SCIENTIFIC PAPERS
OF THE UNIVERSITY OF PARDUBICE
Series A
Faculty of Chemical Technology
8 (2002)

APPLICATION OF SUPERCRITICAL FLUID EXTRACTION TO ISOLATION OF ADDITIVES FROM SMOKELESS GUNPOWDERS

Aleš EISNER, Karel VENTURA[1] and Martin ADAM
Department of Analytical Chemistry, The University of Pardubice,
CZ–532 10 Pardubice

Received September 30, 2002

This paper deals with the application of supercritical fluid extraction to isolation of additives from samples of smokeless powders, as an to classical fluid extractions (using Soxhlet apparatus or ultrasonication). The reasons for introduction of new extraction techniques are the decrease in volume of the solvents used for extraction and shortening the time of extraction, which usually takes several hours or even days. In the supercritical fluid extraction it is necessary to optimize the basic extraction parameters (temperature, pressure, modifier, treatment of the sample by means of grinding and the length of static step).

[1] To whom correspondence should be addressed.

Introduction

The extraction techniques find an increasing application in the treatment of samples. In recent years, various attempts have been made to replace the classical extraction techniques, particularly the Soxhlet extraction, by the techniques that would decrease the volume of the extraction solvent, amount of the sample to be analyzed as well as the time of the extraction process.

Examination of the content of compositions in explosives is interesting and highly topical in the analytical chemistry. Some strong explosives consist of toxic and carcinogenic substances; therefore, their content in soils and groundwater is subject to analysis. The present methods of obtaining the compounds included in the explosives from soils and other solid matrices prior to the analytical determination are the Soxhlet extraction and ultrasonication. These methods utilize relatively high volumes of solvents and are time consuming.

SFE is a dynamically developing method of preparation of samples for analytical processing. In the analytical scale, the SFE starts [1] to appear in the 1970s. However, only in the second half of the 80s started the real analytical application of the supercritical fluid extraction (SFE). The most widely used — as to instrumentation — is the off-line connection [2] of SFE-GC and SFE-HPLC, the on-line connection prevailing for the SFE-GC and SFE-SFC.

The supercritical fluid extraction shows better extraction efficiency compared to the classical fluid extractions (e.g., the Soxhlet extraction, with which it is compared most frequently). The supercritical fluid is under its critical point, which is given by the critical temperature and critical pressure, at which the properties of the phases become identical and, thus, the phases melt into one supercritical phase. For the extraction it is possible to use little-toxic substances as supercritical fluids, whereby utilization of organic fluid solvents harmful for the environment and the working atmosphere is limited. Simultaneously, the application of the above-given substances improves the mass transfer and accelerates the extraction process. The time necessary for the SFE is 15 – 90 minutes compared to the classical Soxhlet extraction, requiring even twenty-four hours.

Some properties of the gases, supercritical fluids and fluids are summarized in Table I. From this table it is obvious that the supercritical fluid, along with its density, viscosity and diffusion coefficient, is in a transition between gases and fluids. A supercritical fluid possesses specific physical and chemical properties, which make it interesting as an extraction medium.

The density of the supercritical fluid [3] is much higher than that of gases, which results in a higher solvating ability compared to gases. Their lower viscosity along with higher diffusion coefficient and nearly zero surface tension enable higher velocity of the transport processes compared to the fluids. These properties enable the supercritical fluid extraction to be performed more quickly and more

Table I Values of typical physical constants for gases, supercritical fluids and liquids [3]

	Density, 10^3 kg m^{-3}	Viscosity, mPa s	Diffusion coefficient, cm^2 s^{-1}
gas			
30 °C; 0.10132 MPa	(0.6 – 2) 10^{-3}	(1 – 3) 10^{-2}	0.1 – 0.8
supercritical fluid			
near the T_c, p_c	0.2 – 0.5	0.1 – 0.3	(0.7) 10^{-3}
near the T_c, $4p_c$	0.4 – 0.9	(3 – 9) 10^{-1}	(0.2) 10^{-3}
liquid			
30 °C; 0.10132 MPa	0.6 – 1.6	0.2 – 3	(0.2 – 2) 10^{-5}

efficiently than the classical fluid extraction, due to quicker and more perfect penetration of the fluid into the solid matrix [4].

