COMPARATIVE ANALYSIS FOR DETERMINATION OF STABILIZER CONTENT IN GUNPOWDER AND DOUBLE BASE PROPELLANT BY HPLC METHOD

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Abstract: *Gunpowders and double-based propellants contain nitrocellulose (NC) as their main energetic component. This type of i.e. NC ammunition has slow decomposition period during the time and even under ambient conditions can cause self-ignition. This reaction is spontaneous and cannot be stopped, but can be retarded using small amount of organic compound. Usually those organic compounds are: diphenylamine (DPA) or urea derivatives (e.g. ethyl or methyl centralite), which are known as stabilizers. One of the most important requirements for keeping gunpowder and double base propellant in the area of good chemical stable state for the long storage period is presence of stabilizer in satisfactory concentration in the ammunition. Content of stabilizer can be determined by high performance liquid chromatography method. Sample preparation for determination of the stabilizer content depends on type of gunpowder or double base propellant tested, according to standard procedures method for chemical stability examination by HPLC. Future more, sample preparation includes a very long time for the extraction (around 48 hours) without any external influence, and finally, large amount of solvent – dichloromethane. This paper presents the comparative analysis of different samples preparation in two different solvents (dichloromethane and acetonitrile) by the same method. Using acetonitrile as solvent for extraction results can be provided for less than 12 hours, with the same precision.*

Keywords: *double-base propellant, gunpowder, stabilizer, nitrocellulose, high performance liquid chromatography.*

1. INTRODUCTION

Single-based gunpowders have nitrocellulose (NC) as energetic component, while double-based propellants have two energetic constituents – NC and nitroglycerin (NG). Both of these type of ammunition are based on nitrate ester polymer, which has negative characteristic – slow thermal decomposition during the time. This chemical process has huge influence and, in the same time changing mechanical, chemical [1] and ballistic [2] properties of energetic materials. This progression, known as chemical aging of ammunition, is happening even under ambient conditions. Free radicals: NO^o and NO_2 are products of NC decomposition responsible for autocatalytic exothermic degradation which effect temperature decreasing and, in extreme situation, can cause self-ignition. This reaction is spontaneous and cannot be stopped, but can be slow down using small amount of organic compounds which are added to increase the stability of NC. Their role is to be main acceptor of free radical nitrogen oxides and acids formed from them [3]. These organic compounds, named stabilizers, are added in ammunition formulations up to 5 wt. %, enough to provide optimal chemical characteristics for longer time. This is the reason why monitoring the stabilizer represents one of the most important methods for chemical stability evaluation.

On the other hand, standard procedures for determination of the chemical stability of NC gunpowder and propellants are based on monitoring and periodical measurement of the content of stabilizer in naturally aged samples. This type of monitoring can only give an information about current chemical stability, without any prediction of total lifetime for ammunition.

Gunpowders and double-based propellants are usually stabilized by diphenylamine (DPA) or urea derivatives (e.g. ethyl or methyl centralite). DPA is usually used in single-based and spherical gunpowder, because it is experimentally proven that DPA accelerates denitration of NG, so DPA is not good choice for double-based gunpowder and propellants. To solve this problem, DPA derivatives (2-NDPA) as primary stabilizer, or urea derivatives are in use in double base gunpowder and in propellants.

During the aging, DFA transits into its derivatives (Fig1.), and, what is more importance, most of them also have stabilizing effect. [4] Despite, the fact that DPA has more than 30 derivatives isolated until now and only a few of them are interesting from the aspect of chemical stability for ammunition – N-NODPA, 2-NDPA and 4-NDPA. Reason for that lies in the fact that the higher DPA derivatives has been consumed at the moment when ballistic shelf life is reached [4].
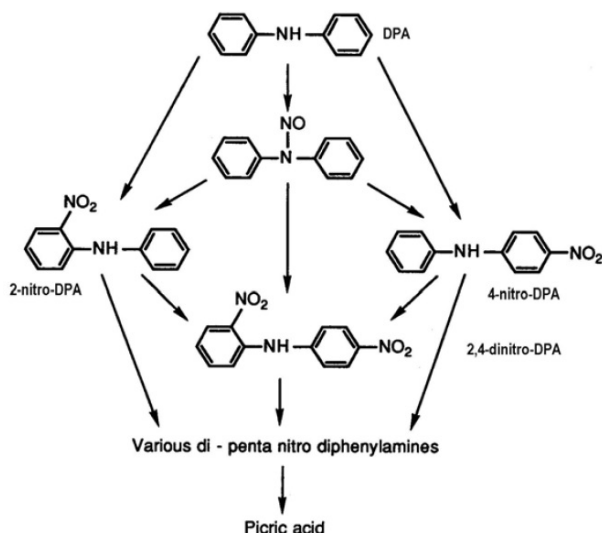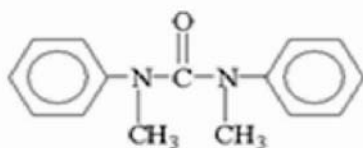

