

## Rapid estimation of explosive nitrates

In view of their recent applications, the study of nitrate esters has aroused great interest. Diethyleneglycol dinitrate (DEGN) and nitroglycerine (NG) are being employed in thixotropic liquid propellants useful in missiles, rockets and torpedo propulsion<sup>1-2</sup>. Ethylene glycol dinitrate (EGDN) together with trinitroaniline is used in shock resistant plastic explosives<sup>3</sup>, whereas in conjunction with NG it finds its application in detonatable emulsions<sup>4-6</sup> and high security mine explosives<sup>7-8</sup>. More recently NG has reduced the oxidizer ratio in polyurethane propellants<sup>9</sup>. Pentaerythritol tetranitrate (PETN) in conjunction with polyvinyl chloride is used in explosive compositions suitable for fabrication of high strength weapon cases<sup>10</sup>, and in slurried blasting explosives having flowability down to  $-15^{\circ}$ <sup>11</sup>. It is also employed in malleable<sup>12</sup> and high density explosives required for loading of projectiles<sup>13</sup>. Mannitol hexanitrate (MHN) along with PETN is utilised in delayed action fuses<sup>14</sup>.

The explosive nitrates have been analysed by several chromatographic techniques, e.g. gas chromatography (GC)<sup>15-16</sup>, column chromatography (CC)<sup>17-19</sup>, paper chromatography (PC)<sup>20-21</sup>, and thin layer chromatography (TLC)<sup>22-30</sup>. GC suffers from limitations due to the decomposition of the nitrate esters<sup>15-16</sup>. CC takes a long time and is unsuitable for micro estimations. These compounds being lipophilic tail on paper chromatograms. After separation on silica gel plates, using TLC, such compounds have been estimated spectroscopically<sup>24</sup>, by measurement of spot area<sup>30</sup>, and radio scanning<sup>20</sup> of <sup>14</sup>C-tagged explosive. All the above procedures are inconvenient, time consuming and cannot be adapted to field conditions. In places where normal laboratory facilities are not available it frequently becomes necessary to estimate the explosive content of a variety of compositions.

The present paper describes a quick method of quantitative estimation of DEGN, EGDN, NG, PETN, MHN and SHN (sorbitol hexanitrate) when present as mixtures. It was observed that their resolution was better and sharper on magnesium silicate and alumina plates than on silica gel, employed by other workers. The compounds, after extraction from the plates, were estimated colorimetrically to 2-4  $\mu$ g with Griess-Romijn reagent.

### Experimental

#### Preparation of the compounds

*Mannitol hexanitrate (MHN)*. Mannitol (5 g) was gradually added to fuming nitric acid (sp.gr. 1.51, 25 g), which had been cooled below  $0^{\circ}$ . The temperature was not allowed to rise above  $0^{\circ}$  and the mixture was stirred during the addition. Sulphuric acid (sp.gr. 1.84, 25 g) was slowly added with careful cooling and stirring resulting in MHN as a white precipitate. It was poured over crushed ice, the compound filtered and washed with water. It was crystallised from ethyl alcohol in the form of needles, m.p. 112-113 $^{\circ}$ .

*Pentaerythritol tetranitrate (PETN)*. Pentaerythritol (2 g) was slowly added to nitric acid (96 %, 10 g) kept at 18-23 $^{\circ}$  and continuously stirred. Then the mixture was further stirred for 20 min, then poured over ice. The compound was washed with water, dried and crystallised from acetone-ethyl alcohol (1:1) as colourless prisms, m.p. 138-140 $^{\circ}$ .

*Diethylene glycol dinitrate (DEGN)*. Diethylene glycol (5 g) was very cautiously

added over 2 h to an acid mixture (nitric acid–sulphuric acid (7:3) 14 g) kept below 10°. The mixture was stirred and after some time DEGN appeared as an insoluble oil. The reaction was quenched over ice, the compound separated, washed with dilute sodium carbonate, followed with water and dried over anhydrous magnesium sulphate; sp.gr. (21°) 1.3841.

