10th INTERNATIONAL SCIENTIFIC CONFERENCE
ON DEFENSIVE TECHNOLOGIES
OTEH 2022
Belgrade, Serbia, 13 – 14 October 2022

CLASSICAL AND INSTRUMENTAL METHODS FOR DETERMINATION OF RESIDUAL SOLVENT IN NITROCELLULOSE GUNPOWDER

MAGDALENA RAKIĆ
Military Technical Institute, Belgrade, magdalenarakic@gmail.com

MIRJANA KRSTOVIĆ
Military Technical Institute, Belgrade, mbkrstovic@gmail.com

MIRJANA DIMIĆ
Military Technical Institute, Belgrade, mirjanadimicjevtic@gmail.com

BOJANA FIDANOVSKI
Military Technical Institute, Belgrade, b.fidanovski@gmail.com

Abstract: *The production of nitrocellulose gunpowder includes as indispensable two solvents: ethanol and diethyl ether. Both solvents, in very high concentration, are present during the production. One of the lasts steps, in standard procedure, is removing the solvents from the system. This operation enables keeping and protecting ballistic performances and stability of gunpowder. However, some of the solvents remains in the gunpowder and the amount of residual solvents must be monitored. Previous technique included only classical method for determination of residual solvents. As a result, the total quantities of residual solvents were obtained. The aim of the presented paper is to develop a new approach to individual residual solvents determination, separately, by instrumental method – gas chromatography method.*

Key words: *nitrocellulose gunpowder, moisture content, residual solvents, classical method, instrumental - gas chromatography method.*

1. INTRODUCTION

Chemical stability of the ammunition which commonly contain nitrocellulose gunpowder is one of the most concerned property of such composition [1]. During the production of nitrocellulose gunpowder, a large quantity of organic solvents (ethanol – EtOH and diethyl ether – Et_2O) are used [2]. High concentration of both solvents (added into system as a mixture - 2:1 of diethyl ether and ethanol, respectively) must be present in process for better gunpowder mass shaping [3, 4]. Furthermore, concentration of 25 % of ethanol in gunpowder has effect on lower friction and impact sensitivity of pure nitrocellulose which providing safe handling in gunpowder production [5].

However, it is well known that, ethanol and diethyl ether are extremely flammable liquids of sweet-smell and high volatility [6]. Therefore, during the manufacturing process of nitrocellulose gunpowder, solvents vapor comes in contact with air making a gas mixture. That gas mixture is highly explosive and could cause a detonation effect with nitrocellulose gunpowder, which indicates the safety and compliance with the production procedure must be at an extremely high level [5].

Near last phases of gunpowder production, the gunpowder mixture has approximately 15-20 % of solvents [4]. This huge percentage of solvents directly affects gunpowder ballistic stability control. Namely, precise and acceptable calculation of solvent percentages should be done before the manufacturing process starts. In the classical approach, maximum solvent concentration should be among the 0.7 to 1.3 %, which would neutralize the potential unwanted gelatinization process and enable safe ammunition storage [7]. So, the crucial step during production, is removing solvents from the gunpowder mixture. Two different operations, which are defined by the gunpowder manufacturing procedure, are involved during the residual solvent elimination process [8]. In practice, the safety of gunpowder is evaluated during the quality-control process i.e. by experimental measurements. As a result, only acceptable safety can guarantee their application.

In addition to measure residual solvents, determination of moisture content is also very important examination from the aspect of preserving ballistic performance. Namely, if the moisture content decreases over time, there will be an increase in the initial gunpowder combustion rate, and also an increase in the maximum pressure of the gunpowder gases. On the other hand, if moisture content increases over time, the gunpowder ignition will be difficult, initial speed will be in decrease and eventually the range of the projectile will be reduced.

This paper presents a new approach of investigations of classical chemical and instrumental method, especially, instrumental method – chromatography. Although, the classical chemical method is mainly and only involved in experimental measurement of residual solvents, the

growing tendency in the world, is to employ modern instrumental methods for monitoring the content of residual solvents.

2. MATERIALS AND METHODS

Two different types of nitrocellulose gunpowder (NC-16 and NC-161), sampled from the different lots (label as *a*, *b*, *c* for NC-16 and *p*, *q*, *r* for NC-161) were examined. All samples were examined according to the classical gravimetric method and instrumental GC (Gas Chromatography) method.

