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DETERMINATION OF COMBUSTION PRODUCTS FROM PROPELLANTS

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The study describes identification of products after combustion of smokeless powders and solid propellants. A sample of smokeless powder was burnt on clean sand and the combustion products were isolated from the sand. The accelerated solvent extraction and ultrasonication were used for the isolation of these compounds. Gas chromatograph GC 17A with mass spectrometry detector QP5050A was used for identification of the compounds.

Introduction

Old propellants must be liquidated because they contain low amounts of stabiliser. This smokeless powder is unstable and dangerous for people. The deactivation of smokeless powders can be realized by burning. Knowledge of compounds produced by burning of smokeless powders is necessary for specification of their

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effect on the environment.

Polynitro organic compounds [1] Diphenylamine (DPA), Centralite, [hexahydro-1,3,5-trinitro-1,3,5-triazine (RDX), octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX) and 2,4,6-trinitrotoluene (TNT)] are typical labile environmental pollutants that can bio transform with soil indigenous micro organisms, photo degrade by sunlight and migrate through subsurface soil to cause groundwater contamination. A comprehensive analytical methodology of sample preparation, separation and detection is thus required to be able to determine the type and concentration of explosives and their (bio) transformation products in different soil environments.

The first step is isolation of these compounds from sample. The classical [2] extraction methods (soxhlet, ultrasonication) and new extraction techniques (accelerated [3] solvent extraction, supercritical fluid [4] extraction) are used for this purpose.

In principle, accelerated solvent extraction (ASE) is an extraction process taking place in the solid / liquid phase system and performed at an increased temperature (50-200 °C), increased pressure (5-20 MPa) and within a relatively short time interval (max. 20 min).

For ASE, the same solvents as for Soxhlet extraction can be used. Moreover, it is possible to choose even such solvents that are less effective when used in classical techniques. This is due to specially enhanced extraction kinetics of the extraction process in ASE. Very advantageous is the fact that extraction by ASE can be performed under conditions of liquid phase. This allows one to use even mixed solvents, as there is no risk of distilling one component separately.

Experimental

The samples of propellant used for these experiments contained nitrocellulose, diphenylamine or centralite I as stabiliser, nitrotoluene, nitroglycerine and nitroguanidine as energetic compounds, and phthalates as plasticizers.

Each sample of smokeless powder and propellants (about 5 g) was burnt on sand alone. Before combustion the sand was washed with water eight times and then dried in an oven (150 °C) for 8 hours. The sample of sand (about 50 g) was extracted with 50 ml solvent in ultrasonic bath for 20 minutes, filtered and most of the solvent was evaporated: residual volume 1 ml.

Also accelerated solvent extraction was used as a comparative extraction technique. After pre-treatment, the weighted amount of sample was placed into extraction cell with glass wool on the bottom. Another portion of glass wool was laid on the surface of the sample, and the remaining volume of the cell was filled up with glass balls. After inserting the prepared cell into extractor heating oven, the desired value of both temperature and pressure were adjusted to fit the

extraction solvent chosen.

Two extraction steps were performed when the extract was entrapped into the same collecting vessel. The conditions of extraction were as follows: about 15 g sand extracted at the temperature of 110 °C and pressure 10 MPa for 2×10 min. Acetonitrile was used as solvent for both extraction methods.

In the next experiments propellants were burnt on a bowl without sand. A rest of propellant was washed down with 20 ml acetonitrile. The extracts were concentrated by evaporation to a volume of 1ml and analysed.

The extracts obtained were analysed using the gas chromatograph GC 17A coupled with mass spectrometry detector QP 5050A (EI, NCI, both Shimadzu) and GC/MS solution data system (Shimadzu). Helium (grade 5.0, Linde) was used as carrier gas. Separations were performed on a 30 m × 250 μm i.d. capillary column coated with a 0.25 μm film of polymethylsiloxane (DB-5 MS). Split injection 1:10 was used. The column oven was isothermally maintained at 45 °C for 5 minutes and then the temperature was increased at the rate of 20 °C min^{-1} to 280 °C which was kept for 5 min. The temperature of injector was 220 °C and that of interface was 230 °C. The identification of compounds was based on the comparison of their mass spectrum with the spectrum in the library (NIST 62 and NIST 12, Shimadzu).

Results and Discussion

The propellants, which contained nitrocellulose, diphenylamine, centralite, nitrotoluene, nitroglycerine, nitroguanidine and phthalates, were burnt on clean sand. Samples of sand were extracted with acetonitrile and were analysed by means of gas chromatography with mass detector. Mass spectra of the peaks were compared with library. Some of the peaks were identified, but others were not identified with the library. We will try to identify these peaks and interpret their mass spectrum. Better extraction efficiency results from our experiments for accelerated solvent extraction than ultrasonic extraction. More peaks were found in the extract from accelerated solvent extraction, but unfortunately these additional peaks were not identified. Diphenylamine and dibutyl phthalate were found there. These compounds come from original propellants. *N,N*-Diethyl-3-methyl-aminobenzene was identified, which can be a degradation product of diphenylamine. These compounds were found in both extracts (accelerated solvent extraction and ultrasonic extraction). One of the chromatograms is shown in Fig. 1. Aliphatic hydrocarbons (undecane, tridecane and hexadecane), benzene and phthalates were identified in extracts from accelerated solvent extraction.

