11TH INTERNATIONAL SCIENTIFIC CONFERENCE
ON DEFENSIVE TECHNOLOGIES
OTEH 2024
Serbia, Tara, 9-11 October 2024

INFLUENCE OF GUNPOWDERS AND ROCKET PROPELLANTS SAMPLE PREPARATION ON TEST RESULTS

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Abstract: *Research, presented in this paper, deals with the influence of the different ways of preparation of gunpowders and rocket propellants, in terms of different granulations, on the results of microcalorimetric and chromatographic tests of the chemical stability of gunpowder. The samples were examined in their original form, where possible, as well as prepared in a way that requires cartain defense standards of the Republic of Serbia and in this way their requirements regarding the preparation of the sample were also reviewed. The conclusion for the optimization of sample preparation for microcalorimetric testing are especially important, which reduces free oxygen to the smallest possible amount, which has a positive effect on the accuracy of sample test results. For comparison of results, methods based on thermal activity monitoring and changes in the chemical composition of samples were used.*

Keywords: *gunpowders and rocket propellants, chemical stability, preparation of samples*

1. INTRODUCTION

Energetic materials such as propellants, pyrotechnics and explosives till nowdays are investigated from different points of view. The results are essential to safe production storage and handling. Nitrocellulose (NC) is main component of smokeless gunpowder and propellants. The spontaneous chemical degradation of nitrocellulose takes place over time, producing nitrogen oxides and excess of heat which causes its further autocatalytic degradation leading to critical conditions for possible self-ignition of propellant. To prevent autocatalysis and minimize degradation effects, components known as stabilizers are added to propellants composition. Diphenylamine (DPA) is one of those components usually used as a stabilizer. Besides diphenylamine, there are several substances that can be added to gun propellants composition like 1,3-diethyl-1,3-diphenylurea (centralite I) and 1,3-dimethyl-1,3-diphenylurea (centralite II). The consecutive nitration and nitrosation products of DPA, are formed over time [1] and some of them also have stabilizing effect.

Important information about behavior of energetic materials can be acquired by thermal methods and high-performance liquid chromatography.

Chemical stability is strongly influenced by storage conditions. After temperature, the most important atmospheric conditions for the stability of propellants is humidity. The measured heat flow increased with increasing relative humidity. In the past many studies were performed, to investigated the influence of oxygen, humidity etc. Less attention is paid to two other important aspects, namely the sample geometry and filling degree during the microcalorimetric test and high-performance liquid chromatography (HPLC). The fact that the decomposition of nitrocellulose is influenced by the amount of oxygen, the best way to investigate the stability of gun propellants is to measure it "ammunition like". This means a combination of the propellant grains and the filling degree of the vessel.

Serveillance of nitrocellulose based propellants is performed without paying much attention to the enviromental conditions of the stored propellants, except for the storage temperature. Effect of the other major aspect like relative humidity (RH), amount of oxygen and the particle size are quite often discussed in the literature, but not adopted for test procedures [2].

The RH will vary with location and time. The relative humidity may change from day to day in coastal areas or from season to season, making incorporation in a standard test procedure complicated. During decomposition of propellants, NO_x is released which reacts with water to nitric acid. Nitric acid accelerates decomposition reaction of NC propellants. In a serveillance procedure a sample preconditioning is not yet performed as a standard.

The effects of the oxygen content as well as the effects of grounding (cutting into appropriate size) to propellants stability will be discussed in this paper.

The methods used in this work, Heat Flow Calorimetry (HFC), High Performance Liquid Chromatography and Karl Fischer method. Test methods have been conducted on ten samples, single based (SB), single based with dinitrotoluene (DNT) and double based (DB) propellants.

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DOI: 10.5937/OTEH24045S

2. EXPERIMENTAL

In this paper experiments with different preparation, in way of different particle size has been conducted. Also, for testing oxygen influence on degradation process, propellants were grounded.

For some propellants moisture was determined using Karl – Fischer titration method.

For purposes of influence sample size and oxygen on test results, Heat Flow Calorimetry was used.

Karl Fisher titration is a method in analytical chemistry that determines trace amounts of water in a sample using volumetric or coulometric titration. Table 1 shows the moisture content of propellant samples.

