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Evaluating the Effectiveness of Different Sample Preparation Routes for Organic Components Quantification in Gunpowder and Double-Base Rocket Propellants for HPLC Analysis

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Monitoring the chemical stability of gunpowder and double-base rocket propellants is a crucial aspect of quality control for stored ammunition. This intricate undertaking seeks to guarantee the accuracy of ammunition at a satisfactory level, encompassing both its practical functionality and safety considerations. The primary reason for monitoring chemical stability is the presence of nitrocellulose (NC) as the basic energetic component in gunpowder and double-base rocket propellants. This particular form of ammunition, known as NC ammo, undergoes a slow process of degradation over time. It is important to note that even when exposed to normal environmental conditions, it has the potential to ignite spontaneously. This reaction is inherently spontaneous and irreversible, however, it can be slowed down by introducing a small quantity of organic or inorganic substances known as stabilizers. Over time, the stabilizer is gradually consumed, and accurately measuring its quantity is essential for evaluating chemical stability. Aside from stabilizers, additional organic additives are used in nitrocellulose-base energetic materials to enhance performance or streamline the production process. Identification and quantification of organic components are also important from the aspect of analyzing unknown samples. The high-performance liquid chromatography (HPLC) method can be used to determine the content of certain organic compounds. The sample preparation for quantifying the organic compound content relies on the specific type of energetic material being examined, following the standard protocols outlined in the HPLC method. The technique of sample preparation, the equipment needed in the laboratory, and the amount of time required to get accurate and repeatable results are all directly impacted by the solvent selection. This research provides a comparison of sample preparation performances using two different solvents (dichloromethane and acetonitrile) indicating the advantages and disadvantages of both preparation techniques.

Key words: **energetic materials, stabilizer, nitrocellulose, plasticizer, explosives, HPLC.**

Introduction

GUNPOWDER and double-base rocket propellants are classified as propellant energy sources, according to the fact that their combustion products are used to propel projectiles [1, 2]. Due to this, they are extensively utilized and manufactured in significant amounts during times of peace, ensuring that the optimal amount of ammunition can be supplied in the occurrence of a war. However, it is imperative to monitor the state of the energetic components during storage to ensure that the ammunition performs as intended when it is used. The stability of energetic materials (EM) refers to their capacity to maintain their chemical, ballistic, and mechanical properties at a level that enables their safe usage and storage under specific conditions. Stability of EM can be characterized based on two key factors: safety and reliability. The term "safety" refers to chemical aspects, while the "reliability" links to mechanical and ballistic aspects [3]. Single-base and double-base gunpowder are composed of nitrate ester polymer, which undergoes gradual thermal decomposition over time. This chemical process has huge influence and, at the same time it changes mechanical, chemical [4] and ballistic [5] properties of energetic materials. This process, referred to as chemical degradation of ammunition, occurs even in normal environmental circumstances. Free radicals, specifically ^{o}NO and $^{o}NO_2$, are derivatives of NC decomposition. These radicals are responsible for an autocatalytic exothermic degradation process that leads to a decrease in temperature. Chemical processes are characterized by the release of heat and gaseous products that are capable of accelerating the process of ageing. In extreme cases, this degradation process can even result in self-ignition. This reaction is inherently spontaneous and irreversible, although its rate can be reduced by the addition of minute quantities of organic

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molecules, which enhance the stability of NC [6, 7].

Stabilizers in EM formulations are used at quantities of up to 5 wt. % to ensure optimal chemical characteristics over an extended duration. Quality and quantity monitoring of the stabilizer is crucial for evaluating chemical stability. Gunpowder and double-base rocket propellants are usually stabilized by diphenylamine (DPA) or urea derivatives (e.g. ethyl or methyl centralite) [6, 8, 9].

Double-base gunpowder and double-base rocket propellants have nitroglycerin as their second energetic compound [10, 11]. The NG/NC ratio can be increased until reaching a specific edge, after which the nitroglycerin becomes unabsorbable. The occurrence of the following can be attributed to an insufficient ratio of nitroglycerin and nitrocellulose - gunpowder exudation, often known as "sweating". That is the phenomenon when nitroglycerin is transferred from the interior of a gunpowder grain to its surface due to variations in external temperature. The migratory process continues until a state of equilibrium is reached in the concentrations of nitroglycerin in both materials [12]. Considering the tendency of nitroglycerin to migrate, it is desirable to track the concentration of nitroglycerin in double-base gunpowder and rocket propellants.

Beside stabilizers, the most frequently used organic additives in gunpowder and double-base propellants are plasticizers and explosives. The most commonly employed plasticizers include dibutyl phthalate – DBP and diethyl phthalate – DEP. They have a crucial role in enhancing the plasticity of the EM throughout the temperature range of -60°C to 60°C. This prevents the gunpowder or double-base propellants from fracturing, hence preserving the ballistic performance.