*Nitroglycerine (NG)*. Glycerine (6 g) was slowly added to a mixture of acids (nitric acid–sulphuric acid (7:3) 25.8 g) kept at 20° for one hour. The mixture was shaken by hand. After the reaction the contents of the reaction vessel were poured over crushed ice and the NG repeatedly washed with sodium carbonate and water. It was dried over anhydrous magnesium sulphate, sp.gr. (21°) 1.5932.

*Ethylene glycol dinitrate (EGDN)*. Anhydrous glycol (10 g) was slowly added to mixed acids (58 % H<sub>2</sub>SO<sub>4</sub>, 41 % HNO<sub>3</sub> and 1 % water; 62.5 g) kept at 10–15° for 3 h. The compound appeared as an oily layer which was separated. The oil was washed with dilute sodium carbonate solution, then with a minimum of water and dried. It was a colourless oil, sp.gr. (21°) 1.4901.

*Sorbitol hexanitrate (SHN)*. Sorbitol (5 g) was carefully added to mixed acids (as used for EGDN, 25 g) maintained at 0–2°. After a reaction period of 2 h, the stirred contents were poured over ice. The compound was extracted with ether, washed with water, dried over magnesium sulphate and the solvent removed. SHN was obtained as a syrup.

*Preparation of the plates, their spotting and irrigation.*

All the solvents were dried and freshly distilled. Kodak photographic plates (22 × 22 cm) were used as supports. The ascending irrigation technique was employed, the temperature of irrigation being 23° ± 1°.

The plates were prepared by pouring on to them a homogeneous slurry of the adsorbent in a suitable solvent. The plates were tilted from side to side so that there was an uniform coating. These were left overnight at room temperature and activated at 110° 1 for h before use. Table I gives the details of various adsorbents, solvents etc. Solutions of all the explosives, as well as of their mixtures, were prepared in ethyl alcohol–acetone (1:1). 10 μl of individual solutions containing 2–4 μg of the compound were spotted at two places on two halves of the same plate.

The plates were left for 1 h in the vapours of the irrigating solvent, after which they were irrigated. The compounds were located under U.V. light (Chromatolite lamp), after spraying a half of the plate with 1 % solution of diphenylamine in ethyl

TABLE I

Sample No.	Adsorbent and weight	Solvent	Wt. of the adsorbent (mg/cm <sup>2</sup> )
1	Silica Gel G (E. Merck), 30 g	Chloroform (60 c.c.) + methanol (30 c.c.)	8.2
2	Magnesium silicate (M. Woelm, 200 mesh, B.S.S.), 30 g.	Water (30 c.c.)	7.6
3	Alumina neutral (M. Woelm, 200 mesh, B.S.S.) with 20 % CaSO <sub>4</sub> , 30 g	Water (60 c.c.)	6.4

alcohol. During spraying the other half of the plate was carefully shielded with a glass plate. Figs. 1 and 2 are two typical chromatograms. Table II gives the  $R_F$  values of the compounds.

#### *Estimation*

*Reagents.* (A) 0.5 N alcoholic KOH; (B) 1 % sulphanic acid in 30 % acetic acid; (C) 0.1 %  $\alpha$ -naphthylamine in 30 % acetic acid.

The corresponding spots from the unsprayed portion of the plates were scraped off, extracted with acetone, filtered and the solvent evaporated off. Reagent A (1 c.c.) was added to this and the solution left at room temperature for 20 min. After this Griess-Romijin reagent (2 c.c.) prepared by mixing equal volumes of B and C was added, which instantaneously gave a pink colour. The intensities were measured with a Hilger Spekker Absorptiometer and amounts of the compounds calculated from a previously established calibration curve.

