Def Sci J, Vol 32, No 2, April 1982, pp 151–155

Analysis of Explosive Mixtures by Thin Layer Chromatography

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Received 25 May 1980

Abstract. Thin layer chromatographic separation of some important military explosive mixtures containing nitro and nitramino compounds have been carried out with new developing systems.

1. Introduction

Nitro as well as nitramino compounds form major component of the explosives employed for filling warheads and shells. It is observed that explosive filling in shells and ammunitions etc. deteriorate on long storage under adverse climatic condition. These deteriorated products usually catalyse further decomposition, which effect the stability and performance of explosives. Therefore it is very essential to analyse the explosive filling from time to time in order to have a check on its deterioration under adverse condition of temperature and humidity. In most of the field areas, normal laboratory facilities do not exist and thus some simple and convenient method is required to check the stability of explosives. Considering the safety aspect such analyses are essential to minimise the explosive hazard. Although some work on identification of explosive mixture have been reported[1–5], yet many explosives and their mixtures require further study. The present work aims to find out new developing systems which could provide an efficient separation of components of explosive mixtures.

2. Materials and Methods

(a) *Samples of various explosive mixtures*

p-mono nitrotoluene (MNT), 2,4, dinitrotoluene (DNT), 2,4,6 trinitrotoluene (TNT), 1,3 dinitrobenzene (DNB), 1,3,5 trinitrobenzene (TNB), trinitro phenylmethyl-N-nitramine (CE), 2,4,6 trinitrophenol (PA), 2,2', 4,4', 6,6', hexanitrostilbene (HNS), 2,2′, 4,4′, 6,6′, hexanitrodibenzyl (HNDB), Hexa hydro-1,3,5 trinitro-s-triazine (RDX), and Octa hydro-1,3,5,7 tetranitro-s-tetrazine (HMX).

(b) *Developing solvents*

Petroleum ether, Benzene, Cyclohexane, Dichloromethane, Chloroform, Ether, Ethyl acetate, and Acetone.

(c) *Visulizers*

Ethylene diamine, Iodine chamber and Greiss reagent.

(d) *Adsorbents*

Silica gel G, Oxalic acid and Zinc powder.

3. Procedure

(a) *Preparation of layers*

Glass plates of 5 × 20 cms were well cleaned with chromic acid, washed with water several times and dried. 25 g silica gel G was mixed with 50 ml of distilled water by shaking. This slurry was then spreaded over plates with the help of spreader within 3 minutes keeping layer thickness 0.25 mm. The plates were left for over night for air drying. On the next day, the plates were kept in oven for 1.5 hrs at 110°C for activation. The plates were stored in a closed chamber to avoid any damage to layers due to exposure to dust or humid atmosphere.

(b) *Preparation of samples*

(*i*) Different combinations of explosive mixture were formed, which were dissolved in non polar and low boiling solvent as far as possible.

(*ii*) Pure compounds were also dissolved in the same solvent for reference sake.

4. Spotting

With the help of Hamilton micro syringe, fine spot of sample and pure compounds were applied to the starting line on the silica gel layer at a height of 1.5 cm from the base.

5. Development

The plates were air dried and put into the tank filled with developing solvent upto the 0.5 cm to 1 cm height. Prior to putting the plates, the atmosphere in the tank was saturated with the developing solvent by wrapping it from inside with filter paper sheet. The tank was closed with lid and developing solvent was allowed to rise in the plates upto 10 cms height from the starting line.

6. Detection

After the development, the plates were removed and dried to make them free from developing solvent. Visulising agent was then sprayed over them which produce the coloured spots.

7. Identification

The coloured spots were compared with the reference coloured spots which helped to identify the component of mixture. Distance of coloured spots and distance of solvent from starting point were measured and *Rf* values for each component in the mixture were found out (Table 1).

Table 1. *hRf* values of the components of explosive mixtures.

Mixture No.	Components of mixture	*hRf* values of components	Colour of spots	Developing solvent in ratios (v/v)	Visualizer
1	DNT TNT	53 45	Blue Brown	Pet ether/dichloromethane (40:60)	Ethylene diamine
2	CE TNT	21 46	Orange Brown	Pet ether/dichloromethane (40:60)	do
3	CE TNT	34 53	Orange Brown	Benzene pure	do
4	CE TNT DNT	20 45 54	Orange Brown Blue	Pet ether/dichloromethane (40:60)	do
5	DNB TNT	52 46	Violet Brown	do	do
6	PA TNT	30 52	Yellow Brown	do	do
7	PA TNT	27 49	Yellow Brown	Pet ether/acetone (70:30)	do
8	PA TNT	39 65	Yellow Brown	Pet ether/ether (60:40)	do
9	PA DNB	33 63	Yellow Violet	Pet ether/dichloromethane (60:40)	do
10	PA DNB	41 61	Yellow Violet	Pet ether/benzene (20:80)	do
11	PA DNB TNT	30 60 52	Yellow Violet Brown	Pet ether/dichloromethane (40:60)	do
12	PA DNB TNT	38 42 55	Yellow Violet Brown	Pet ether/ethylacetate (80:20)	do