Explosives are often in use in gunpowder and rocket propellants. Dinitrotoluene according its characteristics [13] can be used as plasticizer, gelatinizer, and burning rate modifier. TNT functions as a phlegmatizer, and its detonation velocity causes the increase in energy relative to its detonation rate. Modified double-base propellant is a unique type of EM that is produced by incorporating crystalline nitramines into the base matrix of double-base propellants. Introducing nitramines, typically octogen, enhances the density, thermal stability, and energetic efficiency of this type of EM [2].

Newly manufactured ammunition come with a specific timeframe within which the manufacturer ensures that the energetic components will maintain their original properties. Nevertheless, due to the extended storage duration of the ammunition beyond the specified date, it becomes imperative to establish monitoring techniques to assess the state of the ammunition and establish criteria for evaluating its chemical, ballistic, and mechanical integrity. Over time, several measurements and procedures were created worldwide to control the chemical stability of gunpowder and propellants. There are both classical and instrumental methods among them. The primary importance of instrumental approaches lies in various forms of chromatography.

The HPLC approach was used as it enables precise quantification of not only DPA and its derivatives, but also urea derivatives, NG, and other organic substances such as plasticizers and explosives [14, 15, 16]. The paper presents a comparative analysis of sample preparation using dichloromethane and acetonitrile as a solvent for gunpowder and rocket propellants extraction. The objective of this research was to propose potential alterations to the process of sample preparation, with the intention of addressing issues related to the optimization of the duration of extraction.

Experimental part

Materials and samples preparation

Thirteen different gunpowder and double-base propellants were examined. All of them underwent natural aging as a result of being regularly monitored and undergoing technical inspections.

Preparation of samples

The gunpowder or double-base propellants were fragmented into small pieces and then passed through sieves with a 2 mm aperture prior to the extraction procedure. Following the milling process, each of the samples was weighed with a mass of 1.000 g and subsequently transferred into the flask.

Extraction in dichloromethane (CH_2Cl_2)

The analyzed sample was introduced into the flask, followed by the addition of 50 cm^3 of dichloromethane. The flask was then kept in a dark place at room temperature for a duration of 48 hours. Subsequently, 1 cm^3 of the solution was transferred to a 10 cm^3 flask, where dichloromethane was extracted at low temperature conditions (about 40ºC), and then 10 cm^3 of acetonitrile was introduced. In order to obtain satisfactory results, it was imperative to pass the sample through a 0.5 µm PTFE filter prior to utilization [6].

Extraction in acetonitrile (CH_3CN)

The analyzed material was introduced into the flask, followed by the addition of 50 cm^3 of acetonitrile. The extraction process involved a 2-hour period of agitation using a magnetic stirrer, followed by an additional 2-hour period of agitation under ultrasonic conditions, which is the minimum recommended extraction time according to AOP standard [17]. Finally, the test solution, was obtained by separation from the precipitate using a centrifuge. Following the completion of the preceding stages, a volume of 1 cm^3 was transferred to a flask with a capacity of 10 cm^3, adding 9 cm^3 of acetonitrile to make full flask volume. In order to obtain satisfactory results, it is essential to pass the solution through a 0.5 µm PTFE filter prior to usage [6].

