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SAPONIFICATION AS AN ENABLING STEP FOR FAST GC DETERMINATION OF STABILIZERS IN SMOKELESS POWDERS

TEODORA STANČIĆ
Military Technical Institute, Belgrade, teodorastancic@gmail.com

NADA MARINKOVIĆ
Milan Blagojević Namenska, Lučani, nadam966@gmail.com

SUZANA KOVAČEVIĆ
Milan Blagojević Namenska, Lučani, skovacevic135@gmail.com

MIRJANA MILEKIĆ
Milan Blagojević Namenska, Lučani, mirjanamilekic84@gmail.com

VESNA PETROVIĆ
Technical Overhaul Facility Kragujevac, lab@trzk.co.rs

MIRJANA KRSTOVIĆ
Military technical institute, Belgrade, mirjana.krstovic@mod.gov.rs

Abstract: *Smokeless powders represent chemically unstable systems whose safety and performance critically depend on the integrity of their non-energetic organic components. Their primary constituent, nitrocellulose, is inherently prone to thermal decomposition, which under unfavorable or long-term storage conditions may lead to autocatalytic degradation and, ultimately, self-ignition of ammunition. In this context, fast and reliable determination of organic stabilizers and additives by gas chromatography (GC) is not only an analytical requirement but a safety imperative in both production and storage environments. In this work, saponification is examined as a key step in sample preparation with the potential to significantly accelerate the analytical workflow. Its performance was directly compared with conventional preparation procedures that do not include saponification, specifically extraction in methanol and extraction in dichloromethane. These approaches were systematically matched under equivalent conditions prior to GC analysis to clearly assess the impact of the saponification step on both efficiency and analytical performance. All investigated procedures provided reliable and reproducible quantification of the non-energetic organic components present in the analyzed samples by GC. However, the saponification-based method enabled a substantial reduction in total sample preparation time, by several hours, while maintaining analytical accuracy and precision. These findings demonstrate that the introduction of saponification as an initial preparation step offers a practical route toward faster GC analysis without compromising data quality. This improvement is particularly relevant for routine quality control, where reduced turnaround time directly enhances process monitoring and operational efficiency.*

Keywords: *smokeless powders, gas chromatography (GC), sample preparation, stabilizers, saponification.*

1. INTRODUCTION

Although the field of composite propulsion materials is developing rapidly, gunpowder and propellants based on nitrocellulose remain the pillar of ammunition technology in small caliber and standard artillery ammunition. Due to the inherent susceptibility of nitrocellulose to chemical degradation [1-4], extensive research has established various instrumental and classical methods to monitor its chemical aging as quality control procedures [5]. Consequently, precise criteria have been defined for evaluating and categorizing the stability of gunpowder and rocket propellants over time. However, before assessing long-term chemical stability, a critical phase in the ammunition life cycle is rigorous quality control during both production and product-acceptance phases. A key aspect of this process is the precise quantification of essential organic components, especially stabilizers and plasticizers. To meet the rigorous demands of quantifying these critical parameters, chromatographic methods emerge as the premier analytical tool, enabling rapid, efficient, and simultaneous identification and quantification of organic compounds within the propellant matrix. [6]

Therefore, the development and implementation of rapid, reliable, and precise analytical methods is essential for manufacturing facilities dedicated to smokeless powder production. While standard chromatographic protocols provide highly accurate results within brief timeframes, sample throughput remains limited by the pre-analytical

Corresponding author: T.Stančić;
E-mail: teodorastancic@gmail.com

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preparation phase. Gas chromatography (GC) generally requires between 5 and 10 minutes for analysis. Consequently, the primary obstacle in achieving rapid and reliable analytical systems shifts from instrumental analysis to sample preparation, which demands optimization for exhaustive extraction within the shortest possible time.

International [1] and domestic standards [7-8] aim to establish versatile testing methodologies. These protocols must accommodate an exceptionally wide range of propellant grain geometries, dimensions, and shapes, while seamlessly adapting to the diverse chemical compositions found in modern formulations.

