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The Qualitative Analysis of the Selected Explosives using Thin-Layer Chromatography

T. Lutonská[*], Z. Kobliha and Z. Skaličan

NBC Defence Institute, University of Defence, Brno, Czech Republic

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Abstract:

A simple, economical and relatively quick method of thin-layer chromatography (TLC) has been applied to analyse four frequently used explosives, TNT, RDX, HMX and Tetryl that are a common part of significant military, industrial and improvised explosives. Silicon dioxide is proven to separate individual explosives at a stationary phase. Out of 38 tested, three types of two-component mobile phases consisting of petroleum ether and acetone in the ratio of 2:1 or 7:3 of a volume and hexane and acetone in the ratio of 2:1 of a volume are recommended. To detect explosives, the UV radiation with the wavelength of 254 nm is proposed.

Keywords:

TLC, Explosives, TNT, RDX, HMX, Tetryl

1. Introduction

Explosives are condensed substances or mixtures able to undergo extremely quick exothermic reactions connected to the expansion of gases into huge volumes – explosion [1]. The oldest known explosive is gunpowder used from the 9th up to the 19th century. Afterwards, picric acid (2,4,6-trinitrophenol) was brought to the fore competing with trinitrotoluene (TNT), which was firstly used to fill bullets in Prussia in 1902. The next most commonly used component of explosives was ammonium nitrate followed by Pentrite (PETN), Hexogen (RDX), Octogen (HMX) and Tetryl [2].

In practice, the mixtures of these essential and chemically homogeneous substances have been commonly used up to now. The mixtures of TNT and RDX are known as Composition B. The mixtures of TNT and HMX are known as Octol. TNT and Tetryl in the mixtures of so-called Tetrytol were used among sappers [2]. From the chemical point of view, RDX, HMX and Tetryl belong into the group of so-called nitroamines, i.e.

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[*] *Corresponding author: NBC Defence Institute, University of Defence, Víta Nejedlého, CZ-682 01 Vyškov, Czech Republic, phone: +420 737 857 784, E-mail: terezalutonska@seznam.cz*

compounds derived from nitric acid alternatively its amide (nitroamide) and TNT belongs into the group of nitro-aromatic compounds. The basic properties of explosives, widely used in the Army of the Czech Republic, are shown in Table 1.

Tab. 1 The basic properties of the studied explosives [1, 3, 4, 5]

Explosive	**TNT**	**RDX**	**HMX**	**Tetryl**
Molecular formula	$C_7H_5N_3O_6$	$C_3H_6N_6O_8$	$C_4H_8N_8O_8$	$C_7H_5N_5O_8$
Density (g/cm^3)	1.65	1.83	1.96 (β)	1.73
Melting point (°C)	80.2 (α) and 75÷77 (technical)	204	276÷280	129.5
Boiling point (°C)	210 (1333.2 Pa)	*	*	162 decomposition 187 explosion
Explosive velocity (km/s)	6.94 for 1.64 g/cm^3	8.64 for 1.77 g/cm^3	9.12 for 1.9 g/cm^3	7.79 for 1.73 g/cm^3
Detonation pressure (GPa)	18.9	33.8	39.3	26.3
Oxygen balance (%)	–74	–22	–22	–47
Gas volume (dm^3/kg)	567	756	756	604
Explosion temperature (°C) [13]	295	229	335	195
Beginning of thermal decomposition (°C)	250	214	265	100
Activation energy (kJ/mol) [13]	143.105	197.115	220.644	*
Explosion energy Q_{max} (kJ/kg)	4230	5540	5670	5950
Molar mass (g/mol)	227.15	222.6	296.16	287.15

The deployment of military specialists in missions abroad and the need to react to a possible terrorist threat using explosives have introduced the demand for a rapid and simple method to detect explosives. Due to its simplicity, low material demands and relatively quick analysis, the method of thin-layer chromatography (TLC) is seen as suitable for the needs of chemical inspection of explosives by specialists of the Army of the Czech Republic.