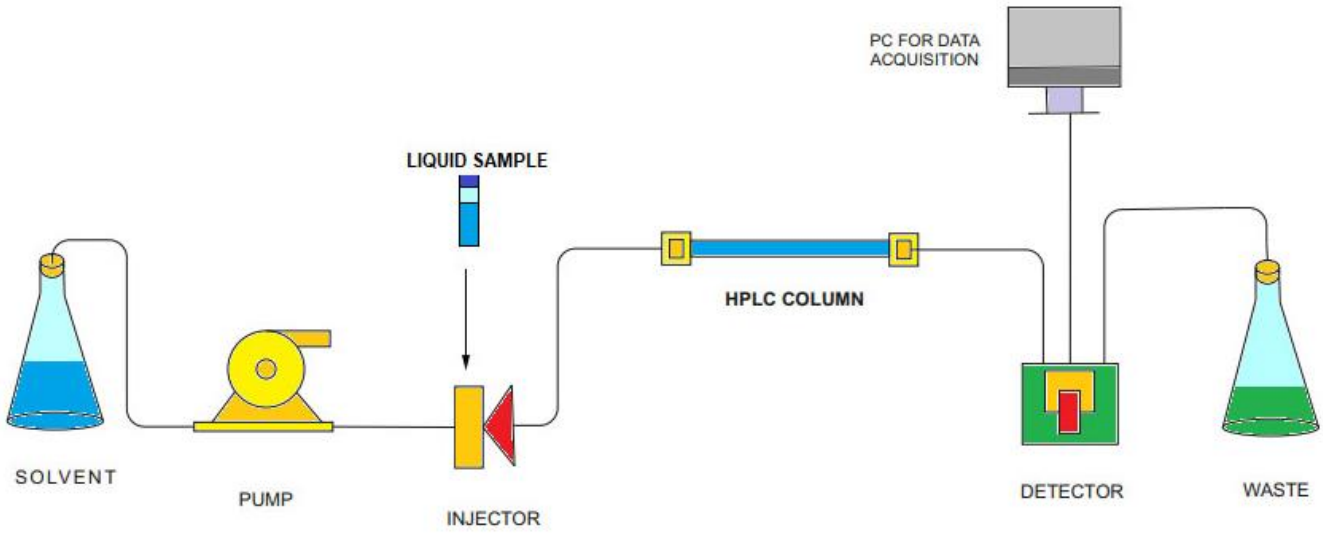

Figure 1. Illustration of the operational concept of the HPLC apparatus

HPLC method

HPLC is an analytical technique used to separate, identify, and measure the amounts of organic compounds. This method relies on the introduction of a high-pressure liquid solvent into a column containing a solid adsorbent material, also known as the stationary phase. Each component in the analyzed sample has a variable retention duration due to its unique interaction with the stationary phase, resulting in the separation of components [15].

The High-performance Liquid Chromatograph "Waters 1525 Binary HPLC Pump" with a column heating thermostat, the manual injector "Rheodine Model 7125", and the photodiode array detector "Waters 2998 PDA" were utilized for quantitatively detecting the organic compound concentration in prepared samples. The operational concept of the HPLC apparatus is illustrated in Figure 1.

Calibration is necessary for detecting, identifying, and quantifying each organic chemical. The calibration curve must span the concentration range of the examined samples, while also considering the mass of the samples. The stabilizer calibration solutions are generated with concentrations ranging from 0.5% to 5%. Plasticizers can have concentrations up to 10%, nitroglycerine up to 50%, TNT and DNT up to 10%, and HMX up to 30%. The calculations were conducted with respect to the sample's weight of 1 g.

It is necessary to examine the calibration and sample using identical chromatographic conditions. For the analysis of those samples and calibration standards, the following elements of equipment were used: detector PDA (220 nm), column C18 (length 150 mm, ID 4.6 mm and particle size 3μm), column temperature (not above 35ºC ± 0.5ºC) and the mobile phase, acetonitrile: water (67:33 v/v), and the flow rate of 1.2 mL min^{-1}[6]. For the analysis of some particular samples it was necessary to use the E2 column (length 250 mm, ID 4.6 mm and particle size 5 μm). In this experimental procedure, the mobile phase consisted of a mixture of methanol and water (50:50 v/v). The column temperature was kept below 30 ºC, and the flow rate was 1.0 mL min^{-1}. The volume of the injection sample solution for each column was 10 μL.

Data processing and instrumental control were accomplished using the Breeze HPLC software. The results were reported in terms of mass percentage, with a precision of two decimal places.

Results and discussion

The organic components content for five different single-base gunpowder, stabilized by DPA, is presented in Table 1. Two of them had DNT in their formulation (SBGP-4, SBGP-5) and one (SBGP-5) had DBP as plasticizer.

The results were reported as mass percentages, scaled to two decimal places. The standard procedures for older single-base gunpowder state that the effective stabilizer content was determined by the sum of DPA, N-NO-DPA, and 4-NDPA content. Conversely, as per the NATO standard [17], the effective stabilizer was determined by adding the DPA and 0.85% N-NO-DPA.

Based on the obtained results, both sample preparation procedures yield to identical results, with a negligible discrepancy on the second decimal point. Given that the effective stabilizer is the sum of DPA and its derivatives, it was imperative to achieve clear distinction between all relevant peaks [6].

The first three samples (SBGP-1, SBGP-2 and SBGP-3) had only a stabilizer in their composition, while the rest additives were inorganic, so the applied HPLC technique could not detect them. A suitable peak separation for DPA and its derivatives and a very good result matching for preparations in two different solvents for sample SBGP-1 can be seen in Figure 2.

Table 1. Result of mass concentration of organic compounds for single-base gunpowder

No	sample	organic compound	Extraction *in solvent [wt.%]*	
			CH_2Cl_2	CH_3CN
1.	SBGP-1	DPA	0.80	0.79
		N-NO DPA	0.31	0.32
		2-N DPA	0.02	0.02
		4-N DPA	0.05	0.06
2.	SBGP-2	DPA	1.22	1.21
		N-NO DPA	0.12	0.13
		2-N DPA	0.03	0.03
		4-N DPA	0.02	0.01
3.	SBGP-3	DPA	1.05	1.04
		N-NO DPA	0.08	0.08
		2-N DPA	0.01	0.02
		4-N DPA	0.01	0.01
4.	SBGP-4	DPA	1.14	1.13
		N-NO DPA	0.21	0.20
		2-N DPA	0.05	0.06
		4-N DPA	0.03	0.04
		DNT	8.53	8.52
5.	SBGP-5	DPA	0.14	0.15
		N-NO DPA	0.18	0.18
		2-N DPA	0.17	0.16
		4-N DPA	0.13	0.13
		DNT	7.91	7.90
		DBP	1.61	1.61

