Testing the Chemical Stability of Smokeless Propellants

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The paper presents a critical analysis of methods used for stability testing of smokeless propellants. The authors shown superiority of TLC and densitometry to other chromatographic techniques used to measure stabilizers content and kinetics of their changes. Basing on the results of the tests on propellant samples subjected to natural and accelerated aging, the basic principles of predicting a time of safe storage of particular propellant lots were worked out.

Glycerine and cellulose esters that are basic components of smokeless propellants, undergo decomposition under natural aging conditions. The main decomposition products are nitrogen oxides that are a catalyst of further accelerated decomposition leading to self-ignition. To prevent autocatalytic decomposition of nitroglycerine or nitrocellulose, a small amount (1.5–3.5 %) of substances that react very fast with nitrogen oxides is added to propellants. These substances, called stabilizers, in a way “absorb” the catalyst that results in an increase in chemical stability of propellants. Thus a basic safety condition for propellant (ammunition) storage is a control of its stability on a regular basis.
Recently used methods of propellant stability testing are widely differentiated in measurement principle, instrument setup as well as accuracy and repeatability. This fact is, to some extent, a result of tradition of manufacturers and users as well as that of capabilities of industrial and control/research laboratories. Searching for updating and unification of a stability assessment procedure used for smokeless propellants in Poland, an attempt of use of high-performance liquid chromatography (column and thin layer) was taken. A need to develop such a procedure was a direct effect of the Warsaw Pact termination that has rendered it possible to leave behind the obsolete propellant testing methods that previously were in force.

This paper presents the crucial elements of the project, i.e. a critical review of the smokeless propellant testing methods, results of chromatographic tests and their verification in experiments involving more than a hundred lots of propellants manufactured in the period of 1945–1990.

Analysis of methods for smokeless propellant stability assessment

The term “propellant stability” was introduced to designate their chemical, mechanical and ballistic stability [1]. In a narrower meaning, this term concerns exclusively chemical stability because both mechanical and ballistic stability of a propellant is a direct effect of its chemical properties. Chemical stability of a propellant, understood as a basic measure of its storage safety assessment, depends mainly on purity of esters, stabilizer type, thickness of propellant grains, storage conditions, etc.

A need to stabilize smokeless propellants and to assess their chemical stability was found as early as in the beginning of the 20th century, soon after some tragic events related to their storage [2]. Testing methods that were developed in that time are still in use in many laboratories, along with intensively developing instrumental analyzing techniques (Table 1). These methods can be divided into two categories, depending on propellant components being analyzed. The first category includes methods that use testing decomposition of esters contained in some representative propellant sample, subjected to heating (sample weight as well as time and temperature of its heating are precisely determined). Differences among particular methods of this category, commonly called tests, consist mainly in a way of measuring nitrogen oxides released during the tests; parameters of particular tests are also non-uniform. The second category includes methods based on assessment of stabilizer content and reaction done, in propellant samples subjected to natural and accelerated aging. These methods differ among themselves mainly in conditions of the accelerated aging and technique of a stabilizer determination.

An obvious disadvantage of the first category methods is low precision and also (except the Bergmann–Junk test) flexibility; they do not provide an estimation of stability and they are only informing that some threshold value is exceeded (or not) under the test condition. Methods of the other group are of a quantitative nature thus the propellant stability estimation based on the measurement of the kinetics of stabilizers change is getting more widely used.
Table 1. Methods of propellant stability assessment