Because only few peaks were found, we tried to burn 5 g propellant without sand on a clean tinny bowl. A rest of propellant was washed down with 20 ml acetonitrile. This solution was evaporated to volume 1 ml and analysed. Morecom-

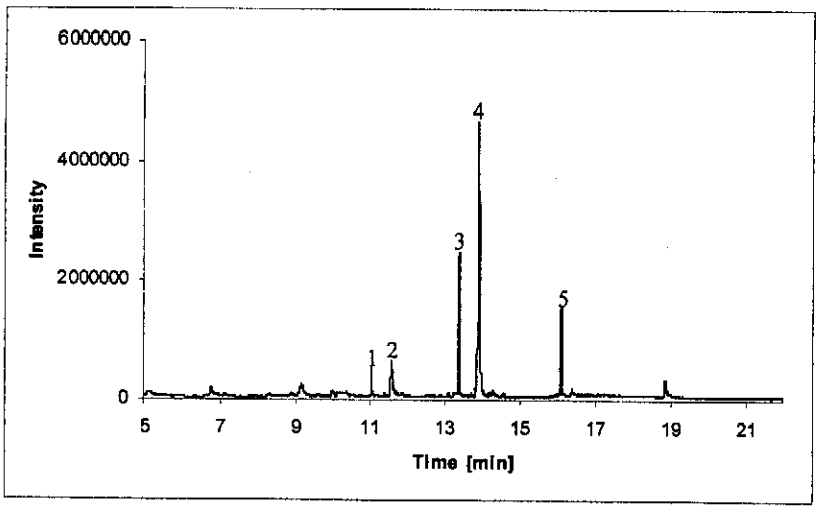

Fig. 1 Chromatogram of extract from sand. Peak 1: 2,3-dinitrotoluene; peak 2: 2,5-dinitrotoluene; peak 3: 2,4,6-trinitrotoluene; peak 4: toluene and peak 5: dioctyl phthalate

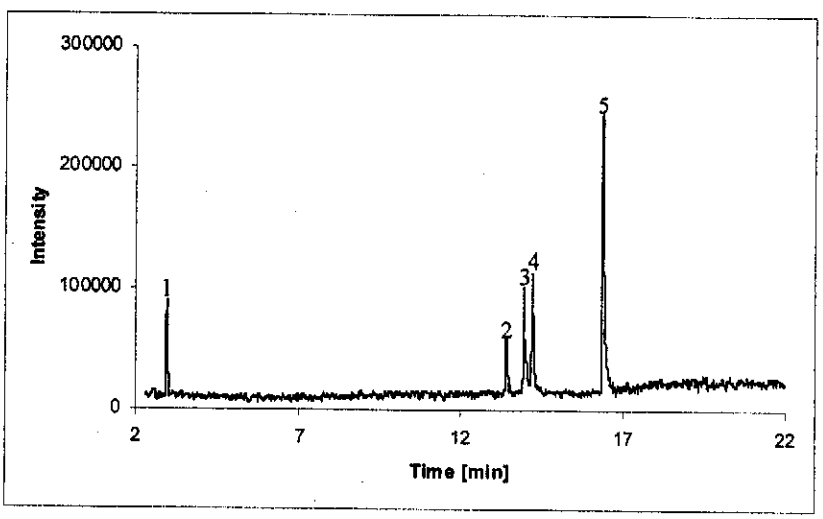

Fig. 2 Chromatogram of acetonitrile extract from tinny bowl. Peak 1: benzene; peak 2: 2,3-dinitrotoluene; peak 3: 2,5-dinitrotoluene; peak 4: diethyl phthalate and peak 5: dibutyl phthalate

pounds were identified in this solution. Diphenylamine, centralite I, phthalates and 2,4,6-trinitrotoluene come from original propellants. 1,3- and 1,4- dinitro-toluene, toluene, benzene, 1-methyl-2-nitrobenzene, 1-methyl-4-nitrobenzene and *N,N*-diethyl-3-methyl-aminobenzene were identified. They can be degradation products

of the compounds which were in original propellants. One of the chromatograms is shown in Fig. 2.

Nitroglycerine and nitroguanidine were not found in any extracts. These compounds are thermally labile and completely burn to carbon dioxide, water and the other gaseous compounds.

Conclusion

The experiments confirmed the fact that accelerated solvent extraction is better than ultrasonic extraction. The propellants almost completely burn to carbon dioxide, water and other gaseous compounds. We achieved the best results after combustion of propellants on a clean tinny bowl.

Acknowledgements

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