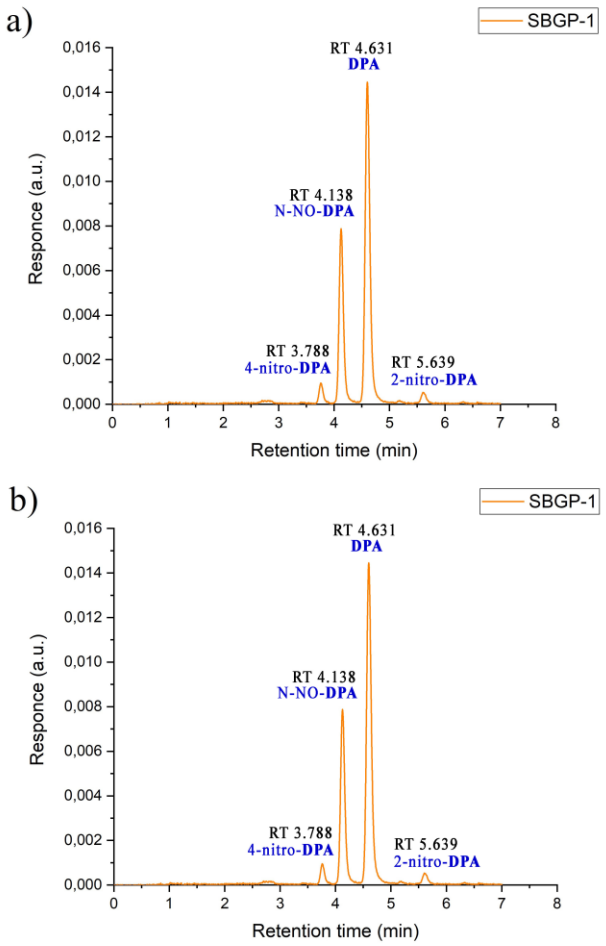

Figure 2. Chromatograms of single-base gunpowder SBGP-1 extraction in acetonitrile (a) and extraction in dichloromethane (b)

Utilizing a C18 column with precise chromatographic conditions [6, 15] enables the analysis of single-base powders devoid of additional organic constituents in a reasonably brief duration of approximately 6.5 minutes.

Sample SBGP-4 (Figure 3) beside stabilizer, DPA and its derivatives, also contained DNT in its composition as a ballistic modifier. The presence of an explosive compound like DNT did not impact the elution duration of the sample in the column.

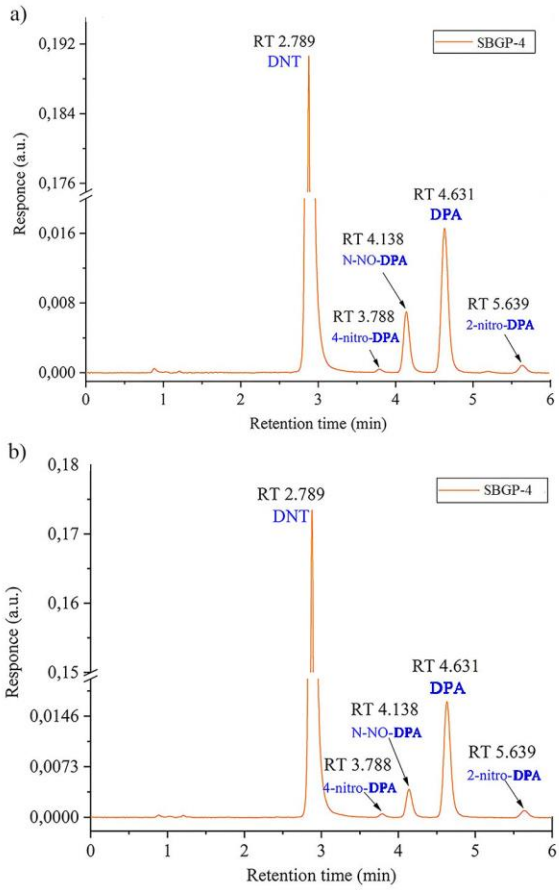

Figure 3. Chromatograms of single-base gunpowder SBGP-4 extraction in acetonitrile (a) and extraction in dichloromethane (b)

The sample SBGP-5 contained stabilizer (Figure 4), DNT and plasticizer dibutyl phthalate (DBP) as organic compounds. Due to different retention periods of the organic components, the C18 column and the specified chromatographic conditions [6, 15] can be employed for the analysis of these specific single-base powders. The primary difference was based on the observation that a plasticizer like DBP emerges from the column at a later stage, which required extended analysis duration.

Considering that all the examined samples included in this study were subjected to natural aging, a few of them exhibited limited content of stabilizers during the examination, although nevertheless in adequate amounts to provide a stabilizing influence. Regarding DPA, it promptly transitions into its derivatives, which also behave as stabilizers, sometimes referred to as secondary stabilizers. This implies that as long as the combined value of DPA and interest derivatives remains above the the crucial threshold, the EMs meets the criteria for chemical stability.

