



Determination of Nitroglycerine Content in Double Base Propellants by Isothermal Thermogravimetry

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Abstract: Thermal methods play an important role among various measuring techniques used in the analysis of explosive materials. These methods are mostly used for the investigation and determination of thermal properties of energetic materials (e.g. melting process, polymorphic transformations, temperature of initiation, etc.), as well as to estimate thermal stability, and to study thermal decomposition.

Furthermore, thermal methods can be also used for analytical purposes, such as identification of some commonly used high explosives, determination of their purity, determination of phlegmatiser content, etc.

The aim of this work was to study the possibility of application of isothermal and non-isothermal thermogravimetry for determination of nitroglycerine content in double based propellants.

It has been found out that thermogravimetry can be used not only to distinguish clearly between nitrocellulose and double based propellants, but also for rough determination of nitroglycerine content in double based propellants.

The difference between an actual and experimentally determined content of nitroglycerine in double based propellants (i.e. accuracy of the method) is dependent on composition of propellant and data treatment method.

Keywords: thermal methods, thermogravimetry, identification, homogeneous propellants, double based propellants, nitroglycerine content

Introduction

Thermal analysis is defined as a group of methods by which the physical

or chemical property of a sample is measured as a function of temperature or time, while the sample is subjected to a controlled temperature program [1]. The program may involve either heating or cooling (dynamic), or holding the temperature constant (isothermal), or any sequence of these. Thermal methods are multi-component techniques and include thermogravimetry (TGA), differential scanning calorimetry (DSC), dynamic mechanical analysis (DMA), and thermomechanical analysis (TMA). These methods find widespread use in both quality control and research applications on industrial products such as polymers, fine organic chemicals and pharmaceuticals, metals and alloys – generally in the field of characterization and investigation of materials.

Thermal methods play an important role among various measuring techniques used in the analysis of explosives materials. These methods are mostly used for the investigation and determination of the thermal properties of energetic materials [2-6], as well as to estimate thermal stability [7-9], and to study thermal decomposition [10-13].

Thermal methods can be used for detecting the presence of an energetic material in a sample of unknown material [14-15]. Furthermore, they can identify the specific type of energetic materials by comparing the measured thermograms for the unknown sample to reference thermograms from reference library. From the shapes of thermograms, characteristic points (e.g. melting temperature, temperature of decomposition, heat of reaction, etc.) it is possible to identify specific energetic materials or specific type of energetic materials. It is important to note that the comparison of thermograms should only be made when their measurements are run under the same conditions (such as mass of the sample, heating rate, atmosphere surrounding the sample, etc.).

Generally for the chemical analysis of explosive materials, besides the classical methods, the following instrumental methods can be used: gas chromatography (GC), thin layer chromatography (TLC), high performance liquid chromatography (HPLC), UV spectrophotometry, atomic absorption spectrophotometry (AAS), etc. [16]. HPLC methods are most frequently used since they are rapid and are performed with high precision.

Besides the above methods, thermal methods can also be used for the analytical purposes [17-20], such as identification of some commonly used high explosives, determination of their purity, determination of phlegmatizer content, etc.

In this work we have studied the possibility to apply thermogravimetry (TGA) for the identification of the homogeneous propellants type, as well as for the determination of nitroglycerine content in the double based propellants.

Experiments

The study was carried out on nitrocellulose (NC) and double based (DB) propellants having different composition (Table 1). The measurements were carried out using differential scanning calorimetry (TA Instruments DSC, Model 2910) and thermogravimetry (SDT, Model 2960).

Table 1. Composition of studied propellants

| | NC1 | NC2 | NC3 | DB4 | DB5 | DB6 | DB7 |
|--------------|----------------------|--------------------------------|--------------------------------|--|---|---|--|
| Composition: | NC-98.5% DPA-1.5% | NC-97% DPA-2% +Additives | NC-97% DPA-2% +Additives | NC-80% NGL-17% DNT-0.9% EC-2% +Additives | NC-56% NGL-26.7% DNT-8.5% EC3% +Additives | NC-57% NGL-28% DNT-11% EC-3% +Additives | NC-51% NGL-41% DNT-2.5% EC-3% +Additives |

Legend: NC – nitrocellulose; NGL – nitroglycerine; DNT – dinitrotoluene; DPA – diphenylamine; EC – ethylcentralite.

The DSC measurements were carried out using samples weighing 4.0 ± 0.2 mg. The samples were tested in aluminium sample pans covered by perforated cap, with a heating rate of $5 \text{ }^\circ\text{C}/\text{min}$ and under nitrogen atmosphere with a flow rate of $100 \text{ ml}/\text{min}$.

Dynamic TGA measurements were carried out using samples weighing 1.0 ± 0.2 mg. The samples were tested in aluminium sample pans, with a heating rate of $2 \text{ }^\circ\text{C}/\text{min}$ and under nitrogen atmosphere with a flow rate of $50 \text{ ml}/\text{min}$.