Among the fluids most frequently utilized for the supercritical fluid extraction are to be mentioned CO_2 and N_2O. The critical parameters of these gases are low and the instrumentation is relatively simple. The substance proper, utilized as a supercritical fluid in the extraction, must be easily separable from the substances extracted and should not interfere with the subsequent analytical determination. Therefore, CO_2 and N_2O are applied, which are gaseous at normal temperature and pressure and can easily be separated [5] after decompression. CO_2 is non-toxic, non-inflammable and little reactive. It is supplied in high purity at an acceptable price and does not build explosive mixtures. It has zero permanent dipole moment and only the non-zero quadrupole moment contributes to its polarity. The polarity and extraction power is comparable with that of hexane; the extraction efficiency decreases with increasing polarity of the analytes. Giddins [6] indicates the following extraction possibilities:

a) Hydrocarbons and other non-polar lipophile substances, such as ethers, esters, ketones, PAU, PCB up to molar masses 300 – 400, can easily be extracted at the pressures extending to 30 MPa.
b) The presence of polar functional groups (-OH, -COOH etc.) makes the extraction more difficult or even impossible. Only derivatives of benzene with the maximum number of three hydroxyl groups can be extracted in a satisfactory way.
c) In the range up to 40 MPa, polar materials, such as sugars, glycosides, amino acids, lecithin, as well as polar polymers, such as proteins, cellulose, polyterpenes and synthetic polymers, are non-extractable. Non-polar oligomers are only slightly soluble.

N_2O is the second most frequently applied extraction medium, which has low critical temperature and pressure. The molecule has non-zero permanent dipole moment, compared to the molecule of carbon dioxide. This is probably the cause of better yields in the extraction of polar substances [7] from some matrices, in spite of the fact that the critical values for both gases are nearly equal. However, the promising perspectives of this gas are destroyed by the fact that it forms explosive mixtures with the air [8].

Practical Advantages of Application of the Supercritical Fluids

1. The fluids utilized are gaseous under the normal conditions; therefore, separation of the extraction medium from the extract is realised by simple expansion under the atmospheric pressure. The extracted substances fall out of the mobile phase flow and are captured in various ways.
2. Low critical temperature of the fluid enables application of the method for separation of thermally unstable substances.
3. The extracting fluid protects the sample from the atmospheric air, thus minimizing the risk of oxidation.
4. The gases applied as the extraction media (CO_2, N_2O) are supplied in a relatively pure condition, therefore, the problems of residual matter — common in the liquid solvents extraction — are not encountered.
5. The extracts obtained are sufficiently concentrated, they need not be post-concentrated, and thereby the sample contamination is limited.

Smokeless Powders

Smokeless powders are substances and mixtures of chemical compositions, if necessary, which are able to release large amount of gases of high temperature by combustion without access of the air, namely, by means of a pre-set mode.

The basic matrix used for the smokeless powders is nitrocellulose (high molecular composition, prepared by esterification of cellulose with nitric acid), whose structure [9] is shown in Fig. 2. In addition to the nitrocellulose, smokeless powders can include energetic components (DNT, TNT, NG), stabilizers (necessary for chemical binding of degradation products of the smokeless powders), plastifiers (dibutyl phthalate, dioktyl phthalate) and additives inhibiting flame blast, occurred after the shot (mostly salts of alkali metals, e.g., K_2SO_4). The most frequent stabilizers used are Cl and DPA, contained in every smokeless powder. In older powders concentration of the stabilizer decreases, whereby the powder becomes unstable.

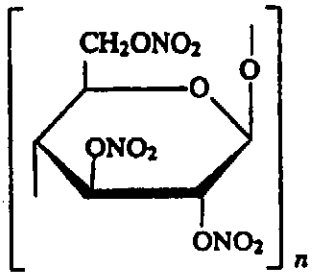

Fig. 1 Structure of nitrocellulose [9]

Smokeless powders are classified into the following groups according [10] to their composition:

a) one-component
b) two-component
c) multi-component powders

As evident from the name of one-component powders, their basic component is cellulose nitrate (or a mixture of cellulose nitrates) in the amount of 95 – 98 %. In addition to this basic component they include a stabilizer and, sometimes, inhibitors of the flame occurring after the shot. The one-component powders used include also the powders in which a part of nitrocellulose is replaced, e.g., by DNT, DPA, etc., which, however, are produced by an identical technological process.

The basic constituents of two-component smokeless powders are nitrocellulose and liquid ester of nitric acid (trinitro glycerol or dinitro glycerol). In addition, small amounts of stabilizers, plastifiers, inhibitors of flame after the shot are added along with other components.

Multi-component smokeless powders differ from the two-component ones in the content of nitroguanidine. Nitroguanidine is utilized as a cooling additive, as its explosion products have low temperature, which influences favorably the wear of barrels, which again is particularly important in large and efficient calibers.

