I on the adsorbent.
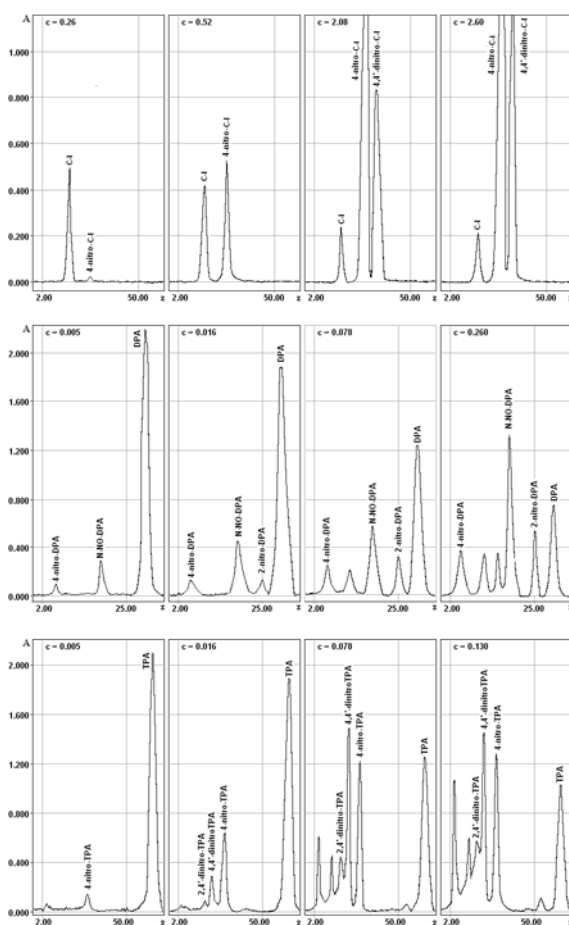

Figure 2. Densitograms of the nitration products of C-I, DPA and TPA with air/N_xO_y mixtures for different concentration c (v/v) of N_xO_y. Other symbols as in Figure 1.

After that, the mixture was filtered off, the adsorbent was dried and divided into samples of 0.75 g in mass. The samples were placed into typical SPE cartridges, and from a few cartridges, the adsorbed stabilizer was eluted with two 1-mL portions of methylene chloride using an SPE set. The masses of eluted stabilizers were determined by analyzing the combined eluates, and in this way information on the amount of stabilizer that had been adsorbed on the silica gel was obtained.

Through the other cartridges, filled with silica gel – containing adsorbed TPA, DPA or C-I – 5 mL portions of N_xO_y/air mixture with increasing concentration c (v/v) of nitrogen oxides were passed. The stabilizers were then nitrated with a rate depending on the concentration of N_xO_y. After finishing the nitration process, remaining stabilizers and their nitration products were eluted and analyzed. Results of densitometric measurements of the obtained chromatograms are shown in Figure 2.

Discussion and Conclusions

The proposed method for observation of the transformation of propellant stabilizers subjected to nitrogen oxides which relies on: (i) adsorption (from a solution) of a known quantity of the stabilizer on a silica gel, (ii) filling a column (applied in SPE) with the obtained gel, (iii) passing a N_xO_y/air mixture of known composition through the column, and (iv) elution and quantitative analysis of the stabilizer and its nitration products, seems to be an effective one. As a matter of fact the method cannot be used for a direct evaluation of the propellant stability, but owing to its simplicity, inexpensiveness and fastness it is especially preferred for a comparative assessment of the stabilizing performance of various stabilizers (Figure 2). It makes the observation of direction and kinetics of the changes of stabilizers possible without the necessity of long-lasting ageing of stabilized propellants.

The obtained results of measurements indicates that the stabilizing properties of TPA are comparable to that of DPA. This is indicated by the similar rate of depletion of the stabilizers subjected to nitrogen oxides under the same conditions, Figure 3.

Instrumental thin-layer chromatography proved to be a useful method for testing propellant stabilizers. The instrumentation of the method provides a possibility of quantitative analysis. The detection limit is low enough and the indications of the densitometer detector are linear within a sufficiently wide range of the concentration of the tested analytes.
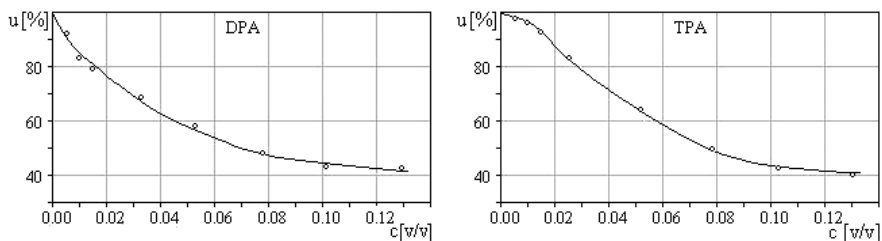
Figure 3. Changes in the amount of unreacted TPA and DPA C-I after their nitration with nitrogen oxides versus concentration of N_xO_y in air (*c*), *u* – relative mass fraction of the analyte in the sample.

Acknowledgment

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