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Safety Monitoring of Storage and Use of Solid Homogeneous Rocket Propellants Through the Chemical Composition Analysis

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ABSTRACT

During storage, munitions and the high-energy materials they contain undergo destructive processes to their properties, which can cause them to be unintentionally initiated, resulting in the release of significant amounts of energy. In such a case, even a powerful explosion is possible, with significant material and human losses. What is crucial regarding storage safety, transportation and operational reliability is the chemical determination of the components of high energy compositions, since during long-term storage their decomposition products and derivatives appear, indicating the aging processes taking place. Analytical tests of chemical composition of high energy materials based on nitrocellulose are carried out using qualitative and quantitative analysis of micromolecular modifying agents. It is an important question due to opinion its service, especially safety for exploitation and rating of quality in production stage. The purpose of the study was to present relevant research on the rocket propulsion system in terms of resistance to long-term storage. As the first stage of an experiment – for separating modifiers from the nitrocellulose matrix – the gel filtration chromatography method (spatial exclusion chromatography, SEC) was used, then the most accurate method. For the next stage – determination of various types of high explosives and initiators in propellant samples – the liquid chromatography with spectrometry (LC/MS) was used. These methods allow the identification of the decomposition products and derivatives that appear over time. Physical and chemical property testing isis an extremely important step in the process of diagnostic testing of rocket propellants. They allow the ageing process of the high-energy material to be monitored, the current and accelerated ageing of the technical condition of the explosives to be assessed and a long-term prediction of their further operation to be made. This article presents the selected methods used in the study of solid homogeneous rocket fuels, which are suitable for separating and identifying the components of interest.

Keywords: Safety; Storage; Ageing; Homogenous rocket propellant; Analysis; Chromatography

NOMENCLATURE

1,3-DNB	: 1,3-dinitrobenzene
2,4-DNT	: 2,4-dinitrotoluene
2,6-DNT	: 2,6-dinitrotoluene
λ	: Wave lenght
ACN	: Acetonitrile
AN	: Ammonium nitrate
AND	: Ammonium Dinitramide
AP	: Ammonium perchlorate
CTPB	: Carboxyl-terminated polybutadiene
DEGN	: Diethyleneglycol dinitrate (2,2'-xybisethanol)
DBP	: Dibutyl phthalate
DPA	: Diphenylamine
EGDN	: Ethylene glycol dinitrate
ESI	: Electrospray Ionizer
FTIR	: Fourier Transform Infrared Spectroscopy
GAP	: Glycidyl azide polymer
GC	: Gas Chromatography
GPC	: Gel Permeation Chromatography
HMX	: Cyclotetramethylenetetranitramine (octogen)
HPLC	: High Performance Liquid Chromatography
HTPB	: Hydroxyl-terminal polybutadiene
LC	: Liquid Chromatography
LC/MS	: Liquid Chromatography-Mass Spectrometry
NB	: Nitrobenzene
NG	: 1,2,3-trinitroxypropane (nitroglycerine)
PETN	: Pentaerythritol tetranitrate
PPINICI	: Pulsed Positive And Negative Ion Ionization
RDX	: 1,3,5-trinitro-1,3,5-triazine, (cyclonite, hexogen)
SEC	: Spatial Exclusion Chromatography
THF	: Tetrahydrofuran
TIC	: Total Ionic Current
TLC	: Thin-Layer Chromatography
TNB	: Trinitrobenzene
TNT	: 1,3,5-trinitrotoluen (trinitrotoluene)
UV	: Ultra Violet
UV-Vis	: Ultra Violet-Visible

1. INTRODUCTION

Since the dawn of history, the most important aspect of building a state's military capability has been maintaining the

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armed forces in combat readiness. This means maintaining the state's defence readiness in one of three states: peacetime, crisis and hostilities. As the range of ammunition has expanded over time, history has recorded cases of malfunction1 or lack thereof, as well as storage incidents and accidents (magazine explosions of ammunition stockpiled over the years in peacetime). These have been linked to ageing processes over time as a result of their long service life or the effects of inappropriate storage conditions. The main factor with a fundamental impact on the safe operation of combat equipment is its technical condition.

It has therefore become very important to monitor the technical condition of combat equipment in the armed forces, which has led to the successive introduction and updating of elements of the testing system and evaluation Algorithms 2. The development of testing techniques and methods has made it possible to develop increasingly effective models for conducting tests on combat equipment, their statistical processing and the processing of the results. This has led to the introduction of numerous standardisation documents (STANAG, AOP, AASTP, MIL-SPEC, MIL-STD) and national standards (civil and military) based on them for the testing and operation of combat equipment.

Condition monitoring is based, among other things, on a series of tests in which the explosive is examined in its current state of use and after an accelerated ageing process. The aim of the physico-chemical tests is to assess the technical condition of the explosives and to provide a long-term prediction of the further service life of the products and their components containing these materials. Depending on the type of explosive contained in a given munition, appropriate physico-chemical test methods are selected. By analysing a wide range of data, it is possible to select parameters that have a fundamental impact on the safety and reliability of the operation of warfare agents, thus making research more efficient. By selecting appropriate research techniques, equipment and instruments, it is possible to improve existing monitoring procedures for the proper monitoring and operation of munitions in order to increase the safety of their operation. Ongoing verification and implementation of new research procedures and standards in laboratories is necessary.

This study used theoretical research methods, reviewed standardised methods for testing the physical and chemical properties of explosives in ammunition, analysed, compared and interpreted the data collected. This approach allowed conclusions to be drawn, the most appropriate test techniques to be selected and test methods to be developed. The application of each test at each stage of the experiment was explained.

1.1 Monitoring The Technical Condition ff Propellants

The production of solid rocket propellants requires strict adherence to technological standards. These standards, in addition to the conditions of the technological process, also determine the output parameters of the products, among others: the content of stabilizers, plasticizers and other organic additives that improve the quality of the powders, solvent content and water content. Therefore, an important aspect is to undertake the work of learning as much as possible about their stability.

During long-term storage of warfare agents containing gunpowder, propellants, and homogeneous and heterogeneous rocket propellants, irreversible aging changes occur, which are catalysts for the decomposition process[1], which can consequently lead to a decrease in performance and safety.