According to the art of the explosives and compositions included, it is necessary to select suitable extraction conditions as well as application of supercritical solvent and modifier. At present, the composition applied most frequently to the extraction of the additives of explosives is CO_2 with modification of various polar compositions. However, problems occur if this solvent is utilized for extractions of amines. Aromatic and tertiary aliphatic amines can be extracted with supercritical CO_2. On the contrary, highly basic primary and secondary amines react with CO_2 to give insoluble products, therefore, their

extraction cannot take place. For these compositions, a more suitable extraction solvent is N_2O (no reaction giving insoluble [11] compositions takes place). However, for the reasons mentioned above the application of supercritical N_2O starts to be abandoned.

Another group of compositions contained in the explosives includes nitro compounds. For these substances, CO_2 is a suitable supercritical fluid. However, it is necessary to choose a modifier, which will increase solubility of these polar compounds.

For this group of substances, the most suitable modifiers are toluene and acetonitrile, according to the results [12] obtained by Deuster R. *et al.* The modifier polarity can be increased using small amount of highly polar additives (triethylamine and trifluoro-acetic acid). These additives interact with reactive sites of the matrix and block them after desorption of molecules of the analyte, thus inhibiting readsorption of the analyte. Due to these substances, reproduction capacity of the extraction increases; on the other hand, the extraction yield decreases compared to the extraction with a modifier, without usage of these polar additives.

At present, Soxhlet extraction is the most utilized method to obtain explosive components from the solid phase, and extraction with ultrasound is used to a smaller extent. Recently, supercritical fluid extraction has started to be used. An advantage of the SFE compared to the liquid extraction is a significally lower consumption of solvents and an important shortening of the extraction times. Mostly, it takes approximately one to two hours at most, compared to the Soxhlet extraction, which takes several hours or even several days. Another advantage of the SFE is that all substances under determination are transferred into a relatively small amount of a solvent (max. 10 ml). Therefore, further handling with the extract (concentration) are not necessary, and an extract contamination with impurity decreases.

Morris J.B. *et al.* [13] investigated the effectiveness of extraction of the nitro amine explosives using supercritical fluid extraction. For the extraction media, pure CO_2, CO_2 modified with organic modifiers and alternative supercritical fluids (ammonia and trifluoromethane) were utilized. The modification of the carbon dioxide was achieved by using acetonitrile, nitromethane, methanol, isopropyl alcohol and water. During the extractions, they especially focussed on isolation of RDX.

First, they extracted pure crystalline RDX, whereupon they investigated the extraction effectiveness with various extraction additives. The modifiers were added directly into the extraction cell. The extraction was executed for 20 min at the pressure of 55 MPa and temperature 50 °C in dynamic mode. The extracts obtained were analyzed using HPLC. The results indicate that acetonitrile is the most effective modifier for increasing RDX solubility in the supercritical CO_2. Then, they extracted RDX directly from the smokeless powders. The results

indicate lower effectiveness of extraction from the powder compared to pure crystalline RDX.

Niehaus *et al.* [14] examined the influence of the modifiers upon the solubility of polar substances in modified CO_2. They extracted samples containing nitroguanidine (NIGU), hexahydro-1,3,5-trinitro-1,3,5-triaza-cyclohexane (RDX), 3-nitro-1,2,4-triazol (NTO), and pentaerythritol tetranitrate (PETN). In the extraction they used a mixture of critical CO_2 with the modifier concentrations below 4 mol. %. A comparison of the extraction efficiency of pure CO_2 and CO_2 is shown in Fig. 1. As obvious from the diagram, different modifiers have different effects upon the samples, which is indicated by the specific interaction between the modifier and the sample.

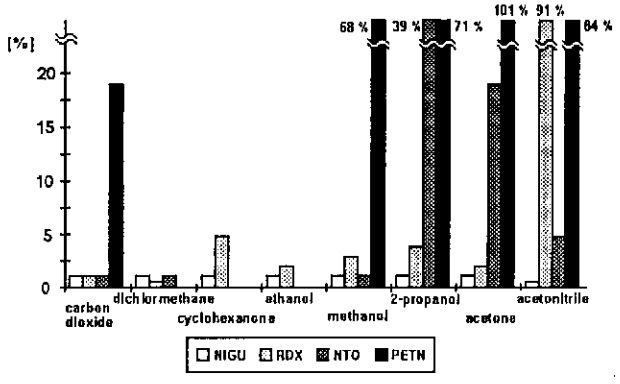

Fig. 2 Effect of modifier on the extraction efficiency [14]

Suitable choice of modifier depends on many factors and it is necessary to optimize a suitable type and concentration of the modifier for the particular matrix and analyte. The modifier solubility in the supercritical fluid depends on the extraction temperature and pressure. The amount of modifier added must be appropriate to these parameters. Furthermore, it is necessary to take into account whether the applied modifier interacts better in the liquid or the supercritical state with the sample. The studies show that it is more suitable to dose the modifier directly into the extraction cell [15] with the sample. In addition, it is necessary to respect the following analytical separation of the substances and, first of all, the way of detection in the analytical method selected.