The primary objective of this research is to develop a rapid sample preparation method for production-line gunpowder samples prior to gas chromatographic testing. Given that the exact chemical composition of the control samples was predetermined, three preparation techniques were employed in parallel. The study aims to achieve the fastest possible analytical workflow time without compromising the accuracy and sensitivity. For this reason, the role of saponification in the sample preparation was rigorously evaluated, focusing specifically on its impact on overall analysis speed and extraction efficiency.

2. MATERIALS AND METHODS

The nitrocellulose-based smokeless gunpowder samples used in this research were produced within the last six months at "Milan Blagojević – Namenska" factory.

These samples vary in shape and size and were specifically chosen to demonstrate the diversity of nitrocellulose powders, not only in terms of composition and application but also regarding grain geometry and dimensions. As can be seen in Figure 1, nitrocellulose-based gunpowder can take on various forms depending on the desired burning rate and the specific purpose of the system it serves. Because these physical properties significantly influence ballistic performance, the development of a universal method applicable under identical conditions to all types of gunpowder and rocket fuel is essential. Establishing such a standard aims to unify methodology across the field, ensuring that analytical results remain consistent and comparable regardless of the propellant's specific geometry and compositions.



Figure 1. from left to right: samples of NGB 261, NC-27 and SB 715

Information regarding the selected non-energetic organic compounds (diphenylamine – DPA, ethyl centralite -EC, dibutyl phthalate – DBP, camphor – camp, triethyl acetate -TAC) of the ten selected powders is presented in Table 1. However, since all compositions are currently in operational use, the disclosure of complete formulations or the mass fractions of individual components is restricted.

Table 1. Selected samples of gunpowder

Sample name	Non-energetic organic compounds				
	DPA	EC	DBP	Camp	TAC
NC-46	+			+	
NC-27	+				
NC-49	+				
NC-261	+		+		
SB 620	+	+			
SB 511	+		+		
SB 411	+				
SB 715	+		+		
NGB 051		+			+
NGB 161		+			+

2.1. Gas chromatography

Gas chromatography with a capillary column works by vaporizing a sample and carrying it through a thin, long column using an inert carrier gas. Inside the column, components are separated based on their unique chemical affinity for the stationary phase coating the internal walls. Each gunpowder organic component exits the column at a specific retention time, allowing the detector to identify and quantify them individually.

In this research, for separation, identification and quantification of components of interests, Agilent gas chromatograph model 7890 with flame ionization detector (FID), with autosampler, was used. Capillary column HP-5 has been employed as separating tool. The chromatographic conditions were as follows:

- Injector temperature: 130 °C,
- Initial oven temperature: 130 °C,
- heating rate of 10 °C/min,
- final temperature of 210 °C,
- Detector temperature: 300 °C,
- Carrier gas: Hydrogen (H_2),
- Hydrogen flow rate: 25 mL/min,
- Air flow rate: 400 mL/min.

While high-performance liquid chromatography (HPLC) [9-12] is the recommended method for analyzing older powders, due to the tendency of diphenylamine (DPA) derivatives to convert back into DPA at the elevated temperatures required by GC, creating a false representation of the active stabilizer content, GC remains a highly favorable method for the quality control of new powders because economic and ecologic efficiency. In newly manufactured powders, the DPA has not yet had time to degrade into its derivatives, therefore, the risk of thermal reversion is non-existent, and the results remain accurate. Furthermore, GC offers several technical advantages for these samples: superior column resolution, high precision separation of other components in

gunpowder (especially if sample contain nitroglycerin (NG), dinitrotoluene (DNT) and trinitrotoluene (TNT).

3. EXPERIMENTAL PART

All ten selected powders were prepared using three different methods, with each test performed in duplicate. Since the powders are intended for ammunition up to 20 mm and possess a small original grain size, no preliminary grinding of the samples was required.