Table 1. Moisture content in the tested samples

Sample name	Humidity (%)
SB1DNT	0,97
Ballistite	0,70
SB2	1,34
SB8	0,75
SB9	1,03

2.1. HFC test

Microcalorimetry can yield information about the stability of propellants and high explosives because the heat flow is a measure of the decomposition rate – function of decomposition rate. It is powerful tool for assessment stability problems.

All experiments are carried out according to procedure of STANAG 4582 at 90°C using Heat Flow Calorimeter, TAM IV TA Instruments [3].

Picture 1. Microcalorimeter TAM IV

Heat flow calorimetric method for establishing chemical stability of single base, double base and triple base (TB) propellants for a minimum of 10 years when stored at 25°C or to an equivalent degree.

Model of TAM IV presented on Picture 1, contains 24 channel-minicalorimeters that are managed like four multicalorimeters consists of six minicalorimeters.

There were used samples of propellants prepared in two ways:

1. Original size
2. Cutted into appropriate size and took fraction as near as possible between 1-2 mm.

Loading density was calculated for each propellant itself and it is showed in Table 2. usually it is between 0.8-1.1 gcm^{-3}.

Table 2. Experimental data and results obtained in microcalorimetry tests

Sample name	Loading density (gcm^{-3})	Max Heat Flow (μWg^{-1})	Length of original propellant grain (mm)	Diameter of original propellant (mm)
SB1DNT grounded	0.81	55.7	7.00±1.00	1.05±0.15
SB1DNT original	0.69	73.8		
SB2 grounded	0.84	133.6	3.35±0.15	1.95±0.10
SB2 original	0.90	148.4		
SB3 grounded	0.88	135.4	4.35±0.15	4.60±0.30
SB3 original	0.85	126.5		
SB4DNT grounded	0.71	60.2	11.00±1.00	3.40±0.20
SB4DNT original	0.86	40.4		
SB5DNT grounded	0.74	134.2	9.00±1.00	5.60±0.35
SB5DNT original	0.76	136.8		
SB6 grounded	0.70	61.5	12.05±0.55	2.00±0.10
SB6 original	0.56	51.6		
SB7 grounded	0.94	50.5	4.00±0.10	3.35±0.10
SB7 original	0.90	55.2		
SB8 grounded	0.83	58.5	4.20±0.20	3.35±0.10
SB8 original	0.92	41.5		
SB9 grounded	0.84	73.9	3.10±0.40	2.32±0.10
SB9 original	0.92	72.0		
Ballistite grounded	0.76	74.1	5.00±0.05	0.52±0.04
Ballistite original	0.77	73.7		

