

Chemical and energetic changes in thermally aged urea-stabilized double-based propellants

Mirjana B. Krstović^a, Teodora D. Stančić^b

Military Technical Institute, Belgrade, Republic of Serbia

^a e-mail: mirjanakrstovic@yahoo.com, **corresponding author**,

ORCID iD: <https://orcid.org/0000-0002-5469-3581>

^b e-mail: teodorastancic@gmail.com,

ORCID iD: <https://orcid.org/0009-0009-1974-5727>

 <https://doi.org/10.5937/vojtehg74-61613>

FIELD: chemical technology

ARTICLE TYPE: original scientific paper

Abstract:

Introduction/purpose: Nitrocellulose-based propellants exhibit satisfactory properties for the majority of conventional munitions, although their tendency to lose effectiveness over time results in less operational efficacy and safety issues. The process of chemical aging and a decrease in certain properties occurs gradually due to the degradation of nitro esters into nitrogen oxides. A comprehensive spectrum of test processes has been established globally as a quality control system to reduce the risk of accidents in warehouses. One method that provides insight into the existing condition and estimates service life is artificial aging at specific temperatures.

Methods: The study examines the chemical stability of double-based rocket propellant after accelerated aging at 70°C for a duration of 60 days. The samples were systematically analyzed every 10 days to assess the variations in important parameters of chemical stability at the laboratory level. High-performance liquid chromatography (HPLC) was applied to determine the concentration of stabilizers, as well as other organic constituents (plasticizers and nitroglycerin), while the isoperibolic calorimeter allowed the evaluation of energetic potential.

Results: The results demonstrate that double-based propellant stabilized with urea derivatives retains significant stabilizer concentrations under artificial aging, allowing this propellant type to preserve chemical stability for extended periods. The variations in the values of nitroglycerin and plasticizer are associated with elevated temperatures and the aging of samples without an inhibitor layer.

ACKNOWLEDGMENT: This work was supported by the Ministry of Science, Technological Development and Innovations (Serbia), Contract No. 451-03-34/2026-03/200325, and the University of Defense, Military Academy, Project No. VA-TT/1/22-24.

Conclusion: Data provided by the artificial aging of double-based gunpowder can be beneficial for assessing the chemical stability of well-preserved ammunition over time.

Key words: double-based rocket propellant, stabilizer, energetic potential, HPLC, calorimetry.

Introduction

Despite continuous developments and research, the military industry continues to primarily depend on nitrocellulose (NC) based propellants. Such energetic materials exhibit satisfactory properties for the majority of conventional munitions. The advantages of this ammunition type (cost, manufacturing methods, characteristics) are counterbalanced by its tendency to lose effectiveness over time, resulting in less operational efficacy. The nitrocellulose problem was noticed already in the final decade of the 19th century and the beginning of the 20th century, following numerous incidents in warehouses and aboard ships transporting gunpowder, leading to concerns regarding the stability of energetic materials based on nitrocellulose (Maksimović, 1985, p. 34-35). Extensive testing revealed that the chemical stability of gunpowder and rocket propellant decreases over time due to the autocatalytic decomposition of nitric acid esters, even at ambient temperatures. A number of reactions occur in nitrocellulose powders, resulting in the formation of breakdown products over time, including carbon oxides, nitric and nitrous oxides, methane, formaldehydes, water and nitrogen (Lindblom, 2004, p. 9). The main concern is nitrogen oxides, as they ultimately result in exothermic processes that establish critical conditions for self-ignition. The process, regrettably, cannot be entirely halted, but can only be mitigated by the incorporation of stabilizers - organic compounds that bind nitrogen oxides. The aging process of gunpowder is characterized by mass decrease, changes in molar masses, variations in nitrogen concentration within nitrocellulose, modifications in stabilizer composition, and heat emission (Grbović, 2025, p. 443). The manufacturer's warranty encompasses a duration of 10 years, in which the ammunition will maintain its mechanical, ballistic, and chemical properties, and after that period, according to the fact that the complete elimination of chemical aging in nitrocellulose energetic materials is unfeasible, an extensive variety of tests has been established globally to assess present chemical stability or estimate the safe shelf life. Each country in peacetime accumulates a large amount of ammunition in order to use it in wartime. To provide safety and reliability



of ammunition, it is imperative to implement protocols that reduce the risk of gunpowder self-ignition and accidents in storage facilities.

Serbia possesses its own standard, which establishes the assessment of the chemical stability of gunpowder and rocket propellants. The referenced standard is broad and highly detailed, although it applies to instruments whose performance is now considerably outdated. Nonetheless, stringent criteria and techniques facilitate the oversight of the situation and the regulation of ammunition storage, thus ensuring the secure management of ammunition resources.

The preparation, duration, and conditions of individual tests may differ considerably based on the type of gunpowder sample being evaluated. Gunpowders have advanced from single-base, mostly composed of nitrocellulose, to double-base, which includes both NC and nitroglycerin (NG), and further to triple-base, comprising NC, NG, and nitroguanidine (Jelisavac et al., 2019, p. 51). The modification of their properties, dependent upon the application and efficacy of the weapon and ammunition in which they are integrated, is accomplished by various additions of either organic or inorganic form. Some have significantly improved energetic characteristics by adding a certain amount of nitramine explosives to the composition, creating composite modified gunpowder. To enhance adequate processability, different plasticizers and chemical treatment agents are incorporated. Moreover, their configurations can vary significantly, ranging from diminutive spheres and flakes to perforated tubes or singular blocks. Certain methods include grinding the gunpowder to exact dimensions to achieve representative results, whereas others aim to replicate the conditions present in a cartridge as closely as possible. Most approaches have a commonality in elevating the temperature to expedite reactions that would otherwise occur within the gunpowder mass over an extended duration. It is essential to note that the majority of the criteria for evaluating chemical stability have been established empirically, serving as a benchmark that is consistently understood to prevent self-ignition.