2.1. Classical method - gravimetric method

Samples preparation

Dimension of samples for classical method were performed by further technique. All nitrocellulose gunpowder grains with dimension of 2.0 mm or less were used as they were, i.e. in their original shape. Larger samples were milled into smaller pieces.

Experimental procedure for measurement of the moisture content in nitrocellulose gunpowder

Firstly, clean and dry measurement vessel with lid was measured. Samples with the mass of 5.000 g whose dimensional preparation has been completed, were placed in it. After drying (two hours at the temperature of 80 °C) and cooling the samples, experimental measurement of moisture content was calculated, according to the following equation (1):

$$moisture\ \ content = \frac{a}{m} * 100\% \qquad (1)$$

a – difference in sample mass before and after drying, g and

m – mass of the examined sample of nitrocellulose gunpowder, g.

Experimental procedure for measurement of the volatility substances in nitrocellulose gunpowder

Firstly, clean and dry measurement vessel with lid was measured. Samples with the mass of 10.000 g whose dimensional preparation has been completed, were placed in it. After drying (five hours at the temperature of 100 °C) and cooling the samples, volatile substances content was determined according the to the following equation (2):

$$volatility\ \ substances = \frac{a}{m} * 100\% \qquad (2)$$

After determination of volatilite substances content, the value of residual solvents can be calculated according to the equation (3):

$$residual\ \ solvents = VS - MC \qquad (3)$$

VS – calculated result of volatility substances, equation (2), mas.% and

MC – calculated result of moisture content, equation (1), mas.%.

2.2. Instrumental method – Chromatography

Samples preparation

For instrumental method dimensional preparation of nitrocellulose sample, i.e. chopping or grinding, is not allowed. So, all nitrocellulose gunpowder was used as it is.

Experimental procedure for measurement of the residual solvents in nitrocellulose gunpowder

First step in identification of residual solvents from the examined samples was distillation process. Therefore, it was necessary to prepare heating bath, the distillation flask, Liebig condenser and Erlenmeyer flask, and connect the distillation apparatus. Nitrocellulose gunpowder samples with the mass of 5.000 g with approximately 80 cm^3 of 15 % of solution of natrium hydroxide were placed into distillation flask. The distilled water was poured into Erlenmeyer flask. The heating was performed in heating bath and the distillation process can started. After two hours of heating or until volume of 100 cm^3 of distillate was separated, distillation process should be in progress.

Second step was the identification process by gas chromatography method. Namely, this instrumental method is based on recognition of compounds using the same pure compounds which are in the examined samples. This step depends on comparation of the chromatography peak from the standard and chromatography peak from the samples. The calculation of each compound concentration, follows next equations (4) and (5):

$$\%EtOH = \frac{P_{EtOH}}{m_{uz} * P_{us}} * \frac{P_{us} * m_{EtOH}}{P_{EtOH}} \qquad (4)$$

$$\%Et_2O = \frac{P_{Et_2O}}{m_{uz} * P_{us}} * \frac{P_{us} * m_{Et_2O}}{P_{Et_2O}} \qquad (5)$$

The gas chromatograph equipped with thermostat for column heating, manual injector and "TCD" detector was used.

Chromatographic conditions: detector (TCD, heated at 220 °C and with reference flow of 20 mL min^{-1}), column HP-PLOT Q, oven (heating on 110 °C) and the hydrogen gas as mobile phase. The GC system has the total flow rate of 39 mL min^{-1} and the pressure of 2.45 psi. The volume of the injection sample solution was 1 µL [9, 10].

Calibration: The calibration was done with ethanol and diethyl ether solution. 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 [9, 10].

3. RESULTS AND DISCUSSION

In order to preserve and protect ballistic performance in the nitrocellulose gunpowder for both types of examined

samples, humidity was tested by gravimetric method. According to the equations (1), (2) and (3), results were obtained and shown in the Table 1 and 2. Besides, results of residual solvents collected using the classical method were also shown in the same Tables. For every examined lot, the values of three measurements are given as mean values obtained from three measurements.

