

## Comparative Analysis of Volumetric and Instrumental Method for Determination of Nitroglycerin Content in Gunpowder

Magdalena Rakić <sup>1)</sup>  
Mirjana Krstović <sup>1)</sup>  
Slavko Mijatov <sup>1)</sup>  
Mirjana Dimić <sup>1)</sup>  
Bojana Fidanovski <sup>1)</sup>

The major energy components of double-based gunpowder are nitrocellulose (NC) and nitroglycerin (NG). In double-based gunpowder NG is used as a plasticizer and, at the same time, as an energetic component. Since the amount of NG in the gunpowder strongly influences and affects its chemical and mechanical properties or/and characteristics, the study of NG content is of great importance. The aim of this paper is to compare the analytical performances of high-performance liquid chromatography (HPLC) and classic analytical volumetric method for the separation and qualitative determination of nitroglycerine in smokeless gunpowder.

**Key words:** double-base gunpowder, nitroglycerine, Soxhlet extraction, high performance liquid chromatography, volumetric method.

### Introduction

SMOKELESS gunpowders are propellants commonly found in ammunition. Single (SB), double (DB), and triple-base (TB) gunpowders contain nitrocellulose (NC), with nitrogen content above 12 wt.%, as a major energy component in propellant formulation. Double-base gunpowders contain a mixture of NC and nitroglycerin (NG). Triple-base powders, typically limited to military ordinance, contain NC, NG, and nitroguanidine [1], [2]. In addition to the presence of NG as a primary propellant, NG may also be added as an additive to enhance the properties of the ammunition of double or triple-base powders only. Propellants may also contain additives, such as stabilizers (up to 5 wt.%), lubricants and plasticizers, as well as chemical constituents to control burn rate and suppress muzzle flash. The presence of trace components may be the result of the manufacturing process [3], [4].

However, gun powders and propellants based on nitrate ester polymers are intrinsically unstable due to the low activation energy ( $155 \text{ kJ mol}^{-1}$ ) of the O-NO<sub>2</sub> (nitrate ester) group. Accordingly, these groups undergo slow decomposition even under ambient conditions, causing the mechanical, chemical [5] and ballistic properties [6] of the gun powders to deteriorate over time. The decomposition reactions cannot be prevented, but the addition of an organic compound, containing secondary amines, such as diphenylamine (DPA), 2-nitrophenylamine (2-NDPA) or urea derivatives (e.g. ethyl or methyl centralyte), absorbs the nitrogen oxides that are the main products released during the decomposition of the nitrate esters, thus delaying autocatalytic degradation and preserving the base components in the original composition [7], which is why they are called stabilizers [8].

Nitroglycerin (Fig.1) is an energetic compound that has been used for many years by the military industry, mostly as a part of double-base gunpowder and propellant formulations. In this context, NG, which is liquid at the room temperature (melting point, 13.2°C) and has a water solubility of  $1.5 \text{ g L}^{-1}$  at 20°C [9], is embedded within a non-water-soluble nitrocellulose matrix. The resulting material is solid at the room temperature and is manufactured in different shapes depending on the type of ammunition for which it is used [10]. In gunpowder compositions, NG acts as a plasticizer and energetic component at the same time.

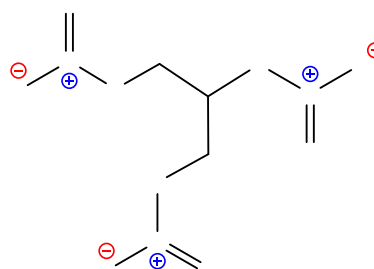


Figure 1. Chemical structure of NG molecule

The manufacture of double-base powders requires the addition of nitroglycerine to the nitrocellulose. Two methods can be used. One method uses organic solvents, the other uses water. The organic solvent method mixes nitrocellulose and nitroglycerine with solvents and any desired additives to form a doughy mixture. The mixture is then pressed into blocks that can be fed into the extrusion press and cutting machine, so NG is physically entrapped into fibrous NC. The resulting granules are screened prior to solvent removal and the

<sup>1)</sup> Military Technical Institute (VTI), Ratka Resanovića 1, 11132 Belgrade, SERBIA  
Correspondence to: Magdalena Rakić, e-mail: [magdalenaracic@gmail.com](mailto:magdalenaracic@gmail.com)

application of various coatings. The powder is dried, screened again, then blended to achieve homogeneity.