The artificially aging method for gunpowder was first designed solely to assess the degradation of stabilizers over time, serving as a quantitative measure of chemical stability. The method outlined in the domestic standard (Jelisavac et al., 2018, p. 81) also facilitated the monitoring of additional parameters, including changes in the content of other organic components and the assessment of mass loss at a specified temperature, while the sample quantity was adequate to evaluate the effect on energetic potential following treatment at an elevated temperature for 60 days.

Materials and methods

This study examines four samples of double-based gunpowder (DBGP) composed of NC, NG, stabilizer (urea derivative - ethyl centralite, EC), plasticizer - dibutyl phthalate (DBP), and a certain amount of inorganic compounds. All of the samples were treated at a temperature of 70°C for 60 days. Table 1 shows data on the initial values for the tested samples before samples were artificially aged.

Table 1 – Initial values for tested materials

Sample	Organic compound (mass %)			MV, 120°C (min)	energetic potential (cal/g)
	EC	DBP	NG		
DBGP 446	2.79	2.02	32.55	46	913.8
DBGP 229	2.78	2.30	32.04	46	909.9
DBGP 515	2.78	2.25	32.74	45	909.6
DBGP 157	2.72	2.26	32.07	45	905.9

All samples are five years old; the inhibitor has been eliminated during the delaboration process, and the samples were exposed outside the rocket engine for a few weeks before analysis.

Sample preparation for artificial aging

Gunpowder samples were inserted into suitable glass test tubes with ground stoppers. If the gunpowder was of substantial size, it was shaped into sticks (Figure 1), with a length corresponding to the mass specified by the standard.

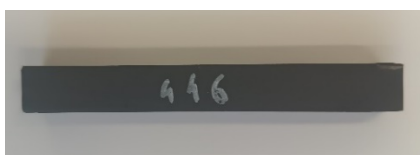


Figure 1 – Left: sample prepared for artificial aging; right: sample prepared for acclimatization in a climate chamber

A sufficient number of pieces are cut for the test, enough pieces for every 10 days and to maintain a reference piece, which will remain at ambient temperature for the whole length of the experiment. Testing is permitted only on materials that have undergone the Methyl Violet

technique for over 45 minutes prior to the test paper's complete transition from purple to salmon color.

Before the beginning of the accelerated aging process, the prepared samples and test tubes must be acclimatized in a climate chamber for 48 hours at a temperature of $20 \pm 5^\circ\text{C}$ and a relative humidity of $65 \pm 2\%$ (Figure 2, left). This step is crucial, as conventional thermoblock tubes exceed the dimensions of the sample, resulting in significant free volume and air that may interact with the gases within the tube throughout the aging process.



Figure 2 – Left: samples in a climate chamber; right: samples placed in thermoblock

Elevated humidity facilitates the evaporation of gases alongside water at increased temperatures, hence enhancing safety for the operators. Upon thorough preparation, the test tubes are sealed with stoppers and sealant to inhibit gas exchange with the external environment. Fully prepared samples are placed in a thermoblock (Figure 2, right), which must maintain a consistent temperature throughout the experiment, allowing for fluctuations of $\pm 1^\circ\text{C}$.

The samples remain sealed inside the thermoblock for the entire experimental period at a constant temperature and are collected and examined at a specified period. At the established temperature of 70°C , it is presumed that one test tube is extracted from the block every 10 days. Considering that the samples are at a temperature much higher than ambient temperature, they are allowed to equilibrate at room temperature for 2-3 hours following their removal from the thermoblock, which is shown in Figure 3, the first figure from the left. Subsequently, they are taken out of the test tube (Figure 3 in the middle), crushed to the requisite dimensions (Figure 3 at the right side), and prepared for analysis by the high-performance liquid chromatography (HPLC) technique. Sample preparation requires cutting the samples into dimensions of 2x2 mm, necessitating the use of a non-sparking tool.

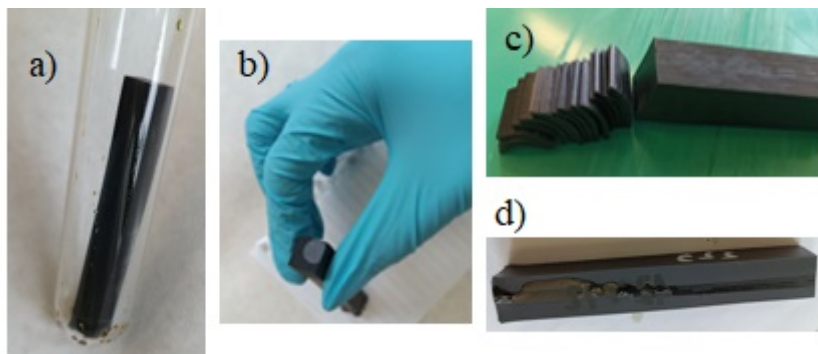


Figure 3 – a) sample in the test tube after removal from the thermoblock; b) sample after removal from the test tube; c) sample in the grinding process; d) a sample on which the consequences of the condensed phase are visible

Given that the mass of the aged samples significantly exceeds the requirements for HPLC analysis, the remaining samples were utilized for isoperibolic calorimetry testing to determine any fluctuations in energetic potential resulting from sample aging and to acquire a more precise understanding of the changes occurring in double-based propellants over time. However, considering the observable evidence of droplets on the samples (Fig. 3d), indicative of wetting and the migration of specific components, these regions were eliminated to ensure the most precise data, and only the areas devoid of visible "wet" signs were analyzed.