It is therefore extremely important to monitor the rocket propulsion system's resistance to long-term storage by carrying out periodic tests[2], both visual inspection of the technical condition and laboratory testing of samples of high-energy materials from batches of products nearing the end of their technical life (guaranteed by the manufacturer or resulting from the results of tests in the previous test cycle). These measures increase the safety of storage, transport and operation of these products[3].

Research carried out for many years by the Military Institute of Armament Technology (MIAT) enables predicting and extending the residual life of munition, thereby ensuring the safety of its storage and the reliability of the operation of a munition and its components at the end of their technical life[4]. Laboratory tests are one element of the developed diagnostic process and are based on the chemical determination of decomposition products and derivatives of high-energy components and their compositions, which occur during long-term storage and indicate the progress of the ageing processes taking place.

Several groups of analytical methods[5-6] are currently used to determine selected components of explosives (propellants)[7]. A number of methods have been developed to test the stability of propellants, the most commonly used of which are instrumental methods (e.g. HPLC) which allow the stabilizer content of the propellant under test to be determined with a high degree of accuracy. On this basis, it is possible to predict the period of time over which the stabilizer will degrade and the propellant will lose its original properties and thus fail to meet the requirements. Other methods of determining the stability of propellants are non-instrumental, such as determining the levels of nitrogen oxides emitted by thermally decomposing gunpowder as a result of high temperatures.

STANAG standardization documents list the parameters to be tested for different types of explosives and the test methods to be used for them in order to assess safety and suitability at all stages of the life cycle of explosives and ammunition. These documents specify which methods can be used to test the most important parameters in a diagnostic evaluation and usually include a choice of several alternative methods or an endorsement of the methods used by the laboratory, subject to equivalence with the proposed methods. Homogeneous solid propellant[8] is a solid propellant in which an oxidizing component and a combustible substance form a chemical compound or mixture (one phase) are part of the same molecule - they are chemically bound oxygen and combustible elements[9]. Its composition is similar to smokeless powders. The term colloidal fuel/powder is also used, since it consists mainly of a mixture of nitrocellulose of varying degrees of nitration dissolved in nitroglycerin (colloid)[10]. Solvents are both gelatinizers of nitrocellulose, which under certain conditions of temperature, pressure and concentration bring it to a plastic state and impart propelling properties.

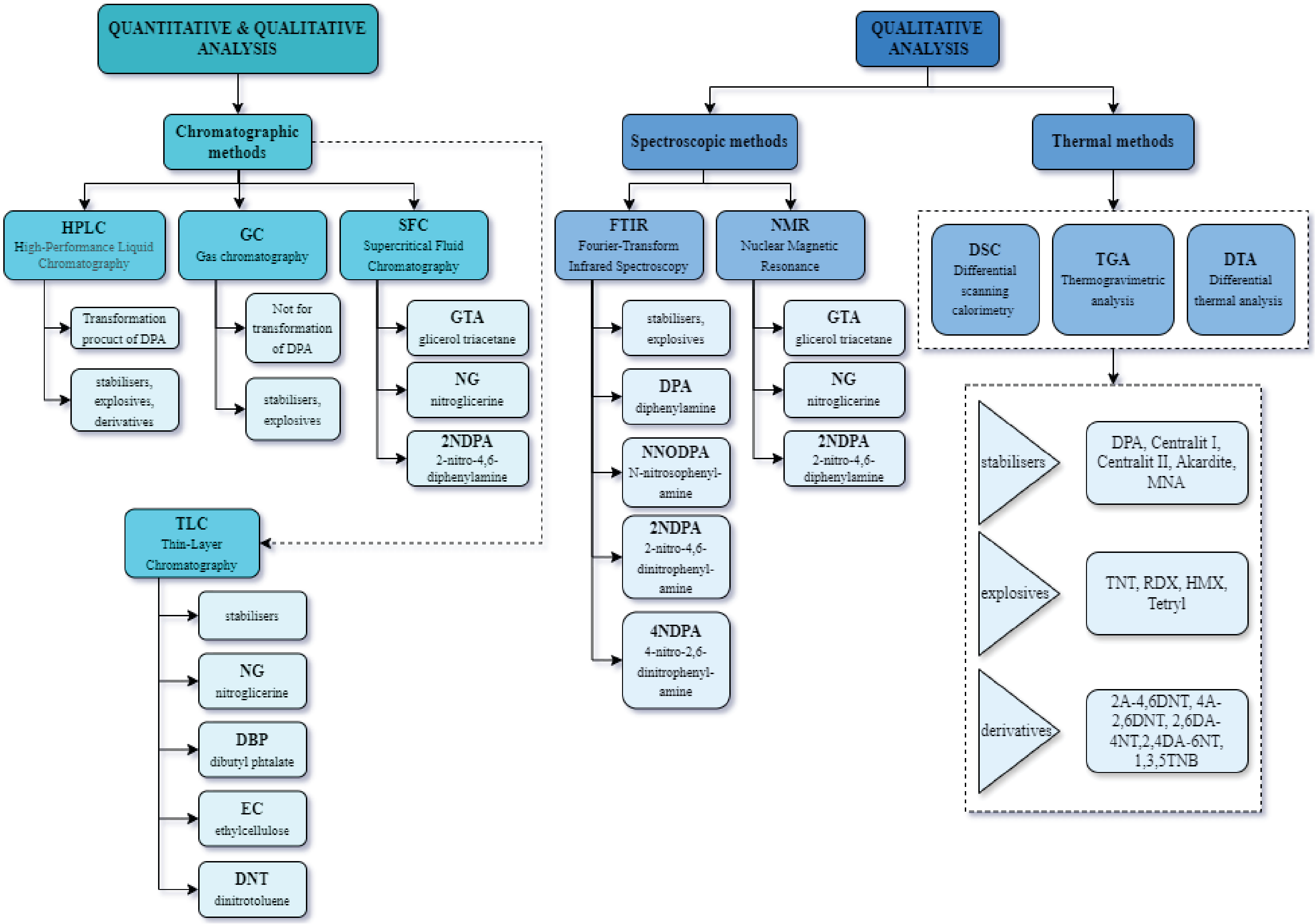

Figure 1. Division of instrumental methods for qualitative and quantitative analysis of explosives (propellants) and its components.