Some studies [11] have shown that chemical and mechanical properties of DB gunpowders significantly change with ageing and can be crucial for their safe service time. Namely, in the course of time, a number of chemical and physical processes (including migration and evaporation of NG) take place in gunpowder grains. Since the amount of NG in the gunpowder strongly influences its chemical and mechanical properties, study of NG content is of great importance. Recent studies have shown that the analytical techniques used for the separation and determination of the main organic components of gunpowders include thin-layer chromatography (TLC), gas chromatography-mass spectrometry (GC-MS), high-performance liquid chromatography (HPLC), Fourier transform infrared spectrometry (FTIR) and capillary electrophoresis (CE) [12]. GC has been applied to the separation and identification of different constituents in smokeless powders but thermal decomposition of NG limits the method's sensitivity and precision. The high GC temperatures have also been shown to cause denitrosation of nitrosodiphenylamines, and consequently DPA and nitrated diphenylamine may be detected instead [13]. EC and HPLC are alternatives to GC that have been shown very useful in characterizing smokeless powders [12].

The purpose of investigation in this study was to find a method with a total time for analysis of about 8 hours using a technique that could be highly automated. Also, the aim of the present study was to compare the analytical performances of high-performance liquid chromatography (HPLC) and classic analytical volumetric method for the separation and qualitative determination of a selected group of nitroglycerine in smokeless gunpowders.

## Materials and methods

Two different types of single base gunpowders (NGB), as well as four different types of double base gunpowders (NGR) were examined. All samples were examined according to the classical volumetric method and instrumental HPLC method.

### Preparation of samples

Dimension and mass of the samples for volumetric and instrumental methods were performed by the further technique. Double base gunpowders with dimension of 2.0 mm or less were used as well as it is in their original shape. Larger samples were milled into small pieces and sifted through sieves of dimension 2.0 mm and 0.84 mm. Samples left on the 0.84 mm sieve were taken for testing. For volumetric method the mass of samples was 2.000 g and for instrumental method the mass of 1.000 g was measured.

### Chemical preparation for volumetric method

After dimensional preparation, the samples were measured and placed in a cellulose fiber for the Soxhlet extraction process. The classical apparatus for extraction by Soxhlet, Fig.2 (a), consists of: 1. Allin glass condenser, 2. classical extractor by the Soxhlet with cellulose fiber in it and 3. distillation flask.

Soxhlet extraction process can be divided in four phases of the extraction cycle, Figure 2 (b). The first one was consisted of filling the flask with solvent. Distillation flask, whose mass was measured, was filled with approximately  $\frac{3}{4}$  of volume with diethylene ether. After assembling the Soxhlet apparatus, the heating was performed in the heating bath. The second

phase required the temperature settings of the heating bath, which implied that temperature should be set so that condensate drips 2-3 drops per second. The third phase represented completion of the extraction process. Namely, extraction is finished when approximately  $\frac{1}{3}$  of volume of solvent from the flask was predestined into the extractor, in Fig.2 a) position 2. The extraction process took at least 48 hours. The last phase was consisted of drying the distillation flasks into the vacuum desiccator above the sulfuric acid or heating at the 45 °C to the constant mass of the samples.