HPLC method and sample preparation

High-performance liquid chromatography is a crucial technique for quantifying organic constituents in gunpowder and double-based rocket propellants. The primary advantage over gas chromatography is the significantly lower operating temperatures that facilitate the detection of thermolabile substances. This is a very precise analytical technique that provides the exact identification and quantification of desired components. Each organic component possesses a distinct time frame at which it manifests on the chromatogram, dependent upon the established parameters of the procedure, and exhibits a clearly defined spectrum and wavelength distinctive of the specific chemical. This technique involves the injection of a high-pressure liquid solvent into a column filled with a solid adsorbent material, referred to as the stationary phase. Each component in the examined sample exhibits a distinct retention time owing to its specific interaction with the stationary phase, leading to the separation of components (Author et al., 2025, p. 4).

The "Waters 1525 Binary HPLC Pump," equipped with a column heating thermostat, the manual injector "Rheodine Model 7125," and the photodiode array detector "Waters 2998 PDA" were employed for the quantitative analysis of organic compound concentrations in prepared samples, with the following method characteristics: detector PDA (220 nm), column C18 (length 150 mm, ID 4.6 mm and particle size 3 μm), column temperature (not above $35^\circ\text{C} \pm 0.5^\circ\text{C}$) the mobile phase, acetonitrile: water (67:33 v/v), and the flow rate of 1.2 mLmin^{-1} .

HPLC operates by introducing known volumes of each component within the suitable range, enabling the software to generate a calibration curve for the identification and quantification of that particular component. Three calibration curves were established for the specified samples: the EC stabilizer ranged from 1% to 3.5%, the plasticizer from 1% to 3%, and NG from 25% to 35%. The processing of data and operational manipulation were carried out with the Breeze HPLC program. The outcomes were presented as mass percentages, with a precision of two decimal places.

Sample preparation for HPLC, which is shown in Figure 4, involves several steps: grinding the propellants into small fragments, passing them through sieves with a 2 mm opening, measuring exactly 1.000 g of the sample, and placing it into a flask. Next, 50 cm^3 of dichloromethane is added, and the flask containing the sample is stored in a dark place at ambient temperature for 48 hours.

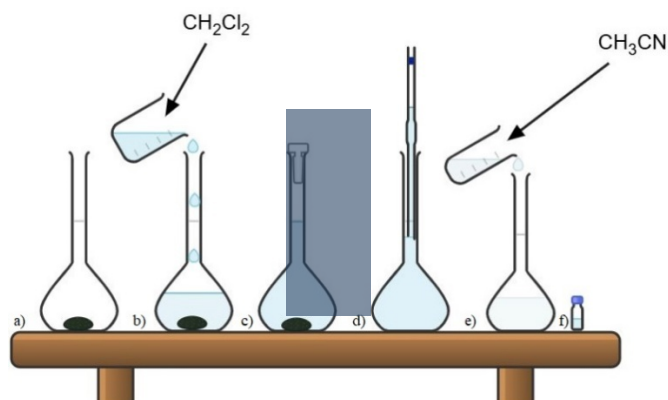


Figure 4 - Sample preparation in dichloromethane: a) 50 cm^3 flask with sample, b) adding dichloromethane to the flask, c) 48 h of extraction in the dark, d) taking 1 cm^3 of the solution for transferring to a 10 cm^3 flask, e) introducing acetonitrile into the flask after evaporation of dichloromethane, f) prepared sample for injecting into the HPLC vial

Subsequently, 1 cm³ of the solution was transferred to a 10 cm³ flask, where dichloromethane was extracted at low-temperature conditions (about 40 °C), followed by the addition of 10 cm³ of acetonitrile. To obtain satisfactory results, it was imperative to filter the sample using a 0.5 µm PTFE filter prior to utilization (Author et al., 2022, p. 140).

To provide the repeatability and reliability of the data, each sample was prepared in duplicate, and each vial's sample was injected twice. The result shown in this study represent mean value of four measurements.

Isoperibolic calorimetry method

Combustion calorimetry is a technique that quantifies the heat released during a deflagration/combustion process. Given that powders and rocket propellants are classified as propellants, the energy released during the deflagration process is a crucial measure for assessing their efficacy. Considering that the combustion of energetic materials occurs in cartridge cases, it is essential to assess the concentration of external oxygen, specifically in an inert gas atmosphere, to accurately evaluate the energetic potential of the material under examination.

The IKA C2000 and the calorimetric bomb C5010 were employed for the experimental evaluation of the energetic potential. This technique comprises a sealed steel chamber containing the sample, immersed in water at a preset temperature. The test sample, possessing a known mass, is burned in a bomb under argon at a pressure of 20 bar. The generated heat is subsequently conveyed to a water jacket, where the temperature fluctuations are monitored (Author et al., 2024, p. 38).

Heat capacity quantifies the quantity of heat necessary to increase or decrease the temperature of a material by 1 K (Halliday et al., 2013, p. 524). The concept pertains to the ratio of heat (Q) exchanged between the material and the surroundings, along with the alteration in body temperature (ΔT). The energetic potential or heat value of combustion per gram of sample mass (m) is then:

$$\frac{\Delta TC_v}{m} = Q, \quad (1)$$

where:

Q – energetic potential, J/g (or Q/4.1868 to express the value in cal/g);

ΔT – temperature change, K;

C_v – calorimeter heat capacity (water equivalent), J·K⁻¹;

m – sample mass.