<table>
<thead>
<tr>
<th>Test name</th>
<th>Temperature °C</th>
<th>Duration</th>
<th>Measured signal</th>
</tr>
</thead>
<tbody>
<tr>
<td>Abel Heat</td>
<td>65.5</td>
<td>10–30 min</td>
<td>color change of a iodo-starch test paper</td>
</tr>
<tr>
<td>Methyl Violet</td>
<td>120.0</td>
<td>40 min</td>
<td>color change of a crystalline violet</td>
</tr>
<tr>
<td>Dutch</td>
<td>105.0</td>
<td>72 h</td>
<td>weight of the sample</td>
</tr>
<tr>
<td>Surveillance</td>
<td>80.0 or 65.5</td>
<td>150 h</td>
<td>occurrence of brown nitrogen oxides</td>
</tr>
<tr>
<td>Small Vessel</td>
<td>100.0</td>
<td>5 days</td>
<td>weight of the sample</td>
</tr>
<tr>
<td>NATO</td>
<td>65.5</td>
<td>60 days</td>
<td>stabilizer loss assessed by means of spectrophotometer</td>
</tr>
<tr>
<td>Woolwich</td>
<td>80.0</td>
<td>3 weeks</td>
<td>stabilizer loss assessed by means of GC or HPLC</td>
</tr>
<tr>
<td>Vieille</td>
<td>110.0 or 106.5</td>
<td>70 h</td>
<td>color change of a litmus paper</td>
</tr>
<tr>
<td>Bergmann–Junke</td>
<td>132.0</td>
<td>2 h</td>
<td>pH-metric or iodometric analysis of nitrogen oxides</td>
</tr>
</tbody>
</table>

Kinetics of the change occurring in the stabilizers under influence of nitrogen oxides emitted in the process of aging of smokeless propellants is well known [3–6]. Diphenylamine (DPA), the basic stabilizer of single-base propellants is initially being changed into N-nitrosodiphenylamine (N-NO-DPA) and next, as the propellant aging process advances, 2-nitro and 4-nitrodiphenylamine (2-NO_2-DPA and 4-NO_2-DPA) is formed out of this. A result of further changes of this stabilizer are higher nitrated derivatives, e.g. 2,2'-(NO_2)_2-DPA. Diphenylidithylene, widely known as centralite (C-I), the basic stabilizer of double-base propellants, changes into N-nitroso-N-ethyl-aniline or into 4-nitrocentralite (4-NO_2-C-I) and further in higher nitrated products. Therefore, there is a possibility to assess a propellant stability by measurement of both stabilizer loss and increase of one or two products of its change. Use of the instrumental analytical methods for such measurements significantly increases precision and repeatability of the assessment in comparison with the methods of the first category. In these assessments reliability of measurement is of special importance because information on an amount of the stabilizers and kinetics of their chemical change provides a basis for not only classification of propellant stability but also for predicting periods of further safe storage of particular propellant lot.

Majority of the works on quantitative determination of the stabilizers and their products deals with chromatographic analyses [7–13] that results directly from a need of their separation from a complex sample of propellant and dividing them into single components that undergo the determination. Via and Taylor [13] showed that the gas chromatography cannot be used for testing single-base propellant stabilizers due to changes of N-NO-DPA at temperatures higher than 65.5°C. The way of preparing a propellant sample for chromatographic analysis is also of some importance; samples containing nitroglycerine or nitrocellulose cannot be analyzed by means of the HPLC because of extremely fast wear-out of the columns. The best effects are achieved by means of the TLC or fluid chromatography. Newer techniques of propellant analyzing, associated with the first category of methods (testing of esters) include microcalorimetry [14] and EPR [15]. However, these methods are of bigger cognitive significance than of useful one.
In Poland, stability of smokeless propellants is assessed by means of a modified Bergmann–Junk method (in testing related to storage) and the Vieille test (in the industry), while in most countries using advanced technologies, insufficiently accurate Vieille, Bergmann–Junk or Abel tests have been replaced by the other category of methods (measurement of stabilizers), including use of advanced instruments. For example in armies of the European NATO countries the NATO test (Table 1) is used and in the US Army – the Surveillance test. Having the above in mind, an attempt of use of liquid chromatography for this testing was taken.