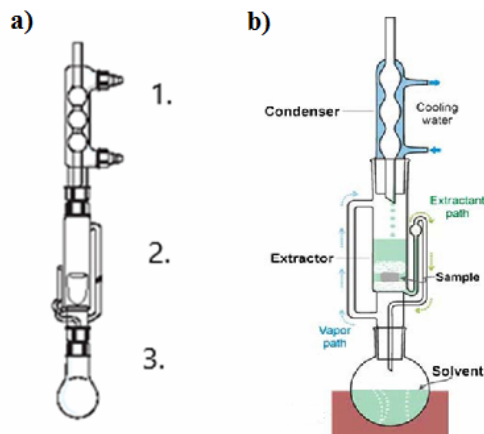


Figure 2. Soxhlet apparatus for extraction (a); the cycle of extraction process (b)

From weight grain of the distillation flasks, the percentage of the ether extract was calculated according to the following equation (1):

$$\% \text{ ether extract} = \frac{a * 100}{m} * \frac{100}{100 - p} \quad (1)$$

Parameters in this equation are:

*A* - the rest of samples in the distillation flasks after the extraction process, g

*M* - mass of double base gunpowder sample, g

*P* - the volatile matter content, mass.%.

### Chemical preparation for instrumental HPLC method

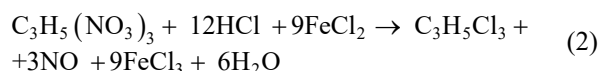
After grinding and sieving of the gunpowder samples, a chemical preparation process follows. This preparation involved simple extraction process which allowed selectively removing a compound from the gunpowder samples by a proper solvent. Test samples was placed in a flask and an organic solvent – methanol was added. The first part, which lasted approximately 4 hours, started by using magnetic stirrer. After that, the second part, which also lasted for 4 hours, involved switching the flask from magnetic stirrer to the ultrasound. Finally, the examined solution, which is used in HPLC method, was obtained by separation from the precipitate using a centrifuge.

### Determination of nitroglycerin (NG) from gunpowder using volumetric method

After the chemical preparation, the ether extract was dissolved in methanol and 25 cm<sup>3</sup> of this solution was transferred into the flasks for titration. Also, next to it, 25 cm<sup>3</sup> of ferrous chloride solution (FeCl<sub>2</sub> x 4H<sub>2</sub>O) and 12 cm<sup>3</sup> of solution of HCl:H<sub>2</sub>O (1:1) was added, too. The flask was connected with condenser and placed on a heating plate. Solution was heating to the boiling temperature and left on that temperature for five minutes. The complete examination was carried out under carbon dioxide atmosphere (for elimination the air from the system), with the flow rate of 15 mL min<sup>-1</sup>.

During the heating time, the color of the solution was changed from dark green to reddish-brown color. This color shift presents the end of the reduction process for nitroglycerin. The flask with condenser was placed in cold water bath. After cooling down the solution to the room temperature, the condenser was removed and 5 cm<sup>3</sup> of ammonium thiocyanate solution was added. The titration goes with 0.2 M titanium (III) chloride, also under carbon dioxide atmosphere, until the solution changed color from red to light orange.

A blank test with 25 cm<sup>3</sup> of methanol was performed in the same way. Namely, NG with ferrous chloride solution was reduced, reaction (2) and (3). The concentration of the nitroglycerine was calculated using the resulting ferric chloride which was titrated with titanium (III) chloride.



According to the volumetric method, concentration of the nitroglycerine was calculated using the following equation (4):

$$\%NG = \frac{(v_2 - v_1) * F * 0.005047 * 250 * 100}{25 * m} * \frac{100}{100 - p} \quad (4)$$

$V_1$  - the volume of TiCl<sub>3</sub> used for blank test, (cm<sup>3</sup>);  
 $V_2$  - the volume of TiCl<sub>3</sub> used for gunpowder, (cm<sup>3</sup>);  
 $F$  - the concentration of the solution of TiCl<sub>3</sub>;  
 $M$  - mass of the gunpowder (g);  
 $P$  - moisture content, (mas. %).

*Determination of nitroglycerin (NG) from gunpowder using instrumental HPLC method*

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 for these experiments, Fig.3.