Compound fuels, on the other hand, consist of two main substances - a combustible substance and an oxidizer. The content of the oxidizer is 50-80 %. In addition, they contain substances that give them appropriate properties that meet the requirements for fuels, both physical, chemical and ballistic[11]. Due to the number of components of rocket fuel[12] (reaching up to a dozen), this is a very complex issue.

The most often used for the analysis of propellants (powders and rocket solid propellants) are: Thin-Layer Chromatography (TLC), Gas Chromatography (GC) or Liquid Chromatography (LC). The methods used must be characterized by accuracy, high sensitivity, precision and speed. Where possible, they should preferably be non-destructive. Figure 1 shows a division of quantitative and qualitative analysis methods with assigned components that can be determined by the method, which were considered during the preparation of the experiment.

It should be borne in mind that, according to good laboratory practice, it is necessary to use several test methods or parameters for a given explosive in order to obtain as much detailed information as possible on its properties and thus to make a reliable diagnostic evaluation and to determine the residual value of the explosive submitted for testing. The method presented in this article is one of the possible ones.

The main problem associated with the analysis of such materials is the incomplete separation of small-molecule components (modifiers) from the nitrocellulose matrix changes occurring over time and the possibility of individual components masking the results. However, it seems possible to analyze a general approach to the analysis of the composition of rocket fuels, test it and solve some smaller research problems related to the topic of the article. For this reason, it was proposed to use chromatographic methods to study the composition of propellants. However, using several methods and confronting the results of the measurements allows for a more precise evaluation. For the purposes of this publication, chromatographic techniques were explored and the HPLC method was chosen for the study due to its speed and versatility.

Thermal techniques are not included in this paper, even though they are also the primary methods used in the study of solid rocket fuels, as the focus is on improving chromatographic techniques. Also, monitoring of stabilizers and evaluation of mechanical properties are provided for a separate publication.

2. SELECTED METHODS OF QUALITATIVE ANALYSIS

Chromatographic methods like Gel Permeation Chromatography (GPC), Liquid Chromatography-Mass Spectrometry (LC/MS), and other techniques are suitable for separating and identifying the components of propellants. The gel filtration chromatography method (spatial exclusion chromatography, GPC, SEC) can be considered the most accurate method for separating modifiers from the nitrocellulose matrix. In the process of solvent extraction of organic substances, acetone is most often used (sometimes, among others: ethanol, diethyl ether, chlorinated methane or toluene), while for inorganic substances - water.

Liquid chromatography (HPLC) and Gas Chromatography (GC) are modern testing methods used for the determination of various types of chemicals, including high explosives and initiators. These methods allow the identification of materials, such as TNT, and the determination of their purity (checking for the presence of derivatives and impurities).

2.1 Gel Permeation Chromatography (GPC)

Spatial Exclusion Chromatography (SEC), also known as Gel Permeation Chromatography (GPC), is a separation technique that uses a non-ionic molecular sieve mechanism. It separates compounds according to their molecular weight and structure in the column[13]. Substances having a higher molecular weight (with an effective volume exceeding the pore dimensions of the gel used) pass unstopped through the column[14]. Smaller molecules enter the internal structure of the gel and are removed later.

The types of stationary phases in gel chromatography can be divided as follows[15]:

- Lyophilic (for low and medium polar polymers),
- Hydrophilic (for highly polar polymers and for biopolymers).

The most commonly used filling for the separation of low- and medium-polar polymers is a copolymer of styrene and divinylbenzene, spatially cross-linked, with spherical grains of 5µm diameter, which is a hard sorbent used under High Pressure/ Performance Liquid Chromatography (HPLC) conditions.

2.2 Liquid Chromatography (LC)

Liquid chromatography (HPLC) and gas chromatography (GC) are modern testing methods used for the determination of various types of chemicals, including high explosives and initiators. These methods allow the identification of materials, such as TNT, and the determination of their purity (checking for the presence of derivatives and impurities).

The LC method uses the effect of chromatographic separation using a liquid as the mobile phase. Steady flow and high pressure are provided by a special pump. An UV spectrophotometer or a refractometric detector coupled to a recorder is most often used as a detector. Columns in HPLC are thick-walled steel tubes with an inner diameter of 2 mm and a length of 10-30 cm[15].Capillaries supplying the mobile phase under pressure have an inner diameter of 0.1 mm. High-performance liquid chromatography usually uses fillers with grain diameters of 5-10 µm. Fine-grained fillings provide a short diffusion path for the molecules of the substances to be analyzed into the interior of the grains, which results in high column efficiencies. The kinetic properties of the sorbent are better for the thinner the thickness of the active layer.

During separation in the normal phase system, silica gel is mainly used as a column filler[15], which is an amorphous, porous material and as a column filler has many advantages, such as grain size of the desired size and appropriate pore size, specific surface area and high mechanical strength.

When analyzing a chromatogram, retention values play an important role, allowing to unambiguously determine the presence of a particular component.

In order to identify the peaks corresponding to individual components of the sample, it is necessary to compare the peak retention time of the identified substance with the peak retention time of the standard, analyzed under the same conditions. The number of components in the sample is proportional to the area or height of the corresponding peaks. During quantitative analysis by the internal standard or normalization method, the area or peak height of the component of the sample being analyzed and the area or peak height of the standard can also be compared[13].

The literature provides several options for HPLC analysis. The first presents a separation between diethylene-glycol dinitrate (DEGN, 2,2'-oxybisethanol dinitrate) and nitroglycerine (NG, 1,2,3-trinitroxypropane), between tetryl (N-metylo-N,2,4,6-tetranitro-anilina) and trinitrotoluene (TNT, 2,4,6-trinitrotoluen), and between NG, 2,4-DNT and ammonium nitrate[13]. Acetonitrile and water in a 50:50 volume ratio, a 10 cm x 4.6 mm RP-8 column and an UV detector (λ=214 nm) were used as the mobile phase. A mixture of nitro aromatic compounds containing TNT, 2,6-DNT and o- and m-nitrotoluene can be separated using a 25 cm LiChrosorb RP-8 column. The mobile phase in this case is a methanol/water system (50:50) with a flow rate of 2 mL/min and an UV detector for 280 nm[13]. A separation of two-phase smokeless powders can be achieved using a 30 cm column µBondapak C18, a mobile phase (acetonitrile/water in a 55:45 ratio) with a flow rate of 2.5 mL/min and a UV detector (λ=230 nm).