EXPERIMENTAL

Assessment of quantity and kinetics of stabilizer change by means of high-performance liquid chromatography

Selection of the chromatography conditions and assessment of quantitative relations were performed using the standard solutions (Merck). The measurement were carried out by means of Liquochrom 2010 liquid chromatography manufactured by Labor-Mim (steel column of dimensions of 250x4.6 mm. Conditions of analyses were as follows:
- double-base propellants: stationary phase – ODS-18, mobile phase – methanol+water (2+1), isocratic elution, wavelength 225 nm;
- single-base propellants: stationary phase – silica gel, mobile phase – hexane+methylene chloride (1+1), isocratic elution, wave length 285 nm.

Separations of the components being analyzed are shown in chromatograms (Figs. 1, 2). Assessment of the quantitative relations was performed by means of the internal standard method. In the test concerning assessment of stability of propellants, samples taken from each lot were divided into two groups. In the first group, content of the stabilizer and 1–2 products of its changes taking place under natural conditions was assessed while the other group underwent an accelerated aging under conditions that allowed the observation of the occurring change. Principles and conditions of accelerated aging were previously described [16].

![Figure 1. Chromatogram of a single-base propellant extract (HPLC), 0 – solvent, 1 – diphenylamine, 2 – 2-nitrodiphenylamine, 3 – 2,4-dinitrotoluene (internal standard), 4 – N-nitrosodiphenylamine, 5 – 2,4-dinitrodiphenylamine, 6 – 4-nitrodiphenylamine](image-url)
An especially interesting result obtained at this stage of the testing was an unfavorable balance of amount of the stabilizers. It was expected that in a sample of propellant subjected to accelerated aging, stabilizer content would be lower (and correspondingly bigger amount of the products of its change). In fact, in an artificially aged sample, a decrease of the stabilizer share in the sum of the all components being determined in comparison with the sample aged under natural conditions was observed. This fact could be explained only by non-uniform effectiveness of the extraction. A hypothesis was taken that in the process of accelerated aging, structure of the propellant grains becomes damaged that results in extraction of an additional amount of the stabilize “trapped” in these grains (in not heated samples, access of an extracting solvent to this part of the stabilizer is more difficult). This hypothesis may be verified only by experiments on fully dissolved propellant samples.

Assessment of extraction effectiveness

Extraction effectiveness was assessed only in relation to the stabilizers. Propellant samples (1 g weight, aged naturally and artificially) of different particle sizes were subjected to extraction with methylene chloride (25 ml). The resulting extract was separated and the remaining part was dissolved in 100 ml of acetone. Chromatographic analysis was applied to both extracts and solutions of post-extraction residues.

Effectiveness of three extraction techniques widely used in propellant analyses was assessed: keeping the sample in a water bath at temperature of 70°C for 2.5 h, keeping the sample at normal temperature for 24 h and ultrasonic technique (the extraction in Soxhlet apparatus is not recommended because of the above-mentioned stabilizer changes). A relation of an amount of a stabilizer in the extract to its total quantity in the extract and post-extraction solution was taken as a measure of extraction effectiveness (Table 2).
Results of the measurement appear to confirm the suggestion on an increased penetration of the solvent into grains of propellant that has been heated. This is especially clearly visible in a propellant of relatively coarse grains. Having the above in mind and also in the light of a resulting need to determine extraction effectiveness in practical testing, we decided to give up the extraction techniques and to subject propellant solutions to the chromatographic analysis only.