Essentially, thin-layer chromatography is based on the division of analysed substances according to various adsorptions of substances within a large specific surface [6]. The results of qualitative analysis or qualitative evaluation of the position of the spots of substances in chromatogram are expressed by retardation factor (R_f), which is given by the ratio of the distance of the spot centre to the distance from a base line to a solvent front. A given substance in given conditions is characterised by R_f factor [7].

The aim of the work is to verify and propose a suitable stationary and mobile phase to separate the selected explosives (TNT, RDX, HMX and Tetryl), as well as the method to detect them. The applicability of TLC method in the technical equipment of NBC defence of the Army of the Czech Republic is taken into consideration.

2. Experimental Part

2.1 Chemicals and Equipment

All solvents used to prepare mobile phases had the purity for analysis, SigmaAldrich (Table 2). Some mobile phases used in this work, were chosen based on results given in [14]. The standard explosives TNT, RDX, HMX and Tetryl had the purity of at least 99 % and were supplied by the company Explosia plc, Pardubice.

As a stationary phase, TLC plates LuxPlate Si 60 F_{254} with the dimensions of 10×20 cm, Merck, BRD, were used. To apply samples on plates, the automatic sampler ATS 3 was used and to develop plates, a chromatographic chamber (20×10 cm) was used. The Camag TLC Sampler 3 is known as a fully automatic device used in thin-layer chromatography for quantitative, qualitative and preparative sample application. The system is comprised of applicator module with built-in interface, software and a PC, via which the module is programmed. To heat chromatographic plates up, a plate heater was used. The devices Scanner 3 and Visualizer were used to read the values of retardation factors under UV radiation and archive chromatograms. The Camag TLC Scanner 3 is designed for densitometric measurement of thin-layer chromatograms and other objects up to 200×200mm in size. All used devices are produced by company Camag, Switzerland. To evaluate chromatographic data, Camag TLC software (CATS for short) version 4.06 was used.

2.2 Procedures

The solutions of explosive standards with the concentration of 1µg/µl were prepared via solving weighed amounts in acetone. Glass chromatographic plates were washed using methanol and dried in a drying chamber at the temperature of 120°C for 20 minutes before being used. Camag TLC was used for the analysis. 38 mobile phases were verified item-by-item. The composition and the ratio of the components in the volume is presented in Table 2. The distance between spots was 10 mm. The development of the chromatographic plates was performed at the normal pressure at the temperature of 23°C in the development chamber covered with the lid. The volume of the mobile phase was approximately 20 ml. After the evaporation of the mobile phase, the values of retardation factors R_f were read using TLC Scanner and the chromatograms were archived (Camag visualizer).

3. Results and Discussion

After the separation of explosives on a thin layer, the mobile systems presented in the literature and proposed by us were verified. Retardation factors values of the sets of the studied explosives (TNT, RDX, HMX, and Tetryl) for separate solutions were read after having been divided in the solid phase of silicon dioxide doped by UV detector and presented in Table 3. The mixtures of solvents with the numbers **7** (hexane:chloroform, in the ratio 4:1 of the volume), the mobile phases **18** (petroleum ether:acetone, 1:1.8), **24** (petroleum ether:chloroform, 7:3) and **35** (chloroform:methanol, 4:3) can be determined as completely unsatisfactory for the division of the four studied explosives (Table 3). The inability to separate individual explosives is illustrated by the retardation factors with the values of approximately 0 or 1.