Isothermal TGA measurements were carried out using approximately rectangular samples having thickness between 0.15 and 0.4 mm and weighing 4.0 ± 0.2 mg. The samples were tested in aluminium sample pans, in the temperature range from $100 \text{ }^\circ\text{C}$ to $140 \text{ }^\circ\text{C}$ and under nitrogen atmosphere with a flow rate of $50 \text{ ml}/\text{min}$.

Results and Discussion

Non-isothermal TGA results

The TGA curves of the tested propellants are presented in Figure 1. As is visible from Figure 1, the TGA curves differ and they are characteristic for particular type and composition of propellant.

For example, NC propellants have one-step mass loss (intensive mass loss starts at about $180 \text{ }^\circ\text{C}$), while DB propellants have two-step mass loss. The first step occurs in the temperature range from $80 \text{ }^\circ\text{C}$ to $150 \text{ }^\circ\text{C}$ and it is predominantly

connected with the evaporation of NGL. The second step occurs between 150 °C and 200 °C and it is connected with decomposition of NC. These two facts allow one to clearly identify type of homogeneous propellant, i.e. to distinguish between single base and double base propellants.

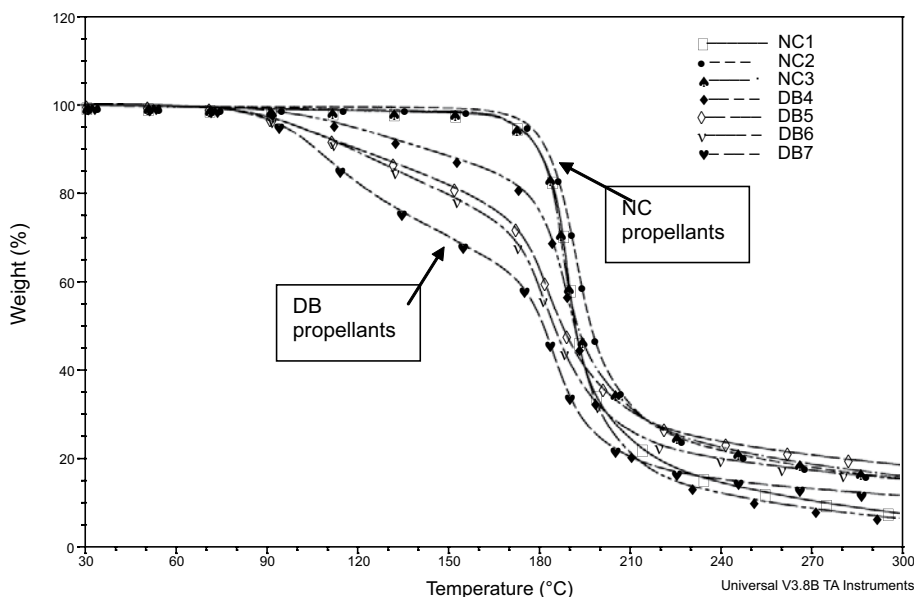
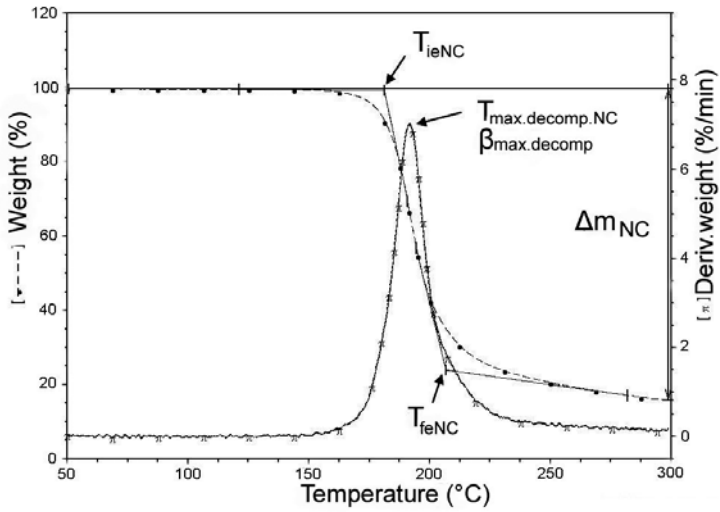


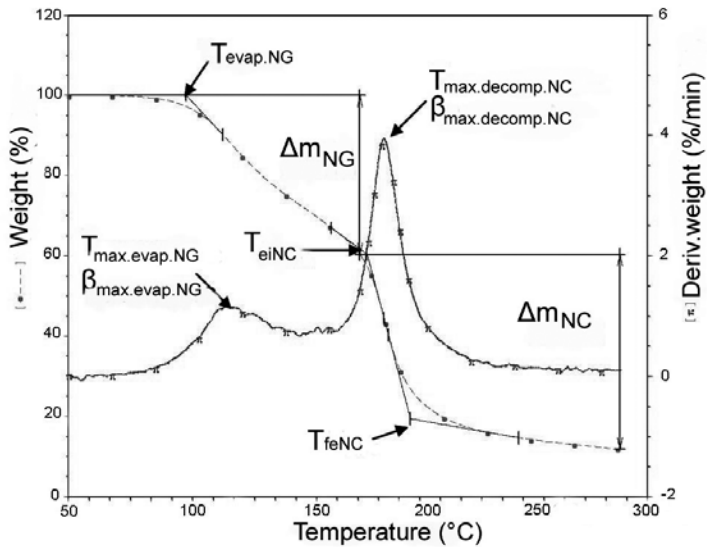
Figure 1. Non-isothermal TGA curves of homogeneous propellants having different composition.