### Table 2. Extraction effectiveness (%)

<table>
<thead>
<tr>
<th>Propellant grains thickness mm</th>
<th>Exposition 2.5 h at 70°C</th>
<th>Exposition 24 h at 20°C</th>
<th>Ultrasonic 4 h at 40°C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Single-base propellants</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>89.3</td>
<td>88.0</td>
<td>87.2</td>
</tr>
<tr>
<td></td>
<td>92.1</td>
<td>91.0</td>
<td>90.6</td>
</tr>
<tr>
<td>0.4</td>
<td>89.5</td>
<td>90.3</td>
<td>91.0</td>
</tr>
<tr>
<td></td>
<td>91.6</td>
<td>95.8</td>
<td>95.0</td>
</tr>
<tr>
<td>0.1</td>
<td>95.4</td>
<td>92.1</td>
<td>92.2</td>
</tr>
<tr>
<td></td>
<td>98.1</td>
<td>98.2</td>
<td>97.9</td>
</tr>
<tr>
<td></td>
<td>Double-base propellants</td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.8</td>
<td>86.6</td>
<td>89.0</td>
<td>90.7</td>
</tr>
<tr>
<td></td>
<td>93.3</td>
<td>93.7</td>
<td>94.7</td>
</tr>
<tr>
<td>0.3</td>
<td>91.2</td>
<td>92.0</td>
<td>92.8</td>
</tr>
<tr>
<td></td>
<td>95.0</td>
<td>94.6</td>
<td>94.7</td>
</tr>
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<td>0.1</td>
<td>93.5</td>
<td>94.2</td>
<td>93.9</td>
</tr>
<tr>
<td></td>
<td>98.4</td>
<td>98.6</td>
<td>97.8</td>
</tr>
</tbody>
</table>

*Numerator: extraction effectiveness for propellants aged under natural conditions only; denominator: for propellants aged both under natural and artificial conditions.

Analysis of propellant solutions using the HPLC technique is troublesome. Both nitroglycerine and nitrocellulose (basic components of propellants migrating into the solutions in the dissolving process) "clog" the chromatographic columns, making measurement more difficult. Thus the afore-mentioned limitations of gas chromatography [13] and low effectiveness of extraction that result in a necessity to subject only completely dissolved propellant samples to the chromatographic analysis (Table 2) that in turn limits the possibilities of the HPTLC technique just imposed a need to use the thin-layer chromatography.

Assessment of quantity and kinetics of change of the stabilizers by means of the thin-layer chromatography

Favorable conditions of proper analysis of propellant samples (dosing volume, solution viscosity, etc.) were obtained in the case of acetone as a solvent and the following proportion: 1 g of a propellant and 100 ml of acetone. Propellant solutions of this concentration and volume of 5 µl applied on a chromatographic plates allow a densitometric measurement of both stabilizers (DPA and C-I) as well as first products of their change and provide satisfactory values of the signals being measured.

It was assumed that the measurements of DPA loss, confirmed by a N-NO-DPA and 2-NO₂-DPA increase in the case of double-base propellants and measurements of C-I loss confirmed by a 4-NO₂-C-I
increase as well as kinetics of these changes, would provide a sufficient information set, necessary to determine a degree of propellant stability. Detailed data related to the separation of these substances on HPTLC plates were given previously [16].

Existence of double bonds in DPA and C-I molecules as well as that of product of their changes allowed to foresee a priori occurrence of the characteristic absorption bands in UV spectra of these compounds. Results of the measurement (CS-9000 densitometer, Shimadzu) confirmed the suggestion (Figs. 3, 4). In Figure 5 the variations of area of the densitometric peak (S) are shown as a function of concentration (c) of DPA and C-I. A linear relationship $S = f(c)$ was obtained also for the remaining compounds in concentration interval of 0.1–3.5 %. Determination errors of the above mentioned components were within an interval of 0.3–0.9 %. They were determined basing on experiences on standard solutions of these substances (two series of measurements, ten determinations in a series).