3.1. Sample preparation in methanol

A sample of gunpowder 1.000 ±0.001 g was weighed and transferred into a 100 cm^3 volumetric flask. Methanol was added to half of the flask's volume, and the mixture was left for 4-6 hours. Subsequently, the flask was filled to the mark with methanol and agitated on a magnetic stirrer for 6 to 8 hours. The sample requires centrifugation to facilitate nitrocellulose precipitation before proceeding with further analytical steps. A 20 cm^3 volume of the prepared solution was pipetted into a 50 cm^3 volumetric flask, followed by the addition of 5 cm^3 of the internal standard solution (1.5 g dimethyl phthalate dissolved in 250 cm^3 of methanol), and then diluted to the mark with methanol. The sample was then transferred to a vial for autosampler, as it can be seen in Figure 2. To obtain satisfactory results, it is essential to pass the solution through a 0.5 µm PTFE filter prior to usage.

Since an internal standard was introduced into the sample, the concentration of the analyzed substances is calculated using the following equation (1):

$$A = \frac{P_A}{m_u * P_{IS}} * k_A \qquad (1)$$

Where are:

- k_A - mean value of two replicates of proportionality constant for the analyzed component, calculated by instruction from [8]
- m_u - sample mass (g),
- P_A - peak area of the analyzed component (%),
- A - content of the analyzed component in the gunpowder sample (%),
- P_{IS} – peak area of the internal standard (%).

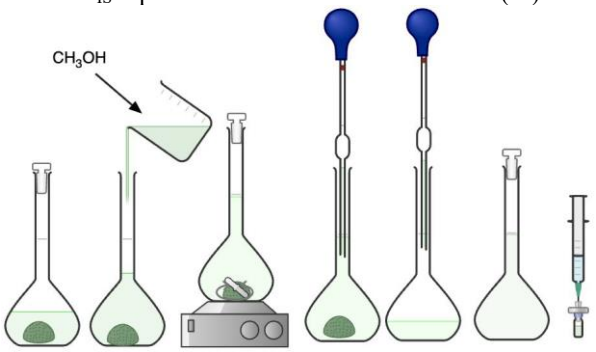


Figure 2. Sample preparation in methanol, from left to right: sample with ½ volume of methanol for 4-6 h, adding methanol to full volume into the flask, stirring sample for 6-8 h, 20 cm^3 volume pipetted and transferred into the new flask, followed by the addition of 5 cm^3 of the internal standard solution, filtrating sample and transferring it to vial

In a 50 cm^3 volumetric flask, weigh the required amount of the component to be determined for calibration and add 25 cm^3 of solvent. Subsequently, add 5 cm^3 of the previously prepared internal standard solution, then dilute to the mark with the solvent. Calibration is performed using standard solutions by testing the organic components under the same chromatographic conditions used for determining organic additives in gunpowder samples.

The calculation of the proportionality constant is performed according to the following equation (2):

$$k_A = \frac{m_A * P_{IS}}{P_A} * 100 \qquad (2)$$

Where are:

- k_A - proportionality constant for the analyzed component;
- m_A - mass of the component weighed for the preparation of calibration solutions (g);
- P_A - peak area (signal) of the analyzed component (%);
- P_{IS} - peak area of the internal standard (%).

3.2. Sample preparation in dichloromethane

A sample of gunpowder 1.000 ±0.001 g was weighed and transferred into a 50 cm^3 volumetric flask. Dichloromethane was added to half of the flask's volume, and the mixture was left for 24 hours, as it can be seen in Figure 3, step by step.