It is important to note that the remaining mass of the samples at 300 °C can be nearly 20% of the initial sample mass (Figures 1, 2). This residue is a charcoal-type material containing mostly carbon.

As shown in our previous papers[15, 23], non-isothermal TGA measurements allow one not only to identify type of homogeneous propellant, but also to determine roughly the amount of NGL in DB propellant. Although the identification is possible simply on the basis of TGA curve shape, we used more reliable approach based on the “quantification” of TGA curves. TGA curves are quantified by determining values of several characteristic parameters/points on the curves, as shown in Figure 2.



a)



b)

Figure 2. Typical non-isothermal TGA and derivative TGA curves of nitrocellulose (a) and double based propellants (b).

Table 2. Values of characteristic parameters/points on non-isothermal TGA curves

| Characteristic points on TGA curves | Unit | NC1 | NC2 | NC3 | DB4 | DB5 | DB6 | DB7 |
|--|-------|-------|-------|-------|-------|-------|-------|-------|
| Extrapolated peak onset temperature of evaporation ($T_{\text{evap.NG}}$) | °C | | | | 99.08 | 78.95 | 84.82 | 87.94 |
| Extrapolated peak onset temperature of decomposition (T_{ieNC}) | °C | 182.3 | 181.6 | 180.9 | 180.7 | 171.6 | 171.3 | 175.8 |
| Extrapolated peak end-set temperature of decomposition (T_{feNC}) | °C | 197.9 | 204.8 | 198.6 | 203.9 | 201.9 | 200.9 | 198.5 |
| Mass loss due to NGL evaporation (Δm_{NG}) | % | | | | 18.40 | 23.02 | 26.57 | 39.58 |
| Maximum evaporation rate ($\beta_{\text{max.evap.}}$) | %/min | | | | 0.429 | 0.535 | 0.584 | 1.151 |
| Maximum decomposition rate ($\beta_{\text{max.decomp.}}$) | %/min | 12.03 | 7.907 | 10.53 | 6.796 | 3.852 | 4.191 | 4.380 |
| Temperature at maximum evaporation rate ($T_{\text{max.evap.}}$) | °C | | | | 124.2 | 100.9 | 110.0 | 106.8 |
| Temperature at maximum decomposition rate ($T_{\text{max.razg.}}$) | °C | 188.6 | 191.7 | 186.9 | 190.3 | 181.9 | 181.4 | 184.2 |

It is clear from the shape of TGA curves (Figures 1 and 2), as well as from the values of characteristic points on TGA curves (Table 2) that one may clearly distinguish between single based and double based propellants.

Furthermore, it follows from the comparison of the experimentally obtained sample mass loss due to NGL evaporation (i.e. in the temperature range ~80-150 °C) and the actual content of NGL in the tested propellants that the difference between them is less than 4% (Figure 3). This means that we can roughly determine content of NGL in a DB propellant from the experimentally obtained sample mass loss data.

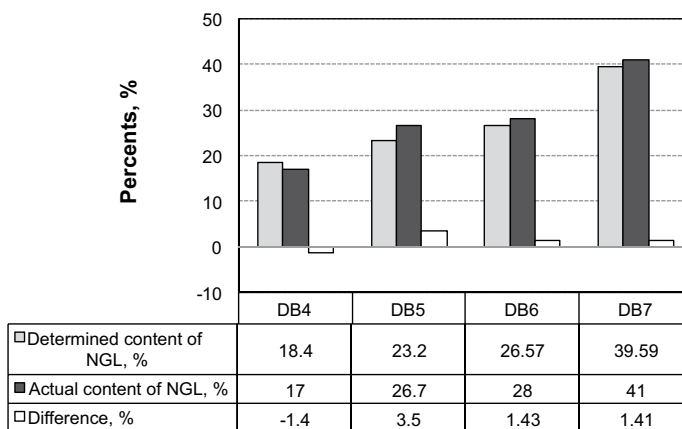


Figure 3. Comparison of experimentally determined and actual amount of NGL in tested DB propellants.

Determination NGL content in DB propellants by isothermal TGA

In order to determinate NGL content from isothermal TGA measurements, the first step was to find optimal experimental conditions, i.e. to find an isothermal temperature at which, within limited experimental time, an intensive mass loss of NGL will occur but decomposition of NC will be very small (or negligible). In other words, the goal was to find a temperature at which we can separate NGL evaporation from NC decomposition.