A separation of a mixture containing NG, TNT, RDX (hexogen), HMX (octogen) and EGDN (ethylene glycol dinitrate), among others, can be achieved using a reversed-phase column, an acetonitrile/water mobile phase (70:30) and an UV detector at 214 nm[16-17]. However, for a mixture containing TNT, 2,4-DNT, 2,6-DNT, RDX and HMX, separation will be achieved using two different columns: 3.3 cm x 4.6 mm and 15 cm x 4.6 mm Supelcosil LC-8 and a mobile phase of methanol (with 2 % THF)/water (30:70) with a flow rate of 2 mL/min and an UV detector (λ=230 nm)[18]. You can also use a Radial-Pak C18 column and a methanol/water in a ratio of 40:60 (2 mL/min flow rate) and an UV detector (λ=254 nm).

A satisfactory separation of NG and EGDN is also possible using a 30 m x 3.9 mm µBondapak C18 column and methanol/water mobile phase using a gradient method - starting with 30 % methanol (7 min.), then ramping up to 100 % methanol for 2 min. and finally maintaining this concentration of solution for 5 min. The UV detector should operate at (λ=254 nm).

2.3 Liquid Chromatography with Mass Spectrometry (LC/MS)

Combining a Liquid Chromatograph (LC) with a Mass Spectrometer (MS) is the most effective method for identifying and determining trace amounts of volatile organic compounds in complex natural matrices, where chromatographic analysis is often insufficient for efficient chromatographic separation and does not provide confidence that a given signal corresponds only to the compound being determined. In the LC/MS system, a liquid chromatograph separates the analyzed mixture into components, and a mass spectrometer records their mass spectra, allowing unambiguous identification of each component of the separated mixture. The resulting ions, radicals and neutral molecules, have a set of ions with different mass-to-charge m/z ratios that are characteristic of a compound[19].

As the LC/MS method is a comparative method, it requires calibration (comparison against a known standard). The method is also limited to those substances that can be eluted from the chromatography column and are not very volatile. Some nitro esters and nitro amines are thermally unstable and break down under analysis conditions. However, various ionization methods allow explosives analysis[20]). Analysis of nitrobenzene, 1,3-DNB, 2,6-DNT, 2,4-DNT, TNB and TNT is possible. To analyze the sample, make a 0.1-10 μg/ mL solution in acetone. The proposed capillary column is a 30 m x 0.32 mm x 0.25 μm BD-5, the analyzer is a Finngan 4021 quadrupole mass spectrometer with pulsed positive and negative ion ionization (PPINICI) option. The temperature program assumes an initial temperature of 40 °C (2 min.), followed by heating to 270 °C at 10 °C/min.

A mixture containing NC, NG, diphenylamine (DPA), C-I, 2,4-DNT and dibutyl phthalates can also be successfully separated by LC/MS and FTIR (Fourier Transform Infrared Spectroscopy), with FTIR identifying NG, while LC/MS identifies NC, 2,4-DNT, stabilizers and plasticizers. The methanol solution was identified using the magnetic sector of a VG 16F spectrometer. Separation was performed on a 15m x 0.32 mm Chromepack CP-Sil 5 CB column in the temperature range of 80-230 °C (16 °C/min). The ion source used had a temperature of 230°C. Another analysis proposal involves using a 30m x 0.32 mm x 0.25 μm BD-5 capillary column and a Finngan 4500 mass spectrometer quadrupole analyzer. The temperature program is an increment from 70 °C to 270 °C at a rate of 15 °C/min.

The separation of the mixture of six explosives (NG, 2,4-DNT, 2,4,6-TNT, PETN, RDX and tetryl), was carried out on a 15m column, because on a 30 m column RDX and PETN did not elute or partially decayed. For a shorter column, the separation was worse, but more important in this case was the selectivity at the entrance to the ion source. Under slightly different conditions[15] i.e., using a 15 m x 0.32 mm x 0.25 μm DB-5 column, a temperature program of 50-170 °C (heating rate 20 °C/min) and chemical ionization, authors obtained satisfactory separation and identification of NG, TNT and DNT isomers.

2.4 Experiment

Typical examples of homogeneous propellants are single-base (NC with additives), double-base (NC, NG with additives) and triple-base (NC, NG, NQ with additives). For composite propellants often contain oxidizers like AP (Ammonium Perchlorate), AN (ammonium nitrate), AND (Ammonium Dinitramide), RDX and HMX. Metal fuel additives (for example. aluminum particles) are widely used in propellant compositions to enhance stability characteristics and motor performance. Moreover HTPB (hydroxyl-terminal polybutadiene), CTPB (Carboxyl-Terminated Polybutadiene) and GAP (glycidyl azide polymer) nowadays are added as binders[21]. Based on the literature data, research methods were selected. As part of the experiment, the following were made:

- Review and analysis of the literature in terms of application of SEC for separation of a nitrocellulose ingredient and LC/MS chromato-graphy for testing of energetic ingredients and their derivatives in rocket fuels.
- Verification of the suitability of individual methods for composition analysis to determine the stability of homogeneous propellants.
- Selection of conditions of the method of separation of macromolecular components by SEC method and determination of decomposition products by LC/MS and its validation:
    - Selection of chromatographic conditions;
    - Evaluation of qualitative and quantitative relations;
    - Analysis of the amount of products,
- Selection of rocket propellants from different vintages of production that indicate changes in stability (Fig. 2).

The research methodology included chromatographic analysis of samples and determination of their mass profile. The reference material consisted of standards of diphenylamine, triphenylamine, toluene derivatives and additional standards (tetryl, 1, 3, 5-trinitrotoluene, 2, 6-dinitrotoluene, hexogen, octogen) at a concentration of 5 mg/mL (dissolved in acetone and dichloromethane). A simple and reproducible method was developed for standards listed above.