Experimental

The apparatus used for SFE was a supercritical fluid extractor SE-1 (SEKO-K, s.r.o., Brno). The design of the apparatus is shown in Fig. 3. The apparatus is equipped with a piston micro-pump, controlled pneumatically, working in the pressure range from 7 to 40 MPa. The size of the piston surfaces is in the ratio of 1:33. The micro-pump volume equals to 10 ml, which is not sufficient for an extraction longer than 5 minutes at 40 MPa. The length and diameter of a restrictor also influence this time. If the extraction agent is spent during the extraction, the valve separating the extraction cell from the pump closes automatically and re-filling starts. The extraction cell can be heated up to 30 °C – 150 °C. Into the extraction cell is inserted an extraction cartridge of various internal volumes (0.7 – 2.7 ml), according to the weighed amount. After the sample weighing into the extraction cartridge, free room is filled with inert material. A silica capillary of inner diameter 25 μm and 20 cm length was used for the restrictor. The restrictor is used to compensate the high pressure in the extraction cell to the atmospheric pressure. The analytes under determination were taken up by submersion of the restrictor end under the level of the organic solvent (methanol). Basic equipment of the extractor used for supercritical fluid extraction includes neither a valve for static extraction nor equipment for continuous modification of the extraction medium. To include the static step into the extraction process, it was necessary to locate a high-pressure six-way valve (Valco Instruments Co. Inc., USA), enabling to perform the static extractions between the extraction cell and the capture vessel. For dosing of modifiers into the extraction medium, the extractor was adapted by insertion of a dosing valve for HPLC with outside loop of 500 μl volume between the CO_2 pressure bottle and the extractor pump. The volume of loop was selected so that the modifier concentration amounted to 5 % approximately (w/w).

First, the sample was weighed on a SARTORIUS automatic scale into the extraction cell, which was closed completely from below with sintered glass. The weighed amount was about 1 g in each sample for all the extractions. After the sample weighing, the remaining free room was filled with siliceous wool. The prepared extraction cell was put into a heated extractor block and the block was closed with a packing screw. The restrictor was submersed into a 2-ml or 5-ml collecting vessel, filled with methanol. Than, the extraction program was initiated. In the first phase, the optimized extraction temperature was (60 °C, 80 °C and 100 °C) and the pressure was (20 MPa, 30 MPa and 40 MPa). In this phase only dynamic extraction took place. The extraction agent used was pure carbon dioxide and carbon dioxide modified with methanol, acetonitrile, diethyl ether, dimethyl formamide, 50-% solution of 1,6-HDA in methanol, 1-decylamine etc. The extraction agent was modified using a dosing valve for liquid chromatography (outside loop of 500-μl volume), inserted between the pressure bottle of carbon dioxide and the extraction pump. If a modified supercritical fluid was applied for

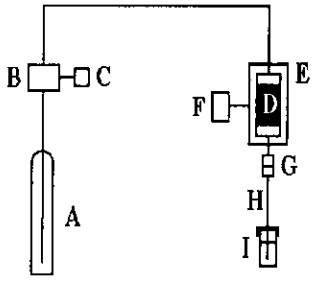

Fig. 3 Design of the supercritical fluid extractor: A – cylinder of CO_2; B – high pressure pump; C – extraction vessel; D – heater of restrictor; F – restrictor; G – vial with solvent

the extraction, the modification solution was added using a dosing loop into the extraction medium flow during each pump filling. The experiments showed that it was not possible to make use of the dosing loop for dosing of aliphatic amines, as the amines form insoluble carbamates with carbon dioxide and both the capillary vessels and the pump are clogged. That is why 300 µl of a 5-% amine solution was dosed directly into the reaction cell.