This task was done on the basis of a series of non-isothermal DSC measurements, and isothermal and non-isothermal TGA measurements on NC and DB propellants (Figures 4-6). From non-isothermal TGA curves (Figure 4) it is obvious that a measurable mass loss of NC propellant starts above 150 °C, while a measurable mass loss of DB propellant starts above 80 °C. At the same time, it is visible from non-isothermal DSC curves (Figure 5) that there is no any measurable exothermic process until approximately 140 °C for both DB and NC propellants. This means that the mass loss of DB propellants in the range 80-150 °C is due to NGL evaporation, while the mass loss of NC propellant above 180 °C is due to NC decomposition. In other words, we can separate NGL evaporation process from NC decomposition if we use temperature below 140 °C.

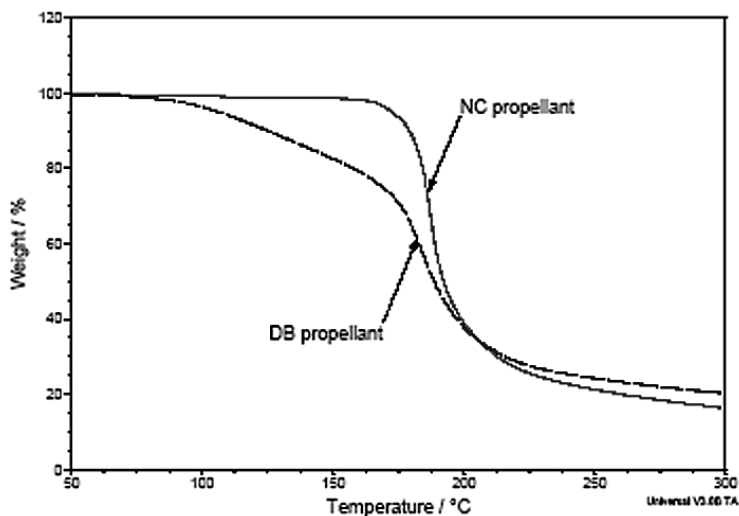


Figure 4. Non-isothermal TGA curves of NC and DB propellants.

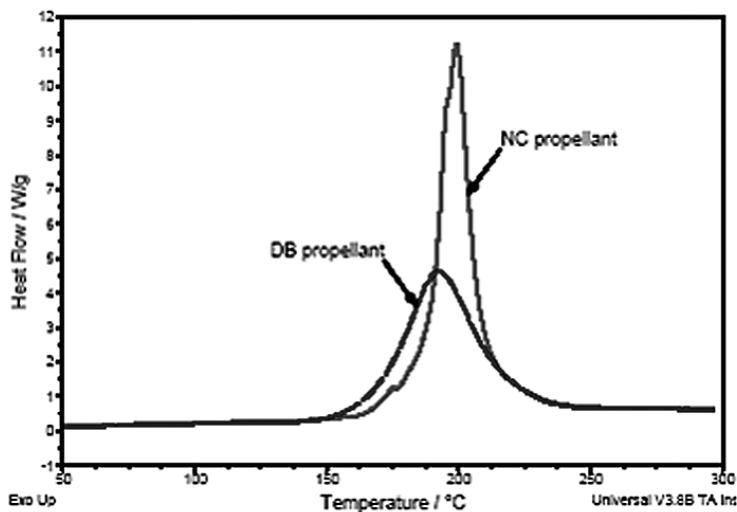


Figure 5. Typical DSC curves of NC and DB propellants.

Additional tests were done to find the temperature at which the mass loss due to NC decomposition is minimal but at the same time the mass loss due to NGL evaporation is considerably within limited experimental time period – in this case up to 1400 min.

From Figure 6, showing isothermal TGA curves of NC propellants at different temperatures, it is visible that the mass loss for temperatures below 120 °C is very small, less than ~2 % at 1400 min. It was found that 0.65% of that mass loss is due to residual solvent evaporation at the early beginning of heating, while the rest (about 1.3%) is probably due to DPA evaporation. At temperatures above 120 °C the mass loss is considerable. From these tests, the temperature of 110 °C was selected as optimal temperature to study NGL evaporation, i.e. to determine NGL content in DB propellants.

Isothermal TGA curves of the studied DB propellants, obtained at 110 °C temperature, are shown in Figure 7.