The selected parameters depicted here include accuracy, precision and limit of detection and limit of quantification are shown in the Table 1.

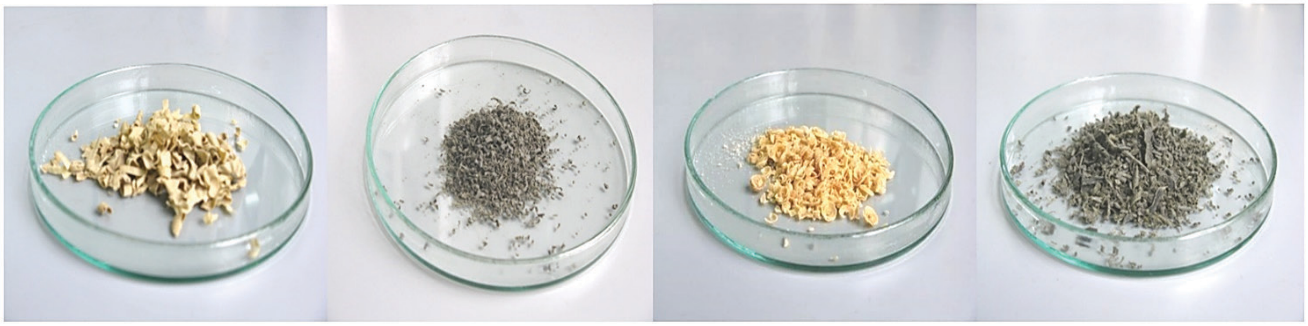

Figure 2. Samples of homogeneous solid rocket propellants prepared to test.

Table 1. LC/MS validation parameters for limit of detection, limit of quantification, precision and accuracy

Name of substance	LOD [ng/mL]	LOQ [ng/mL]	Precision [CV %]	Accuracy [RSD %]
TNT	1,8	4,7	2,84	5,72
HMX	1,33	2,1	2,95	5,11
RDX	1,2	2,28	3,1	4,89
Tetryl	1,44	3,27	2,56	5,3
2,6-DNT	1,87	2,34	1,98	4,54
Toluene	1,21	3,56	1,33	4,56
DPA	1,04	3,24	1,22	4,23
TPA	1,15	2,91	1,34	4,72

Based on the literature data, tetrahydrofuran was selected as the eluent in the spatial exclusion chromatography (SEC) method. This solvent ensures solubility of virtually all propellant samples tested and is compatible with the column packing used. The method allowed complete separation of nitrocellulose into low molecular weight components. An LC-10AD liquid chromatograph with Shimadzu's LCsolution interface consisting of a pump, equipped with a Macherey-Nagel 300 mm x 7.7 mm gel chromatography column and refractometric and UV-Vis spectrophotometric detectors were used to study selected fuel samples. Tetrahydrofuran (for HPLC) was used as the eluent at a flow rate of 1.0 mL/min. Prepared solutions of the tested rocket fuels in tetrahydrofuran, at a concentration of 20 mg/mL, were injected onto the column. For each sample, the optimum collection time for the fraction of low-molecular-weight components was determined based on the indications of the UV-Vis detector.

Table 2. Gradient conditions used during the analysis

Time [min]	Pump	Value [%]
0.10	B	0
5.00	B	0
5.10	B	100
54.00	B	100
55.00	B	0
60.00	B	0

The HPLC method was initially optimized by performing a gradient phase elution from 10 %ACN/0.1 %TFA to 98 %ACN/0.1 %TFA, over a period of 54 min. (Fig. 5). The experiment was conducted on reference standards and sample fractions. Blinded analysis was performed.

A 4000 Q TRAP LC/MS/MS System coupled liquid chromatograph with two constant flow pumps, with a variable wavelength UV detector - Shimadzu® UFLC, equipped with a Luna 5 µm C18(2) 100Å 25 cm x 4.6 mm column from Phenomenex® with a C18(2) pre-column (30 mm x 4.6 mm) and a UV-Vis spectrophotometric detector was used for the study. The eluent used was 10:90 ACN:H_2O / 0.1 %TFA (phase A) and 40:60 ACN:H_2O/0.1 %TFA (phase B) at a flow rate of 1.0 mL/min. Solutions of the rocket fuels under study were injected onto the column at concentration of 0.25 mg/mL of phase A. The oven temperature was set at T=40 ºC, the analysis time at about 60 min., and UV detection at λ=254 nm. The gradient conditions are shown in Table 2.

Chromatographic analysis using A 4000 Q TRAP LC/MS/MS System coupled with UFLC liquid chromatograph with a variable wavelength UV and UV-Vis detector for the reference material dissolved in 0.1 %HCOOH/H_2O (concentration 0.002 mg/L).

The determination of the mass profile of the test samples was carried out using a 4000 Q TRAP LC/MS/MS System mass spectrometer with a Harvard Apparatus 11Plus pump. The scan type was adopted Q1+ and the mass scan range was 50 to 600 amu, with a time of 0.17 sec. Other parameters were set as follows: CUR=10, IS=5500, TEM=25ºC, GS1=25, GS2=0, ihe=on. The determination was carried out for a phase flow of 10µl/min in MCA mode for 3 min.