Figure 5 shows the sample preparation for calorimetry measurement, which involves cutting the sample to an appropriate size of 2x2 mm cubes, weighing between 2.0-2.4 g, inserting the sample into a quartz container, attaching the chrome-nickel wire for electrical connections, and sealing the bomb.



Figure 5 - Left: positioning the sample within the quartz container of the bomb; right: bomb prepared for the experiment

Given that the test is performed in an inert atmosphere, it is essential to initially evacuate the residual air from the bomb using a vacuum pump before subsequently introducing argon. Subsequently, the bomb is positioned in the calorimeter, and the remainder of the experiment proceeds autonomously.

Monitoring mass reduction

Mass loss is a significant parameter that indicates aging processes and alterations to energetic materials. While thermogravimetric analysis is predominantly employed as an instrumental technique that efficiently replicates specific processes in energetic materials, this research tracked the mass change in the tested samples using a standard gravimetric method during the entire experiment. The weight of every sample was initially measured before placement in the test tubes and exposure to the conditions within the climate chamber. Subsequently, the mass was remeasured after the samples were extracted from the test tubes, before the crushing process for further analysis started. The measurement of the mass reduction was determined as follows:

$$\frac{m_b - m_a}{m_b} \times 100 = m_l, \quad (2)$$

where:

m_b – mass before artificial aging, g;

m_a – mass after artificial aging, g;

m_l – mass reduction, %.

Results and discussion

All samples were tested consecutively; they were prepared and analyzed dynamically as they were taken from the thermoblocks every 10 days. The values obtained by the HPLC method are presented in Table 2. The accelerated aging method is solely designed for assessing the stabilizer concentration in gunpowder and rocket propellants, as this component decreases with time due to interactions with nitrocellulose degradation products.

Table 2 – Organic compounds content in DBGPs

DBRP 446							
day	10.	20.	30.	40.	50.	60.	ref.samp.
NG	31.49	31.46	30.64	30.46	30.20	29.0	32.18
EC	2.66	2.62	2.5	2.45	2.37	2.26	2.88
DBP	2.23	2.23	2.22	2.26	2.28	2.26	2.30
DBRP 229							
day	10.	20.	30.	40.	50.	60.	ref.samp. ¹
NG	32.27	32	31.76	31.52	31.38	28.86	/
EC	2.64	2.59	2.51	2.40	2.35	2.20	/
DBP	2.34	2.36	2.33	2.30	2.40	2.35	/
DBRP 515							
day	10.	20.	30.	40.	50.	60.	ref.samp.
NG	32.27	32.10	31.80	30.9	30.74	29.0	32.10
EC	2.80	2.62	2.54	2.41	2.30	2.24	2.83
DBP	2.24	2.23	2.20	2.19	2.18	2.22	2.21
DBRP 157							
day	10.	20.	30.	40.	50.	60.	ref.samp.
NG	33.1	31.28	31.22	31.09	30.74	30.37	31.78
EC	2.79	2.71	2.54	2.47	2.33	2.26	2.80
DBP	2.31	2.31	2.26	2.21	2.32	2.28	2.27

The results indicate that the temperature and duration of the experiment initiated rapid aging processes, as seen by the significant reduction in the starting stabilizer value. Despite the apparent degradation of the stabilizer, it did not result in a decline considered critical by the

¹Due to an insufficient quantity of propellant, there was not enough substance for a reference sample for DBRP 229.

domestic standard. The observation that the stabilizer content decreased by no more than 20% over a 60-day period signifies that it is a fuel exhibiting considerable chemical stability.

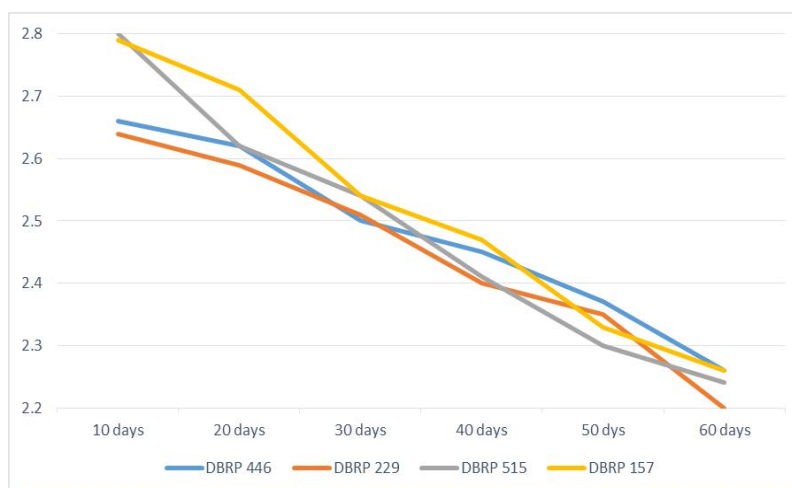


Figure 6 – Correlation between stabilizer consumption and time for DBRP 446, DBRP 229, DBRP 515 and DBRP 157

Figure 6 illustrates the correlation between stabilizer consumption and time, demonstrating a consistent decline in stabilizer value across all four samples, indicative of their identical compositions. The consumption of EC over time is minimal, a characteristic of the urea derivatives, which serve as the predominant stabilizers of double-based compositions, thus ensuring prolonged chemical stability of this category of energetic materials.