The extracts obtained were analyzed using liquid chromatography. A column with Biospher Sl C18 7 µm filling, 250 × 4 mm (Ecom s.r.o., Prague) was used for the separation. A protective pre-column Separon SGX C18 7 µm, 30 × 3.3 mm (Tessek, Prague) was placed ahead of the column. The sample was dosed into the column by means of a valve of outside loop volume of 20 µl. The mobile phase flow through the column was ensured by means of a high-pressure pump LCP 4000 (Ecom s.r.o. Prague) and was kept at 0.8 ml min^{-1}. For the analysis was utilized a mobile phase gradient, which was created using a gradient programmer GP 5 (Ecom s.r.o. Prague). The mixture of mobile phases is prepared prior to the entry into the pump. Methanol and water were selected for gradient formation. Various programs of gradient elution were tested to reach an optimum separation of the substances, especially in 2,6- and 2,4-DNT, for the shortest possible time. Table II summarizes the program of gradient elution during which all substances were separated sufficiently within an adequate time. The mobile phase stock solutions were deaerated in the ultrasound and were bubbled with helium during analysis. A UV detector LCD 2040 (Laboratorní přístroje Prague) was applied for the detection. The wavelengths for the UV detection during the HPLC analysis were determined from the UV spectra measured with a GBC 916 from GBC Scientific Equipment, Australia. The wavelengths of 280 and 220 nm were chosen for one-component smokeless powders, containing DNT, and for other smokeless powders inclusive of two-component ones, respectively.

Table II Program of the gradient elution

Time, min	30 % CH_3OH in water, %	100 % CH_3OH, %
0	100	0
8	29	71
12	29	71

Results and Discussion

This work includes SFE of additives from samples of smokeless powders. The effectiveness of this process was related to the results obtained by the Soxhlet extraction, i.e., the process utilized in Synthesia a. s. for the release of smokeless powders.

In Experimental extractions of non-polymer organic components from various samples of one-component smokeless powders (Lovex S-040) and two-component smokeless powders (Balistit) were carried out using pure CO_2 and CO_2 modified with various organic substances. The influence of the extraction temperature and pressure upon the extraction process effectiveness was studied as well.

One-Component Smokeless Powders

Lovex S-040

Lovex S-040 is a one-component smokeless powder, surface-treated by graphitization, produced in the form of rollers of approximate diameter equal to 1 mm and height of 2 mm. This sample contains DPA and Cl (stabilizer). For the Soxhlet extraction a 2.5 g sample and 50 ml dichlormethane were utilized for a period of 8 hours. It follows from the following HPLC analyses of the extracts obtained that the sample contained 0.91 % DPA and 0.98 % Cl. The liquid extraction effectiveness in the state above the critical point was related to the above-mentioned values.

Influence of Temperature and Pressure upon Extraction Effectiveness

This section of work investigated the possibility of application of SFE to isolation of these substances from the smokeless powder. The extraction was carried out at the pressures of 20 MPa, 30 MPa and 40 MPa for 60 min at three different tempe-

Table III Influence of temperature upon the extraction effectiveness; conditions of SFE: m = 1 g, t = 60 min, p = 50 MPa (average from six extractions), content of the components determined by Soxhlet: 0.91 % DPA and 0.98 % Cl

DPA, %	Cl, %	Modifier	t, °C	Pressure, MPa
0.91 ± 0.04	0.98 ± 0.10	HDA	100	
0.66 ± 0.07	0.95 ± 0.06	HDA	80	40
0.41 ± 0.02	0.91 ± 0.05	HDA	50	
0.77 ± 0.06	0.81 ± 0.07	HDA	100	
0.58 ± 0.04	0.74 ± 0.03	HDA	80	30
0.34 ± 0.05	0.68 ± 0.05	HDA	50	
0.64 ± 0.03	0.74 ± 0.06	HDA	100	
0.48 ± 0.06	0.68 ± 0.05	HDA	80	20
0.22 ± 0.04	0.54 ± 0.07	HDA	50	
0.88 ± 0.03	0.99 ± 0.11	DA	100	
0.70 ± 0.07	0.91 ± 0.08	DA	80	40
0.50 ± 0.04	0.88 ± 0.06	DA	50	
0.74 ± 0.04	0.78 ± 0.05	DA	100	
0.57 ± 0.03	0.64 ± 0.08	DA	80	30
0.31 ± 0.05	0.61 ± 0.06	DA	50	
0.61 ± 0.08	0.72 ± 0.04	DA	100	
0.45 ± 0.03	0.62 ± 0.06	DA	80	20
0.19 ± 0.04	0.05 ± 0.06	DA	50	

ratures. The temperatures used were 50 °C, 80 °C and 100 °C. During SFE, partial decomposition of DPA occurs (max. one fifth of the total content of diphenylamine present in the sample). An approximately identical decomposition occurs also during the Soxhlet extraction with dichloromethane (boiling point 40.6 °C). It is interesting that at higher temperatures (80 °C and 100 °C) the DPA decomposition occurs, as it was found that a complete reverse transition of *N*-nitrosodiphenylamine to diphenylamine — takes place during gas chromatography at 65.5 °C and higher temperatures. The extracted quantity of the substances under determination was found out using HPLC with UV detector. Each extract was analyzed four times after suitable dissolution. Standard deviation of the components to be determined did not exceed 0.02 %.

