

## Note

### Two-dimensional thin-layer chromatography for the separation and identification of nitro derivatives in explosives

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The annual consumption of explosives in Italy (averaging not less than 50 000 tons per year) indicates their economic and commercial importance. The specific effects desired as well as police regulations regarding the handling, transport and use of explosives, necessitate a preliminary method of characterization. Subsequent accurate detection of the components could then be undertaken by thin-layer chromatography (TLC) or high-performance liquid chromatography (HPLC), coupled with mass spectrometry<sup>1</sup>.

The present report considers the active organic components of bursting explosives. There is no lack of previous investigations into the subject. Nevertheless, those studies dealt with separation within the limits of each individual class of explosives, without trying to characterize, even to a first approximation, the various components of a mixture. Thus, descriptions have been given regarding the separation of nitroesters<sup>2-4</sup>, nitroarenes<sup>5-7</sup>, nitroamines<sup>8</sup>, aromatic nitro compounds in general—mixtures of nitroarenes, nitrophenols and nitroanilines<sup>9</sup>, mixtures of nitroesters and nitroarenes<sup>10</sup> and of nitroesters [nitroglycerine (NGL), ethylene glycol dinitrate], nitroamines (nitroguanidine) and nitroarenes [*p*-nitro-, 2,4-dinitro- and 2,4,6-trinitrotoluene (MNT, DNT, TNT)], but only with regard to the compounds specified in brackets<sup>11</sup>. More comprehensive investigations took into account various and significant components, but some did not achieve satisfactory separations<sup>12,13</sup>, unless several solvent systems were employed<sup>14,15</sup>.

We thought it useful to develop, for a series of components chosen according to the criterion of the highest commercial and military significance, a two-dimensional TLC separation by selecting those eluent mixtures which allowed, on the whole, the best detection. Some eluent mixtures were also found adaptable to the separation of particular components, thus being suitable for the resolution of some typical formulations.

## EXPERIMENTAL

*Reagents and products*

Solvents and reagents utilized were of RPE-ACS grade or the equivalent. As chromatographic standards, either analytical grade products were used where available, or commercial products recrystallized from suitable solvents<sup>16</sup>. The latter technique was applied for purification of DNT, TNT, HMX, RDX, PETN and TNMA (see Table I for meaning of abbreviations). NGL and NDGL were obtained as a solution of approximately known titre by Soxhlet extraction with diethyl ether from unstabilized double-base propellants.

*Analytical procedure*

In preliminary tests, 10  $\mu$ l of a 1% solution of each product in ethanol-acetone (1:1, v/v), or in acetone (RDX, HMX), were chromatographed, under the optimum conditions described in the literature<sup>17</sup>, on silica gel 60 plates, 20  $\times$  20 cm (Merck, Cat. No. 5721), by utilizing either binary mixtures (light petroleum-dichloromethane, light petroleum-acetone, light petroleum-ethyl acetate, chloroform-acetone) or ternary ones (light petroleum-benzene-acetone), at various ratios. After conditioning the plates to 100°C for 10 min, detection was carried out by means of a freshly prepared solution of 1% diphenylamine in ethanol-acetone (1:1). The appearance of spots, essentially coloured and/or fluorescent to UV light, was immediate; those corresponding to HMX and RDX even became directly visible after 24 h.

For developing the two-dimensional chromatogram, a suitable mixture of all

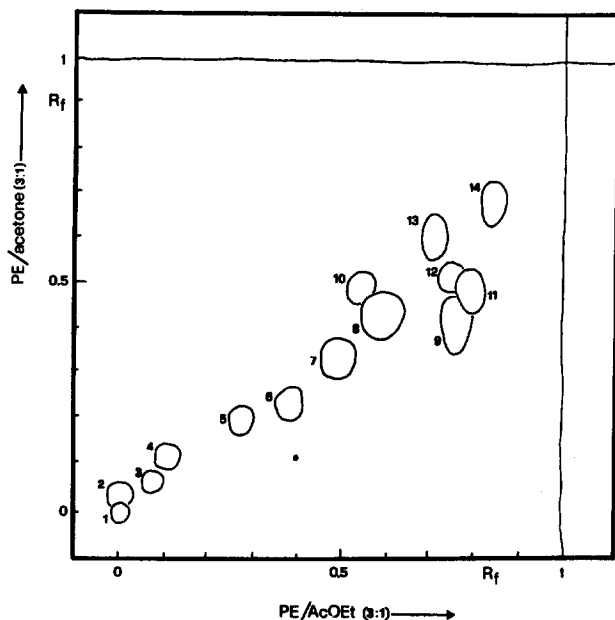


Fig. 1. Two-dimensional chromatogram on silica gel obtained for a mixture of the components listed in Table I by eluting successively with light petroleum-acetone (3:1) and light petroleum-ethyl acetate (3:1).

