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Optimization of focused ultrasonic extraction of propellant components determined by gas chromatography/mass spectrometry

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ABSTRACT

A method for focused ultrasonic extraction of nitroglycerin, triphenyl amine and acetyl tributyl citrate presented in double-base propellant samples following by the gas chromatography/mass spectrometry analysis was developed. A face-centered central composite design of the experiments and response surface modeling was used for optimization of the time, amplitude and sample amount. The dichloromethane was used as the extractant solvent. The optimal extraction conditions with respect to the maximum yield of the lowest abundant compound triphenyl amine were found at the 20 min extraction time, 35% amplitude of ultrasonic waves and 2.5 g of the propellant sample. The results obtained under optimal conditions were compared with the results achieved with validated Soxhlet extraction method, which is typically used for isolation and pre-concentration of compounds from the samples of explosives. The extraction yields for acetyl tributyl citrate using both extraction methods were comparable; however, the yield of ultrasonic extraction of nitroglycerin and triphenyl amine was lower than using Soxhlet extraction. The possible sources of different extraction yields are estimated and discussed.

1. Introduction

In the analyses of explosives, specifically smokeless powders, the appropriate techniques of sample preparation prior to analysis are usually required based either on liquid–liquid [1] or solid–liquid equilibria [2–4]. The selection of proper extraction technique for the isolation of target analyte depends on the sample nature and on the presence and concentration of other compounds in the sample, i.e. sample matrix. Propellant components such as nitroglycerin (NG), diphenyl amine (DPA), centralite or akardite II can be determined in water, in soil, directly in the smokeless powders immediately after their production, or in gunshot products.

Extraction techniques prevailing in the analysis of explosives in water are solid phase extraction (SPE), solid phase microextraction (SPME), or single-drop microextraction (SDME). SPE with a divinylbenzene/N-vinylpyrrolidone sorbent was used to prepare samples of water for the determination of NG and ethylene glycol dinitrate [2,3]. Zhou and Cunling [4] reported the application of SDME for the preparation of water samples for determination of DPA. Conventional liquid–liquid extraction techniques were also used, e.g. by Sherperel et al. [1] who used methanol as an extraction agent and subsequently separated the extract in a centrifuge. This method facilitated determination of DPA and centralites not only in the water but also in the gunshot products stuck onto clothing.

For the analysis of smokeless powders, Soxhlet extraction or its modifications are usually used [5–7]. For instance, a so-called high-rate Soxhlet extractor was used for the preparation of propellant samples [5,6] to determine explosive gellifying agents of nitrocellulose (NG, ethylene glycol dinitrate and triethylene glycol dinitrate (TEGDN)), chemical stabilizers (DPA, triphenyl amine (TPA), centralite and arkadite II) and the non-explosive gellifying agents of nitrocellulose (dibutyl phthalate, acetyl tributyl citrate (ATBC) and trimethyl citrate (TMC)). Soxhlet extraction was also used by Mathis and McCord [7] to determine the same substances as in studies [5,6]. An interesting mode of SPME application can be found in a paper by Joshi et al. [8], who used SPME to prepare the propellant samples for determination of DPA, centralites and nitroguanidine. A new method of preparing smokeless powder samples for the analysis was presented in a paper by Wilker et al. [9], where a sample is dissolved in acetonitrile. Subsequently, nitrocellulose was precipitated with water and separated from an extract in a centrifuge. This method could be applied for the determination of TPA and its decomposition products.

Abbreviations: ATBC, Acetyl tributyl citrate; CCD, central composite design; DPA, diphenyl amine; DPU, diphenyl urethane; ISTD, internal standard; NC, nitrocellulose; NG, nitroglycerin; RSM, response surface modeling; SDME, single-drop microextraction; SPE, solid phase extraction; SPME, solid phase microextraction; TEGDN, triethylene glycol dinitrate; TMC, trimethyl citrate; TPA, triphenyl amine; USE, ultrasonic extraction

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The above described research implies that the progressive methods of extraction, e.g. ultrasonic extraction (USE), pressure solvent extraction, supercritical fluid extraction or subcritical water extraction, do not yet find applications in the analysis of smokeless powders even though they can often provide more advantages than Soxhlet extraction. Our experience with Soxhlet extraction also suggests the urgency to adequately replace this technique with a less laborious and less time consuming technique. The methods described in our preceding publications [5,6] were in compliance with Czech National Standard ČSN 668102 (part 23). This method was developed in the 1970s by the Research Institute of Industrial Chemistry (VÚPCH) of the company Explosia, a.s. (Pardubice, Czech Republic) and has been used in its unaltered form to this date. However, it has not been optimized for the extraction of newly tested substances (TEGDN, ATBC, TMC, TPA and akardite II) and newly manufactured powders (e.g. spherical propellants with an NG surface finish and chemical stabilizers). The increasing volume of the extract and the decreasing charge of the powder in case of Soxhlet extraction can also significantly change the extraction efficiency. In the present work, we have therefore developed and optimized the focused ultrasonic extraction of main components of smokeless powders as possible alternative method to the Soxhlet extraction procedure.

