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Identification and quantitative determination of poly(ethylene glycol) dimethacrylate deterrent in single-base gun propellants

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The identification and quantitative determination of poly(ethylene glycol) dimethacrylate deterrent in single-base gun propellant was carried out. Using different analytical methods, the presence of tri(ethylene glycol) dimethacrylate deterrent was determined, along with the content of its monomer and polymer components.

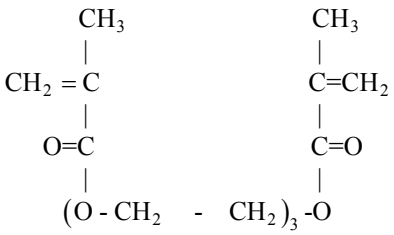
Key words: **explosive materials, single-base propellants, phlegmatizer, poly(ethylene glycol) dimethacrylate, tri(ethylene glycol) dimethacrylate, quantitative analysis.**

Introduction

ALONG with the existence of classical deterrents, there is a worldwide tendency towards using new kinds of deterrents [1,2,3,], especially unsaturated organic esters on the bases of poly(ethylene glycol) dimethacrylate. Propellants with poly(ethylene glycol) dimethacrylate deterrents have a constant gradient burning rate and good ballistic stability, due to only a slight migration of deterrent to interior of the propellant grain during storage.

Tri(ethylene glycol) dimethacrylate (tri-EGDMA) is the most widely used deterrent in the previously mentioned group of compounds. Molecular formula of tri-EGDMA is $C_{14}O_6H_{22}$ and its molecular weight is $M(C_{14}O_6H_{22}) = 286.3\,\text{g/mol}$.

Structural formula of tri-EGDMA is:



In order to identify and qualitatively determine poly(ethylene glycol) dimethacrylate deterrent presence in single-base gun propellant, different analytical methods have been used: nuclear magnetic resonance (NMR) spectroscopy, infrared (IR) spectrophotometry, thin layer chromatography (TLC), gas chromatography (GC), reversed phase high performance liquid chromatography (RP HPLC) and Soxlet extraction.

Experimental and discussion of results

The propellant sample was ground to the approximate size of 2 × 2 × 2 mm. After 48 hours of extraction in dichloromethane, the following analyses were performed:

Qualitative analysis of propellant dichloromethane extract

1. Identification of deterrent using NMR spectroscopy

Identification of deterrent in single-base gun propellant could not be done using NMR spectroscopy and IR spectrophotometry, but it was assumed that the deterrent was a compound, from homologous series of poly(ethylene) glycoldimethacrylate [4].

Further more, NMR spectroscopy was used for analyzing of standard compounds of poly(ethylene) glycoldimethacrylate homologous series, in order to identify the deterrent exactly [4]. Analyses were performed on Gemini-200, NMR spectrophotometer.

Dichloromethane was evaporated from propellant sample extract. Residual sample and standard compounds of poly (ethylene) glycol dimethacrylate homologous series were dissolved in chloroform in preparation for the analysis. Internal standard was tetra methyl silicone, Si (CH3)4.

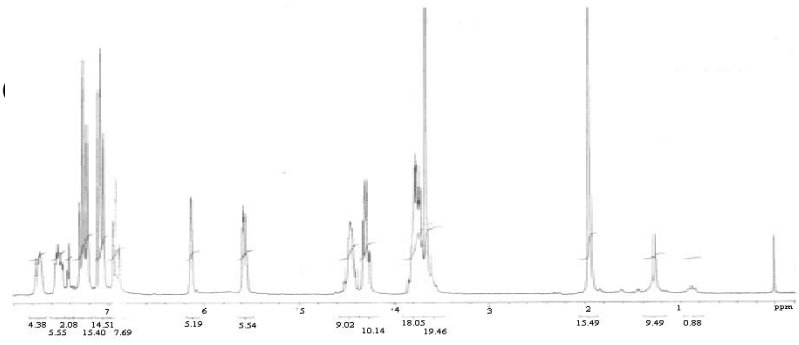


Figure 1. NMR spectrum of propellant sample

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Operating temperature was ambient.