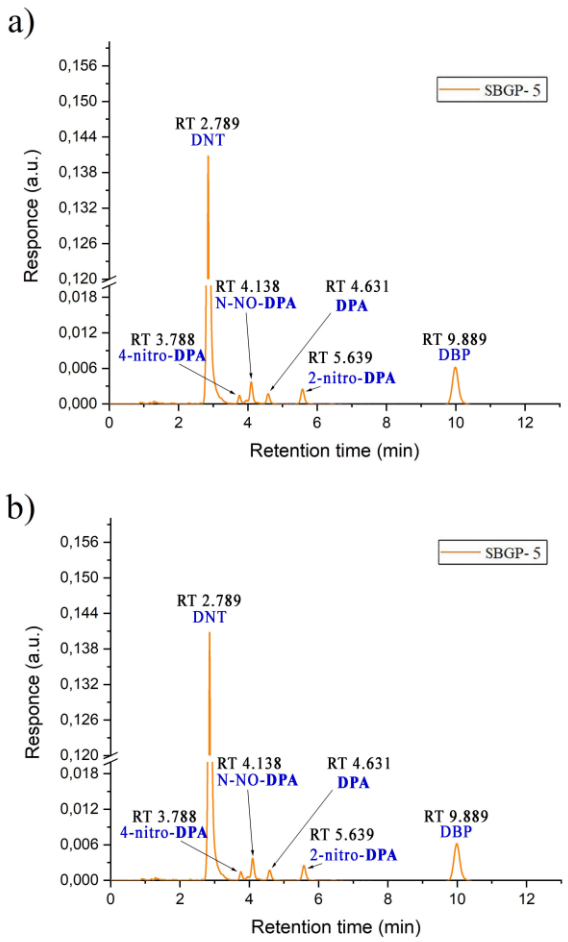

Figure 4. Chromatograms of single-base gunpowder SBGP-5 extraction in acetonitrile (a) and extraction in dichloromethane (b)

Table 2. Result of mass concentration of organic compounds for double-base gunpowder and propellants

No	DBRP	organic compound	Extraction *in solvent* [*wt.%*]	
			CH_2Cl_2	CH_3CN
1.	DBRP1	C II	1.24	1.23
		NG	28.36	28.14
		DINA	8.95	8.95
2.	DBRP2	C II	1.34	1.34
		NG	37.9	37.24
		DNT	4.87	4.88
		TNT	2.68	2.67
		DBP	3.11	3.09
3.	DBRP3	C I	2.47	2.46
		NG	28.41	28.59
		DEP	5.87	5.86
4.	DBRP4	C II	2.83	2.84
		NG	22.64	22.19
		DNT	2.51	2.53
		TNT	0.96	0.98
		DBP	4.38	4.37
5.	DBRP5	C I	2.55	2.54
		NG	26.95	26.47
		DNT	4.32	4.32
		TNT	1.17	1.18
		DBP	2.4	2.39

The results of organic compound content determination for five double-base rocket propellant samples are shown in Table 2. All of the samples were stabilized by urea derivatives (ethyl or methyl centralite). These samples contained nitroglycerin, which serves as an additional energetic component, along with stabilizers, explosives, and plasticizers. Results are given in wt.%, in two decimals. Given the extensive range of uses for double-base gunpowder and double-base propellants, their composition frequently varies in numerous aspects. In this instance, the identification of a distinct peak was effortlessly accomplished because to the insensitivity of this particular stabilizer to elevated temperatures. Furthermore, it exhibited remarkable stability, remaining intact without undergoing any disintegration into its constituent derivatives over an extended period of time.

The DBRP1 sample contains DINA explosives (dioxyethylnitramine dinitrate). This substance is classified as a secondary explosive and is comparable in strength to pentrite. However, its primary use is as a nitrocellulose gelatinizer in double-base propellants.

Given the specific chromatographic conditions for the C 18 column [6, 15], which do not result in any peak overlap, it was feasible to efficiently identify and quantify the three organic components in the mentioned sample within a relatively brief timeframe of approximately 4 minutes. As it can be seen in Figure 5, all the peaks were well separated, and according to the result from Table 2 it is obvious that both solvents were suitable for the extraction of the mentioned organic components from this type of double-base propellant.