In view of the major benefit of Soxhlet extraction, i.e. a very simple and inexpensive apparatus and minimum requirements for extraction agents (dichloromethane and diethyl ether) that can be reused after separation from the extract, we chose focused USE with an ultrasonic probe. It is relatively simple, inexpensive and fast in comparison to the others extraction methods [10]. The possible use of chlorinated solvents or diethyl ether presents a major advantage over, for instance, pressure solvent extraction.

There are several parameters, which can be varied to achieve highest extraction efficiency by the focused USE (i.e. extraction time, power of ultrasonic waves, temperature, and amount of the sample). To effectively optimize extraction technique, a response surface modeling (RSM) statistical approach is usually used. The RSM technique uses fitting of polynomial equation to the experimental data to describe the behavior of data sets including interactive effects among the examined variables. The main advantage of this technique is the reduced number of experimental trials needed to evaluate multiple parameters and their interactions and thus it is less laborious and time-consuming than other optimization approaches, e.g. the one-variable-at-a-time optimization [11]. The key parameter affecting the application of RSM optimization technique is the choice of experimental design type covering the region of studied parameters. Then, adequate mathematical function is fitted to the experimental data and the quality of the model and its accuracy is evaluated. Selection of suitable models has been recently summarized in several review articles [12–14]. For the development of the analytical procedures, the central composite design (CCD) is probably the most frequently utilized methodology. The CCD, introduced by Box and Wilson [15], consist of a full or fractional factorial design, an additional design, often denoted as a star design employed to estimate the square terms and a central point [12]. The replicates of the experiments, usually at the central point, are important to estimate the error and improve the precision of the experiment.

In recent years, the CCD has been widely applied on the optimization of ultrasonic extraction procedures of polysaccharides [16,17], non-volatile and volatile compounds occurring in plant materials [18–22] and other types of organic compounds [23,24]. The application of ultrasonic extraction for the analysis of explosives is, however, not yet sufficiently covered by literary sources. Conventional extraction in an ultrasonic bath is usually used to modify the samples of contaminated soils. Tian et al. [16] determined hexogen in soils by extracting samples in acetonitrile in an ultrasonic bath for 18 h. New ultrasonic method, concretely direct ultrasound-assisted dispersive liquid–liquid microextraction was introduced by Cortada et al. [25] for determination of the nitroaromatic explosives (derivatives of benzene and toluene) in water samples. To best of our knowledge, the RSM approach has not been yet applied on the focused USE isolation of compounds from propellant samples.

In the present work, we applied multivariate approach for the optimization of focused USE experimental conditions of extraction of NG, TPA and ATBC. We have described and statistically evaluated the extraction efficiency of these compounds by multiple non-linear regression. The propellant components were analyzed by gas chromatography coupled to mass spectrometry (GC/MS) in the electron ionization mode, which is faster and more accurate than liquid chromatography with ultraviolet detection and facilitates detection of substances that do not absorb the ultraviolet part of the spectrum (ATBC). We have compared the experimental results with the results obtained using Soxhlet extraction reference method, which was described and validated in our previous publications [5,6].

2. Materials and methods

2.1. Chemicals and propellant sample

Diphenyl urethane and dichloromethane were purchased from Sigma-Aldrich (Steinheim, Germany). Nitroglycerin and acetyl tributyl citrate were kindly provided by Explosia a.s. (Pardubice, Czech Republic). Triphenyl amine was obtained from Lobachemie (Mumbai, India). All standards used were of analytical grade purity.

Double-base propellant YD073-13/09 (containing NC, NG, chemical stabilizer TPA and gellifying agent ATBC) was kindly provided by Explosia. Expected contents of individual components were as follows: 10.0–10.5% (w/w) NG, 0.9–1.1% (w/w) TPA and 4.5–5.5% (w/w) ATBC.

2.2. Ultrasonic extraction

The process of NG, TPA and ATBC extraction from double-base propellant by ultrasonic treatment was performed in ultrasonic probe Sonopuls HD 3200 apparatus produced by Bandelin Electronic GmbH & Co. KG (Berlin, Germany). It allows setting the working time, ultrasonic power (amplitude) and pulsation. The instrument was equipped with titan probe (SH 70 G, 65% maximum amplitude corresponding approximately to 98 W) and 50 mL thermostatic vessel KG 3.