Figure 1. Schematic reaction routes for degradation of DPA in an aging propellant [5]

Ethyl (Fig.2) and methyl (Fig.3) centralite are also common stabilizers in double base propellants and gunpowders formulations.
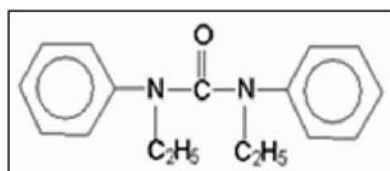
Figure 2. Ethyl centralite

Figure 3. Methyl centralite

During the long time, a whole range of measures and procedures for the control of chemical stability of gunpowder and propellants were developed all around the world. Some of them are classical methods and some are instrumental. The main focus of instrumental methods are in different kinds of chromatography – high performance liquid chromatography (HPLC), gas chromatography (GC), thin-layer chromatography or UV-ViS spectrophotometry.

HPLC or GC methods are widely used because they can provide results in short time with satisfactory precision. GC method works on high temperature, so it is not appropriated for double base propellant and gunpowder samples with diphenylamine (DPA) stabilizers. Namely, increase in temperature has a direct effect on derivation: N-NO DPA, 2-NDPA and 4-NDPA, which became instable and undergo partly or completely into the DPA [6]. To prevent hazards and get realistic information about existence of stabilizer, it is better to use some other chromatography methods to analyze sample based on DPA stabilizer.

HPLC method prevents this problem completely and represent optimal method for determination not only thermal sensitive DPA derivatives, but also thermally sensitive NG, second energetic compound in double-based energetic materials.

For gunpowder and propellant samples which are stabilized with urea derivatives, preparation is not limited by temperature, as it is in the case with DPA samples. It allows samples preparation with saponification method, a grain gunpowder or propellant is treated by NaOH with heating. In short time, approximately 2 hours, sample dissolved completely. In next step, in separation funnel, extraction is performed in dichloromethane. The solution prepared in this way, can be detected on GC.

However, HPLC method was chosen as method which allows quantitative detection not only for thermally sensitive DPA and its derivatives, but also for: urea derivatives, NG and other organic compounds (plasticizers and explosives). Results shown in this paper present comparative analysis of samples preparation in dichloromethane and acetonitrile for different type of ammunition which were subject of periodic control and technical inspection in Military technical institute for the most common stabilizers in Serbian Military ammunition – diphenylamine (DPA) or urea derivatives (e.g. ethyl or methyl centralite).

The aim of this paper was to present some possible modifications for sample preparation which gave an opportunity to resolve samples preparation problems regarding the handling of large amount of solvent and a long time of extraction.

2. EXPERIMENATAL PART

Materials and samples preparation

Ten different gunpowders and double based propellants were examined. All of them were subjected to natural aging, due to the fact that they were subject of periodic control and technical inspection.

Preparation of samples

Gunpowder or double based propellants were milled in small pieces, sifted through sieves with aperture of 2mm before the extraction process. After milling, each of the samples were measured with mass of 1.000 g and placed into the flask.

Extraction in dichloromethane

Examined sample was placed into the flask, 50 cm^3 of dichloromethane was added and flask was left in dark place at room temperature for 48 hours. After that time, 5 cm^3 of solution was transmitted to a 10 cm^3 flask, dichloromethane was removed at low temperature (approximately 40ºC) and 10 cm^3 of acetonitrile was added. To provide adequate result, it was necessary to filtrate the sample through 0.5 μm PTFE filter before use.

