



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

Ondřej Fryš, Petr Česla, Petra Bajerová\*, Martin Adam, Karel Ventura

University of Pardubice, Department of Analytical Chemistry, Faculty of Chemical Technology, Studentská 573, CZ-532 10 Pardubice, Czech Republic

## ARTICLE INFO

### Article history:

Received 3 February 2012

Received in revised form

26 May 2012

Accepted 29 May 2012

Available online 12 June 2012

### Keywords:

Explosives

Focused ultrasonic extraction

Face-centered central composite design

Optimization

Soxhlet extraction

Gas chromatography/mass spectrometry

## 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.

© 2012 Elsevier B.V. All rights reserved.

## 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

\* Corresponding author. Tel.: +420 466 037 078; fax: +420 466 037 068.

E-mail address: [petra.bajerova@upce.cz](mailto:petra.bajerova@upce.cz) (P. Bajerová).

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<sup>-1</sup>.

### 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

Download English Version:

<https://daneshyari.com/en/article/7685464>

Download Persian Version:

<https://daneshyari.com/article/7685464>

[Daneshyari.com](https://daneshyari.com)