Tab. 2 Used mobile phases

Mobile phase (ratio)	**No**	**Ref**	**Mobile phase** (ratio)	**No**	**Ref**
Hexane:ether (1:1)	**1**	14	Petroleum ether:acetone (7:3)	**20**	8
Chloroform:acetone (1:1)	**2**		Petroleum ether:ether (3:2)	**21**	8
Petroleum ether:acetone (3:1)	**3**	14	Petroleum ether:benzene (1:4)	**22**	
Petroleum ether:acetone (2:1)	**4**		Petroleum ether:ethyl acetate (4:1)	**23**	8
Benzene	**5**	14	Petroleum ether:chloroform (7:3)	**24**	
Petroleum ether:acetone (4:1)	**6**	14	Dichloromethane	**25**	8
Hexane:chloroform (4:1)	**7**	6	Cyclohexane:acetone (3:2)	**26**	8
Hexane:acetone (3:1)	**8**	6	Petroleum ether:dichlorometh ane (3:2)	**27**	
Hexane:chloroform (1:2)	**9**	6	Petroleum ether:ethyl acetate (1:1)	**28**	8
Hexane:acetone (2:1)	**10**	6	Petroleum ether:dichlorometh ane (1:4)	**29**	
Toluene:ethyl acetate (10:1)	**11**	6	Petroleum ether:ether (1:1)	**30**	
Chloroform	**12**	6	CCl_4:chloroform:acetonitrile (5:3:1)	**31**	11
Toluene	**13**	12	Chloroform:CCl_4 (7:5)	**32**	11
Petroleum ether:ethyl acetate (3:1)	**14**		Diisopropyl ether:ethyl acetate:hexane (2:1:1)	**33**	11
Petroleum ether:ethyl acetate (8:1)	**15**		Diisopropyl ether:ethyl acetate:hexane (2:1:2)	**34**	11
1,2-dichloroethane:methanol (2:1)	**16**	9	Chloroform:methanol (4:3)	**35**	11
Chloroform:acetone:methan ol (4:1:1)	**17**	9	CCl_4:acetonitrile (2:1)	**36**	11
Petroleum ether:acetone (1:1.8)	**18**	10	Hexane:chloroform (2:1)	**37**	
Petroleum ether:dichloromet hane (2:3)	**19**	8	Hexane:chloroform (1:1)	**38**	

On the other hand, the mobile phases **3** (petroleum ether:acetone, in the ratio 3:1 of the volume), **4** (petroleum ether:acetone, 2:1), **6** (petroleum ether:acetone, 4:1),

8 (hexane:acetone, 3:1), the mobile phases **10** to **12**, the phases **19** (petroleum ether:dichloromethane, 2:3), **20** (petroleum ether:acetone, 7:3), **26** (cyclohexane:acetone, 3:2) and three-component mobile phase **31** (CCl_4:chloroform:acetonitrile, 5:3:1) satisfy the criteria to divide all four explosives. As observed in Table 3, the values of these retardation factors differ in at least 0.1 and none of the studied explosives stays at the start after the development or migrates towards with the front of the mobile phase.

Tab. 3 Values of measured retardation factors

Mobile phase	**Explosive**				**Mobile phase**	**Explosive**			
	Values R_f					Values R_f			
	TNT	RDX	HMX	Tetryl		TNT	RDX	HMX	Tetryl
1	0.74	0.00	0.00	0.18	**20**	0.58	0.30	0.19	0.42
2	0.90	0.71	0.55	0.88	**21**	0.79	0.02	0.00	0.16
3	0.41	0.11	0.04	0.20	**22**	0.69	0.07	0.00	0.03
4	0.64	0.36	0.24	0.47	**23**	0.63	0.02	0.00	0.06
5	0.75	0.10	0.00	0.46	**24**	0.07	0.00	0.00	0.03
6	0.41	0.12	0.04	0.21	**25**	0.84	0.36	0.00	0.67
7	0.04	0.00	0.00	0.00	**26**	0.55	0.34	0.29	0.41
8	0.47	0.17	0.10	0.26	**27**	0.24	0.02	0.00	0.07
9	0.27	0.04	0.03	0.09	**28**	0.95	0.35	0.34	0.91
10	0.53	0.30	0.20	0.39	**29**	0.71	0.16	0.00	0.44
11	0.84	0.12	0.06	0.58	**30**	0.90	0.03	0.00	0.24
12	0.56	0.10	0.03	0.24	**31**	0.71	0.30	0.09	0.50
13	0.70	0.07	0.10	0.42	**32**	0.30	0.05	0.00	0.10
14	0.92	0.17	0.13	0.51	**33**	0.92	0.72	0.65	0.91
15	0.61	0.04	0.02	0.17	**34**	0.89	0.50	0.40	0.81
16	0.97	0.85	0.78	0.97	**35**	0.95	0.96	0.96	0.96
17	0.96	0.85	0.72	0.96	**36**	0.78	0.66	0.56	0.77
18	0.99	0.95	0.96	0.98	**37**	0.12	0.03	0.03	0.04
19	0.55	0.12	0.02	0.30	**38**	0.17	0.03	0.02	0.05