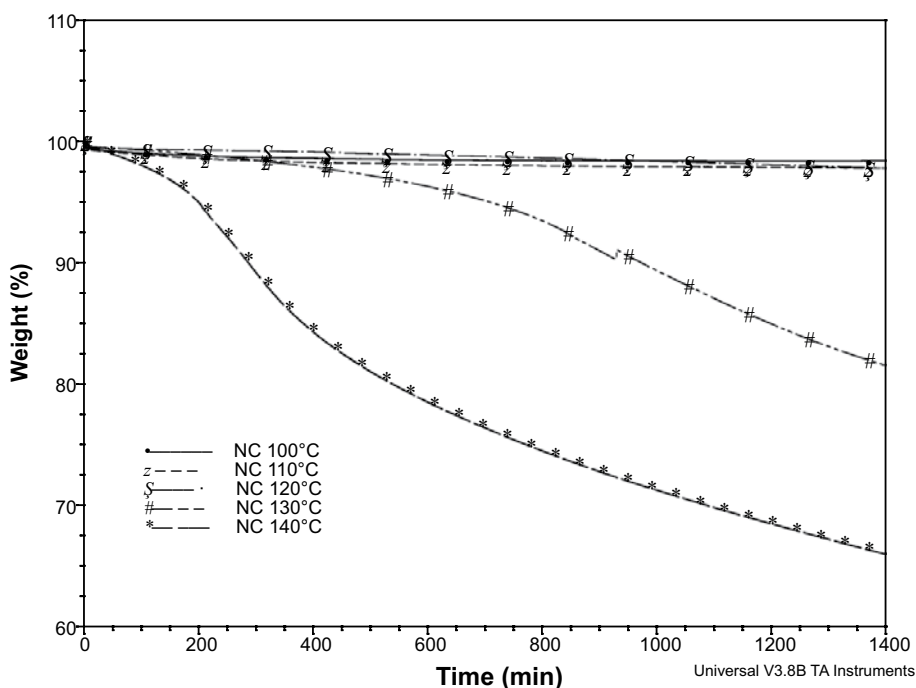


Figure 6. Isothermal TGA curves of NC propellants during isothermal heating at 100 °C, 110 °C, 120 °C, 130 °C and 140 °C.

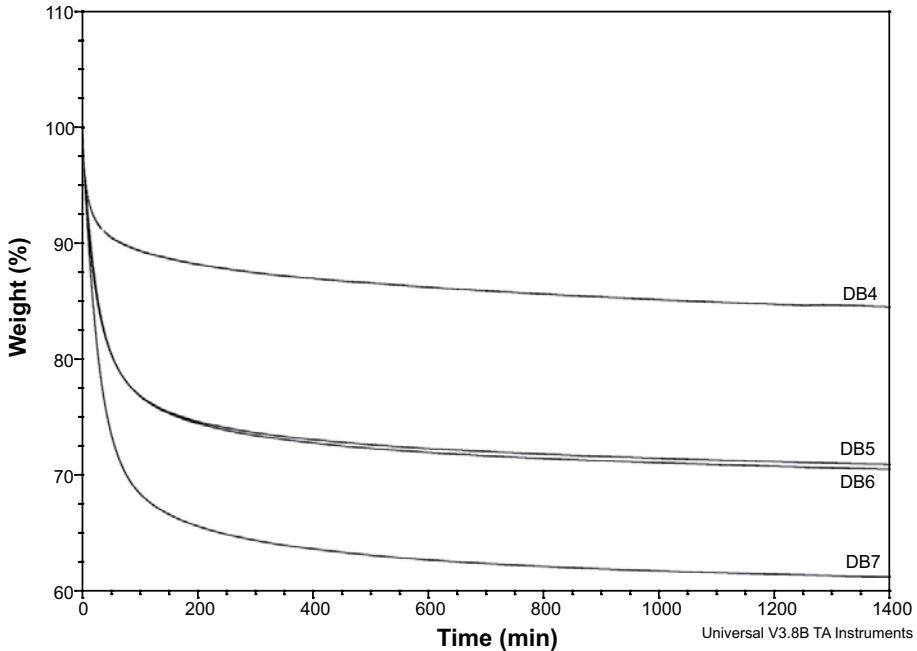


Figure 7. Isothermal TGA curves of tested DB propellants at 110 °C.

It is visible from Figure 7 that the mass loss rate is very high at the beginning of the heating, and almost constant after 600 min. The difference in mass loss at 600 min and 1400 min is less than 2.5%. That means that NGL evaporation process approaches to its completeness after 600 min.

Two approaches were applied for the determination of NGL content on the basis of data given in Figure 7. The first approach is based on the following assumptions: a) after 1400 minutes NGL is completely removed (evaporated), b) the mass loss due to NC decomposition is negligible, and c) the mass loss due to evaporation of any other compound present in a propellant is also negligible. This means that the sample mass loss after 1400 minutes is entirely due to NGL evaporation and it serves as a measure of NGL amount in the sample. The results obtained in this way are presented in Figure 8.

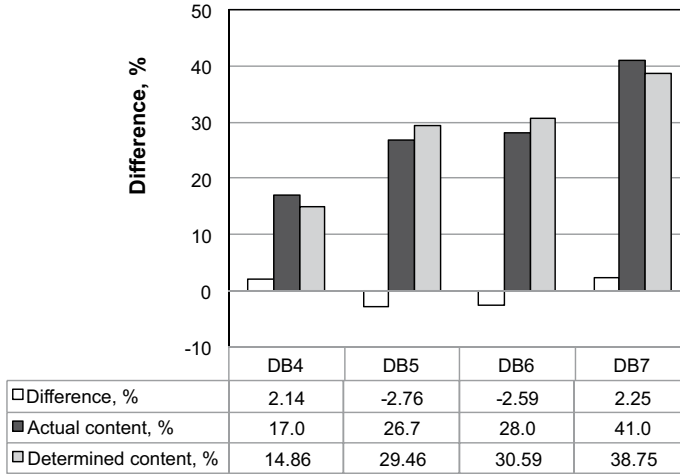


Figure 8. Comparison of actual and experimentally determined content of NGL in tested DB propellants.