Note: Max Heat Flow Calorimetry-test at 90°C is 350μWg^{-1}

grounded sample grounded sample original sample original sample

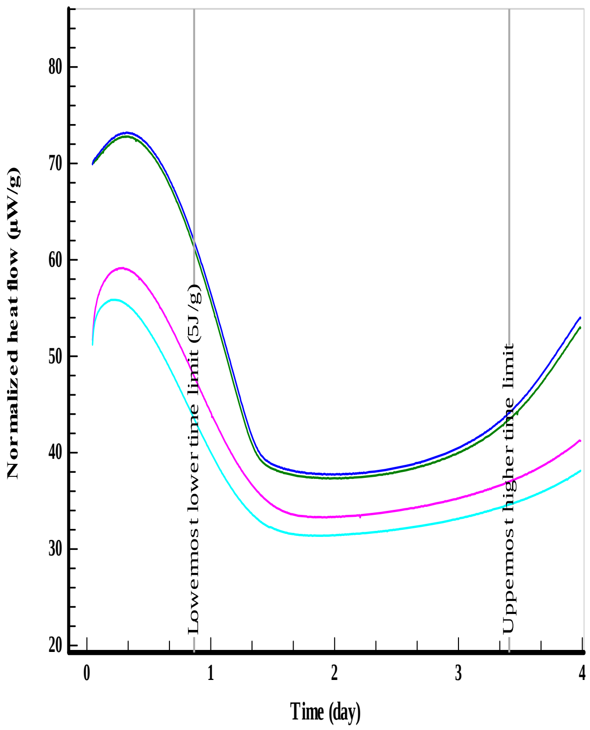

Figure 1. Heat flow against time for SB4DNT

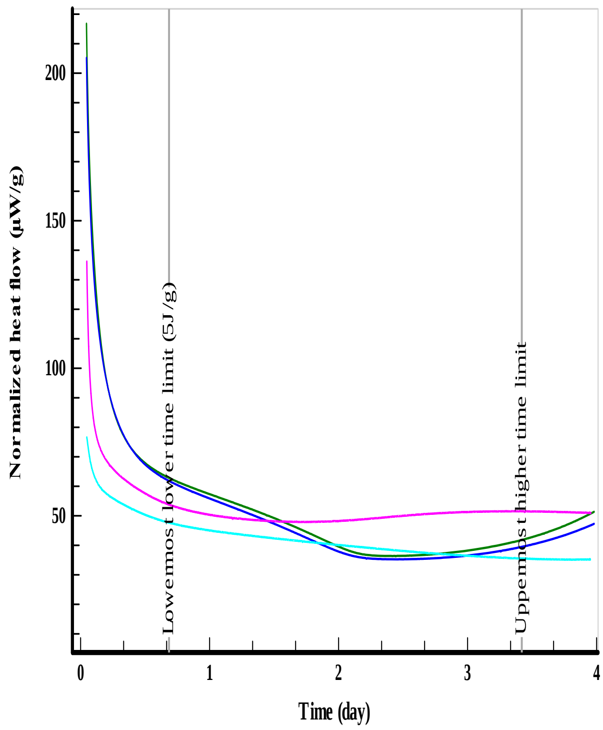

Figure 2. Heat flow against time for SB6

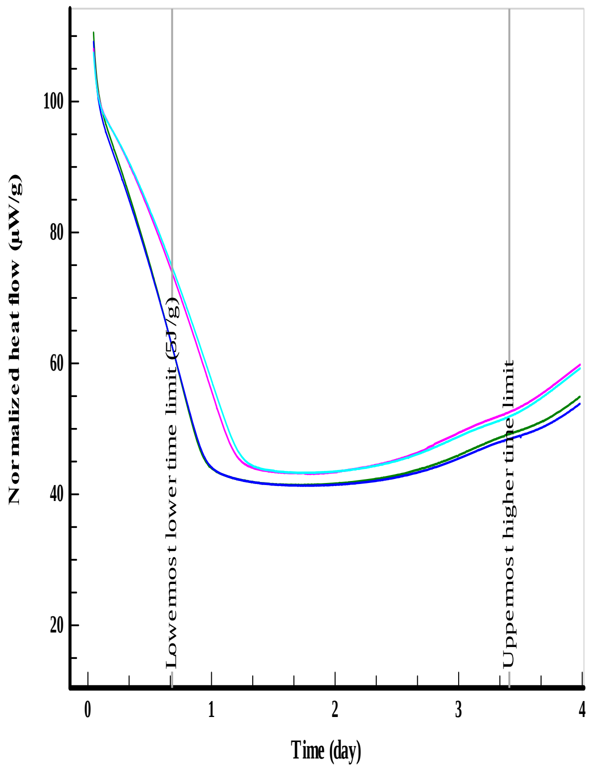

Figure 3. Heat flow against time for SB1DNT

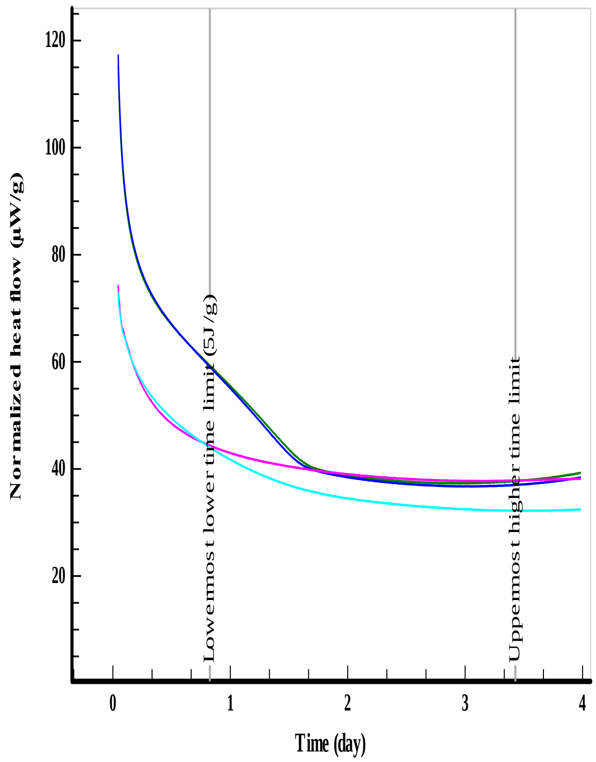

Figure 4. Heat flow against time for SB8

grounded sample grounded sample original sample original sample

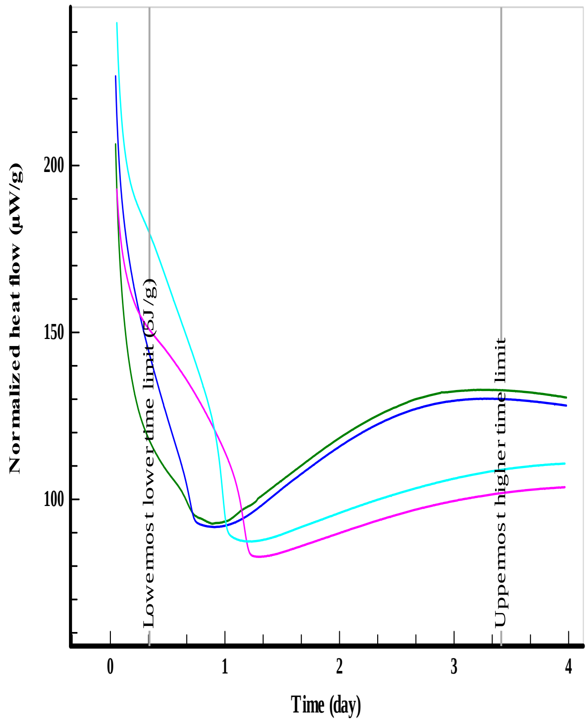

Figure 5. Heat flow against time for SB5DNT

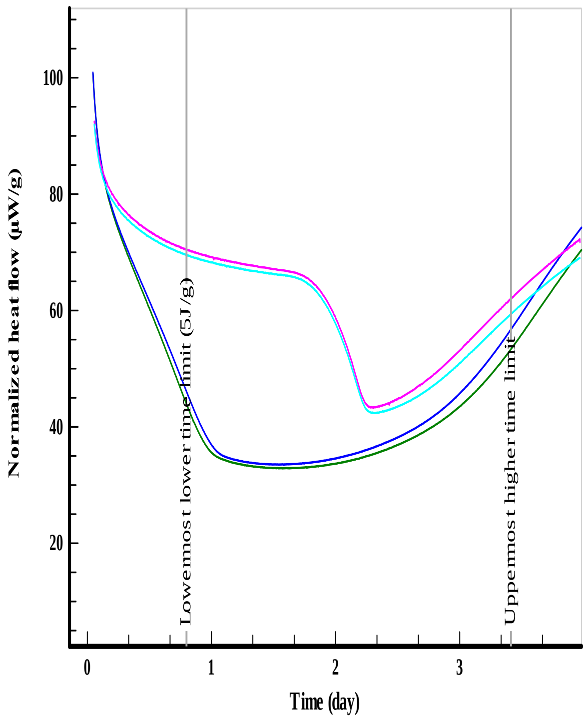

Figure 6. Heat flow against time for SB7

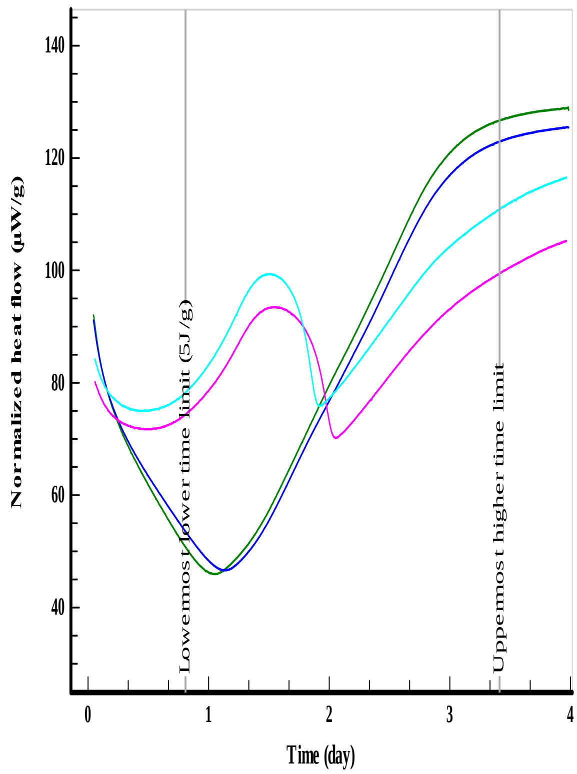

Figure 7. Heat flow against time for SB3

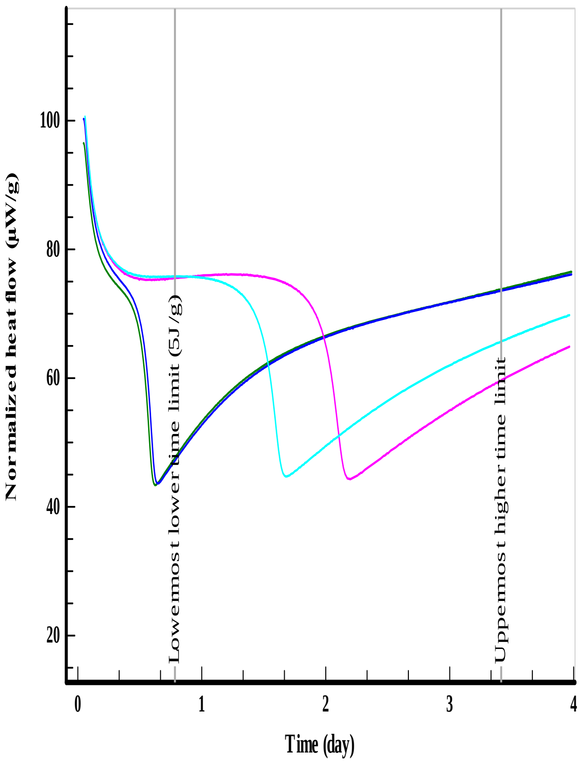

Figure 8. Heat flow against time for ballistite