Analyses of the NMR spectrums were performed. Relation intensity of deterrent peaks in propellant sample (Fig.1.) were compared to relation intensity of standard compounds of poly(ethylene glycol) dimethacrylate homologous series peaks [4]. Tri(ethylene glycol) dimethacrylate was identified as a propellant deterrent (Fig.2.).

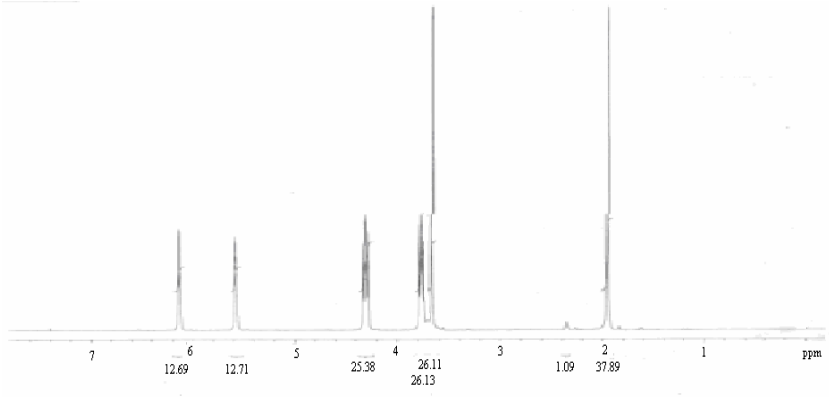

Figure 2. NMR spectrum of tri(ethylene-glycol) dimethacrylate standard

2. Identification of tri(ethylene glycol) dimethacrylate using IR spectrophotometry and GC

Aiming at identifying the tri-EGDMA by IR spectrophotometry, the prior separation of tri-EGDMA from the stabilizer diphenylamine (DPA) and its derivatives was performed by TLC method.

The sample of propellant dichloromethane extract was put on aluminium TLC plate, size of which was 20 × 20 cm, with the Silica gel 60 adsorbent and thickness of layer 0.2 mm (DC-Alufolien Kieselgel 60). The mixture of solvents, chloroform: n-hexane, in relation of 10:1, was used as a developer.

Successfully separation of dichloromethane extract components was performed successfully on TLC plate. After this, separated zones along with silica gel were isolated from the TLC plate.

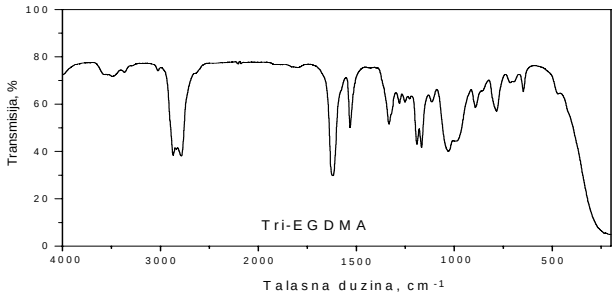

Figure 3. IR- spectrum of tri-EGDMA monomer standard

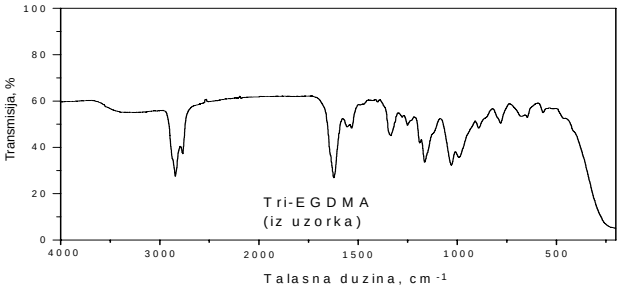

Figure 4. IR-spectrum of tri-EGDMA monomer isolated from propellant

Tri-EGDMA was extracted from silica gel using dichloromethane and analyzed by IR- spectrophotometer, Perkin Elmer (PE) 783, by film technique on kalium bromide (KBr) plate.