**Figure 3.** Absorption spectra of components being determined in measurements of single-base propellants

**Figure 4.** Absorption spectra of components being determined in measurements of double-base propellants. DNT – dinitrotoluene, DBP – dibutyl phthalate
Figure 5. Calibration curves. Dependence of peak area (S) on stabilizer concentration in a propellant sample: a) DPA, b) C-I

Practical testing

The method was verified on samples taken from more than 50 lots of single-base, more than 50 lots of double-base and 15 lots of emulsion-type ball propellants. This means that practically all types of propellants were included in the testing (rocket, artillery and small arms ones). “Age” of the propellants was within 1–50 years. Large-grain propellants were disintegrated into chips 0.1 mm thick; small-grain and small arms propellants were not disintegrated. From each propellant lot two representative samples were taken and (1 g), seasoned for 24 h. One of the samples underwent an accelerated aging. Both samples, aged and non-aged; were dissolved in 100 ml of acetone to obtain the solution for chromatographic analysis. The same propellant lots were subjected to the Bergmann–Junk test that allowed to assess if and to what degree the proposed analytical method (measurement of the stabilizer) is in agreement with esters decomposition measurement.

A differentiation of chemical stability of particular propellant lots was observed. Neither the stabilizers nor any products of their changes were found in three lots of single-base propellants and six double-base ones. In six lots of single-base propellants and two double-base ones a nearly complete consumption of stabilizers and a large amount of products of their changes were found. A large content of the stabilizers (small changes under conditions of natural aging) and an extremely large extent of their reaction products after accelerated aging was observed in seven lots of single-base propellants and six double-base ones. The remaining propellants were considered to be stable. They featured both a sufficiently high stabilizers content and small changes under conditions of accelerated aging.
DISCUSSION AND CONCLUSIONS

Results of the measurements have confirmed the usefulness of the thin-layer chromatography and densitometry for propellant stability assessment. All the propellant lots that were found to be unstable (both due to lack of the stabilizer or due to an excessive speed of its change under condition of accelerated aging) passed the Bergmann–Junk test unsuccessfully. The propellant qualified as stable passed this test successfully. Here, the superiority of the TLC method not only over the Bergmann–Junk one but also over the HPLC method should be emphasized. This superiority is visible first of all in a large peak capacity of the TLC and a possibility to analyze many samples simultaneously. Due to this, duration of one sample analysis, is only 3–4 min and is nearly 10-fold shorter than the determination by means of the HPLC and 15-fold shorter than iodometric analysis used in the Bergmann–Junk test.

The superiority of the second group of propellant stability testing methods based on the determination of the stabilizers is obvious. Only dependable, repeatable and accurate measurements of stabilizer content and kinetics of its change may provide a basis to develop tables of safe storage times and frequency of subsequent control tests of particular lots of propellants.

The analytical method used in herein described research and proposed for implementation seems to be the most proper one for measurements and quantitative determination of propellant components, because:

- condition of separation of components of a propellant mixture should be recognized as a necessary one: this condition just imposes chromatographic methods,
- a need to dissolve completely the samples, resulting from difficulties in extraction effectiveness, limits the possibilities of the HPLC application due to the matrices (nitroglycerine or nitrocellulose) that will cause a very fast wear-out of the chromatographic columns,
- physical and chemical properties of the stabilizers, first of all their low stability in an elevated temperature, limit the possibilities of use of the column gas chromatography,
- the afore-mentioned limitations do not concern the thin-layer chromatography; TLC features the lowest cost of the above-mentioned methods, simplicity of determination and a possibility to analyze up to 20 propellant samples simultaneously,
- densitometric measurements ensure high precision and repeatability of determinations, that are necessary in so important analyses as tests on chemical stability of propellants.

A relatively extensive set of the test data allows also some generalization not concerning analytical technique. The most important of them seems to be the lack of relationship between stability and storage time. It has been found that the reaction of stabilizer under natural aging conditions and also the speed of its change at an elevated temperature do not depend on the “age” of propellant. Some lots of propellants stored for several dozen years featured a higher stability than ones manufactured just several years ago. This may mean that the critical factor for a propellant stability
is not propellant "age" but rather purity of the esters. This suggestion is confirmed by quality of propellants that is decreasing within a dozen or so of recent years (understood, of course, in the light of their stability). This fact may be a consequence of natural environment pollution, i.e. unintended, trace impurities in the raw material used in manufacturing of propellants.

REFERENCES


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