Extraction in acetonitrile

Examined sample was placed into the flask, 50 cm^3 of acetonitrile was added. Extraction included 4 hours using magnetic stirrer and then 4 hours using the ultrasound. Finally, the examined solution, was obtained by separation from the precipitate using a centrifuge. After all this steps, 5 cm^3 of volume was transmitted to a 10 cm^3 flask, and 5 cm^3 of acetonitrile was added. To provide adequate result, it is necessary to filtrate the sample through 0.5 μm PTFE filter before use.

HPLC method

HPLC is an instrumental method for separation, identification and quantification of organic compounds. This technique relies on injecting a pressurized liquid solvent through column filled with a solid adsorbent material (stationary phase). Due to the fact that each component interacts slightly different with stationary phase, different component has different retention time, which provided separation of component in examined sample [7].

Figure 4. High Performance Liquid Chromatograph

For quantitative detection of stabilizer content in prepared samples High Performance Liquid Chromatograph "Waters 1525 EF Binary HPLC Pump" with a thermostat for column heating, the manual injector "Rheodine Model 7125", and the photodiode array detector "Waters 2998 PDA" were used, Fig.4.

Detection, identification and quantification for each of the organic compounds requires calibration which is prepared in adequate solvent (acetonitrile) in optimal concentration. Calibration curve has to cover the range of concentration of the exanimated samples, taking into account the mass of the samples, as well. To provide best result, each stabilizer has its own curve, made by 5 solvents with different concentration and satisfying precision. Stabilizer calibration solutions are prepared in the concentration range of 0.5 to 3%. All calculations were performed in relation to the sample weight of 1g.

It is mandatory to analyze calibration and sample under same 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}. The volume of the injection sample solution was 10 μL [8].

According to the device working instructions, chromatogram was took of the calibration sample solutions, and then automatic data processing was performed. The results were given in %mass, with an accuracy of two decimal places.

3. RESULTS AND DISCUSION

The results of determination stabilizer content for samples based on DPA are shown in Table 1. There were four samples of single-based gunpowder stabilized by DPA and one double-based rocket propellant (DBRP) stabilized with 2-NDPA.

Table 1. Result of mass concentracion of samples sabilized with DPA and/or it derivatives
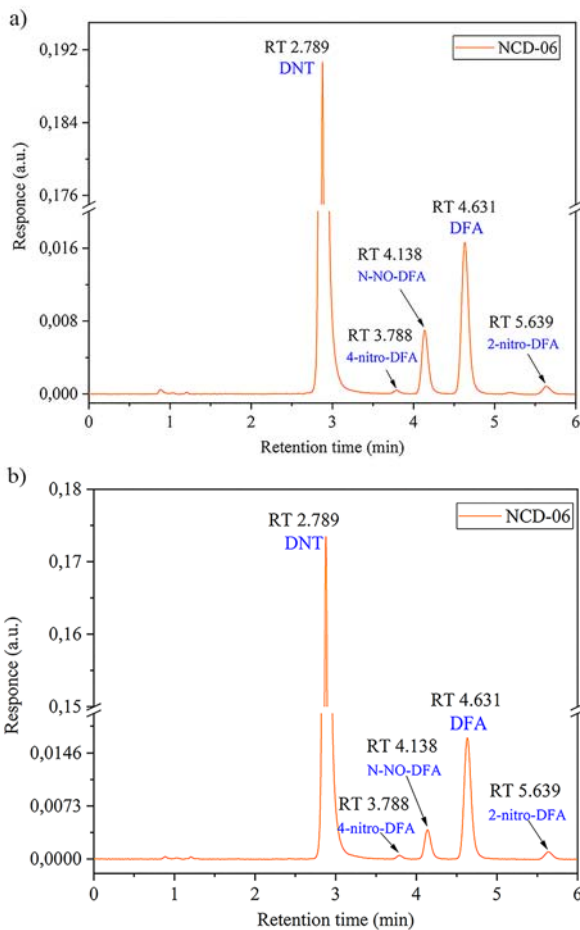
No	Samples of gunpowder and propellant	Stabilizer		Extraction	
				Dichlorome-thane solvent	Acetonitrile solvent
1.	NC-01	DPA and derivatives DPA	DPA	0.79	0.79
			N-NO DPA	0.31	0.32
			2-N DPA	0.02	0.02
			4-N DPA	0.05	0.06
2.	NC-16	DPA and derivatives DPA	DPA	1.21	1.21
			N-NO DPA	0.12	0.13
			2-N DPA	0.03	0.03
			4-N DPA	0.02	0.01
3.	NC-42	DPA and derivatives DPA	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.	NCD-06	DPA and derivatives DPA	DPA	1.13	1.13
			N-NO DPA	0.21	0.20
			2-N DPA	0.05	0.06
			4-N DPA	0.03	0.04
5.	DBRP 1	2-NDPA		1.80	1.80