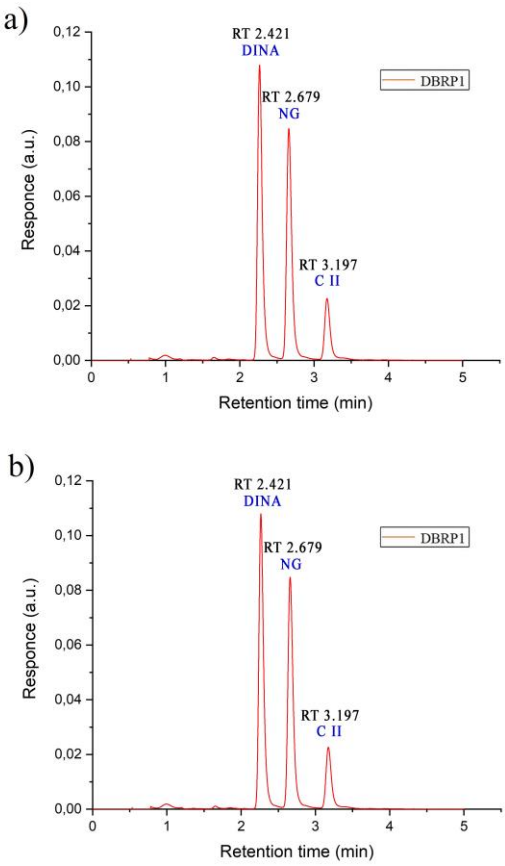

Figure 5. Chromatograms of double-base propellant DBRP1 extraction in acetonitrile (a) and extraction in dichloromethane (b)

In order to analyze samples containing NG, DNT, and TNT, it was imperative to employ a column specifically designed for the quantification of explosives (E2) and a compatible mobile phase. This was needed because when applying the C18 column under the conditions of acetonitrile: water (67:33, v/v) and temperature of 35°C the

desired peaks tend to overlap, making their detection feasible but not their accurate measurement. The chromatogram of the DBRP2 sample examined on the C18 column is depicted in Figure 6 and the same sample examined on the E2 column is depicted in Figure 7.

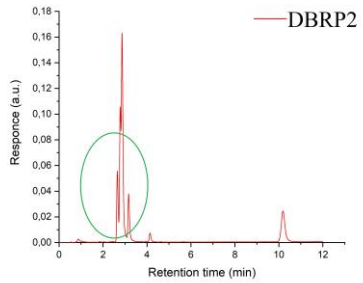

Figure 6. Chromatograms of double-base propellant DBRP2, analyzed by column C18

It is evident that the peaks have overlapped, requiring optimization of chromatographic settings or a replacement of the column to separate them.

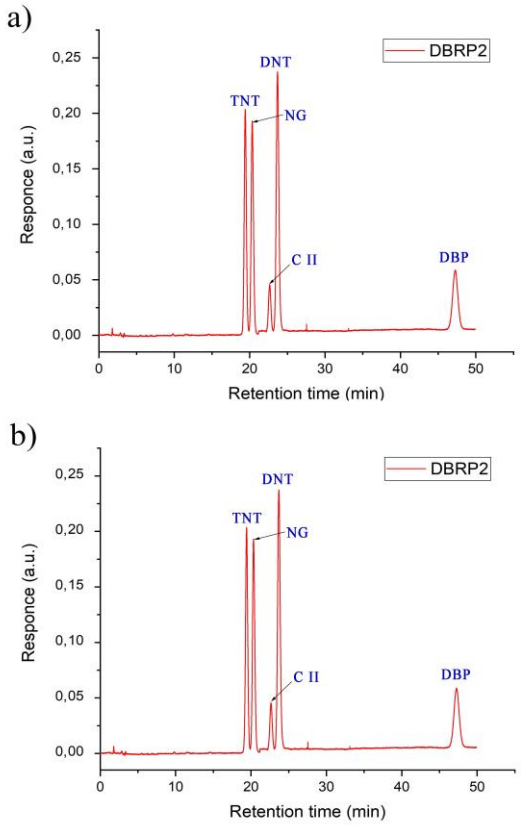

Figure 7. Chromatograms of double-base propellant DBRP2 extraction in acetonitrile (a) and extraction in dichloromethane (b)

Sample DBRP3, despite the absence of peaks that could overlap resulting from a combination of NG, DNT, and TNT), is an intriguing for HPLC investigation. When examining the chromatogram, it is possible to mistakenly identify the presence of NG, C II, and C I in the sample. This suggests that it possesses two stabilizers, which is not implausible, as C I was occasionally used as a method for treating grain surfaces [18]. However, in this situation, the issue lied in the fact that DEP and C II in these particular chromatographic conditions eluted from the C18 column at extremely similar retention times, as previously indicated. Miscalculation can be avoided by examining the spectra (Figure 8) of the studied EMs.

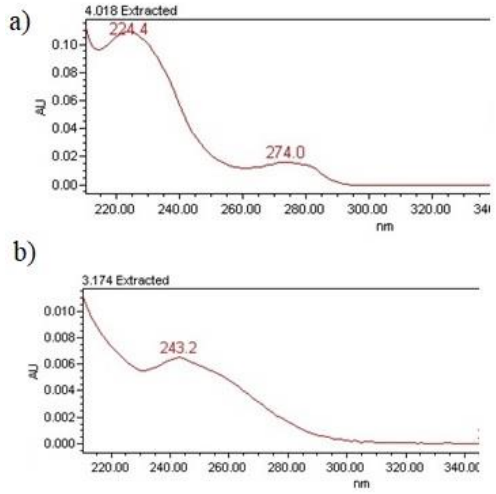

Figure 8. Spectra of DEP (a) and C II (b) in HPLC software

DBRP3 (Figure 9) represents a sample that can be analyzed on the C18 column in a very short time (approximately 6.5 min) with the identification of all three peaks of interest - NG, DEP and C I.