Tested amounts of propellant sample (0.5; 1.5 and 2.5 g) were extracted with 35 mL of dichloromethane in the vessel. Water bath was used to maintain the temperature of solution at 25 °C during whole extraction processing. Ultrasonic probe was immersed into the sample solution and the extraction was performed for three different times (10, 20, 30 min) at variable amplitudes (15, 35, 55%). Extract was transferred into the 50 mL volumetric flask and filled up using dichloromethane. Solutions were diluted and the internal standard (DPU) was added to all samples at concentration 10 mg mL^{-1}.

2.3. GC/MS analysis

The analyses were performed using gas chromatograph model GC-2010 coupled with mass spectrometer QP 2010 and autosampler AOC-20i (all from Shimadzu, Tokyo, Japan). A capillary SLB-5ms column (30 m × 0.25 mm i.d., 0.25 μm film thickness, Supelco, Bellefonte, PA, USA) was used. Helium was used as carrier gas at constant linear velocity 30 cm s^{-1}. Sample volume of 1 μL was injected in the split mode 1:100 with an injector temperature of 150 °C. Interface and ion source temperatures were kept at 230 °C. The temperature gradient program was optimized for the determination of wide range of compounds that may be possibly presented in the propellant samples. Thus the program was used as follows: the initial temperature 80 °C (0 min)→10 °C min^{-1} to 150 °C (4 min)→10 °C min^{-1} to 180 °C (11 min)→25 °C min^{-1} to 280 °C (3 min). The electron energy was set to 70 eV. Initially, mass spectra were recorded in full-scan mode (m/z=30–400) to obtain a set of masses of measured compounds. To improve the sensitivity of the measurement, selected-ion monitoring (SIM) mode was employed for the masses acquired from full-scan mode. Diagnostic ions monitored in SIM mode are listed in Table 1. GC/MS total ion current chromatogram of all analyzed compounds is shown in Fig. 1.

2.4. Experimental design

Three extraction variables considered for this research were extraction time (X_1 with coded levels x_1), sample weight (X_2 with coded levels x_2), and extraction power represented by amplitude of ultrasonic waves (X_3 with coded levels x_3). Table 2 summarizes the whole design consisted of 20 experimental points, which were used to estimate effects of each factor on the extraction efficiency. The experimentally obtained responses (peak areas related to internal standard) for all three compounds determined using GC/MS were fitted using multiple non-linear regression using STATISTICA data analysis software system, version 10, StatSoft, Inc. (2011), www.statsoft.com.

Table 1
Conditions of analysis for GC/MS in SIM mode.

Compound	Molar mass (g mol^{-1})	m/z of diagnostic ions	Relative intensity of ions (%)
ATBC	402	129, 185, 259	69, 100, 40
NG	227	30, 46, 76	25, 100, 5
TPA	245	51, 167, 245	29, 20, 100
DPU (ISTD)	241	51, 168, 241	47, 100, 74

3. Results and discussion

3.1. Experimental design and statistical evaluation

Several parameters can be varied for the selection of the best experimental conditions of sample preparation using focused USE. We have selected three parameters for the optimization of extraction of NG, TPA and ATBC from the samples of double-base propellant, i.e. time of the extraction, weight of the sample and amplitude of the ultrasonic waves. To find the conditions that will result in a maximum yield of USE and to produce detailed quantitative model, we have employed statistical central composite design of the experiments. The coded levels of the CCD used are listed in Table 2. The three factor CCD consisted of three elements, full factorial experiments (run 1–8 in Table 2) used to estimate linear trends and interactions terms, star element (run 9–15 in Table 2) employed to estimate the square terms and finally five replications to estimate the error of the measurement. The boundaries of the factors affecting extraction were selected according to the instrumental capabilities of the ultrasonic probe (amplitude is 15–55%; time of the analysis is 10–30 min) or to be in agreement and comparable with the reference Soxhlet extraction method (weight of the sample up to the 2.5 g) [6]. Amount of the sample was used to estimate the effect of the ratio of extractant solvent dichloromethane with the sample on the yield of extraction, as the amount of solvent was kept constant at 35 mL because of the total volume of the extraction vessel. Also the extraction solvent dichlormethane was used to be compared with the reference Soxhlet extraction method and to prevent the solubility of the nitrocelulose presented in the propellant samples, which may be the case using different solvents. Thus the coded level 1,1,1 represents 30 min extraction of 2.5 g of sample using 55% amplitude, the coded level 0,0,0 states for 20 min extraction of 1.5 g of sample using 35% amplitude and level −1,−1,−1 is the 10 min extraction of 0.5 g of sample at 15% of ultrasonic power. The dependent variable for evaluation of the experimental design of the ultrasonic extraction was the ratio of the peak area of analyzed compound with the peak area of internal standard DPU, both determined using GC/MS analysis in SIM mode. The experimental results are also shown in Table 2.