Since the HPLC method supports simultaneous analysis of all organic components in the sample, it was used in this investigation to also observe the behavior of NG and plasticizers during the accelerated aging process. However, this method is not primarily designed for such purposes. The explanation for the phenomenon is that, while the stabilizer decreases over time, the NG and plasticizer do not degrade but rather tend to migrate. This movement was notably demonstrated under artificially induced conditions, such as accelerated aging in the laboratory. The temperature of 70 °C is sufficiently elevated, and the absence of the inhibitor, which was eliminated from the fuel for this test, further expedited those processes. It became evident after the first 20 days that migration and reaction were occurring, as the elevated temperatures in the thermoblock caused a condensed phase to form on the surface of the test tube, which

then descended to the bottom during the cooling process (Figure 3). Furthermore, the samples progressively lost their original shape due to thermal exposure, as shown in Figure 7.

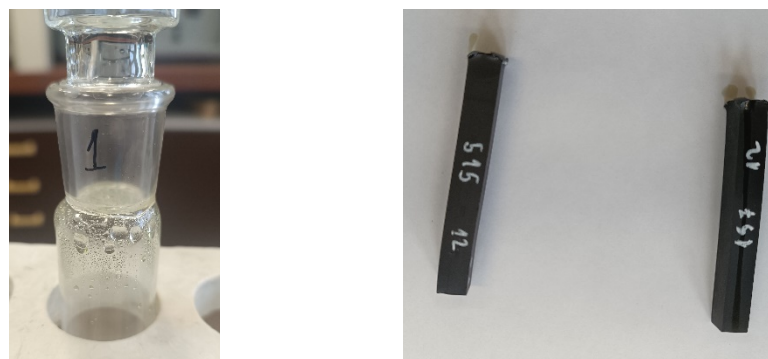


Figure 7 – Left: condensed phase on the surface of the test tube; right: change in shape due to heat

Table 2 shows a specific regularity in the value of NG, which progressively fluctuates over time. However, it is imperative to emphasize that this change should not be interpreted as a universal regularity applicable to all energetic materials, nor does it suggest that migration will occur in an actual inhibited rocket propellant chamber. Nitroglycerin is known to migrate into compatible materials with which it comes into contact, but it rapidly attains equilibrium.

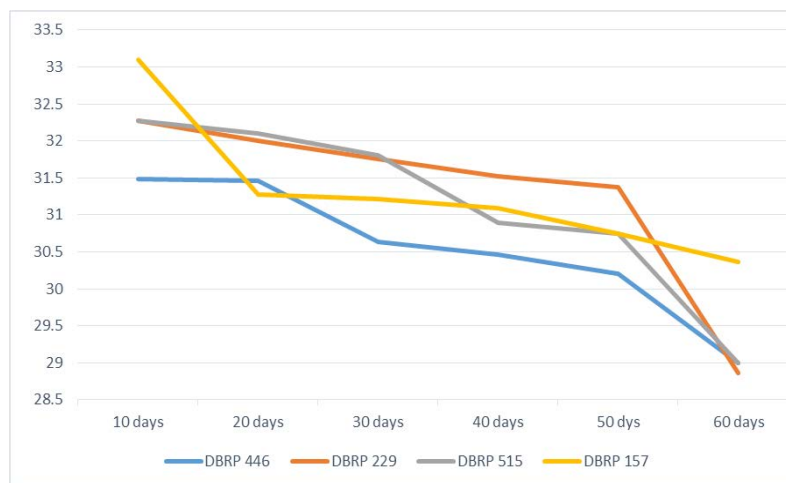


Figure 8 – Correlation of NG consumption and time for DBRP 446, DBRP 229, DBRP 515 and DBRP 157

The elevated temperature maintained during the experiment for 60 days, along with the lack of any barrier to inhibit migration, resulted in specific alterations. Although a reduction in NG content was observed throughout the experiment, it is important to highlight that on the 10th day, samples 515 and 157 exhibited values surpassing those of the reference sample. It was observed throughout all four samples that by the end of the experiment (the 60th day), a decrease of around 3% in NG was recorded relative to the original value, indicating that this quantity had migrated from the fuel.

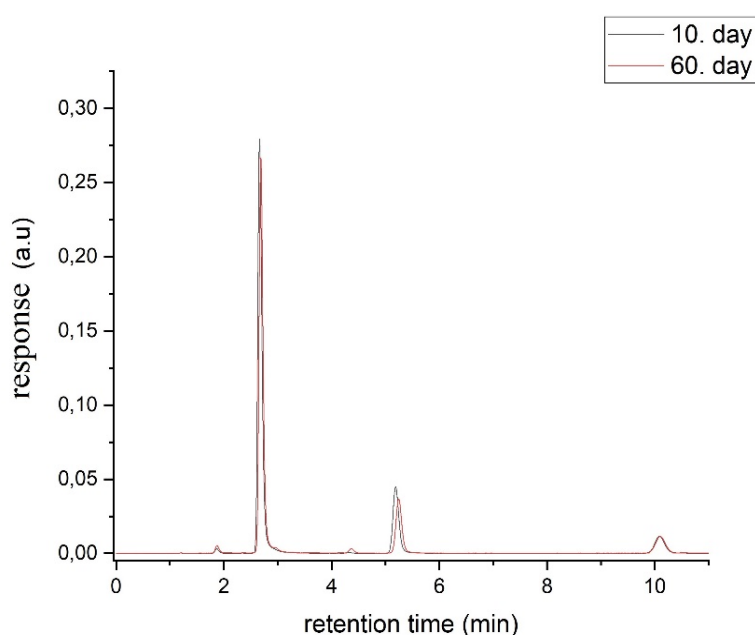


Figure 9 – Chromatogram of sample DBRP 157, 10th and 60th days

The results mentioned above should be evaluated based on the presence of the condensed phase in the test tube and the absence of the inhibitor. An optimal setting that would provide a definitive answer about the behavior of NG in double-based propellant would involve aging samples in their real dimensions and in the original cartridge. This will ascertain the direction of NG migration, whether from the center to the periphery of the grain, from top to bottom, or the opposite, and to what degree these activities are slowed down by inhibitor presence.