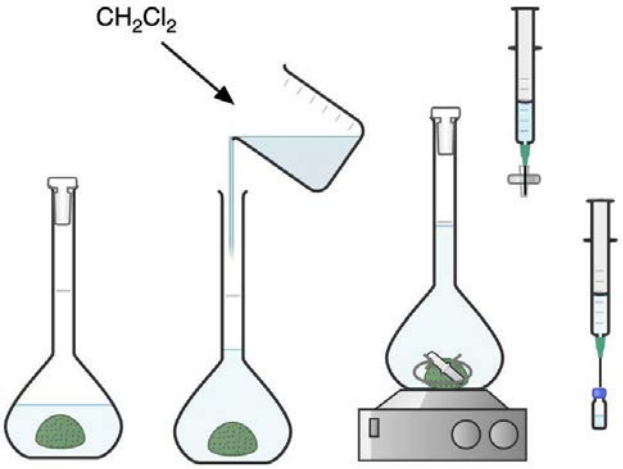


Figure 3. Sample preparation in dichloromethane, from left to right: sample with ½ volume of dichloromethane 24h left in dark place, introducing 5 cm^3 internal standard and adding dichloromethane to full volume into the flask, stirring sample for 4-6 h, filtrating sample and transferring it to vial

Subsequently, the in flask was added 5 cm^3 of the internal standard solution (1.5 g dimethyl phthalate dissolved in 250 cm^3 of dichloromethane) and filled the flask to the mark with dichloromethane. Sample prepared into that manner was agitated on a magnetic stirrer for 4 to 6 hours. The undiluted sample was then transferred to a vial for autosampler. To obtain satisfactory results, it is essential to pass the solution through a 0.5 µm PTFE filter prior to usage. With the internal standard incorporated, the

calculation of target component concentrations is performed using equations (1) and (2) from the section 3.1.

3.3. Sample preparation by saponification

Approximately 5 g of gunpowder was weighed into a flat-bottomed flask, followed by the addition of 80 cm^3 of a 20% (m/m) NaOH solution. The apparatus was assembled for reflux using a reflux condenser. The flask was placed on a heating mantle and refluxed for approximately 2 hours. Without removing the condenser, the flask was cooled in a water bath to room temperature. The condenser was then rinsed with 15 to 25 cm^3 of dichloromethane (Figure 4), and the contents of the flask were transferred to a laboratory separatory funnel, which was firstly added 200 cm^3 of a 5% (m/m) NaCl solution.

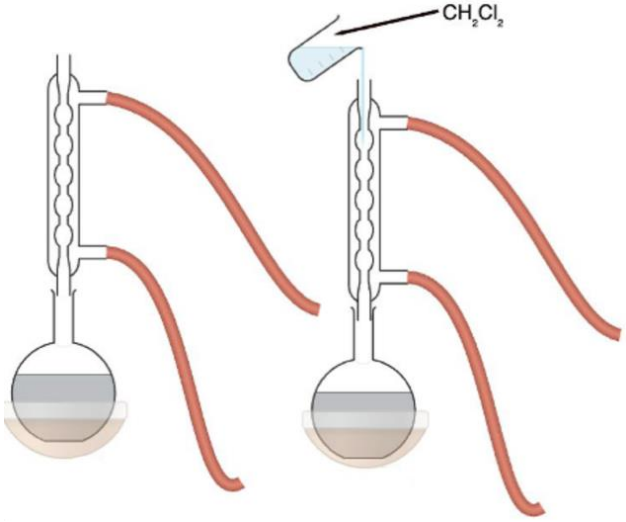


Figure 4. Heating solution of gunpowder and NaOH with reflux for 2h, colling down to the room temperature and rinsed by dichloromethane

The content in separatory funnel was then stoppered and shaken vigorously. The lower layer from the funnel was transferred into a 200 cm^3 volumetric flask. The extraction process from the flask and the separatory funnel was repeated twice more with dichloromethane to ensure quantitative transfer is done. The volumetric flask was then filled to the mark with dichloromethane, as it can be seen in Figure 5.

The sample prepared in this manner was used for the determination of organic components via gas chromatography as follows: 5 cm^3 of the internal standard was added to a 50 cm^3 volumetric flask, which was then filled to the mark with the previously prepared sample. The prepared sample was transferred without dilution into a vial, from which it was injected into the chromatographic column via autosampler or manual injection. At least two replicates were prepared and analyzed for each gunpowder sample.