The multiple regression analysis was applied on the experimental data and the results of analysis are presented in Table 3 for all analyzed compounds. The second-ordered polynomial equations were constructed for the response variables (peak area determined by GC/MS in ratio with internal standard) related to the coded factors for all three compounds, i.e. for NG (Eq. (1)), TPA

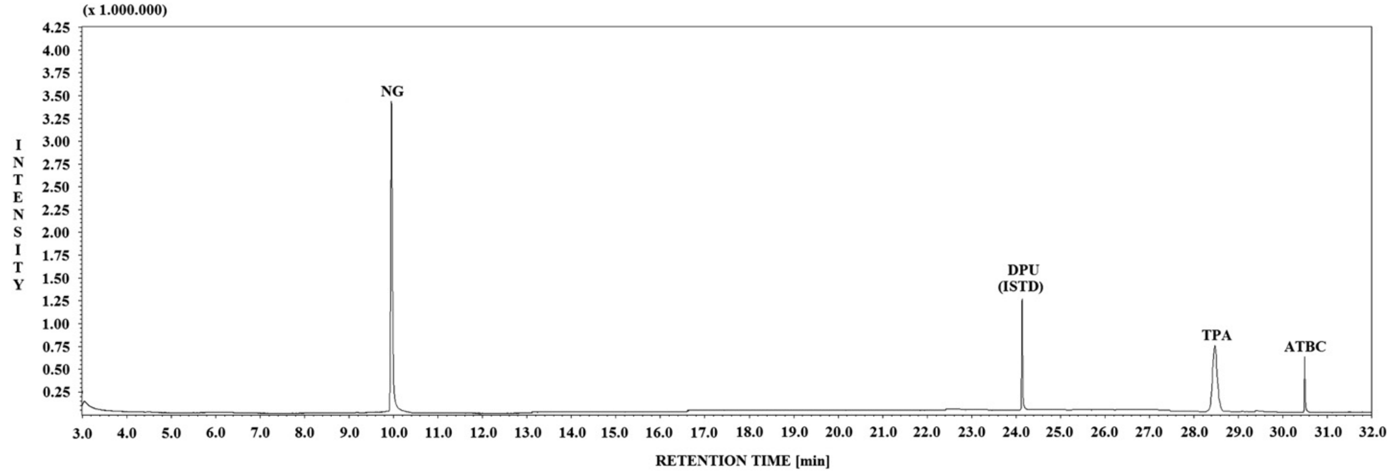

Fig. 1. GC/MS total ion current chromatogram of standards of analyzed compounds.

Table 2
Central composite design-coded independent variables, corresponding experimental conditions and results for the ultrasonic extraction of compounds in propellant sample represented by the ratios of peak areas of extracted compound, A_i, and peak areas of internal standard diphenyl urethane, A_{DPU}.

Run	x_1 (X_1) Extraction time (min)	x_2 (X_2) Weight of the sample (g)	x_3 (X_3) Amplitude (power) (%)	A_{NG}/A_{DPU}		A_{TPA}/A_{DPU}		A_{ATBC}/A_{DPU}	
				Observed	Predicted	Observed	Predicted	Observed	Predicted
1	1 (30)	1 (2.5)	1 (55)	18.74	18.54	1.11	1.15	7.28	6.31
2	1 (30)	−1 (0.5)	1 (55)	8.27	8.48	0.37	0.35	1.59	1.05
3	1 (30)	1 (2.5)	−1 (15)	19.59	18.49	1.02	1.06	6.20	6.43
4	1 (30)	−1 (0.5)	−1 (15)	9.56	9.94	0.56	0.56	1.26	1.97
5	−1 (10)	1 (2.5)	1 (55)	14.07	13.33	0.97	1.02	5.15	4.44
6	−1 (10)	−1 (0.5)	1 (55)	6.96	7.69	0.35	0.36	1.07	0.84
7	−1 (10)	1 (2.5)	−1 (15)	13.48	13.28	0.90	0.92	4.18	4.56
8	−1 (10)	−1 (0.5)	−1 (15)	8.95	9.15	0.60	0.56	0.95	1.76
9	0 (20)	−1 (0.5)	0 (35)	9.14	7.62	0.63	0.67	0.90	0.15
10	0 (20)	1 (2.5)	0 (35)	12.47	14.71	1.41	1.25	3.13	4.18
11	0 (20)	0 (1.5)	1 (55)	7.08	7.08	0.56	0.47	1.67	1.51
12	0 (20)	0 (1.5)	-1 (15)	7.07	7.79	0.55	0.53	1.57	2.03
13	1 (30)	0 (1.5)	0 (35)	8.46	9.17	0.60	0.54	1.45	2.01
14	−1 (10)	0 (1.5)	0 (35)	6.16	6.17	0.53	0.48	1.24	0.98
15	0 (20)	0 (1.5)	0 (35)	7.01	6.96	0.56	0.612	1.25	1.00
16	0 (20)	0 (1.5)	0 (35)	7.12	6.96	0.56	0.612	1.19	1.00
17	0 (20)	0 (1.5)	0 (35)	7.00	6.96	0.56	0.612	1.09	1.00
18	0 (20)	0 (1.5)	0 (35)	7.26	6.96	0.59	0.612	1.06	1.00
19	0 (20)	0 (1.5)	0 (35)	7.57	6.96	0.60	0.612	1.07	1.00
20	0 (20)	0 (1.5)	0 (35)	7.20	6.96	0.58	0.612	0.96	1.00