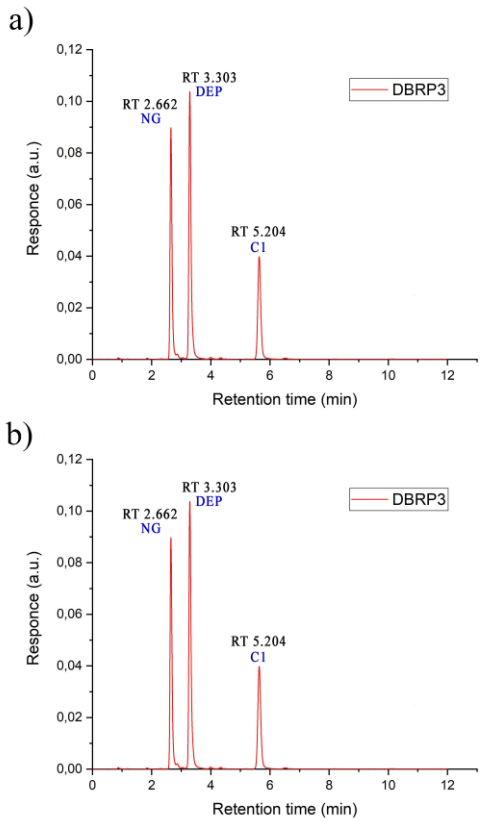

Figure 9. Chromatograms of double-base propellant DBRP3 extraction in acetonitrile (a) and extraction in dichloromethane (b)

The results of organic compound content determination for three modified double-base propellant (MDBRP) samples are shown in Table 3.

Analysis of the data shown in Table 1 and Table 2. suggests that a 4-hour extraction in ACN (2-hour by a magnetic stirrer and a 2-hour under ultrasonic conditions) is sufficient to obtain dependable results for the type of the samples that were investigated.

Table 3. Result of mass concentration of modified double-base rocket propellants

No	MDBRP	organic compound	Extraction *in solvent* [*wt.%*]	
			CH_2Cl_2	CH_3CN
1.	MDBRP1	C II	1.34	1.34
		NG	17.12	17.56
		HMX	4.61	23.96
2.	MDBRP2	C II	1.28	1.29
		NG	14.56	14.93
		HMX	5.62	25.33
3.	MDBRP3	C II	1.47	1.47
		NG	17.39	17.86
		HMX	4.09	23.79

The results presented in Table 3 demonstrate that dichloromethane was unsuitable for extracting HMX from MDBRP. Although the sample prepared in dichloromethane could detect the presence of HMX, the measurement of its quantity in that solvent would not accurately reflect the actual condition (Figure 10b, MDBRP1). By utilizing acetonitrile as a solvent (Figure 10a, MDBRP1), the issue was resolved and an accurate representation of the explosive component's content in MDBRP formulations was achieved.

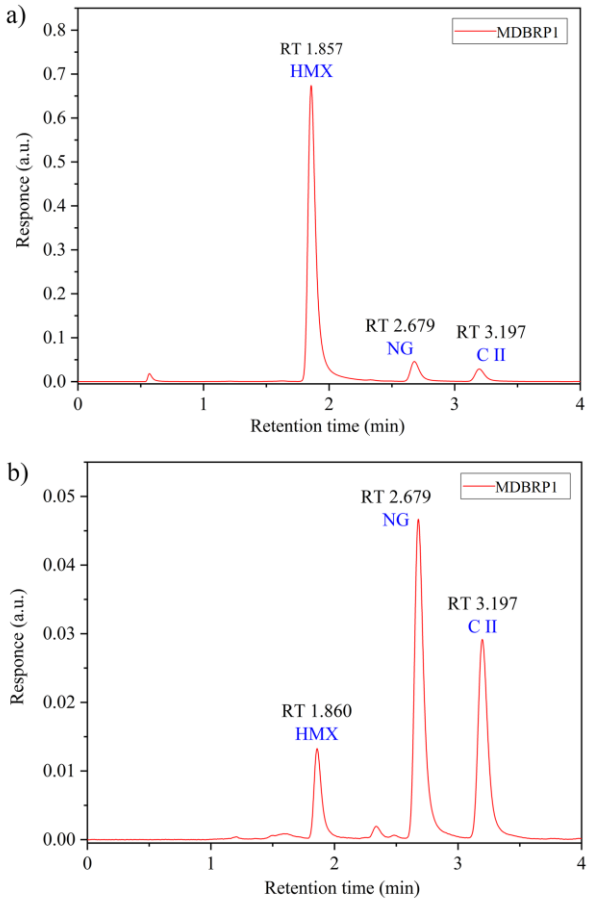

Figure 10. Chromatograms of double-base propellant MBRP1 extraction in acetonitrile (a) and extraction in dichloromethane (b)

Based on the results acquired using the HPLC method, both sample preparation methods yield data regarding the presence of DNT or TNT explosives, as well as facilitate the calculation of mass percentages for these organic compounds in the samples. However, only samples processed in acetonitrile provide accurate data for HMX determination in MDBRP. The reason for this is that HMX and RDX are not fully soluble in dichloromethane. Therefore, HMX and RDX extraction demand assistance of magnetic stirrer and ultrasound.