TABLE I

## SPOT IDENTIFICATION FOR THE CHROMATOGRAM IN FIG. 1

Abbreviations for colours: y = yellow, gr = grey, b = blue, lb = light blue, br = brown, or = orange, v = violet, UV = visible in ultraviolet region.

No.	Compound	R <sub>F</sub>		Colour with diphenylamine
		Ethent A	Ethent B	
1	2,4,6-Trinitrophenol (picric acid)	0	0	y (b after 24 h)
2	2,4-Dinitrophenol	0.04	0	y, lemon
3	Cyclotetramethylene-tetranitroamine (HMX)	0.07	0.07	gr-lb (after exposure to 100°C for 1/2 h), UV (v)
4	Cyclotrimethylene-trinitroamine (RDX)	0.13	0.11	gr-lb (after exposure to 100°C for 1/2 h), UV (v)
5	<i>p</i> -Nitrotoluene ( <i>p</i> -MNT)	0.20	0.27	y, light
6	<i>N</i> -Methyl- <i>N</i> ,2,4,6-tetranitroaniline (Tetryl or TNMA)	0.24	0.38	y-br
7	Nitroglycol (NDGL)	0.33	0.50	gr, light
8	Nitroglycerine (NGL)	0.43	0.60	gr (after exposure to 100°C for 1/2 h), UV (green)
9	Tetranitropentaerythritol (PETN)	0.42	0.76	gr, light (after exposure to 100°C for 1/2 h), UV (v)
10	2,4-Dinitrotoluene (DNT)	0.49	0.55	y, UV (br)
11	2,4,6-Trinitrotoluene (TNT)	0.49	0.80	or
12	<i>o</i> -Nitrotoluene ( <i>o</i> -MNT)	0.51	0.76	y, light; UV (br)
13	$\alpha$ -Nitronaphthalene	0.60	0.72	y, straw-coloured
14	Diphenylamine	0.68	0.85	UV (v)

the products was prepared, in the same amounts as in the preliminary test; elution was carried out with light petroleum (b.p. 40–70°C)–acetone (3:1, v/v; solvent system A) in one direction and with light petroleum (b.p. 40–70°C)–ethyl acetate (3:1, v/v; solvent system B) in the other direction.

## RESULTS AND DISCUSSION

Fig. 1 gives a schematic representation of the two-dimensional chromatogram obtained, under the described conditions, for the mixture of the various components. A sufficiently reliable identification of the chromatographed compounds was obtained, based not only on their respective  $R_F$  values, but also on the specific colour of the spots (Table I). The ordering of the components is basically according to their decreasing polarity, starting from picric acid which remains at the start.

Fig. 2 shows the chromatograms obtained for two typical formulations based on TNT–RDX–HMX and MNT–DNT–TNT with light petroleum–acetone (2:1) and light petroleum–ethyl acetate (8:1). By varying the elutotropic properties of the basic mixtures, optimum separations can be obtained in specific cases: thus, a slight increase in polarity of the first light petroleum mixture led to a sharper separation between RDX and HMX, whereas a decrease in the polarity of the second allowed a better resolution between *o*-MNT and TNT.

The methods described above are currently employed by us for preliminary forensic investigations, giving satisfactory results in the detection of aromatic and aliphatic nitro derivatives (nitroglycerine, nitrodiglycol, etc.; mono-, di- and trinitro-

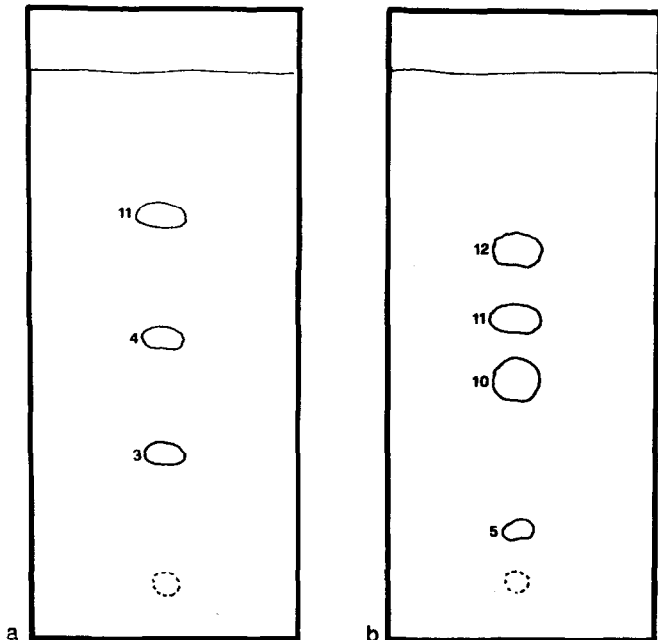


Fig. 2. Silica gel chromatograms of (a) TNT–RDX–HMX mixture eluted with light petroleum–acetone (2:1), (b) *p*-MNT, TNT, DNT, *o*-MNT mixture eluted with light petroleum–ethyl acetate (8:1).