It is obvious from Figure 8 that using this approach one can roughly determine NGL content in DB propellants of unknown compositions. The obtained difference between actual and experimentally determined content of NGL is less than 3%.

Another approach to determine content of NGL starts from the assumption that the mass loss of the tested DB propellant is the consequence of simultaneous evaporation of NGL and DNT (if present). Thus, neglecting evaporation or decomposition of any other propellant's components, one can write:

$$m_{DB} = m_{NGL} + m_{DNT}, \quad (1)$$

where m_{DB} is experimentally obtained mass loss, m_{NGL} is mass loss due to NGL evaporation, and m_{DNT} is mass loss due to DNT evaporation.

It is realistic also to suppose that NGL and DNT cannot completely evaporate during the studied time period of 1400 min. Introducing the parameter called "degree of evaporation", at a given heating time, as a ratio of experimentally obtained mass loss due to NGL and DNT evaporation and their actual contents in the DB propellant (w_{NGL} and w_{DNT} respectively):

$$k_{NGL} = \frac{m_{NGL}}{w_{NGL}}, \quad \text{and} \quad k_{DNT} = \frac{m_{DNT}}{w_{DNT}}, \quad (2)$$

where k_{NGL} is degree of evaporation of NGL and k_{DNT} is degree of evaporation of DNT, Eq. 1 can be rewritten in the following form:

$$m_{DB} = k_{NGL} \cdot w_{NGL} + k_{DNT} \cdot w_{DNT} \quad (3)$$

The degrees of evaporation (k_{NGL} and k_{DNT}) can be calculated from the experimentally obtained mass loss data if actual amounts of NGL and DNT in propellants are known. For example, applying Eq. 3 to the mass loss data at $t = 1400$ min, one can write the following equations:

$$\begin{aligned} \text{For DB4: } & 14.86 = k_{NGL} \times 17.0 + k_{DNT} \times 0.9 \\ \text{For DB5: } & 29.46 = k_{NGL} \times 26.7 + k_{DNT} \times 8.5 \\ \text{For DB6: } & 30.59 = k_{NGL} \times 28.0 + k_{DNT} \times 11.0 \\ \text{For DB7: } & 38.75 = k_{NGL} \times 41.0 + k_{DNT} \times 2.5 \end{aligned} \quad (4)$$

From the above equations the degrees of evaporations at $t = 1400$ min are calculated (as a mean values) to be: $k_{NGL}(1400 \text{ min}) = 0.89$ and $k_{DNT}(1400 \text{ min}) = 0.59$. This means that 89% of NGL evaporated in the time period of 1400 min, while in the same time period 59% of DNT evaporated.

The value $k_{NGL} = 0.89$ is in good agreement with the experimentally obtained value for DB4 propellant containing only 0.9% of DNT. Neglecting the presence of DNT in a DB propellant, the Eq. 3 reduces to:

$$m_{DB} = k_{NGL} \cdot w_{NGL} , \quad (5)$$

thus giving for DB4 propellant $k_{NGL}(1400 \text{ min}) = 14.86/17 = 0.87$.

It should be noted that the degrees of evaporation depend on the experimental conditions; first of all on sample shape and size.

Using this approach the degrees of evaporation were also calculated for 600 and 1000 min heating times. The values obtained are: $k_{NGL}(600 \text{ min}) = 0.85$ and $k_{DNT}(600 \text{ min}) = 0.52$, $k_{NGL}(1000 \text{ min}) = 0.88$ and $k_{DNT}(1000 \text{ min}) = 0.55$. Applying these values of the degrees of conversion, the mass losses are calculated for tested DB propellants applying Eq. 3 and using actual contents of NGL and DNT. The calculated results are compared to the experimentally determined mass losses of DB propellants (Figure 9).

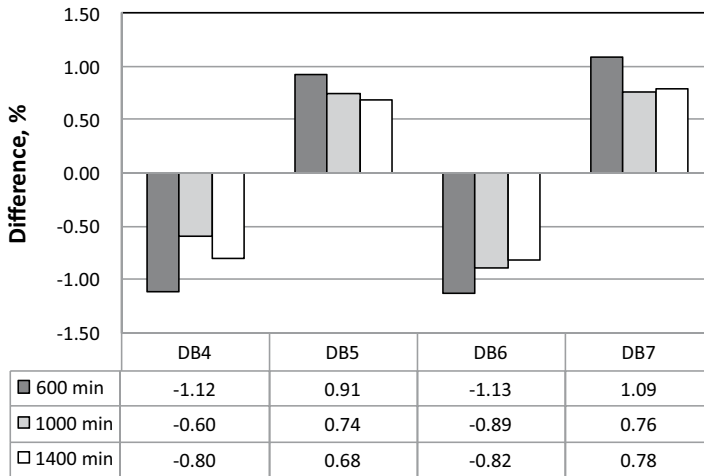


Figure 9. Difference between experimentally obtained mass loss of DB propellants and calculated mass loss using known values of k_{NGL} and k_{DNT} and actual content of NGL and DNT.