Table 3
Coefficients of the central composite design for NG, TPA and ATBC fitted with the second-order polynomial model and analysis of variance (ANOVA) for the experimental results.

Compound	Parameter	Estimated value	Standard error	Degree of freedom	Sum of squares	*F*-value	*p*-value
NG	Lack-of-fit			5	11.2407	50.47	0.0003
	Pure error			5	0.2227		
	b_0	6.953	0.073				
	b_1	1.500	0.067	1	22.5	505.09	0.0000
	b_{11}	0.716	0.127	1	1.41	31.68	0.0025
	b_2	3.547	0.067	1	125.81	2824.28	0.0000
	b_{22}	4.211	0.127	1	48.77	1094.87	0.0000
	b_3	−0.353	0.067	1	1.25	27.97	0.0032
	b_{33}	0.481	0.127	1	0.64	14.30	0.0129
	b_{12}	1.108	0.075	1	9.82	220.27	0.0000
	b_{13}	-0.093	0.075	1	0.07	1.54	0.2701
	b_{23}	0.378	0.075	1	1.14	25.59	0.0039
TPA	Lack-of-fit			5	0.0562	36.24	0.0006
	Pure error			5	0.0016		
	b_0	0.612	0.006				
	b_1	0.031	0.006	1	0.00	31.00	0.0026
	b_{11}	−0.103	0.011	1	0.03	93.61	0.0002
	b_2	0.290	0.006	1	0.84	2712.90	0.0000
	b_{22}	0.352	0.011	1	0.34	1100.85	0.0000
	b_3	−0.027	0.006	1	0.00	23.52	0.0047
	b_{33}	−0.113	0.011	1	0.04	112.73	0.0001
	b_{12}	0.035	0.006	1	0.01	31.61	0.0024
	b_{13}	0.010	0.006	1	0.00	2.58	0.1691
	b_{23}	0.075	0.006	1	0.05	145.16	0.0000
ATBC	Lack-of-fit			5	2.7798	52.71	0.0003
	Pure error			5	0.0527		
	b_0	1.003	0.035				
	b_1	0.519	0.032	1	2.69	255.39	0.0000
	b_{11}	0.491	0.062	1	0.66	62.95	0.0005
	b_2	2.017	0.032	1	40.68	3857.42	0.0000
	b_{22}	1.161	0.062	1	3.71	351.69	0.0000
	b_3	0.260	0.032	1	0.68	64.10	0.0005
	b_{33}	0.766	0.062	1	1.62	153.14	0.0000
	b_{12}	0.415	0.036	1	1.38	130.64	0.0000
	b_{13}	0.040	0.036	1	0.01	1.21	0.3208
	b_{23}	0.200	0.036	1	0.32	30.34	0.0027

(Eq. (2)) and ATBC (Eq. (3)):

$$A_{NG}/A_{DPU} = 6.953 + 1.500x_1 + 3.547x_2 - 0.353x_3 + 0.716x_1^2 + 4.211x_2^2 + 0.481x_3^2 + 1.108x_1x_2 + 0.378x_2x_3, \quad (1)$$

$$A_{TPA}/A_{DPU} = 0.612 + 0.031x_1 + 0.290x_2 - 0.027x_3 - 0.103x_1^2 + 0.352x_2^2 - 0.113x_3^2 + 0.035x_1x_2 + 0.075x_2x_3, \quad (2)$$

$$A_{\mathrm{ATBC}}/A_{\mathrm{DPU}} = 1.003+0.519x_1+2.017x_2+0.260x_3 +0.491x_1^2+1.161x_2^2+0.766x_3^2+0.415x_1x_2+0.200x_2x_3, \quad (3)$$

The square root of the determination coefficients of the models were 0.9614 for NG, 0.9563 for TPA and 0.9598 for ATBC which indicates, that less than 5% of the total variations could not be explained by the models. Adjusted square root of the determination coefficients adjust for the number of explanatory terms in a model. As such, it increases if the new term entered in the model significantly improves the model goodness-of-fit to the experimental data. The adjusted R2 considering only linear effects in the model is 0.4109 for NG, 0.5831 for TPA and 0.5545 for ATBC and increases to 0.8893 for NG, 0.8747 for TPA and 0.9058 for ATBC with introduction of the quadratic terms. Finally, using model with linear terms, quadratic terms and interactions between linear terms, the values of 0.9268 for NG, 0.9171 for TPA and 0.9238 for ATBC were obtained, confirming proper selection of the model for description of the correlation between the experimental values of extraction yield and coded levels of the experimental variables.