Table 1. Results of the mass concentration of moisture content and residual solvent for NC-16 by gravimetric method

Nitrocellulose gunpowder samples	Classical method - gravimetric method	
	moisture content	residual solvents
NC-16, *a*	1.00	0.49
NC-16, *a*	0.99	0.56
NC-16, *a*	1.01	0.59
NC-16, *b*	0.82	0.68
NC-16, *b*	0.75	0.53
NC-16, *b*	0.94	0.52
NC-16, *c*	0.84	0.53
NC-16, *c*	0.76	0.48
NC-16, *c*	0.88	0.51

Table 2. Results of the mass concentration of moisture content and residual solvent for NC-161 by gravimetric method

Nitrocellulose gunpowder samples	Classical method - gravimetric method	
	moisture content	residual solvents
NC-161, p	0.93	0.63
NC-161, p	0.86	0.53
NC-161, p	0.80	0.59
NC-161, q	1.03	0.46
NC-161, q	0.87	0.39
NC-161, q	1.03	0.55
NC-161, r	0.82	0.43
NC-161, r	0.75	0.58
NC-161, r	0.67	0.54

A precisely defined range for amount of moisture minimizes the potential risk of initiation of unwonted gelatinization process. Nitrocellulose gunpowder NC-16, sampled from the different lots label with *a*, *b*, *c* shown in Table 1, gave satisfactory concentration of moisture content. The results of moisture content for NC-161, sampled from the lots label: *p*, *q*, *r* (Table 2.); were slight lower than results of NC-16 samples, but they are also in the range. Considering that the moisture content test was very sensitive, due to the large influence of humidity from the atmosphere. Minor deviations within the 3 measurements in both samples for all examined lots were expected. Although, NC-16 and NC-161 nitrocellulose gunpowder have approximately similar composition, the possibly explanation for difference between the results could lie in residual solvents.

On the other hand, obtained values for residual solvents, by gravimetric method, were in the range for both tested samples, Table 1 and 2. Acceptable agreement between 3 measurements in every lots indicated good homogeneity of the samples.

Since two different types of solvents remained in the nitrocellulose gunpowder, in addition to the standard gravimetric method, an instrumental method was employed for monitoring the content of residual solvents. Namely, the base of our research was checking the residual solvent using chromatography. The gas chromatography was chosen as an instrument method which could identify and give the precise value of each solvents separately. In order to recognize and identify each solvent in NC samples the special preparation of the calibration solution, as well as described distillation process, should be done.

The average values of the residual solvents, which were calculated using equations (4) and (5), were shown in Table 3 and 4. The average value presented the value of three measurements, as mean values obtained from three measurements.

Table 3. Results of average value of concentration of each residual solvents separately, ethanol (EtOH) and diethyl ether (Et_2O), from NC-16 by instrumental method

Nitrocellulose gunpowder samples	Instrumental method – gas chromatography	
	EtOH	Et_2O
NC-16, *a*	0.49	1.40
NC-16, *b*	1.08	1.61
NC-16, *c*	0.93	2.19

Observing independently the results of each solvent, in all three lots, disagreement between measurements appeared probably due to differences in batch production. Particularly, batch production involves small batches which are always checked by quality control. If the results are inconsistent, it can be fixed without big losses compared to the mass production [11]. In this case lot with label *a*, needs to be changed or modified depending on requirements and needs of examined nitrocellulose gunpowder, or should be use in less percentages in final mixture of end product.

On the other hand, comparing the results from NC-16 sample, Table 1, the values of the residual solvents obtained by gravimetric method were much lower than the total amount of average value of residual solvents obtained by GC method, Table 3.

According to the results it is obvious that gravimetric method gives an information only for residual ethanol. Namely, procedures for measurement the residual solvents required drying on the temperature of 100 °C, by classical method. Knowing the fact that boiling temperature of ethanol is 78.4 °C [6, 12] and for diethyl ether is 346.0 °C [6, 12], obviously, more ethanol was released than diethyl ether, by first method. Besides, GC method used oven and detector, TCD which was heated at 220 °C, so the diethyl ether, as a second solvent can be relisted, identified and calculated with minimal error.

The instrumental method was also used for obtaining the results for NC-161, for all three lots, Table 4.