3. RESULTS

Using liquid chromatograph with a Macherey-Nagel 300 mm x 7.7 mm gel chromatography column and refractometric and UV-Vis spectrophotometric for fuel samples in tetrahydrofuran the range of fraction collection times for each sample was given that are shown on the corresponding chromatographs with arrows - green (start of collection) and red (end of collection) in the Fig. 3. It shows an example of the chromatographic separation of the test sample for

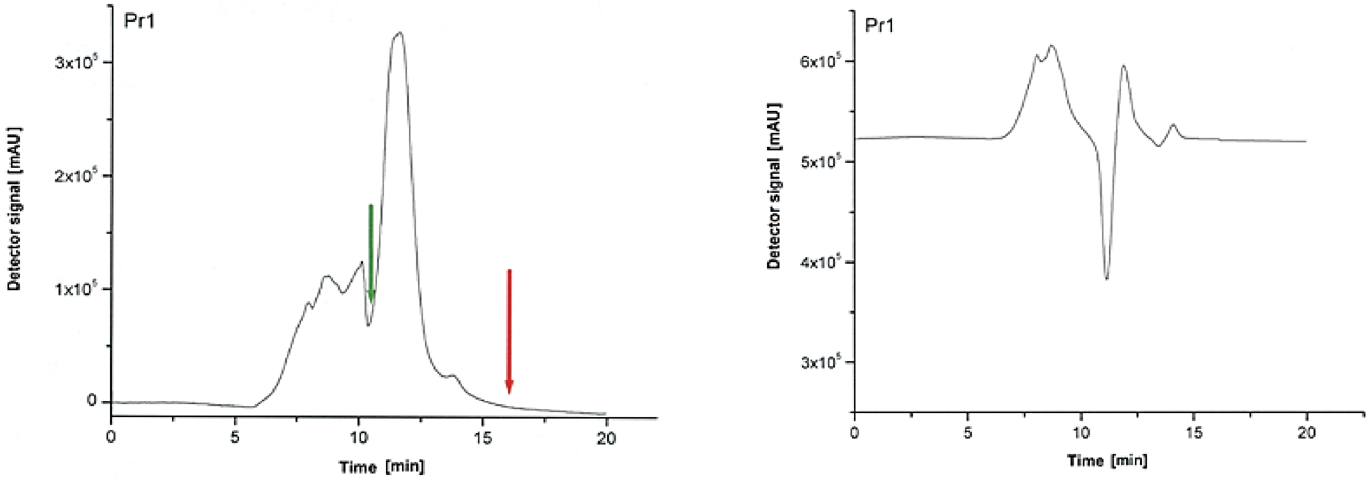

Figure 3. Chromatogram of sample 1 obtained for UV detection (left) and for UV detection (right) for a time of 6-11 min covering the elution range of nitrocellulose.

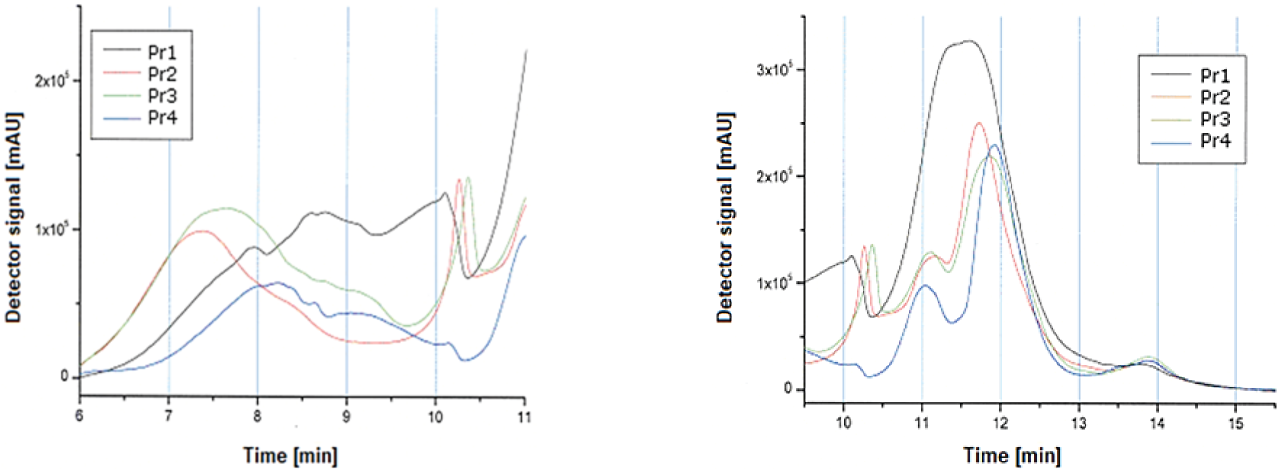

Figure 4. **Summary of chromatograms of samples 1-4 obtained for UV detection for a time of 9.5-15.5 min, covering the elution range for low-molecular-weight components.**