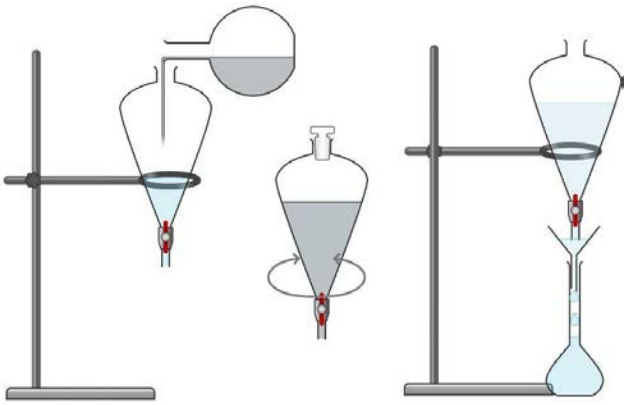


Figure 5. Separation process by using separatory funnel

For the quantification of the target components, it is necessary to prepare calibration solutions for all analyzed components within an appropriate concentration range. Calibration is performed under the same chromatographic conditions as those used for sample testing.

4.RESULTS AND DISCUSION

The stabilizer and other non-energetic organic components content for four different singlebase gunpowder, for all three sample preparation technique, are presented in Table 2. The results were reported as mass percentages, scaled to two decimal places.

Table 2. Results of measuring of other non-energetic organic compound in selected single-based gunpowder

Sample name	Non-energetic organic compounds			
	sample prep.	DPA	DBP	Camp
NC-46	dichloromethane	1.30	/	1.34
	methanol	1.32	/	1.36
	saponification	1.26	/	1.29
NC-27	dichloromethane	1.53	/	/
	methanol	1.50	/	/
	saponification	1.52	/	/
NC-49	dichloromethane	1.33	/	/
	methanol	1.30	/	/
	saponification	1.28	/	/
NC-261	dichloromethane	1.46	3.36	/
	methanol	1.41	3.41	/
	saponification	1.42	/	/

As it can be seen, the relative error between different methods of sample preparation ranges from 1.9 to 2.1%. Furthermore, no consistent trend was observed to indicate that a specific preparation method systematically yields higher values across all sample types. Additionally, a notable deviation was detected in the results for each evaluated component across all three preparation protocols. Nevertheless, all observed values remain within an acceptable margin of error.

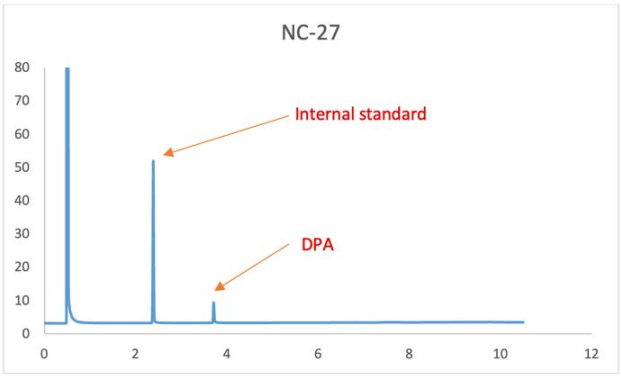


Figure 6. Chromatograms of single-base gunpowder NC-27, extraction in methanol

Regarding spherical (ball) gunpowder, the results for the determination of the content of non-energetic compounds, obtained by analyzing three selected compositions and employing three different sample preparation techniques, are presented in Table 3.

Table 3. Results of measuring of non-energetic organic compound in selected spherical (ball) gunpowder

Sample name	Non-energetic organic compounds			
	sample prep.	DPA	DBP	EC
SB-511	dichloromethane	1.33	5.30	/
	methanol	1.32	5.21	/
	saponification	1.31	/	/
SB-411	dichloromethane	1.37	/	1.32
	methanol	1.36	/	1.31
	saponification	1.39	/	1.30
SB-715	dichloromethane	1.18	6.61	/
	methanol	1.20	6.52	/
	saponification	1.18	/	/

For spherical powders, the determination of non-energetic organic components yields significantly better reproducibility. Specifically, the relative error is approximately 1%, and often lower, for the quantification of stabilizer and plasticizer contents across all three sample preparation techniques evaluated for GC analysis.