**Figure 3.** High Performance Liquid Chromatograph

*Calibration:* Before starting the examination with the gunpowder samples that were chemical treated, HPLC instrument should be calibrated first. The calibration was done with nitroglycerin solution. The selection of the solvent for this preparation was made on the base of the solvent which was used for the extraction of the test samples. The concentration of the calibration solution corresponded to the mass of the test samples and, at the same time, it should

satisfy the range of concentrations in the examined samples.

*Chromatographic conditions:* detector PDA (220 nm), column C18 (length 150 mm, ID 4.6 mm and particle size 3µm), column temperature (not above 35°C ± 0.5°C and the mobile phase, acetonitrile: water (67:33 v/v). The HPLC system has the possibility of application in the analytical mode (with a flow rate of the mobile phase in the range between 0 mL min<sup>-1</sup> and 10 mL min<sup>-1</sup>). The flow rate for this examination was 1.2 mL min<sup>-1</sup>. The volume of the injection sample solution was 10 µL [14].

## Results and discussion

The results of determination of the NG mass concentration of the gunpowder by volumetric and instrumental method, are shown in Table 1. The results of the six different types of the gunpowder, using both methods are presented in Table 1 [15]. Four measurements of each sample were done.

**Table 1.** Results of the mass concentration of nitroglycerin (mas. % NG) from the gunpowder by volumetric and instrumental method

| No | Samples of gunpowder | mas %NG by volumetric method | mas %NG by instrumental method |
|----|----------------------|------------------------------|--------------------------------|
| 1. | NGB 051              | 40.05                        | 39.92                          |
|    | NGB 051              | 39.05                        | 39.97                          |
|    | NGB 051              | 40.67                        | 40.00                          |
|    | NGB 051              | 40.59                        | 40.00                          |
| 2. | NGB 221              | 40.08                        | 39.97                          |
|    | NGB 221              | 39.80                        | 39.95                          |
|    | NGB 221              | 39.85                        | 40.00                          |
|    | NGB 221              | 40.17                        | 40.00                          |
| 3. | NGR 195              | 27.22                        | 27.08                          |
|    | NGR 195              | 26.81                        | 27.10                          |
|    | NGR 195              | 26.50                        | 27.00                          |
|    | NGR 195              | 27.18                        | 27.10                          |
| 4. | NGR 255              | 25.17                        | 25.20                          |
|    | NGR 255              | 25.60                        | 25.15                          |
|    | NGR 255              | 25.07                        | 25.20                          |
|    | NGR 255              | 25.10                        | 25.20                          |
| 5. | NGR 135              | 25.91                        | 26.20                          |
|    | NGR 135              | 26.07                        | 26.15                          |
|    | NGR 135              | 25.81                        | 26.20                          |
|    | NGR 135              | 26.10                        | 26.20                          |
| 6. | NGR 275              | 29.87                        | 30.05                          |
|    | NGR 275              | 30.25                        | 30.10                          |
|    | NGR 275              | 30.15                        | 30.07                          |
|    | NGR 275              | 29.90                        | 30.10                          |

All presented results of mas. % NG, for both volumetric and the HPLC method, are satisfactory and are within the expected limits.

On the other hand, analyzing the results obtained by volumetric method the difference in the value of mas. % NG, in the same tested NGB or/and NGR samples, were indicated. The disagreement in values was in the range from 0.10 to 0.75 mas. % of nitroglycerin. Therefore, this difference represented a problem. Two main problems, which are closely interrelated with oxidation-reduction reaction, can be identified. Namely, during the extraction process using the Soxhlet extraction the reduction reaction begins. Thus, this process must have a precise and well-defined temperature set, which allows condensate drips of 2-3 drops per second, and it requires the executor to have an extensive experience. In support of this, the executor necessarily needed to notice when approximately 1/3 of volume of solvent from the flask was predestined into the extractor, and in that moment stopped the extraction process. If the extraction process is not stopped, an error occurs in the results. But nevertheless, the evaporation of diethyl ether during heating in the extractor process, as well as

the lag of the extract on the wall of the distillation flask can also lead to an error in the results. The sum of such errors in the results is further increased within the titration reaction with titanium (III) chloride. Namely, the reduction reaction is considered as a completely finished reaction at the moment of the appearance of the first color change of the test solution. If the executor does not have an extensive experience, the volume of titanium (III) chloride used for gunpowder titration will be increased and automatically leads to a decrease in the value of mas. % of nitroglycerin, equation (2). In addition, there will be miscalculation in the results of the same sample.