The values obtained by monitoring the DBP content demonstrate that the specified plasticizer exhibits considerable thermal resistance,

revealing not a decline but rather fluctuations within the samples, ranging from 0.06% to 0.1%, thereby maintaining relatively stable values, as shown in Figure 10.

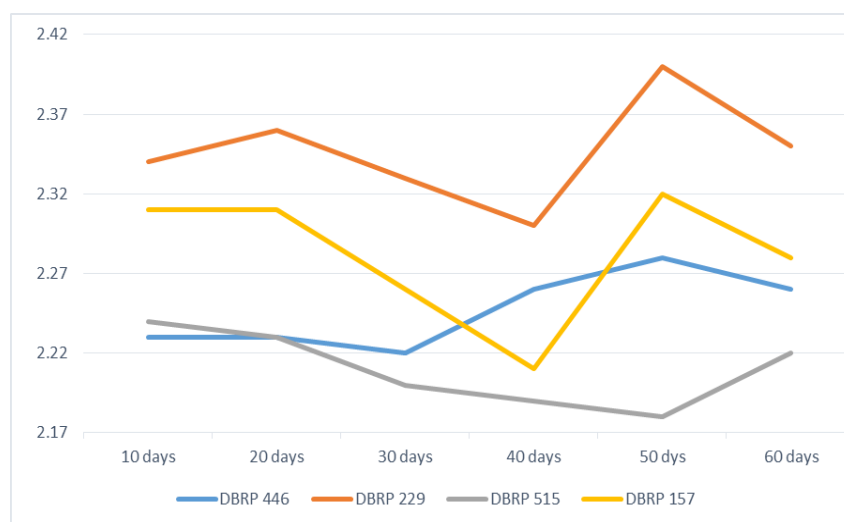


Figure 10 – Correlation of DBP consumption and time for DBRP 446, DBRP 229, DBRP 515 and DBRP 157

The energetic potential is an indicator that provides insight into the operational capacity of the composition of energetic materials such as propellants. Given that the heat of combustion (energetic potential) is a thermodynamic characteristic that directly correlates with the components of gunpowder and rocket propellants, the energetic potential was measured post-aging of the samples to assess the effect of the reduction in specific organic constituents. The variation in the energy released during combustion is directly attributable to the decrease in the concentration of the most energetic substance (NG), along with alterations in the stabilizer content. The first sample (DBRP 446) was analyzed post-removal of each test tube, revealing that changes in energetic potential values occur at a slow rate. Consequently, the remaining samples were assessed in a bomb calorimeter at intervals of 10, 30, and 60 days. The data obtained, representing the average of two measurements, with an allowable inaccuracy of 1 cal/g, are presented in Table 3.

Table 3 – Energetic potential values for samples DBRP 446, DBRP 229, DBRP 515 and DBRP 157

Day	Energetic potential (cal/g)			
	DBRP 446	DBRP 229	DBRP 515	DBRP 157
Ref. sample	913.6	/	909.1	908.5
10.	905.3	906.0	905.8	908.2
20.	908.2	/	/	/
30.	905.1	900.1	900.6	903.1
40.	901.7	/	/	/
50.	898.5	/	/	/
60.	887.4	880.1	885.2	900.7
Decrease in energetic potential from ref. to 60. day	26.2	25.9	23.9	7.8

The results in Table 3 correspond with the data from Table 2 about the NG content. Specifically, it is evident that the values measured on the 10th day align with the trend of energetic potential values for the samples; higher measured NG content correlates with elevated energetic potential values. On the 10th day, DBRP 157 had the largest energetic potential, although the values of samples DBRP 229 and DBRP 515 were very consistent, as were their NG contents. The minimum energetic potential was recorded for sample DBRP 446, which concurrently exhibited the lowest measured NG concentration. A similar trend is noted in the findings from the 60th day, with DBRP 157 exhibiting the highest values and DBRP 446 the lowest, while the other two samples display relative uniformity. Nonetheless, despite the apparent trend, it must be approached with caution, as there were clear indications that excess moisture, along with various components, migrated from the sample, and since it was unable to leave the test tube after cooling to room temperature, it accumulated on both the test tube and the sample. The removal and selection of samples devoid of wet traces may have affected the accuracy of the assessment of the condition of double-based propellants following accelerated aging.

Knowing that mass loss can serve as an indicator of the aging of gunpowder and double-based propellants, a gravimetric approach was employed to monitor the temporal variations in mass. The samples were weighed prior to their placement in the climate chamber and subsequent to removal from the thermoblock, with the mass differential computed in accordance with Equation 2. Tables 4-7 shows data on monitoring mass reduction for the tested samples.