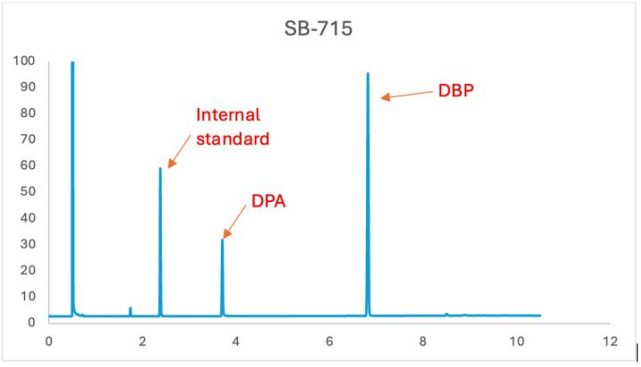


Figure 7. Chromatograms of spherical (ball) gunpowder SB-715, extraction in dichloromethane

Table 4. Results of measuring of non-energetic organic compound in selected double-based gunpowder

Sample name	Non-energetic organic compounds		
	sample prep.	EC	TAC
NGB-051	dichloromethane	1.79	0.40
	methanol	1.76	0.40
	saponification	1.79	/
NGB-161	dichloromethane	1.74	0.29
	methanol	1.79	0.28
	saponification	1.75	/

The results presented in Table 4 indicate nearly ideal agreement between the saponification and dichloromethane preparation protocols for double-base gunpowder. In contrast, the methanol-based preparation yields variations without a consistent trend, the values obtained by methanol preparation are higher for one sample but lower for another. For the stabilizer content, the relative error ranges between 1% and 1.5% when evaluating the results across all three sample preparation technique.

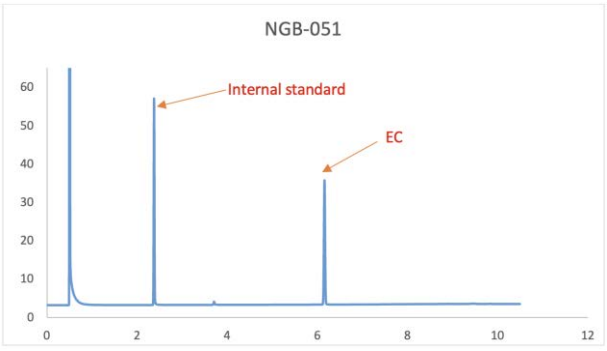


Figure 8. Chromatograms of double-base gunpowder NGB-051, preparation by saponification

5. CONCLUSION

This study focused on evaluating diverse sample preparation methods for gas chromatographic analysis to determine primaly stabilizer and secondary, the other non-energetic compounds in propellants, which serve as essential intermediate and final quality control parameters in manufacturing plants. Based on the findings, every evaluated preparation protocol provides highly reproducible data. The maximum relative error was observed in single-base powders, though it strictly remained below 2.5%, while for all other propellant types, this value was approximately 1% or lower. The primary advantage of the saponification method lies in its rapid sample processing time, less then few hours, compared the other two which demand more between 14 and 30 hours. However, it lacks the capability to determine DBP and triacetin (TAC). Consequently, saponification represents the method of choice when rapid turnaround times are required to obtain immediate feedback on stabilizer concentrations. These stabilizers are critical factors for propellant stability and constitute the primary checkpoint during in-process monitoring, final product

release, and throughout the entire propellant lifecycle. Nevertheless, if the analytical objective requires the comprehensive determination of all non-energetic compounds within the formulation, preparation via methanol or dichloromethane extraction becomes the preferred approach.