Conclusion

A comparative examination was conducted to determine the content of organic compounds in 13 different types of gunpowder and double-base propellant using the HPLC method. Two distinct solvents, dichloromethane and acetonitrile, were used, and different approaches were employed for sample preparation. The comparative study revealed that similar values were obtained in the case of preparation in various solvents. Three measurements were performed for each sample, and the result represents the average value. The acquired results confirmed the repeatability of the preparation process.

Extraction of samples processed in dichloromethane demands a 48-hour duration, but without the need for any involvement of laboratory equipment or personnel. Preparation of an extensive number of samples is highly convenient. One of the disadvantages is undoubtedly the necessity to eliminate dichloromethane. That task involves evaporation of solvent at a temperature of 40°C. Uncontrolled temperature during this process could potentially affect the thermal sensitivity of DPA derivatives or also thermally sensitive NG. Dichloromethane, effective for dissolution of many organic components commonly present in energetic materials, has a significant limitation in its capacity to fully extract HMX from the sample. Only about 20% of HMX could be detected with sample preparation in dichloromethane.

While acetonitrile as a solvent offers the advantage of time saving and providing results within a timeframe of less than 5 hours, its usage requires active preparation and specific equipment with a magnetic stirrer, ultrasound, and centrifuge. Consequently, it is not appropriate for preparation of a large number of samples at the time. Utilizing acetonitrile as a solvent yielded consistent outcomes that closely aligned with the results obtained from dichloromethane extraction. Nevertheless, its most significant benefit is seen in its utilization for analyzing MDBRP that contain HMX.

With the exception of modified double-base propellants, both preparation procedures include distinct advantages and limitations, yet both offer adequate outcomes and give acceptable results. The use of acetonitrile offers an obvious benefit as it significantly reduces the time required for sample preparation and analysis to up 5 hours. In addition, with this solvent the HPLC approach allows the identification and quantification of all present organic components.

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Procena efikasnosti različitih načina pripreme uzoraka za kvantifikaciju organskih komponenata u barutima i dvobaznim raketnim gorivima za analizu HPLC metodom

Praćenje hemijske stabilnosti baruta i dvobaznih raketnih goriva je ključni aspekt kontrole kvaliteta uskladištenih ubojnih sredstava (UbS). Ovaj složeni proces nastoji da garantuje ispravnost municije, obuhvatajući njenu praktičnu funkcionalnost i bezbednosni aspekt. Primarni razlog za proveru hemijske stabilnosti je prisustvo nitroceluloze (NC) kao osnovne energetske komponente u barutima i dvobaznim raketnim gorivima. Ova grupa UbS, poznata kao NC municija, podložna je sporom procesu degradacije tokom vremena. Važno je napomenuti da čak i kada je izložena normalnim uslovima okoline, NC municija ima potencijal da se spontano zapali. Ova reakcija je sama po sebi spontana i nepovratna, međutim, može se usporiti uvođenjem male količine organskih ili neorganskih supstanci koje su poznate kao stabilizatori. Tokom vremena, stabilizator se postepeno troši, a precizno merenje njegove količine je ključno za procenu hemijske stabilnosti. Pored stabilizatora, dodatni organski aditivi se koriste u energetskim materijalima na bazi nitroceluloze kako bi se poboljšale performanse ili optimizovao proizvodni proces. Identifikacija i kvantifikacija organskih komponenti je takođe važna sa aspekta analize nepoznatih uzoraka. Metoda tečne hromatografije visokih performansi (HPLC) se može koristiti za određivanje sadržaja određenih organskih jedinjenja. Priprema uzorka za kvantifikaciju sadržaja organskog jedinjenja zavisi od tipa energetskog materijala koji se ispituje, u skladu sa standardnim postupcima navedenim u HPLC metodi. Način pripreme uzoraka, potrebna laboratorijska oprema i vreme neophodno za dobijanje pouzdanih i reproducibilnih podataka direktno zavisi od odabira rastvarača. Ovo istraživanje daje poređenje pripreme uzorka korišćenjem dva različita rastvarača (dihlorometan i acetonitril) ukazujući na prednosti i nedostatke obe tehnike pripreme uzoraka.

Ključne reči: **energetski materijali, stabilizator, nitroceluloza, plastifikator, eksplozivi, HPLC.**