Sets suitable to divide chemically similar explosives out of the studied sets have also been verified. The mobile phases suitable for the division of the mixtures of two explosives are presented in Table 4. The phases with the values of the retardation factors differing from the values in at least 0.1 were dealt with. To divide the mixtures RDX and HMX, the mobile phase **31** (CCl_4:chloroform:acetonitrile, in the ratio of 5:3:1) is seen as the most suitable one. The values of the retardation factors used for the given phase differ in 0.2, which states the biggest difference in comparison with other values of retardation factors in comparison with other mobile phases. The mobile phase **2** (chloroform:acetone, 1:1) is the next suitable one for the division of the mixture. The difference in the values of the retardation factors is 0.16.

The mobile phases **7** (hexane:chloroform, 1:2), **18** (petroleum ether:acetone, 1:1.8), **24** (petroleum ether:chloroform, 7:4) and the mobile phase **35** (chloroform:methanol, 4:3) are not suitable for the separation of the mixture of TNT and RDX. The difference in the values of the retardation factors while using these mobile phases is lower than 0.09.

The mobile phases suitable for the division of the mixtures of TNT and Tetryl, RDX and Tetryl and HMX and Tetryl are presented in Table 4.

Tab. 4 Mobile phases suitable for division of mixtures of similar types of explosives

Division of mixtures	Mobile phase number
RDX and HMX	2,4,8,10,20,26,31,33,34,36
TNT and RDX	3,4,5,6,8,10,11,12,13,19,20,25,26,29,31,34,36
TNT and Tetryl	3,4,5,6,8,10,11,12,13,15,19,20,21,25,26,29,31,32
RDX and Tetryl	2,3,4,5,6,8,10,11,12,13,14,15,19,20,21,25,26,29,30,31,34,36
HMX and Tetryl	2,3,4,5,6,8,10,11,12,13,14,15,19,20,21,25,26,29,30,31,34,36

4. Conclusion

According to the values of the retardation factors, the ability to separate the mixtures of TNT, RDX, HMX and Tetryl in the stationary phase formed by silica-gel with a UV detector and the corresponding mobile phase were evaluated. Concerning the need to divide and subsequently to detect separate explosives using UV radiation, three two-component mobile phases were proposed, namely the mixtures of petroleum ether:acetone (in the ratio of 2:1 of the volume), hexane:acetone (2:1) and petroleum ether:acetone (7:3).

The suitable sets to divide the mixtures formed by a pair of explosives, namely RDX- HMX, TNT-RDX, TNT-Tetryl, RDX-Tetryl and HMX-Tetryl, were recommended.

Concerning the needs of the chemical defence of the Army of the Czech Republic in stationary and mainly mobile means, the results prove that thin-layer chromatography is a suitable method for a very rapid and relatively accurate qualitative analysis of explosives. The current apparatus, the availability of the laboratory equipment, the separation plates and the chemicals in the mobile field containerised chemical laboratory

AL-2/ch of the Army of the Czech Republic allow the immediate use of the TLC method to analyse the explosives TNT, RDX, HMX and Tetryl.

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