To find which selected factors affect focused USE preparation of propellant sample for the analysis, we have performed analysis of variance (ANOVA) of the experimental data. To evaluate the model, we have performed the lack-of-fit test, based on the calculation of the ratio between sum of squares of the lack-of-fit and sum of squares of the pure error. The ratio and thus the statistical difference between the two sum of squares is compared using Fisher–Snedecor *F*-test. The model well fitted to the data should present non-significant lack-of-fit [12]. In our case, the *F*-values for all tested compounds (50.47 for NG, 36.24 for TPA and 52.71 for ATBC; Table 3) indicate, that all the models are adequate for the prediction of the extraction yield in the selected range of evaluated parameters. The models were also evaluated using *p*-value. The *p*-value of the lack-of-fit is lower than 0.05 for all three compounds also suggesting that the models are satisfactory. The experimental values of extraction yield correlate well with the values predicted by the models (shown in Table 2).

The significance of each regression coefficients determined using multiple non-linear regression were tested using *F*- and *p*-value. The factors that present the *p*-value less than 0.05 (at confidence level of 95%) and the *F*-value higher than the critical *F*-value can be considered statistically significant. According to the determined values, all tested parameters (extraction time, weight of the sample and amplitude) can be considered significant in the linear and also in the quadratic terms for the model of focused USE of propellant compounds. The interactions are statistically significant between the terms of extraction time with weight of the sample and between the weight of the sample and amplitude of the ultrasonic waves. The Eqs. (1)–(3) are showing the dependency of the peak area ratios with internal standard DPU on the coded variables considering statistically significant regression parameters. The results from Table 3 indicate, that the weight of the sample is the major factor affecting the extraction yield in both, linear and quadratic term (*F*-value >2700, *p*-value close to zero), followed by the time of the extraction, while the ultrasonic power has the least effect.

3.2. *Response surfaces and optimization of extraction procedure*

The response surfaces obtained by displaying Eqs. (1)–(3) in three-dimensional plots, with the contour plot projections at the base, were constructed using Statistica software and are presented in the Fig. 2A for NG, 2B for TPA and 2C for ATBC. Each of the three graphs for target compound represents dependency of the extraction yield (ratio of the peak areas of the compound to the peak area of the internal standard DPU) on two independent variables. The third variable is kept on the coded level 0, thus the constant amplitude 35% corresponds to the left-hand side graphs, constant sample weight 1.5 g to the middle graphs and constant extraction time 20 min to the right-hand side graphs.

The effects of selected parameters on the extraction yield of analyzed compounds and interactions between them can be estimated from the shape of the three-dimensional surface and from the contour plots depicted at the base of the three-dimensional plots. The effects of parameters are increased with the increasing response on the surface and darker color of the contour plots. The significant interactions between the parameters are signalized, if the contour plots are of elliptical shape, as can be seen for the NG in the Fig. 2A, left- and right-hand side graphs. Correspondingly, the interactions are negligible with circular shape of the contour plots (e.g. Fig. 2A, middle graph). For all three compounds, the response significantly increases with increasing weight of the sample and the highest response is obtained at the border conditions (corresponding to the extraction of 2.5 g of propellant sample; Fig. 2A–C, left and right graphs). The influence of extraction time and amplitude on extraction yield for NG and ATBC is similar with the optimal conditions at the border conditions (30 min extraction time, 55% amplitude) with local minimum at the level zero (Fig. 2A and C, middle graphs). In contrary, the extraction yield of TPA reveal concave character in the studied segment with the shallow maximum of extraction yield at the conditions of 35% amplitude and 20 min extraction time (Fig. 2B, middle graph). As response surface model of focused USE possesses different optimal conditions for all the studied compounds, we have to select the compromise conditions, which would be suitable for the determination of NG, TPA and ATBC in the single analysis. We decided to use the optimal conditions determined for TPA (20 min extraction time, 2.5 g of sample, 35% amplitude) as it is expected to be present in the double-base propellant sample in the lowest concentration level (between 0.9% and 1.1% (w/w)) and thus the highest possible extraction yield is needed to isolate the significant amount of this compound from the sample.