In contrast to the results from the volumetric method, the results obtained from the instrumental HPLC method gives a good agreement in value of mas. % NG in the same tested NGB or/and NGR samples. Precisely, disagreement in values, observing the same tested samples, was in the range from 0.02 to 0.10 mas. % of NG. This deviation is within the limits, and can also be classified as a statistical error of the instrumental HPLC method measurements. Besides, the calculation of mas.% NG was performed over the peak area on the chromatograph by automatic data process [15], which was set within the calibration and which also minimizes the possible mistakes. However, this is not particularly surprising given the fact that the precise instrumental method provides more reliable and reproductive results than the classical method. Also, according to the presented results, Table 1, it can be noticed that the results obtained for the same samples by HPLC method have high accuracy and reproducibility, compared with the results from the same sample using the volumetric method.

### Conclusion

This paper presents comparative results for two different methods, classical and instrumental method, for determining of nitroglycerin in gunpowders.

Despite the fact that all presented results of mas. % NG using both methods within the expected limits, the differences in the results for the same tested samples are noticeable.

Particularly, a discrepancy between the results for the same sample by volumetric method was between 0.10 to 0.75 mas. % NG compared to the value of 0.02 - 0.1 mas.% NG for the results obtained from the instrumental method. The deviations in the results, between the two observed methods, are due to different chemical sample preparation.

Namely, chemical preparation for classical method is consisted of extraction process and titration process. This actually means that there are two consecutive processes in which it is possible for an error to occur. In order for the extraction process performed in the Soxhlet apparatus with diethylene ether to run continuously and correctly, it is crucial to set an adequate temperature condition. Secondly, observing the titration process, which is based on oxidation-reduction reaction, which proceeded until the complete reduction, it is necessary to monitor the first color change of the solution. Therefore, in order to avoid an error in the final results, it is fundamental to have an executor with a huge experience in both of these classical methods.

On the other hand, chemical preparation for the instrumental method is also based on the extraction process. This process takes about 8 hours and it is based on the methanol extraction using magnetic stirrer and ultrasound. However, the chemical preparation for instrumental method takes less time than the chemical preparation for the classical method, which minimizes the error and allows getting the final result faster. It should also be emphasized that the

chemical preparation for the instrumental method takes less mass of the sample than the mass which is needed to be used for the chemical preparation for the classical method. In addition, for the HPLC method, a small amount of samples still gave a complete agreement between the results of the same tested samples, beside an excellent reproductivity of the results, compared to the classical method.

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## Uporedna analiza volumetrijske i instrumentalne metode za određivanje sadržaja nitroglicerina u barutu

Glavne energetske komponente dvobaznih baruta su nitroceluloza (NC) i nitroglicerina (NG). Nitroglicerina se u dvobaznim barutima koristi i kao plastifikator ali i kao energetska komponenta. Budući da količina prisutnog NG u dvobaznom barutu utiče na mehaničke ali i hemijske karakteristike, izučavanje količine NG je od velikog značaja. Cilj ovog rada je da se izvrši uporedna analiza razdvajanja i kvantitativnog određivanja NG u okviru ispitivanih dvobaznih baruta metodama: tačne hromatografije visokih performansi (HPLC) i klasične analitičke volumetrijske metode.

*Ključne reči:* dvobazni barut, nitroglicerina, Sokslet ekstrakcija, tačna hromatografija visokih performansi, volumetrijska metoda.