It is obvious that such an approach will give better accuracy, however, in order to apply it for determination of NGL content in DB propellants, it is necessary to know the content of DNT, as well as the degrees of evaporation of NGL and DNT for given experimental conditions.

However, if we assume that DNT is not present, i.e. that mass loss is completely due to NGL evaporation ($m_{DB} = k_{NGL} \times w_{NGL}$), then we can apply Eq. 5 to calculate the mass loss due to NGL evaporation using known value of k_{NGL} and actual content of NGL. Such calculations have shown that there is very good agreement between mass loss of DB propellants and calculated amount of NGL for the propellants not containing (or containing very small amount) of NGL (e.g. propellants DB4 and DB7). However, for the propellants containing considerable amount of DNT (e.g. DB5 and DB6), the difference will be much greater (Figure 10).

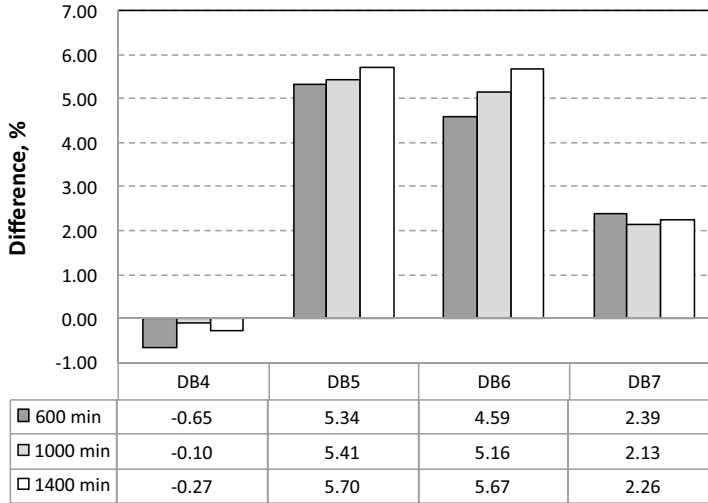


Figure 10. Difference between experimentally determined mass loss of DB propellants and calculated content of NGL using known value of k_{NGL} and neglecting presence of DNT.

This approach gives very good agreement for a propellant without DNT, but in the case of DNT presence the error increases proportionally to DNT content. It can be shown by simple analysis that the error is proportional to DNT content in the propellant. It follows from the experimental results that the ratio of the degrees of evaporation of DNT and NGL equals approximately 0.6 ($k_{DNT}/k_{NGL} \approx 0.6$). Taking this value and assuming that NGL has completely evaporated (i.e. $m_{NGL} = w_{NGL}$, which means that $k_{NGL} = 1$), the following equation can be derived from Eq. 3:

$$m_{DB} - m_{NGL} = 0.6 w_{DNT}. \quad (6)$$

Since we have supposed that $m_{DB} = m_{NGL} = w_{NGL}$, it follows that the difference between experimentally obtained mass loss and true content of NGL is equal to $(0.6 \cdot w_{DNT})$. For example, if a propellant contains 10% of DNT, the difference will be 6%. This agrees very well with the results given in Figure 10. For example, in the case of DB5 the difference is around $\sim 5.5\%$ (actual content of DNT is 8.5%), in the case of DB6 the difference is $\sim 5.5\%$ (actual content of DNT is 11%), and in the case of DB7 the difference is $\sim 2\%$ (actual content of DNT is 2.5%).

Conclusions

The results presented in this paper have shown that isothermal and non-isothermal thermogravimetry can be used for identification of the homogeneous type of propellants, as well as for rough quantitative determination of nitroglycerine content in DB propellants.

The results have shown that using either non-isothermal or isothermal thermogravimetry, nitroglycerine content in double based propellants can be roughly determined from the mass loss data. A simple approach based only on DB propellants sample mass data has shown that NGL content in DB propellants containing NGL and up to 10% of DNT, can be determined within less than 4% difference between the actual and experimentally determined content.

In the case of DNT-free DB propellants, and when taking into account an actual degree of evaporation of NGL at given experimental conditions, the amount of NGL can be determined within the difference of even less than 1%. However, this approach gives less accurate results for propellants containing considerable amount of DNT. The error will be proportional to the amount of DNT.

However, it should be mentioned that many parameters can affect mass loss of DB propellants (e.g. sample shape and size, properties of ingredients, experimental conditions, etc.). It was demonstrated in our previous paper [23] that it is highly recommended to use thin samples in order to completely remove NGL at a suitable experimental temperature and reasonably long experimental time, as well as to use the same experimental conditions.

The described method can be used to distinguish NC and DB propellants, as well as for the rough determination of the amount of NGL in DB propellants. However, the method described is not aimed to replace well established methods for the analysis of propellants (chromatographic methods: TLC, HPLC, GC; spectroscopic methods: IMS, AAS, UV etc.) [16, 21, 22], but to demonstrate a possible application of thermal methods for analytical purposes in the field of explosives.