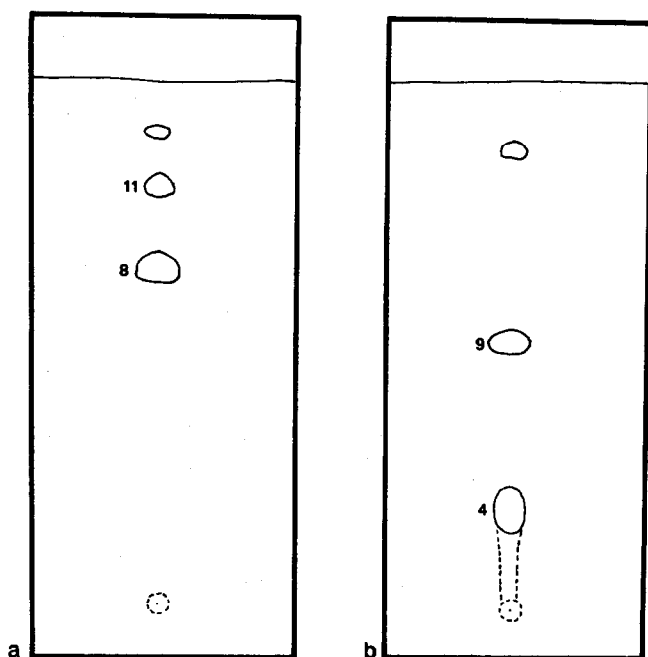


Fig. 3. Silica gel chromatogram of two commercial mixtures: (a) TNT, NGL and vaseline oil eluted with light petroleum-ethyl acetate (3:1); (b) RDX, PETN and vaseline oil eluted with light petroleum-acetone (3:1).

toluene, nitronaphthalene, etc.), as well as heterocyclic ones (cyclotrimethylene-trinitroamine and cyclotetramethylene-tetranitroamine, etc.). For example, Fig. 3 shows the chromatograms obtained from two commercial products (acetone extracts) in which also paraffin-based plasticizing agents appear ( $R_F = 0.88$ ).

#### REFERENCES

- 1 J. Yinon and D.-G. Hwang, *J. Chromatogr.*, 268 (1983) 45.
- 2 D. B. Parihar, S. P. Sharma and K. K. Verma, *J. Chromatogr.*, 31 (1967) 551.
- 3 R. W. Barnes, *J. Chromatogr.*, 31 (1967) 606.
- 4 J. Vich, J. Churaček and V. Kučera, *Explosivstoffe*, 18 (1970) 42.
- 5 L. H. Klemm, D. S. W. Chia and H. P. Kelly, *J. Chromatogr.*, 150 (1978) 12.
- 6 J. C. Hoffsommer, *J. Chromatogr.*, 51 (1970) 243.
- 7 M. Bieganowska and E. Soczewiński, *J. Chromatogr.*, 205 (1981) 451.
- 8 E. Sthal, *Thin-layer Chromatography*, Academic Press, New York, 1965, pp. 368-369.
- 9 S. K. Yasuda, *J. Chromatogr.*, 50 (1970) 453.
- 10 G. F. Macke, *J. Chromatogr.*, 38 (1968) 47.
- 11 A. W. Archer, *J. Chromatogr.*, 108 (1975) 401.
- 12 J. Hansson, *Explosivstoffe*, 11 (1963) 73.
- 13 R. Jenkins and H. J. Yallop, *Explosivstoffe*, 18 (1970) 139.
- 14 R. G. Parker, J. M. McOwen and J. A. Cherolis, *J. Forensic Sci.*, 20 (1975) 254.
- 15 J. M. F. Douse, *J. Chromatogr.*, 234 (1983) 415.
- 16 M. Giua, *Lezioni di Esplosivi*, Regia Accademia della Scuola di Applicazione di Artiglieria e Genio, Torino, 1932.
- 17 C. L. Wilson and D. W. Wilson, *Comprehensive Analytical Chemistry*, Vol. IIC, Elsevier, Amsterdam, 1968, pp. 83, 84.