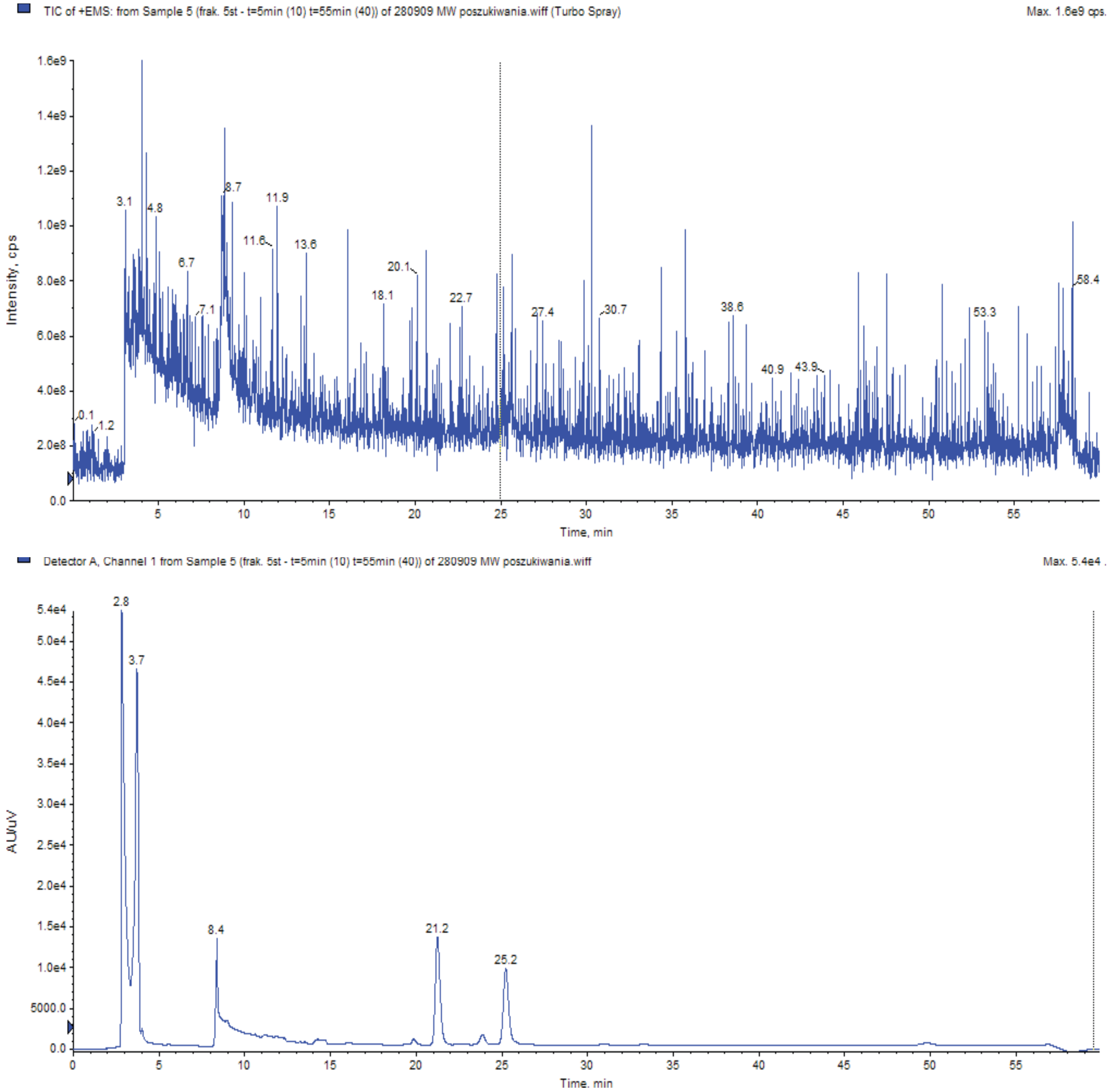

Figure 5. HPLC method optimization (10%->98%ACN/0.1%TFA) (top chart – TIC of +EMS, bottom chart – chromatogram (λ=254 nm).

spectrophotometric detection, while Fig. 4 for refractometric detection obtained as a result of the experiment.

Figures 4, shown below, illustrate the component separations of the fuels tested. The time range of 6-11 min covers the elution range for nitrocellulose, while 9.5-15.5 min. covers the elution range for small molecule components. Both UV and refractometric detection confirm that good separations of nitrocellulose and small-molecule components were obtained. The chromatographs obtained are qualitative only and do not allow quantitative comparisons of nitrocellulose or small-molecule components in rocket fuel samples. For further studies, fractions of low-molecular-weight components were collected according to time ranges and further investigated.

In the experiment the high explosives analysis by HPLC a spectrophotometric detector with ultraviolet (UV) absorbance measurement at a wavelength optimal for the group of nitro aromatic compounds as reference substances (254 nm) was used. Optimization of the MS method (TIC - total ionic current) of samples of unknown composition was carried out by direct injection on an electrospray ionizer (ESI-Electrospray) and checked on a 2,6-DNT standard.

Chromatographic analysis using A 4000 Q TRAP LC/MS/MS System coupled with UFLC liquid chromatograph given the results (chromatograms) that are shown in in Figure 6. For the example sample labeled "fr. 1" (blue line) and the standard sample, as an example 2,6-DNT (green line) at retention time t_R=21,2 min the same peak is visible. It was found that the retention time of 2,6-DNT was consistent with one component of the analyzed fractions with t_R=21 min - it was possible to unambiguously determine that 2,6-DNT was included in the test samples. The retention times of other reference samples did not match the retention times of the main components of the test mixtures. In order to obtain a higher resolution of the signals on the chromatogram of the test sample, the B phase was exchanged for a B' phase with a composition of 35:65 ACN:H2O/0.1 %TFA. Triphenylamine derivatives are not determined by this method and require a much stronger elution.

The determination of the mass profile using a 4000 Q TRAP LC/MS/MS System given in result the mass profile obtained for the sample labeled fr. 1. According to the study, there were not detected signal of diphenylamine, triphenylamine, toluene derivatives in propellants samples. Additional explosives searched (tetryl, hexogen, octogen) were not included in samples.

The mass spectrum at m/z=181.3 is interpreted as the deprotonated ion peak $[DNT–H]^-$. The obtained MS/MS spectrum of the peak at m/z=181.3 corresponds to $[DNT-H]^-$, while this identification is confirmed by the observed fragment peaks: at m/z=152.3 specific to $[DNT-NO]^-$ and at m/z=116.3 specific to $[DNT-2H_2O-NO]^-$.

4. DISCUSSION

The data collected on the composition of selected homogeneous rocket fuels, are applicable in the process of assessing the safety of further rocket operation.

Gel chromatography made it possible to separate nitrocellulose from the other components of the sample, so it did not interfere with the results when analyzing the collected sample fractions by liquid chromatography. In the obtained chromatograms, the peak coming from NC was slender and unambiguous.

A 4000 Q TRAP LC/MS/MS System coupled with UFLC liquid chromatograph is very effective method to detect explosives and derivatives. Liquid Chromatography using UFLC gives as a result peaks of analyzed explosives in samples according to a retention time of standards used. Analyses using mass spectrometry of selected explosives gave parent ions of the standards of explosives Dinitrotoluene (DNT)