IR-spectrum of tri-EGDMA monomer standard component (Fig.3.) was compared to IR-spectrum of tri-EGDMA monomer isolated from the propellant (Fig.4.). Characteristic peaks on the same wavelengths appeared.

After TLC isolation of DPA and its derivatives, there is only tri-EGDMA deterrent in propellant dichloromethane extract remained.

Monomer and polymer components of the same compounds cannot be identified simultaneously using IR-spectrophotometry. Therefore, monomer tri-EGDMA was identified by GC method [4].

Using GC and IR spectrophotometry, it was confirmed that propellant dichloromethane extract consisted of deterrent tri-EGDMA and stabilizer DPA and its derivatives. Subsequently, this is an important fact for tri-EGDMA polymer component content determination.

Quantitative analysis of propellant dichloromethane extract

1. Determination of the tri-EGDMA monomer content

A Hewlett Packard Model 5890 gas chromatograph, equipped with a flame-ionization detector determined tri-EGDMA monomer content. Data was processed using a Hewlett Packard Model 3396A integrator. The carrier gas was nitrogen and a Model 7525 Hydrogen generator was used for preparation of hydrogen.

Optimum operating conditions of separation monomer tri-EGDMA from the other dichloromethane extract components were defined: Flame-ionization detector (FID) temperature was 300°C, column temperature was programmed from 100°C to 200°C at heating rate 10°C/min.

A 5 m × 0.53 mm I.D. capillary column DB-1 with dimethylpolysiloxane stationary phase and $2.65 \cdot 10^{-6}$m film thickness was used. The injected sample volume was $1 \cdot 10^{-3}$ cm^3. The sample and calibration mixture were prepared in the standard way [4].

The concentration of tri-EGDMA monomer component (0.67 mass %) was measured in propellant sample, using GC method (Figures 5 and 6).

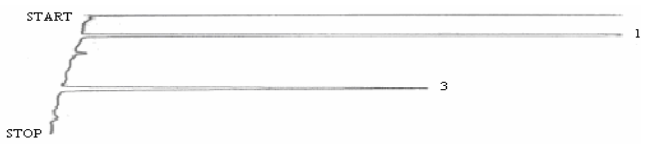

Figure 5. GC chromatogram of tri-EGDMA monomer standard solution

Peaks (retention time, min): 1 = acetanilide (1.84 min), 3 = tri-EGDMA (6.66 min)

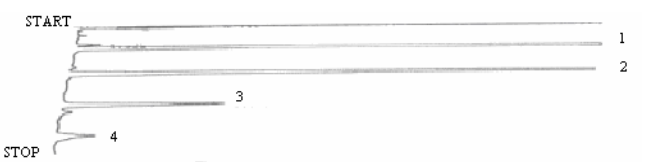

Figure 6. GC chromatogram of propellant sample

Peaks (retention time, min):1=acetanilide (1.84 min), 2 = DFA (3.98 min), 3 = tri-EGDMA (6.64 min), 4 =4-NO_2-DFA (9.29 min)

2. Determination of the tri-EGDMA polymer (soluble in dichloromethane) content

On the basis of the propellant extract qualitative analyses results, the content of tri-EGDMA polymer was determined by calculating the difference between experimental values overall content of dichloromethane extract components and the sum of the monomer tri-EGDMA, DPA and DPA derivatives contents.

Using Soxhlet extraction, overall content of dichloromethane extract components (4.71 mass%) was determined [4].

Measurement of the contents of DPA and its derivatives in propellant dichloromethane extract were carried out using RP HPLC method. A LDC/Milton Roy 3000, HPLC instrument was used. It consisted of a Spark Holland, SpH 99 column heater and a Rheodyne, Model 71, syringe loop injector. The LDC/Milton Roy 3100 variable wavelength UV-detector was connected to the HPLC instrument. Data were processed using an LDC/Milton Roy CI-4100 integrator. A $3 \cdot 10^{-6}$ m particle size Supelcosil LC-18-DB column, 15 cm × 4.6 mm was used. A mobile phase, consisting of 60 %(v/v) of HPLC grade acetonitrile and 40 % (v/v) of distilled water, was used at a flow rate of 1,2 cm^3/min. Operating column temperature was 30°C. The UV-detector was set at a wavelength of $220 \cdot 10^{-9}$m. Injection sample size was $5 \cdot 10^{-3} cm^3$. The sample and the standard components were prepared in the standard way [4].