3.3. *Comparison of optimized ultrasonic extraction with Soxhlet extraction*

The focused USE extraction of NG, TPA and ATBC under optimal conditions was compared with the validated Soxhlet extraction method described elsewhere [6]. The same sample of double-base propellant was prepared three times using each extraction method and further analyzed by GC/MS. The calibrations of GC/MS method was performed by the similar procedure as in our previous publication [6]. The dynamic range for NG was 2–12% (w/w), for TPA 0.1–6% (w/w) and for ATBC 0.5–8% (w/w). The constructed calibration dependencies were fitted with linear equations for the NG, TPA and ATBC and the parameters of slopes of calibration equation (0.9019 for NG, 0.5644 for TPA and 0.2920 for ATBS) and intercepts (-1.1582 for NG, $-9.27\cdot10^{-4}$ for TPA and -0.1558 for ATBC) were obtained. The correlation coefficients >0.99 (0.9980 for NG, 0.9999 for TPA and 0.9955 for ATBC) indicates high degree of linearity and the dynamic ranges are satisfactory for the determination of target compounds in the samples of propellants.

The results obtained using both methods are presented in the Table 4 and the comparison of the focused USE efficiency in relation to the Soxhlet extraction is also shown. The relative standard deviations for the three experiments (Table 4) lower than 5% suggests that both focused USE and Soxhlet extraction methods are highly precise and it can be successfully applied for

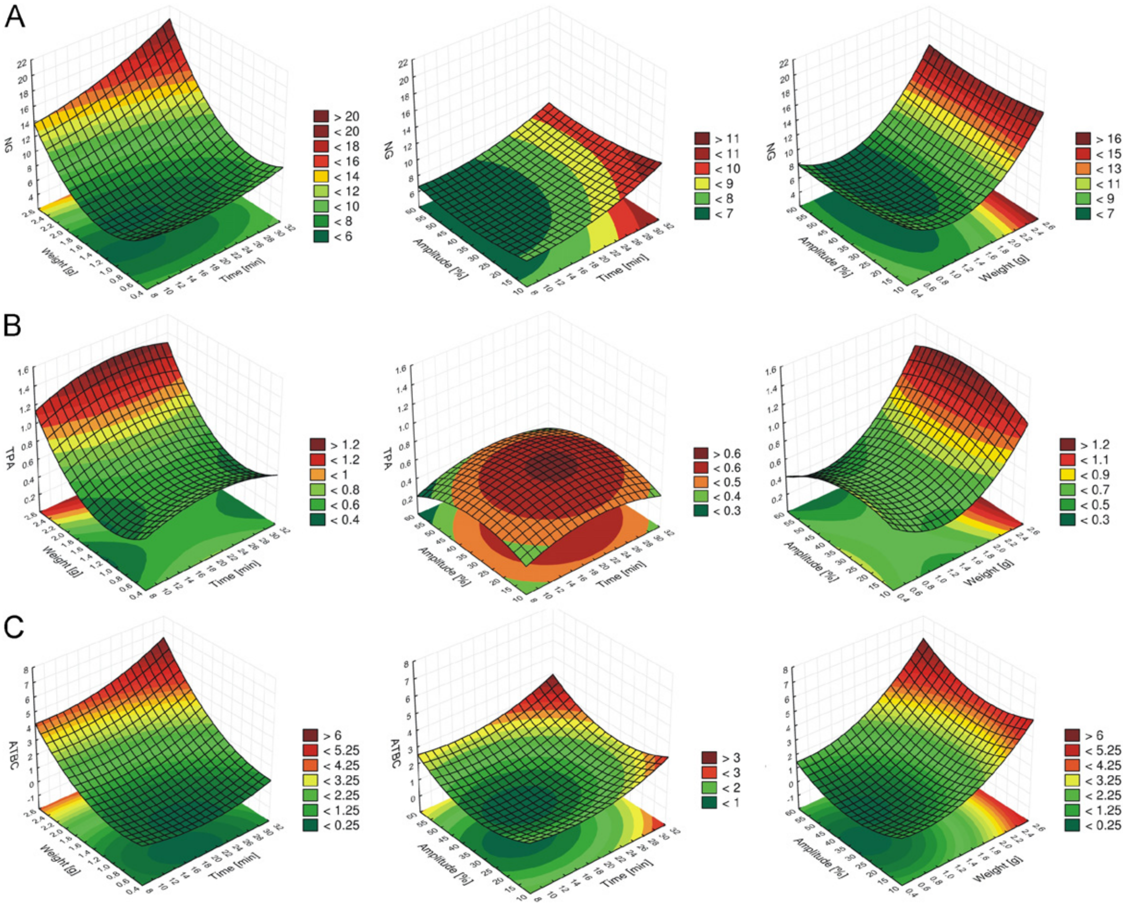

Fig. 2. Response surface plots showing the effects of sample weight, extraction time and amplitude of ultrasonic waves on peak areas related to the internal standard DPU for NG (**A**), TPA (**B**) and ATBC (**C**). On each three-dimensional graph, the third parameter is kept constant on the coded level 0 (35% amplitude, 20 min extraction time or 1.5 g sample weight).