References

- [1] Haines P.J., *Thermal Methods of Analysis – Principles, Application and Problems*, Blackie Academic & Professional, London **1995**.
- [2] Quintana J.R., Ciller J.A., Serna F.J., Thermal Behaviour of HMX/RDX Mixtures, *Propellants, Explos., Pyrotech.*, **1992**, 17, 106-109.
- [3] Zeman S., Thermogravimetric Analysis of Some Nitramines, Nitrosamines and

- Nitroesters, *Thermochim. Acta*, **1993**, *230*, 191-206.
- [4] Zeman S., Gazda Š., Štolceva A., Drab J., New Correlation of the Thermogravimetric Analysis Data of Some Commercial Explosives, *ibid.*, **1993**, *230*, 177-189.
- [5] Zeman S., The Thermoanalytical Study of Some Aminoderivatives of 1,3,5-Trinitrobenzene, *ibid.*, **1993**, *216*, 157-168.
- [6] Rajić M., Sućeska M., Influence of Ageing on Nitrocellulose Thermal Properties and Hazard Potential Figures-of-Merit, *High Temperature – High Pressure*, **2000**, *32*, 171-178.
- [7] Johnson D.C., Using Thermal Analysis for Pyrotechnic Reliability Predictions, *Proc. 22nd International Pyrotechnics Seminar*, Fort Collins, 15-19 July, IIT Research Institut, **1996**, 227-234.
- [8] Reddy G.Om, Srinvasa Rao A.S., Stability Study on Pentaerythritol Tetranitrate, *Propellants, Explos., Pyrotech.*, **1992**, *17*, 307-312.
- [9] *Standard Test Method for Assessing the Thermal Stability of Chemicals by Methods of Differential Thermal Analysis*, ASTM standard E, **1992**, 537-86.
- [10] Kishore K., Thermal Decomposition Studies on Hexahydro-1,3,5-Trinitro-S-Triazine (RDX) by Differential Scanning Calorimetry, *Propellants and Explos.*, **1977**, *2*, 78-81.
- [11] Hussain G., Rees G.W., Thermal Decomposition of RDX and Mixtures, *Fuel*, **1995**, *74*(2), 273-277.
- [12] Rajić M., Sućeska M., Kinetika Termičke Razgradnje Amonijevog Perklorata u Temperaturnom Području 240-250 °C, *Kem. Ind.*, **1998**, *47*(12), 437-441.
- [13] Stanković M., Kapor V., Petrović S., The Thermal Decomposition of Triple-Base Propellants, *J. Therm. Anal. Cal.*, **1999**, *56*, 1383-1388.
- [14] Bannister W.W., Chen C.C., Chen E.B., Curby W.A., Damour P.L., Morales A., *Thermal Analysis for Detection and Identification of Explosives and Other Controlled Substances*, United States Patent, US, **2004**.
- [15] Fiamengo I., Sućeska M., Matečić Mušanić S., Applicability of Thermal Methods for Identification of Homogeneous Propellants, *Proc. 11th seminar "New Trends in Research of Energetic Materials"*, Pardubice, Czech Republic, **2008**, 515-523.
- [16] Stanković M., Vujović B., Filipović M., Capillary Gas Chromatography of Double Based Propellants, *Chromatographia*, **1996**, *9*(42), 593-594.
- [17] Krien G., Thermoanalytical Determination of Tetrazene in Primer Mixtures, *Propellants, Explos., Pyrotech.*, **1979**, *4*, 53-5.
- [18] Sućeska M., Rajić M., Termoanalitičko Određivanje Trinitrotoluena u Smjesi s Heksogenom, *Kem. Ind.*, **1998**, *47*(1), 11-16.
- [19] Sućeska M., Rajić M., Čuljak M., Characterisation and Quantitative Determination of Trinitrotoluene in Mixtures with Hexogen by Differential Scanning Calorimetry, *Proc. 29th Int. Annual Conference of ICT*, Karlsruhe, Germany, **1998**, pp. 144/1-144/12.
- [20] Sućeska M., Rajić M., Analytical Application of Thermal Methods in the Field of Explosive Materials, *Proc. 4th Seminar "New Trends in Research of Energetic Materials"*, Pardubice, Czech Republic, **2001**, 290-302.

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- [21] Kohlbeck J.A., Determination of Nitroglycerin and Resorcinol in Double-base Propellant Following Separation by TLC, *Anal. Chem.*, **1965**, *37*, 1282-1283.
- [22] Colon Y., Ramos C.M., Rosario S.V., Castro M.E., Hernandez S. P., Mina N., Ion Mobility Spectrometry Determination of Smokeless Powders on Surfaces, *International Journal for Ion Mobility Spectrometry*, **2002**, *5*(3), 127-131.
- [23] Fiamengo I., Sućeska M., Matečić Mušanić S., Applicability of Thermal Methods for Determination of Nitroglycerine Content in Double Based Propellants, *Proc. 12th Seminar Pardubice "New Trends in Research of Energetic Materials"*, Czech Republic, **2009**, 526-534.