The influence of extraction temperature and pressure upon the extraction effectiveness using a modified extraction agent was studied with a 5 % methanolic solution of 1-decylamine or 1,6-hexanediamine. Table III summarizes the yields of the substances determined at three different temperatures and pressures.

It is obvious from the table that the required effectiveness was not reached during the extraction carried out at lower temperatures and pressures (50 °C and 20 MPa). Therefore, it was necessary to increase the extraction temperature and pressure. At 80 °C and 30 MPa the extraction yield increased, however, the yield comparable with the Soxhlet extraction was not yet obtained. After increasing the temperature and pressure to the highest values (100 °C and 40 MPa) the extraction effectiveness required was obtained. It also follows from this table that the two modifiers influence approximately equally the extraction effectiveness for the substances determined.

An advantage of the primary and secondary aliphatic amines used as the modifiers is that they react with carbon dioxide giving an unstable *N*-alkylcarbamic acid, which disintegrates to give alkylammonium salts, which again are insoluble in the carbon dioxide.

The insoluble particles deposit at the walls of the supply capillaries as well as in the pump cylinder and clog them after some time. Then replacement of the capillaries and difficult cleaning of the extractor pump are necessary. This behaviour of the primary and secondary aliphatic amines excludes them from utilization in the continuous modification of carbon dioxide using a dosing valve (the amines can be easily used for modification of dinitrogen oxide). The amines can be applied to the modification of carbon dioxide as well, however, they must be dosed directly into the extraction cell along with the sample.

Influence of the Modifier upon the Extraction Effectiveness

Pure CO_2 without modifier was used as an extraction medium at the beginning. Its extraction effectiveness, however, was not sufficient, therefore, for further measurements we started to use CO_2 modified with various modifiers, as an extraction medium. The values measured after the extraction with CO_2 modified with various modifiers (ACN; METOH; DEE; 1,6-HDA and a mixture of ACN and DEE), are summarized in the Table IV.

It is obvious from the table that the DPA yield [%] is best after extraction with CO_2 modified with 1,6-HDA + ACN (0.93 %). The yield of Cl [%] is best after extraction with CO_2 modified with the same modifier (0.99 %). The results obtained are summarized in Fig. 4. It is evident from comparison with the results given above that the application of a 5-% solution of 1,6-hexanediamine directly into the extraction cell with the sample produced equal extraction effectiveness as if this modifier was dosed using the dosing valve in the course of each pump fill-

Table IV Influence of modifier upon the extraction effectiveness; SFE conditions: m = 1 g, t = 60 min, p = 50 MPa, t = 100 °C (an average from six extractions); contents of the components, determined using Soxhlet: 0.91 % DPA and 0.98 % CI

DPA, %	Recovery, %	CI, %	Recovery, %	Modifier
0.26 ± 0.02	28.57	0.64 ± 0.07	66.33	None
0.72 ± 0.04	79.12	0.71 ± 0.08	72.45	ACN
0.55 ± 0.08	60.44	0.77 ± 0.03	78.57	METOH
0.38 ± 0.05	41.76	0.89 ± 0.07	90.82	DEE
0.46 ± 0.01	50.55	0.87 ± 0.05	88.78	ACN + DEE
0.64 ± 0.19	70.33	0.84 ± 0.07	85.71	5 % sol. 1.6-HDA, into cell
0.73 ± 0.03	80.22	0.85 ± 0.02	90.82	5 % 1.6-HDA, into cell 15 min before extraction
0.84 ± 0.09	92.31	0.87 ± 0.05	88.78	5 % 1.6-HDA, into cell 30 min before extraction
0.94 ± 0.08	103.29	0.98 ± 0.04	100	5 % 1.6-HDA, into cell + ACN
0.93 ± 0.05	102.2	0.99 ± 0.05	101.2	5 % 1.6-HDA, into cell 30 min before extraction + ACN

ing. It follows from the results indicated that the centralite yield is not influenced by the time of amine action upon the sample prior to the extraction start. On the other hand, the DPA yield increases with the time of amine addition prior to the extraction itself. If the amine is used along with acetonitrile, the extraction effectiveness of diphenylamine is no more influenced by the amine action prior to the extraction.

Kinetic Study of Extraction

Further measurements were focused on the study of dependence of the yield upon the extraction time. Extractions of Lovex S-040 with CO_2 without modifier and CO_2 modified with 1,6-HDA and ACN, added over a loop, were carried out. The values measured have been processed into Fig. 5.

Obviously from the sample after extraction with CO_2 free of modifier, the yield of only 34.19 % DPA and 67.54 % Cl is obtained after 90 minutes extraction.