2.2. Liquid chromatography tests

It has been used liquid chromatography for stabilizer content. Equipment was the Waters Alliance System 2695 with 2996 PDA detector.

High-performance liquid chromatography is analytical chemistry technique used to separate compounds in a chemical mixture. These separations utilize the pressure-driven flow of a mobile phase through a column packed with a stationary phase.

Propellant in original size or cutting in appropriate size were extracted in methylene chloride in a volumetric flask of 50 ml for 48 hours.

Sieves with 2 mm and 1 mm pore size and nylon membrane and syringe filters pores 0.20 µm were used. C18 column 150*4.6 mm with particle size of 3 µm were used and column temperature 35°C and flow rate 1,2 $mlmin^{-1}$ were conducted in a method. Eluent is mixture of solvents acetonitrile and water in appropriate ratio.

Table 3. HPLC results for gun propellants of different granulation

Sample name	4 nitro DPA	N-NO-DPA	DPA	2 nitro DPA	C1
SB1DNT grounded	0.03	0.17	1.07	0.08	
SB1DNT original	0.03	0.17	1.05	0.09	
SB2 grounded	0.04	0.19	0.94	0.06	
SB2 original	0.03	0.18	0.93	0.06	
SB3 grounded	0.03	0.40	0.56	0.05	
SB3 original	0.03	0.38	0.55	0.05	
SB4DNT grounded	0.02	0.07	1.20	0.06	
SB4DNT original	0.02	0.07	1.20	0.06	
SB5DNT grounded	0.05	0.32	0.39	0.09	
SB5DNT original	0.07	0.33	0.38	0.10	
SB6 grounded	0.03	0.15	1.23	0.05	
SB6 original	0.03	0.15	1.20	0.05	
SB7 grounded	0.03	0.21	0.76	0.05	
SB7 original	0.03	0.21	0.76	0.05	
SB8 grounded	0.09	0.34	1.38	0.09	
SB8 original	0.05	0.17	0.81	0.05	
SB9 grounded	0.17	0.33	0.30	0.17	
SB9 original	0.16	0.28	0.28	0.16	
Ballistite grounded					1.48
Ballistite original					1.48

Note:The results represents mean value of tree probes for each propellant sample.