The overall content of DPA and its derivatives in propellant sample, measured by RP HPLC method [4, 5] was S=1.40 mass%. It consists of: 1.11 mass% DPA; 0.24 mass% N-nitroso-DPA (N-NO-DPA); 0.02 mass% 2-nitro-DPA (2-NO_2-DFA) and 0.03 mass% 4-nitro-DPA (4-NO_2-DPA).

On the bases of the results of quantitative analysis propellant extract [4], the content of tri-EGDMA polymer component soluble in dichloromethane was calculated (2.64 mass%), since yet another aim of this work was to determine the content of tri-EGDMA polymer insoluble in dichloromethane. The sample, which remained on porous thimble after Soxhlet extraction by dichloromethane, was extracted once more, but this time with tetrahydrofuran (THF). Nitrocellulose from the propellant sample was dissolved in THF and during extraction transferred from porous thimble to flask. Graphite and salts were remained in the thimble. Tri-EGDMA polymer component insoluble in dichloromethane was not found in the thimble[4].

Conclusion

The identification and quantitative determination of poly(ethylene glycol) dimethacrylate deterrent in single-base gun propellant was carried out.

Tri(ethylene glycol) dimethacrylate was identified as a propellant deterrent using NMR spectroscopy.

Tri-EGDMA monomer component content was 0.67 mass% and it was measured by GC method.

On the bases of experimental results of quantitative analyses of propellant dichloromethane extract, content of tri-EGDMA polymer component soluble in dichloromethane was calculated to be 2.64 in mass%.

The overall content of propellant dichloromethane extract components was 4.71 mass% consisting of: 0.67 mass% tri-EGDMA monomer, 2.64 mass% tri-EGDMA polymer and 1.40 mass% DPA and its derivatives.

Tri-EGDMA polymer component insoluble in dichloromethane was not found in the analyzed propellant sample.

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Identifikacija i kvantitativno određivanje poli(etilen glikol) dimetakrilatnog flegmatizatora u jednobaznim barutima

Izvršena je identifikacija i kvantitativno određivanje poli(etilen glikol) dimetakrilatnog flegmatizatora u jednobaznom barutu. Primenom različitih analitičkih metoda utvrđeno je prisustvo tri(etilen glikol) dimetakrilata kao flegmatizatora i određen je sadržaj njegove monomerne i polimerne komponente.

Ključne reči: **eksplozivne materije, jednobazni baruti, flegmatizator, poli(etilen glikol) dimetakrilat, tri(etilen glikol) dimetakrilat, identifikacija, kvantitativna analiza.**

L'identification et la détermination quantitative de polyétylèneglycoldimétacrilat flegmatisant chez les podres monobasiques

Ce papier traite l'identification et la définition quantitative chez la poudre monobasique. Par l'application des différentes méthodes analytiques, on a constaté la présence de triè - tylènoglycolmétacrilat comme flegmatisant et on a défini le contenu de ses composantes monomère et polymère.

Mots clés: **matériaux explosifs, poudre monobasique, flegmatisant, polyétylèneglycoldi - métacrilat, triètylènoglycol-métacrilat, analyse quantitative.**

Идентификация и количественное определение поли(этилен гликол) диметакрилового флегматизатора в однобазисных порохах

Здесь сделана идентификация и количественное определение поли(этилен гликол) диметакрилового флегматизатора в однобазисных порохах. Применением различных аналитических методов установленно присутствие три(этилен гликол) диметакрилата в роли флегматизатора и определен состав его мономерной и полимерной составляющей.

Ключевые слова: **взрывчатые вещества, однобазисный порох, флегматизатор, поли(этилен гликол) диметакрилат, три(этилен гликол) диметакрилат, количественный анализ.**