Table 4 – Mass reduction over time for sample DBRP 446

Day	m _b (g)	m _a (g)	loss (%)
10.	21.1456	20.9012	1.16
20.	21.7886	21.4273	1.66
30.	19.6592	19.2923	1.87
40.	23.3835	23.0188	1.56
50.	20.7589	20.3282	2.07
60.	21.1776	20.8126	1.72
Ref.	22.1516	22.1650	+0.06

Table 5 – Mass reduction over time for sample DBRP 229

Day	m _b (g)	m _a (g)	loss (%)
10.	22.3855	22.1288	1.15
20.	22.2850	21.9908	1.32
30.	22.3698	22.0296	1.52
40.	22.1296	21.7641	1.65
50.	22.2389	21.9797	1.17
60.	22.3457	21.8692	2.13
Ref.	/	/	/

Table 6 – Mass reduction over time for sample DBRP 515

Day	m _b (g)	m _a (g)	loss (%)
10.	22.4548	22.2456	0.93
20.	22.0278	21.7731	1.16
30.	22.1609	21.8881	1.23
40.	22.0922	21.7269	1.65
50.	22.8253	22.5884	1.04
60.	22.2459	21.9909	1.15
Ref.	22.2837	22.2955	+0.05

Table 7 – Mass reduction over time for sample DBRP 157

Day	m _b (g)	m _a (g)	loss (%)
10.	22.4483	22.2092	1.07
20.	22.4625	22.1945	1.19
30.	21.8810	21.6189	1.20
40.	22.2996	22.0091	1.30
50.	22.6924	22.4584	1.03
60.	22.4100	22.1293	1.25
Ref.	21.7591	21.7700	+0.05

Tables 4-7 clearly demonstrate the tendency for mass loss to increase with the duration of exposure of the samples to elevated temperatures in the thermoblock. Despite a decline of approximately one percent within the initial 10 days, and up to 2% by the 60th day, individual variances may manifest as early as the 40th or 50th day. These discrepancies are directly correlated with the quantity of condensate retained on the samples during the cooling process, ultimately influencing the mass measured when the test tubes are opened. The most notable instance of this is sample DBRP 229 on the 50th day (Figure 3d), which exhibits a mass loss of about 1.17%, although ten days prior, the loss was 1.65%, and ten days subsequently, it increased to 2.13%. Additionally, it is notable that the samples DBRP 515 and DBRP 157, which exhibited mild deformation owing to heat, as illustrated in Figure 7, demonstrate behavior similar to that observed on day 50, when a divergence from the decreasing mass loss values occurs. For instance, a significant alteration was observed at the lower section of the sample, particularly in the area that contacted the test tube, where the highest concentration of condensate accumulated post-cooling. The results indicate that mass loss over time is apparent during the aging process and can be monitored using the gravimetric method, acknowledging that certain deviations may arise due to the

presence of moisture and the initiation of specific reactions at elevated temperatures.

Conclusion

This study focused on double-based propellants and their aging in accordance with the domestic standard requirements. In addition to the fundamental approach of monitoring the stabilizer over time, the samples were analyzed for the presence of other organic constituents (NG and DBP) and submitted to further assessments, including the evaluation of energetic potential and the measurement of mass loss.

Based on the findings, the following conclusions were reached:

- The implementation of the domestic standard facilitates the monitoring of stabilizer consumption over time and allows for the evaluation of chemical stability based on the data received from the stabilizer,
- EC exhibits relatively low consumption over time, maintaining chemical stability and preventing self-ignition in warehouses for extended durations, which is essential for rocket propellants kept for several decades,
- A gradual decrease in the NG content of the samples was noted over time, exhibiting an obvious trend. Nonetheless, observing the migration of NG is unfeasible within such a limited sample; it is only able to document its occurrence, but not the direction it would assume under real propellant dimensions or the influence of inhibitors on this process,
- The measurement of the change in plasticizer content revealed a minor deviation in the mass distribution of the double-based propellant during the aging process. This phenomenon is related to the fact that plasticizer does not form hydrogen bonds with the polymer. By penetrating the macromolecule, it separates them and forms the plastic mass. This characteristic is identifiable by variations in the plasticizer content rather than its reduction,
- A substantial quantity of samples aged according to the national standard criteria facilitates adequate samples for additional analyses,
- The evaluation of energetic potential using calorimetry revealed a significant correlation between the reduction of the "most energetic" component (NG) and a reduction in energetic potential, which characterizes functionality rather than the chemical stability of double-based propellants,

- The gravimetric method for mass reduction measurement reveals that mass loss occurs over time due to nitrocellulose degradation processes, the consumption of stabilizers, and the migration of nitroglycerin and the sample itself. Nevertheless, the presence of moisture, increased temperatures, and degradation processes, which are partially stored in the sample post-cooling, induce distinct deviations.

The outcomes of the current study indicate that the national standard possesses several significant deficiencies: large free volume in the test tube, the introduction of moisture at the experiment's outset, and a sample of considerable mass that cannot be entirely employed for subsequent research. Minimizing the free volume and eliminating the climatic chamber phase would provide a more precise understanding of the mechanisms occurring during aging. The efficacy of monitoring NG migration and its impact on various parameters, including energetic potential, can be assessed by contrasting the results of this study with those derived from the aging of identical double-based propellants under actual conditions, encompassing total mass and dimensions, alongside the inclusion of inhibitors.