(*Table contd.*)

Table 1. (*Contd.*)

Mixture No.	Components of mixture	*hRf* vlaues of components	Colour of spots	Developing solvent in ratios (v/v)	Visualizer
13	DNB	52	Violet	Pet ether/dichloromethane (40:60)	Ethylene diamine
	TNB	34	Red		
14	DNB	62	Violet	Pet ether/chloroform (30:70)	do
	TNB	50	Red		
15	TNT	45	Brown	Pet ether/dichloromethane (40:60)	do
	TNB	34	Red		
16	TNT	68	Brown	do (20:80)	do
	TNB	60	Red		
17	TNT	68	Brown	Pet ether/ether (50:50)	do
	TNB	59	Red		
18	CE	20	Orange	Pet ether/dichloromethane (40:60)	do
	TNT	45	Brown		
	DNT	55	Blue		
	TNB	35	Red		
	DNB	52	Violet		
19	MNT	72	Yellow	do	Iodine
	DNT	55	Yellow		
	TNT	45	Yellow		
20	HNS	28	Pink	Dichloromethane (pure)	Ethylene diamine
	TNT	45	Brown		
21	HNS	28	Pink	do	do
	HNDB	42	Pinkish Brown		
22	HNS	28	Pink	do	do
	HNDB	42	Pinkish Brown		
	TNT	45	Brown		
23	RDX	52	Pink	Pet ether/ethylacetate (50:50)	Greiss reagent
	HMX	47	Pink turns to violet		
24	RDX	57	Pink	Cyclohexane/acetone (60:40)	do
	HMX	43	Pink turns to violet		

8. Results and Discussion

The *hRf* values for each component of the various mixtures are given in Table 1. It is observed that the resolution of the components is mainly governed by the type of developing solvent system as well as its degree of polarity keeping the other factors same. It is evident from Table 1 (examples 11 & 12) that the solvent system has profound effect on the mobility of compound on TLC plate. The *hRf* value of DNB is greater than TNT in petroleum ether/dichloromethane (40:60) system but it becomes less than TNT in petroleum ether/ethyl acetate (80:20) system. It may also be mentioned that out of all solvent system employed in the analysis, the petroleum ether/dichloromethane has given better separation of the components of explosive mixtures.

The higher *hRf* values of TNT than TNB (Table 1, example 15 to 18) in different solvent systems is mainly attributed to the C-methyl group, which reduces the adsorption capability and thereby increases the *Rf* value. It is further observed that the adsorption increases with increase of nitro group in the ring, which lowers the *Rf* value as is evident in (Table 1, examples 1, 13, 14 & 19) in which *Rf* values of DNT > TNT, DNB > TNB & MNT > DNT > TNT.

When picric acid was present in the mixtures (Table 1, example 6 to 12) the difficulty in separation of the componsnt was noticed because it exhibited tailing during the movement of the spot. To get sharp spot, the plates were further impregnated with oxalic acid by eluting it in 3% alcoholic solution of oxalic acid. The plates were dried and used as usual for mixtures containing picric acid. The plates were prepared by incorporating 10% zinc powder to the silica gel to identify the spots with Greiss reagents for separation of RDX and HMX.

Data in the table helps in finding out the impurities like MNT, DNT present in the TNT, because in nitration some impurities are always present which can be easily detected by TLC technique. Moreover this data is able to assist in detecting the degradation products produced during the storage of explosive under adverse field condition. The evaluation by this technique can guide the user to assess the safety of handling explosives.

In the synthesis of HNS from TNT, hexanitrodibenzyl is generally formed depending upon the reaction condition and concentration of sodium hypochlorite used and the detection of hexanitrodibenzyl in HNS becomes easy by TLC technique. This method also finds application in elucidating mechanism during the nitration of aromatic compounds by isolating the intermediates and finding out with TLC the nature of isolated products.

Acknowledgement

The authors are thankful to Col V. V. K. Rao, Director, Terminal Ballistics Research Laboratory, Chandigarh for his encouragement and keen interest in the work.

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