Results are given in mass%, in two decimals. According to standard procedures for older single based gunpowder content of effective stabilizer represent sum of content DPA, NNO-DPA and 4-NDPA. On the other hand, according to NATO standard [9], effective stabilizer is calculated as sum of DPA and 0.85% NNO-DPA.

According to obtained results, both sample preparations give the same results, with a minor error on the second decimal place.

Due to the fact that effective stabilizer represents sum of DPA and its derivatives, it was crucial to ensure good separation of all peaks of interest.

Proper peak separation for sample of NCD-06, stabilized by DPA is shown in Figure 5, for preparation in dichloromethane. Except DPA and it derivatives, one more peak was detected. It was DNT explosive, which is added to gunpowder formulation for ballistic modification.

Figure 5. Chromatograms of single-based gunpowder NCD-06, a) extraction in acetonitrile, b) extraction in dichloromethane

The results of stabilizer content determination for five double-based propellant samples, based on urea derivatives (e.g. ethyl or methyl centralite) are shown in Table 2. Results are given in mass%, in two decimals.

Table 2. Result of mass concentracion of samples sabilized with urea derivatives

| No	Samples of gunpowder and propellant	Stabilizer	Extraction	
			Dichlorome-thane solvent	Acetonitrile solvent
1.	DBRP 2	C I	1.55	1.55
2.	DBRP 3	C I	2.47	2.46
3.	DBRP 4	C II	2.83	2.84
4.	DBRP 5	C II	1.34	1.34
5.	DBRP 6	C II	1.83	1.84

Double-based propellant stabilized by urea derivatives also had a good matching result for samples preparation in different solvents. In this case, separated peak was detected very easy, because this type of stabilizer is insensitive to high temperature and quite stable, without decomposition into its derivatives, for a long time.

Another separated peak of great importance, ethyl centralite (CI), was registered, Fig.6, in sample DBRP 3 prepared in acetonitrile. Beside CI, two more peaks were identified on this chromatogram. The first peak was for NG, expected for double based propellants, and the other one presented the peak from plasticizer, i.e. diethyl phthalate.
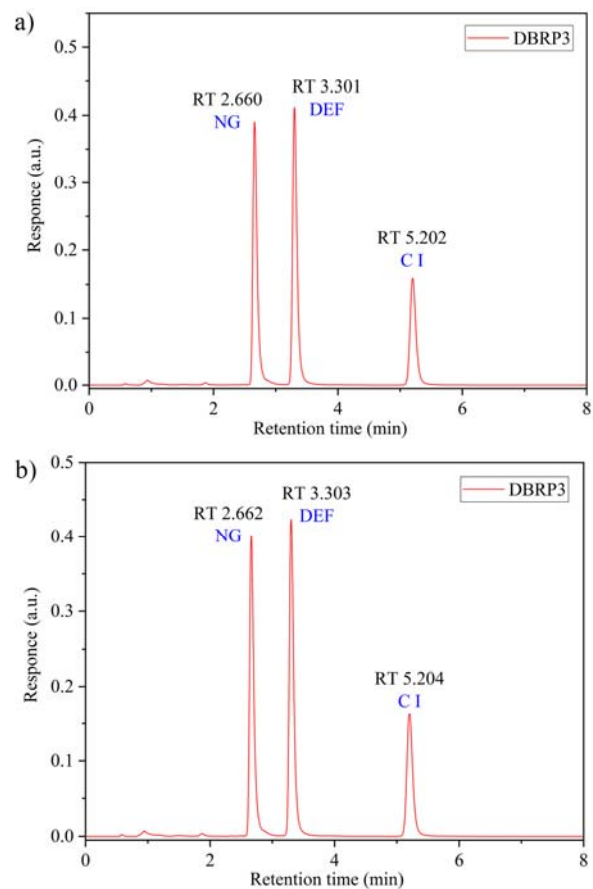
Figure 6. Chromatograms of double-based propellant DBRP 3, a) extraction in acetonitrile, b) extraction in dichloromethane