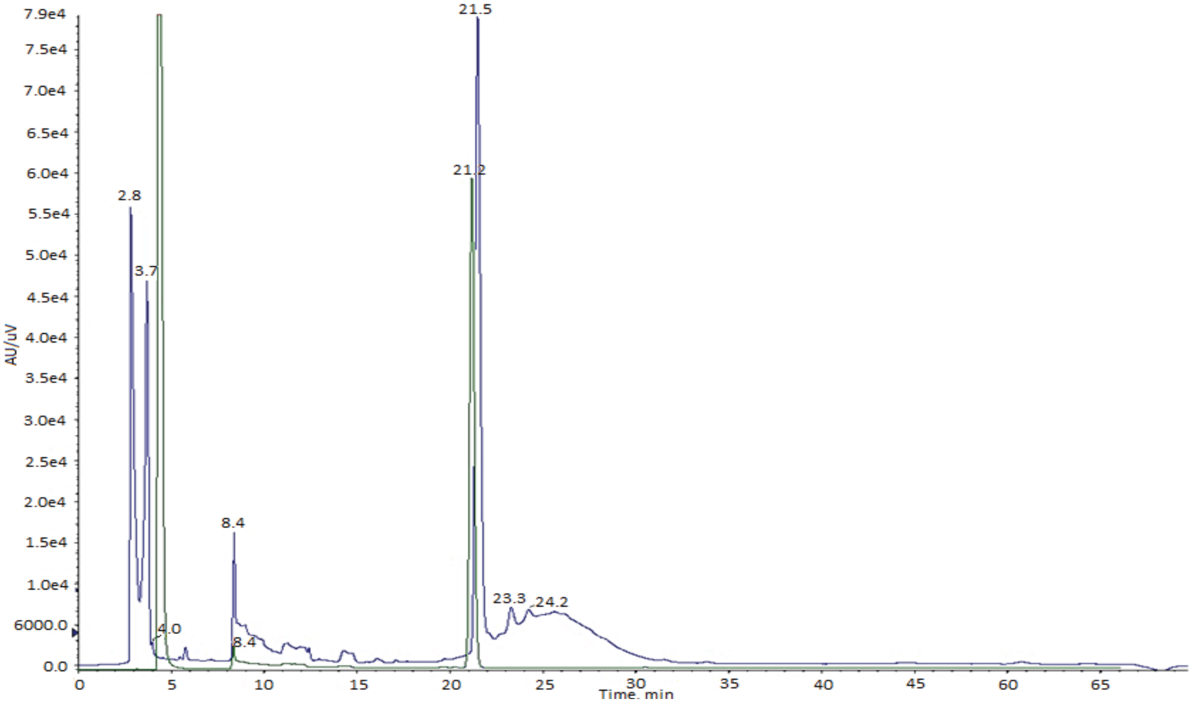

Figure 6. The resulting chromatogram of the tested sample - as an example Sample "fr. 1" (blue line) and the standard sample - as an example 2.6-DNT (t_R=21.2 min) (green line).

and trinitrotoluene (TNT) were observed as [M–H]–. For rest of used explosives (RDX, HMX, PETN) as [M+HCOO]– . These results confirm the usefulness of the research using and explosives detection accuracy using MS and MS/MS methods.

The absence of signals from diphenylamine, triphenylamine and toluene derivatives may indicate the use of another stabilizer (Centralite I and, in some samples, acardite, confirmed by TLC in the collaborating laboratory). The presence of toluene in the samples analyzed may be due to two main sources. Firstly, it may originate from the solvent used in the material plastification process, a common practice in the chemical industry. Secondly, toluene may be present as a contaminant resulting from the synthesis of toluene diisocyanate (DNT), which is a key intermediate in the manufacture of some explosives and polymers. Its presence at trace levels may therefore be indicative of the specific manufacturing process used to produce the test samples.

However, when used as a plasticizer, 2,4-dinitrotoluene affects the burn rate of rocket fuel. It is an effective burn rate modifier because it remains stable over time and is chemically compatible with propellants such as nitrocellulose. Confirmation of its presence is also important from a safety perspective, not only because of its toxicity and potential carcinogenicity, but also because of its explosive properties. In addition to its role as a combustion accelerator, dinitrotoluene is also an explosive breaker, which can have a significant impact on the safety of rocket fuel storage.

Under certain conditions, in particular improper storage, it can lead to an increased risk of uncontrolled detonation or degradation of the stability of the propellant mixture. Awareness of its presence in the fuel composition allows potential hazards to be anticipated and storage and transport conditions to be adjusted accordingly, minimising the risks associated with both accidental initiation and long-term effects on the chemical structure of the fuel.

The absence of derivative signals and degradation products in particular confirms the stability of the rocket fuels tested, which is a key aspect of their long-term storage and use. High chemical stability means that there are no significant degradation processes in the analysed samples that could lead to the formation of unstable decomposition products that could negatively affect fuel performance.

Furthermore, the absence of derived signals may indicate that rapid degradation processes that would result in detectable levels of degradation products do not occur during fuel storage and ageing. This confirms that the fuels tested retain their chemical stability over time, which is an important factor in ensuring their safe storage and subsequent use.

It is also important to note that these fuels are stored under controlled conditions that minimise the influence of external factors that could accelerate their degradation. However, the detailed parameters of these conditions, such as temperature, humidity or possible protection against chemical and physical agents, cannot be fully described in this article. However, their controlled nature provides additional evidence that the observed stability of fuels is due to both their chemical composition and appropriate storage conditions.

5. CONCLUSIONS

Detailed studies of thermal properties, chemical resistance and sensitivity ensure the safety of storage, transport and handling of a given munition and its operational reliability in use. This is an important issue for the safety of use and storage, especially of aged materials (rocket propellants) during long-term storage Using minimum two methods and confronting the results of the measurements allows for a more precise evaluation.. An alternative method to the literature solutions, methodologies and techniques commonly suggested in standardization documents (usually not precisely described and that gives the possibility of adjusting) was proposed. It allows the use of combined techniques and fewer reagents is used (or wasted). The methods used by other authors (cited in the second section of the article) do not take into account all derivatives and decomposition products of stabilizers.

The effectiveness of the proposed alternative test sequence in the rocket fuel health monitoring process has been demonstrated, using separation of the large molecular fraction from the small molecular fraction by SEC, one of the most effective methods, followed by an LC/MS/MS system to analyse and confirm the accuracy of the determination. It is also a relatively inexpensive yet effective method for the determination of high-energy components, stabilizers and modifiers. It can be successfully used as an equivalent method with equivalent accuracy to discriminate between stabilizers and their derivatives and other powder constituents in laboratories equipped with these two analytical instruments when assessing the technical condition and extending the service life of ammunition, thereby increasing the safety of its use and storage.

It should be remembered that the process of ammunition diagnostics must be carried out in a comprehensive manner. The developed principles and procedures, together with the acquired knowledge and technological progress, require continuous improvement in order to obtain, on the basis of the test results obtained, the broadest possible picture of the condition of the combat equipment of the units responsible for maintaining a state of defence readiness in peace, crisis and war.

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