References

- Grbović, L. & Stojiljković, S. 2005. Korelacija hemijske stabilnosti prirodno i ubrzano starenih baruta. *Vojnotehnički glasnik/Military Technical Courier*, 5(25), pp. 442-450 (in Serbian). Available at: <http://www.vtg.mod.gov.rs/arhiva/2005/vojnutehnicki-glasnik-5-2005.pdf>
- Jelisavac, Lj., Stojiljković S., Brzić S., Nešić J., Fidanovski B., & Tanaskovski B. 2019. Modification of AOP-48 Ed.2 Extrapolation Expression by Introduction of Real Storage t-T Conditions of Naturally Aged Nitrocellulose Gun Powder. *Scientific Technical Review*, 69 (3), pp. 49-54. Available at: <http://www.vti.mod.gov.rs/ntp/rad2019/3.pdf>
- Jelisavac Lj., Stojiljković S., Gačić S., Milojković A. & Petković-Cvetković J., Temperature Parameterization of the Stabilizer Consumption in Naturally and Artificially Aged Single Base Gunpowder, *Scientific Technical Review*, 68 (1), pp. 80-87, Available at: <http://www.vti.mod.gov.rs/ntp/rad2018/1.pdf>
- Krstović, M., Rakić, M., Jelisavac, Lj., Dimić, M., Mojsilović, J. & Fidanovski, B. 2022. Comparative Analysis for Determination of Stabilizer Content in Gunpowder and Double Base Propellant by HPLC Method. In: 10th International Scientific Conference on Defense Technologies, OTEH 2022, Belgrade, pp. 138-143, October 13-14. Available at: <http://www.vti.mod.gov.rs/oteh22/elementi/rad/zbornik.pdf>

Krstović, M., Bajić, D., Timotijević, M., Nešić, J. & Fidanovski, B. 2024. The Influence of Nano-Scale Aluminum on the Energetic Potential of Energetic Materials—Theoretical and Experimental Observations, *Scientific Technical Review*, 74 (1), pp. 36-42. Available at: <http://www.vti.mod.gov.rs/ntp/rad2024/1/4.pdf>

Krstović, M., Rakić, M., Mijatov, M., Mojsilović, J., Aleksić, S., & Fidanovski, B. 2025. Evaluating the Effectiveness of Different Sample Preparation Routes for Organic Components Quantification in Gunpowder and Double-Base Rocket Propellants for HPLC Analysis, *Scientific Technical Review*, 75 (1), pp. 3-10. Available at: <http://www.vti.mod.gov.rs/ntp/rad2025/1/1.pdf>

Lindblom, T., 2004, Reactions in the System Nitro-cellulose/Diphenylamine with Special Reference to the Formation of a Stabilizing Product Bonded to Nitro-cellulose, Uppsala, Comprehensive Summaries of Uppsala Dissertations from the Faculty of Science and Technology, ISBN: 91-554-5868-8.

Maksimović, P. V., 1985. Eksplozivne materije. Beograd. Vojnoizdavački zavod (in Serbian).

Praćenje hemijske stabilnosti baruta i raketnih goriva. 1991. Beograd. SORS 8069/91 (In Serbian).

Hemijske i energetske promene u termalno starenim uzorcima dvobaznih raketnih goriva stabilisanih urea derivatom

Mirjana B. Krstović, **autor za prepisku**, Teodora D. Stančić
Vojnotehnički institut, Beograd, Republika Srbija

OBLAST: hemijske tehnologije
KATEGORIJA (TIP) ČLANKA: originalni naučni rad

Sažetak:

Uvod/cilj: Pogonska goriva na bazi nitroceluloze pokazuju zadovoljavajuća svojstva za većinu konvencionalne municije, iako imaju tendenciju da vremenom gube efikasnost, što rezultira manjom operativnom efikasnošću. Proces hemijskog starenja i smanjenja određenih svojstava odvija se postepeno zbog razgradnje nitroestara u azotne okside. Sveobuhvatan spektar analiza razvijen je širom sveta kao sistem kontrole kvaliteta za smanjenje rizika od nesreća u skladištima. Jedna od metoda koja pruža uvid u postojeće stanje i procenjuje vek trajanja je veštačko starenje na određenim temperaturama.

Metode: Studija ispituje hemijsku stabilnost dvobaznog raketnog goriva nakon ubrzanog starenja na 70°C tokom 60 dana. Uzorci su sistematski analizirani svakih 10 dana kako bi se procenile varijacije važnih parametara hemijske stabilnosti na laboratorijskom nivou. Tačna hromatografija visokog pritiska primenjena je za određivanje koncentracije stabilizatora, kao i drugih organskih komponenti (plastifikatora i nitroglicerina), dok je izoperibolički kalorimetar u inertnoj atmosferi omogućio merenje energetskog potencijala.

Rezultati: Dobijeni rezultati pokazuju da dvobazna raketna goriva stabilizovana derivatima uree zadržavaju značajne koncentracije stabilizatora tokom perioda ubrzanog starenja, što omogućava ovoj vrsti pogonskog goriva da očuva hemijsku stabilnost tokom dužeg perioda. Varijacije u vrednosti nitroglicerina i plastifikatora povezane su sa povišenim temperaturama i starenjem uzoraka bez sloja inhibitora.

Zaključak: Podaci dobijeni analiziranjem uzoraka ubrzano starenih dvobaznih raketnih goriva mogu biti korisni za procenu hemijske stabilnosti pravino skladistene municije.

Ključne reči: dvobazno raketno gorivo, stabilizator, energetski potencijal, HPLC, kalorimetrija.

Paper received on: 21 September 2025.

Manuscript corrections submitted on: 28 October 2025.

Paper accepted for publishing on: 28 October 2025.

© 2026 The Authors. Published by Vojnotehnički glasnik / Military Technical Courier (www.vtg.mod.gov.rs). This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution license (<http://creativecommons.org/licenses/by/4.0/rs/>)