Table 4. Results of average value of each residual solvent separately, ethanol (EtOH) and diethyl ether (Et_2O) from NC-161 by instrumental method

Nitrocellulose gunpowder samples	Instrumental method – gas chromatography	
	EtOH	Et_2O
NC-161, *p*	1.02	1.32
NC-161, *q*	1.11	1.25
NC-161, *r*	1.08	1.35

The results of residual solvents for NC-161 sample, by obtained by GC method, shown better mutual agreement than the results for NC-16 presented in Table 3. That implicated more appropriated batch production, i.e. easier joining of lots for final product placement.

Although the sums of these values are, again, higher than the results obtained by classical method, the same conclusion can be made. Despite the preparation process – distillation, allowed collecting of all released gasses which evaporated in a closed system, the chromatography method enables better agreement between the results from the aspects of collecting and giving much more precise individual values for each residual solvent, than the classical method.

4. CONCLUSION

Two different type of methods, classical and instrumental method, were in used for determination the residual solvents from the nitrocellulose gunpowder NC-16 and NC-161 (analyzing the tree different lots for each NC samples, separately).

The moisture contents were determined using the classical method as a standard method for measured the water contend in the laboratory. The obtained results of moisture content in gunpowder were based on classical – gravimetric method which leads to the qualitative monitoring of released humidity by heating gunpowder on the precise temperature and time. The collected results for both NC samples for all lots are in the range, which minimized the potential risk of the degelatinization process and satisfied the conditions of safety. This information is important from the aspect of safety and application of gunpowder in ammunition.

The residual solvents were, firstly, analyzed by classical method. The obtained results presented the difference between moisture content and volatile substance. Although this approach satisfied the standard of quality-control for manufacturing the nitrocellulose gunpowder, it does not provide the precise value for each solvent.

On the other hand, inclusion of an instrumental method – gas chromatography method, in determination the exact concentration of individual solvent can be of great importance. Preparation process for instrumental method was consisted of distillation process, which enabled the collection of all released gasses that evaporated in a closed system. The GC method was depending on recognition of compounds using the same pure compounds which are in the examined samples. After comparation of the chromatography peak for the standard and chromatography peak from the samples, calculation of concentration of the ethanol and diethyl ether gave their precise results. This separated concentration of ethanol and diethyl ether can be of great influence for the removing process during manufacturing and can facilitate calculations for the batch production. Our results are encouraging and should be validated by a larger sample size.

ACKNOWLEDGEMENT

This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia, Contract No. 451-03-68/2022-14/200325

References

[1] Gang Lia, Chaoyang Zhan, Review of the molecular and crystal correlations on sensitivities of energetic materials, Journal of Hazardous Materials, 398, (122910), (2020), , 1-15

[2] RAKIĆ M.: Classical methods of chemical stability - comparison of analyses for gunpowder, Scientific technical review, *,Vol.71, (1), (2021), 25-29*

[3] Zhanhong.You, Chapter -Gunpowder, Thirty great investigation of China, (2020), 647-662

[4] Bob Ashford, A new interpretation of the historical data on the gunpowder industry in devon and cornwall, Baltimor, J. Trevithick soc. 43, (2016), 65-73

[5] E.P.Boltrukevich, G.S. Ratanov, Experimental determination of the mean particle size of the condensed phase in the combustion products of gunpowder, Combustion explosion and shock waves, 15, (2), (1979), 284-286

[6] VOLLHARDT K.P.C, SCHORE N.E.: *Organska hemija,struktura i funkcija*, IV izdanje, Data status, Beograd, (2004).

[7] Petar Maksimovic, Tehnologija eksplozivnih materija, Beograd, (1972).

[8] Gawera Habyesali, Design of a production line for nitrocellulose-based gunpowder, thesis, Makerere University, (2018).

[9] Jelisavac Lj., Hemijska stabilnost i vek upotrebe baruta I raketnih goriva (Chemical stability and lifetime of the propellants), KumNTI, Vojnotehnički institut, Belgrade, Vol. LXIII, No.2, (2009).

[10] Geoffery A. Dorsey, Detection of volatile components in solids and thin films by gas chromatography of evolved gases, Anal. Chem. 41, (2), (1969), 350-352

[11] Marek Wirkus, Alicja Kukulika, Issues of Measuring the Course of Batch Production Processes, Procedia engineering, 182, (2017), 387-395

[12] Robert Neilson Boyd and Robert Thornton Morrison, Organic Chemistry, Prentice Hall; 6th edition, (1992).