According to the results obtained by HPLC method, both sample preparation methods provide information about presence of DNT or TNT explosives and enablemass% calculation for those organic compound in samples. On the other hand, only samples prepared in acetonitrile provide realistic information about RDX or HMX presence. As it shown in Figure 7b, sample DBRP 5 prepared in dichloromethane had HMX in very low concentration, according to sample prepared in acetonitrile (Figure 7a).
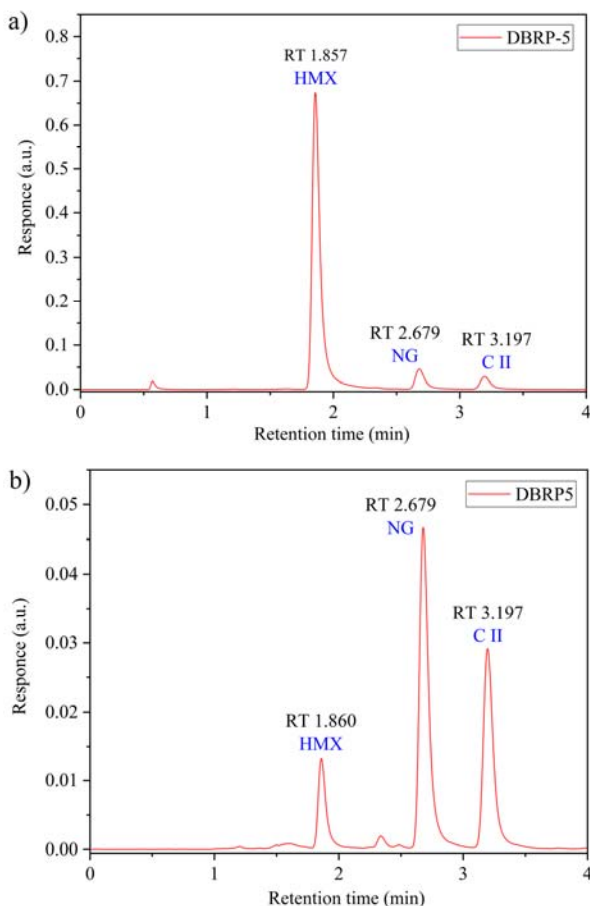
Figure 7. Chromatograms of double-based propellant DBRP 5, a) extraction in acetonitrile, b) extraction in dichloromethane

Reason for that is the fact that those types of explosives (HMX, RDX) are not completely soluble in dichloromethane and require assisted extraction by magnetic stirrer and the ultrasound.

4. CONCLUSION

Comparative analysis was performed of determination of stabilizer content in 10 types of gunpowder and double base propellant by HPLC method, in two different solvents, dichloromethane and acetonitrile, with different approach in samples preparation. The comparative analysis of the samples found that approximately the same values were obtained for preparations in different solvents. For each sample three injects were performed and the result represent the mean value. The obtained results confirmed reproducibility in related to the preparation method.

Both samples preparations have advantages and disadvantages, but both give satisfactory results.

Samples prepared in dichloromethane requires 48 hours extraction, but without any active laboratory equipment or personnel participation. It is quite convenient for preparation of large number of samples. After the extraction process, dichloromethane should be removed from the samples, which required solvent evaporation on 40C. This process might have influence on thermal sensitive DPA derivatives if temperature is not strictly controlled.

On the one hand, using acetonitrile as solvent saves time and gives results for less than 12 hours, but demands active preparation and equipment (magnetic stirrer, ultra sound and centrifuge), so it is not suitable for preparation a large number of samples. However, this solution had one huge benefit – it provides separation not only for stabilizer and NG, but also for explosives such as RDX and HMX which cannot be found using the dichloromethane solution. It means that sample preparation in acetonitrile provides more information – stabilizer content, NG and explosives if the examined sample contain them. The uniform method for detection of the organic compound from only one sample preparation can be create according to the obtained results. Moreover, all of those information can be provided for less than a day, which represent the standard to which most countries strive.

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