Therefore, CO_2 modified with 1,6-HDA and ACN, added over the loop, was used to increase the yield. In the course of this extraction, the yield of the two components under study increased significantly (103.95 % DPA and 97.34 CI).

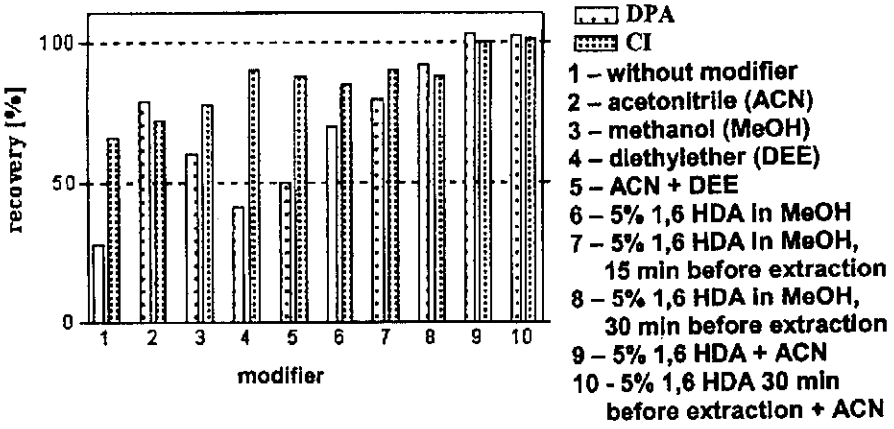

Fig. 4 Influence of a modifier upon the extraction effectiveness

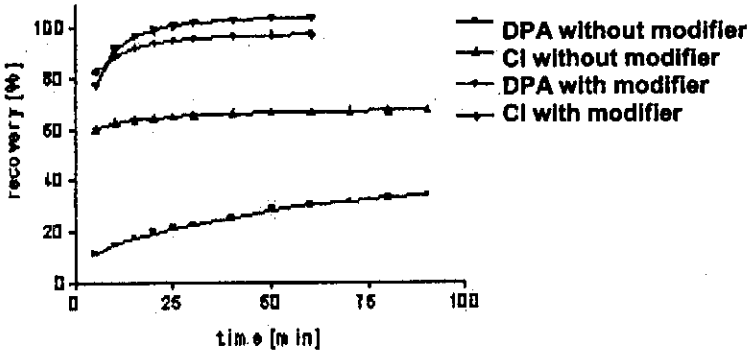

Fig. 5 Kinetic study of extraction (Lovex S-040)

Two-Component Smokeless Powders

Only the influence of the modifier type upon the extraction effectiveness was studied in these samples. The other extraction parameters (extraction pressure, temperature and time) were taken from the optimization of one-component smokeless powders and were evaluated as the best ones (extraction temperature 100 °C, pressure 40 MPa and time 60 min).

Balistit

Unlike the previous sample, this is a two-component smokeless powder, surface-treated by graphitization. Its composition was investigated after the Soxhlet extraction under equal conditions as that used for Lovex S-040. The subsequent HPLC analyses discovered that the sample contained 47.95 % nitroglycerol and 1.33 % centralite I.

Influence of Modifier upon Extraction Yield

The extractor temperature equal to 100 °C and extraction pressure equal to 40 MPa were used for a sixty-minute SFE. These extraction conditions were adopted in all extractions on the basis of the previous results. First, pure carbon dioxide was used as an extraction medium. However, as obvious from Table 5, the extraction effectiveness for the two substances under determination is low with the carbon dioxide. The insufficient effectiveness of the pure carbon dioxide is due to the large difference in the polarity between CO_2 and the substances under determination. Therefore, CO_2 modified with methanol or methanolic solution of the acetic acid (in the ratio of 1:9) was used in the following experiments. The SF extracts were analyzed using HPLC.

After addition of methanol to the carbon dioxide (as a modifier) a significant increase in the yield of the two substances under determination was observed, nevertheless, a lower yield compared to the Soxhlet extraction. It follows that methanol improves the extraction effectiveness, however, only to an insufficient extent. In the following experiments, methanolic solution of the acetic acid (in the ratio of 1:9) was tested as a modifier. As evident from Table V, nearly equal extraction effectiveness for the two substances under determination was reached with this modified carbon dioxide as in an eight-hour Soxhlet extraction.

After suitable thinning, each extract was analyzed four times and the maximum standard deviation of the analysis of one extract was 0.02 % for NG and 0.01 % for CI.