Table 4
Comparison of the concentrations of propellant compounds determined by GC/MS after extraction of samples using USE and validated Soxhlet extraction.

Compound	USE Average value (%, w/w)	SD (%, w/w)	RSD (%)	Soxhlet extraction Average value (%, w/w)	SD (%, w/w)	RSD (%)
NG	4.380	0.040	0.92	10.490	0.076	0.71
TPA	0.264	0.009	3.58	0.800	0.011	1.38
ATBC	2.900	0.110	3.81	2.900	0.086	2.97

the preparation of propellant samples. The determined concentrations of compounds in the sample of propellant are generally lower for focused USE, which may be probably attributed to the lower volume of extraction solvent dichloromethane used in this method. The concentration and thus extraction yield of NG and TPA is approximately three times lower in focused USE in comparison to the value obtained by Soxhlet extraction. The extraction yield obtained for ATBC by both methods is comparable. The low extraction yield of NG and TPA is probably observed due to the shape and constitution of propellant particles. During manufacturing process of the spherical propellant, the NG and TPA are mixed and small droplets are formed by the emulgation, which are then covered by the ATBC. Therefore ATBC is presented mainly in the surface layer of the propellant particles while NG and TPA are encapsulated in the core of the particles. Hence the focused USE is capable to extract all the ATBC presented in the surface layer, but only part of the material from the inside of the particles. The homogenization of propellant sample is extremely difficult due to the high hardness of the material and also due to the undesirable possibility of accident explosion during mechanical disintegration. The differences between extraction yield of NG and TPA using both methods can be probably attributed to the lower hydrophobicity of NG in comparison to the TPA; octanol–water partition coefficients log *P* is 2.15 for NG, 5.74 for TPA and 5.23 for ATBC [26], and thus higher volume of the organic solvent dichloromethane is necessary to extract all NG presented in the sample. Second possible source of lower extraction yield of NG with respect to the TPA can be found in the degradation of NG by aging of the propellant [9]. The further research effort will be focused on the detailed explanation of the mechanisms of NG and TPA degradation. Finally, we have performed successive extractions after the end of the extraction step presented in Table 4 in order to evaluate the extractable capacity in each focused USE extraction step and thus to improve the recovery of NG and TPA. The results of three successive extraction steps followed after the first extraction are summarized in Table 5. As can be seen, the extraction efficiency of NG after total four USE steps are close to the value obtained for Soxhlet extraction method, however, the extraction efficiency of TPA is still half of this value. Although the correction of recovery of the

Table 5
Comparison of the concentrations and recoveries of propellant compounds determined by GC/MS after successive extraction of samples using focused USE.

Compound	Successive extractions			Total concentration (%, w/w)	Efficiency in comparison to Soxhlet extraction (%)
	2nd step (%, w/w)	3rd step (%, w/w)	4th step (%, w/w)		
NG	1.851	1.538	1.448	9.217	87.9
TPA	0.062	0.027	0.020	0.373	46.6

extraction method can be generally performed using the surrogate compound, in this case it would be difficult to use this approach. The surrogate cannot be incorporated into the propellant particles, while the TPA is mainly incorporated in the shell of the particles and it is difficult to be extracted.

4. Conclusions

The central composite design of the experiment and response surface modeling method has been successfully applied for the optimization of focused ultrasonic extraction of NG, TPA and ATBC in double-base propellant sample. This optimization approach reduces the number of experiments needed to achieve the highest extraction yield and reveals also the interactions between studied effects. The optimal conditions for analysis of propellant compounds were selected with respect to the lowest abundance compound TPA as follows: 20 min extraction time, 35% amplitude (power) of ultrasonic waves and 2.5 g of sample used for extraction. The results were further compared with the Soxhlet extraction method recently validated for the analysis of propellant compounds by our group [6]. The results obtained with both extraction methods were comparable for ATBC; however, lower extraction yield was observed for the NG and TPA. Despite the fact that the lower yield was due to carrying out USE for NG and TPA than using Soxhlet extraction, the USE method has advantage in less time needed for preparation of the sample (20 min for USE extraction step in comparison to the 8 h using Soxhlet extraction) and in the energy and solvent savings. Finally, the extraction efficiency of the NG and TPA in real sample was improved using successive extraction steps.

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