3. DISCUSSION

Table 2 shows the results of the HFC test, the samples were cutted in the appropriate size and in their original form. The loading density is shown, which is calculated from the volume of the appropriate vessel for the HFC test and the mass of propellant, grounded or original. Results shows impact of propellant sample preparation to heat flow results.

3.1. Influence of particle size

The Figure 1,2,3 and 4 show the influence of particle size. Besides experiments with original propellant grains also experiments were carried out with ground sample of varying particle size. There were investigated single base propellants, single base with dinitrotoluene and ballistite propellants. During the experimental program in Figure 1,2,3,4 it was observed that from the propellants the heat generation was relatively high during the first days of the experiment. The initial heat effect of original propellant is lower than that of grounded propellants. An explanation for the resulting effects is that due the grounding operation more oxygen reacts with the surface of the propellants parts than with original propellant grains. It can be observed on Figure 1, single base propellant with DNT, with the loading density higher at original propellant has heat flow results lower and therefore it should be analysed in its original form. Figure 2 describes propellant with a long length, where the loading density is better when grounded, but the heat flow is greater due to the influence of oxygen, because of the opening of the grain itself. Figure 3 describes gunpowder with a small surface area, and during the preparation of gunpowder, oxygen does not have a large effect.

3.2. Influence of oxygen

Parameter that influence the chemical stability is oxygen. The presence of excess of oxygen is reported to increase the heat production of the propellant as NO can be oxidized to NO_2 which catalysis the decomposition of the propellant [4]. Indirectly the filling degree of the test vessel determines the amount of free oxygen. In case of a complete filled sample vessel, the amount of oxygen, available for the oxidation reaction is less, in correlation with amount of reaction surfaces. This will lead to decreased value of heat flow. In Figure 5,6,7,8 are shown single base propellants, single base propellants with DNT and ballistite propellant. It can be observed the results of the HFC test, where the heat flow of grounded propellant with half-filled container was measured. The presence of free oxygen affects the course of reactions mechanism during the experiments.

In Table 3 is showed the HPLC results for gun propellants of different granulation. There is no difference in the stabilizer content except for propellant SB8 (foreign production propellant) which, probably has a sort of membrane around a grain that does not allow the stabilizer to be extracted by the solvent.

4. CONCLUSION

In this paper it has been made conclusion, as follows:

- Whenever it is possible to obtain correct loading density of propellants in a testing vessel, either HFC or HPLC testing takes place, no preparation or grinding of samples should be carried out.
- The amount of available oxygen influence the reaction rate and as a results, the heat generation. Therefore, it is advisable to carry out the HFC tests as the propellant grains are originaly stored, so "ammunition like", if loading density is satisfied, meaning as high as possible to obtain 0.8 gcm^{-3} at least.

References

[1] E.o'N.ESPINOZA AND J.I.THORNTON, Characterization of smokeless gunpowders by means of diphenylamine stabilizer and its nitrated derivates, Analytica Chimica Acta, 288(1994) 57-69.

[2] WIM P.C.de KLERK, JOS M. MUL, MARCO N.BOERS, Reasearchgroup, TNO Prins Laboratory: How critical the sample geometry could be in propellant research, TNO Prins Maurits Laboratory, Rijswijk, Netherlands. R.B.BARENDREGT: Thermal investigation of unstable substances, including different thermal analytical techniques.

[3] STANAG 4582 (EDITION 1) EXPLOSIVES, NITROCELLULOSE BASED PROPELLANTS, STABILITY TEST PROCEDURE AND REQUIREMENTS HFC, NATO, Military Agency for Standardization, Brussels, 2004.

[4] E. CAMERA, G. MODENA, B. ZOTTI, Propellants, Explosives, Pyrotechnics, 8, 70, 1983.