Comparison of the values in Tables V and VI shows a large deviation from the values set in Synthesia a.s. for nitroglycerol with carbon dioxide, modified with an acetic acid solution in methanol. The difference is probably due to instability of NG in the acid environment in dependence on time. Acetic acid behaves as a strong acid in the water-free medium and, probably, acts as a catalyst of nitroglycerol hydrolysis (free nitric acid and glycerol are produced; the latter can be further oxidized to carbonyl compounds). Nitric acid increases acidity of the solution and reacts with methanol to give volatile methyl nitrate. The nitric acid methyl ester decomposes with production of methanol and nitrogen oxides, which can be bound to the other substances contained in the extract (mainly to the

substances used as stabilizers), thus decreasing their yield. The deviation is obvious, as the analyses for Table V were made immediately following the extraction or half-an-hour after its termination at the latest. On the other hand, the analyses made in Synthesia a.s. were carried out only several days after the extraction.

Due to the inaptitude of application of the acetic acid as a modifier, it was no more used for the other samples. Another extraction medium modifier used was a 5-% methanolic solution of 1,6-HDA, added directly into the extraction cell along with acetonitrile, added over a dosing valve. This modifier was tested for the extraction of one-pack smokeless powders. As evident from the results in Tables V and VI, comparable results even with the two-pack smokeless powders were obtained as in the Soxhlet extraction.

Conclusion

The present work compares the effectiveness of supercritical fluid extraction with the classical liquid extraction technique (Soxhlet extraction). The additives (DPA, CI and NG) were extracted from one-component smokeless powders (Lovex S-040) and from two-component smokeless powders (Balistit). The supercritical fluid extraction was made at pressures of 20 MPa, 30 MPa and 40 MPa and temperatures of 50 °C, 80 °C and 100 °C. It was found from these measurements that the highest extraction effectiveness is obtained at 100 °C and 40 MPa. Pure CO_2 and CO_2 modified with various modifiers were used as extraction media. It follows from the results obtained that the highest extraction effectiveness for the two samples investigated was obtained when applying a 5-% methanolic solution of 1,6-HDA directly added into the extraction cell and acetonitrile dosed by means of a valve.

The values obtained by the supercritical fluid extraction with CO_2 modified with the above-mentioned modifier mixture for 60 min are comparable with the values obtained from the Soxhlet extraction of the two samples. Therefore, it can be stated that the quantitative yields were obtained, which are reached by the Soxhlet extraction only after 8 hours. It is evident from the data obtained that SFE can be applied as an alternative technique in the extraction of smokeless powder additives and could replace the classical Soxhlet extraction.

Acknowledgements

Financial support from the Ministry of Education, Youth and Sports of the Czech Republic (projects No. MSM 2531 00002 and GA 203/01/0023) is gratefully acknowledged.

References

[1] Itahl E., Schill W.: Z. Anal. Chem. **280**, 99 (1976).
[2] Mikešová M., Vejrosta J.: Chem. Listy **89**, 217 (1995).
[3] Clifford A.A.: *Introduction to supercritical fluid extraction in analytical science*, in: *Supercritical fluid extraction and its use in chromatographic sample preparation* (S.A. Westwood, ed.), Blackie Academic & Professional, Glagow, 1993.
[4] Camel V., Tanbuté A., Caude M.: J. Chromatogr. **642**, 263 (1993).
[5] Hitchen S.M., Dean J.R.: Properties of supercritical fluids. in: *Application of supercritical fluids in industrial analysis* (J.R. Dean, Ed.), Blackie Academic & Proefessional, Boca Raton, 1993.
[6] Giddings J., Myers M., McLaren L., Keller R.: Science **162**, 67 (1968).
[7] Janda V., Bartle K.D., Clifford A.A.: J. Chromatogr. **642**, 283 (1993).
[8] Sievers R.E., Hansen B.: Chem. Abstr. **116**, (1991)
[9] Zinon J., Zitrin C.: *Modern methods and applications in analysis of explosives*, John Wiley & Sons, Chichester, 1993.
[10] Vetlický B.: Střeliviny, VŠChT Pardubice, 1987.
[11] Ashraf-Khorassani M., Taylor L.T.: Anal. Chem. **62**, 1177 (1990).
[12] Deuster R., Lubahn N., Friedrich C., Kleiböhmer W.: J. Chromatogr. **785**, 227 (1997).
[13] Moris J.B., McNesby K.L., Pesce-Rodriguez R.A., Shroeder M.A., Fifer R.A.: ICT Jahrestagnung (1993).
[14] Niehaus M., Teipel U., Bunte G., Krause H.H.: Propellants, Explos., Pyrotech. **22**, 176 (1997).
[15] Friedrich C., Cemman K., Kleiböhmer W.: Fresenius J. Anal. Chem. **352**, 730 (1995).