Although sample preparation for HPLC is less time-consuming, GC offers a far higher justification, thus, the results of this research carry significant value, as they provide critical insights into the capabilities of various preparation techniques to deliver reliable results through a method that, while perhaps not time-efficient, remains fundamentally sound from both an economic and ecological perspective. The utilization of GC offers distinct advantages, particularly in high-throughput industrial settings such as gunpowder factories, where numerous routine samples are analyzed daily. Economically, GC significantly minimizes operational expenses by employing inert carrier gases instead of the expensive, high-purity solvents required as mobile phases in HPLC. Furthermore, it mitigates the substantial costs associated with high-pressure pump maintenance and column degradation caused by aggressive solvent. From an environmental standpoint, GC operation is fundamentally cleaner and more sustainable, as it virtually eliminates the generation of hazardous liquid chemical waste, thereby bypassing the stringent and costly disposal regulations inherent to HPLC operations. Consequently, for routine quality control in manufacturing plants with heavy daily sample loads, GC represents a highly cost-effective and ecologically viable analytical framework.

Acknowledgement

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References

[1] AOP-48 Ed.2. *Explosives, nitrocellulose-based propellants - stability test procedures and requirements using stabilizer depletion*, Brussels. North Atlantic Treaty Organization, Military Agency for Standardization, 2008.

[2] RAKIĆ M, KRSTOVIĆ M, MIJATOV S, DIMIĆ M, FIDANOVSKI B. *Comparative analysis of volumetric and instrumental method for determination of nitroglycerin content in gunpowder*. Scientific Technical Review, 2021, 2, pp.41-45. doi: 10.5937/str2102041R

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

[4] KRSTOVIĆ M, RAKIC M, JELISAVAC LJ, DIMIĆ M, MOJSILOVIĆ J, FIDANOVSKI B. *Comparative analysis for determination of stabilizer content in gunpowder and double base propellant by HPLC method.* In: Proceeding of 10th International Scientific Conference on Defense Technologies, OTEH 2022, Belgrade, Serbia, 2022, pp 138-143, ISBN 978-86-81123-85-0 86

[5] BHON M. *Principles of Ageing of Double Base Propellants and its Assessment by Several Methods Following Propellant Properties.* STO-MP-AVT-268

[6] MATEČIĆ MUŠANIĆ S., SUĆESKA M., ČULJAK R. *The Applicability of Chromatographic Methods in the Investigation of Ageing Processes in Double Base Rocket Propellants.* Central European Journal of Energetic Materials, 2013, 10(2), 245-262 ISSN 1733-7178

[7] SORS 8069/91, *Praćenje hemijske stabilnosti baruta i raketnih goriva.* 1991. Beograd.

[8] SORS 1008/85, *Metode analitičkih ispitivanja malodimnih baruta,* 1985. Beograd.

[9] SEROL M., AHMAD S. M., QUINTAS A., FAMILIA C., *Chemical Analysis of Gunpowder and Gunshot Residues*, Molecules 2023, 28(14), 5550; https://doi.org/10.3390/molecules28145550

[10] LÓPEZ-ĹOPEZ, M.; BRAVO, J.C.; GARCIÁ-RUIZ, C.; TORRE, M. *Diphenylamine and Derivatives as Predictors of Gunpowder Age by Means of HPLC and Statistical Models.* Talanta 2013, 103, 214–220.

[11] ŠULTANS J., STOJILJKOVIĆ S., PETROVIĆ V., *Influence of gunpowders and rocket propellants sample preparation on test results*, In: Proceeding of 11th International Scientific Conference on Defense Technologies, OTEH 2024, Tara, Serbia, 2024, pp 252/257 ISBN 978-86-81123-94-2

[12] KRSTOVIĆ M., RAKIĆ M., MIJATOV S., MOJSILOVIĆ J.,ALEKSIĆ S., FIDANOVSKI B. *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, Vol. 75, No.1 (2025), pp. 3-10, doi: 10.5937/str2500001K