#### *Discussion and results*

It was seen that magnesium silicate and alumina plates gave sharper resolution of the compounds than Silica Gel G. The nitrates could not be distinctly resolved from their mixtures on silica gel plates. Alumina neutral (M. Woelm) proved to be the best adsorbent for the separation of individual compounds from a mixture of EGDN,

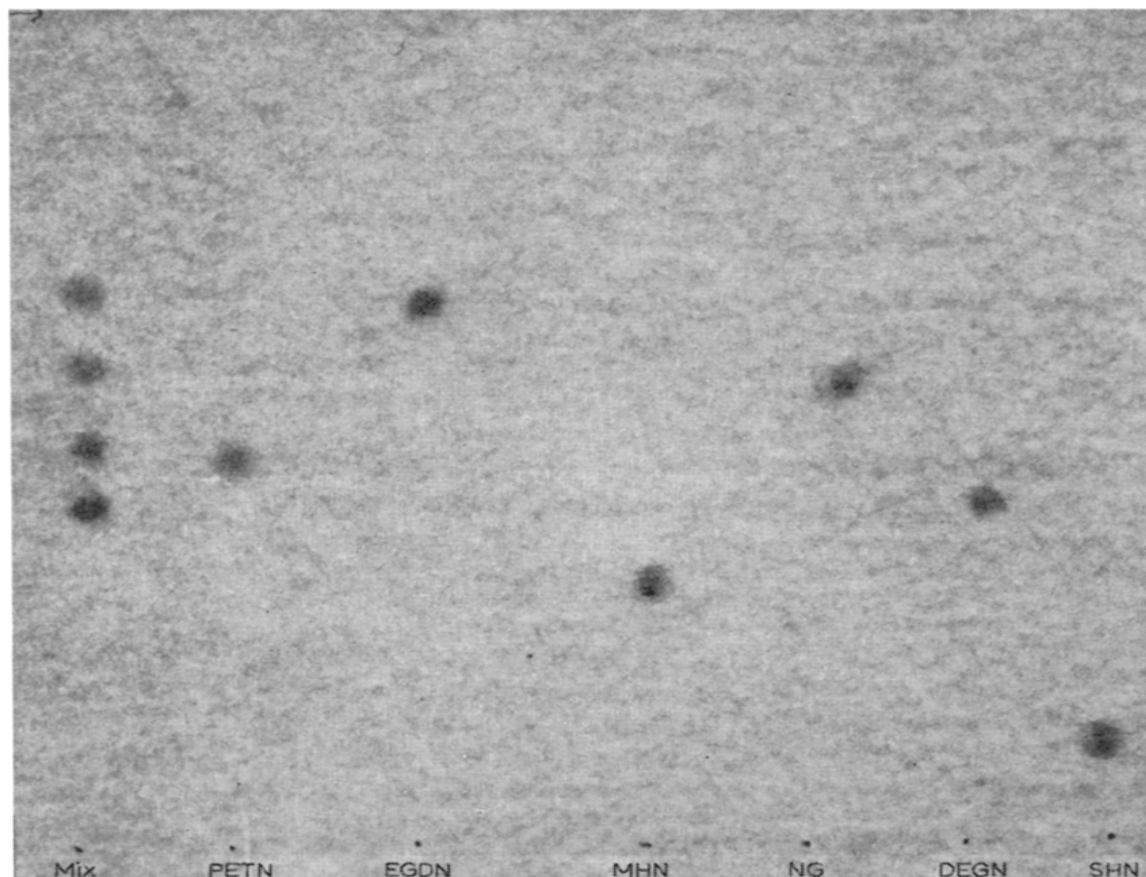


Fig. 1. Thin layer chromatogram showing the separation of explosive nitrates and their mixture on magnesium silicate. Photograph taken under U.V. light after spraying with diphenylamine. Solvent: xylene; system: ascending.

TABLE II

*R<sub>F</sub>* VALUES OF SOME NITRATE ESTERS ON VARIOUS ADSORBENTS AND IN VARIOUS SOLVENT SYSTEMS

Sample No.	Compound	Adsorbents	Alumina, neutral			
		Solvents	Toluene	Mono-chloro-benzene	Xylene	Petroleum ether-ethylene dichlorid (80:20)
1	Pentaerythritol tetranitrate		0.27	0.48	0.38	0.25
2	Ethylene glycol dinitrate		0.82	0.70	0.73	0.77
3	Mannitol hexanitrate		0.10	0.11	0.21	0.09
4	Nitroglycerine		0.68	0.60	0.55	0.40
5	Diethyleneglycol dinitrate		0.64	0.69	0.48	0.51
6	Sorbitol hexanitrate		0.04	0.20	0.13	0.08

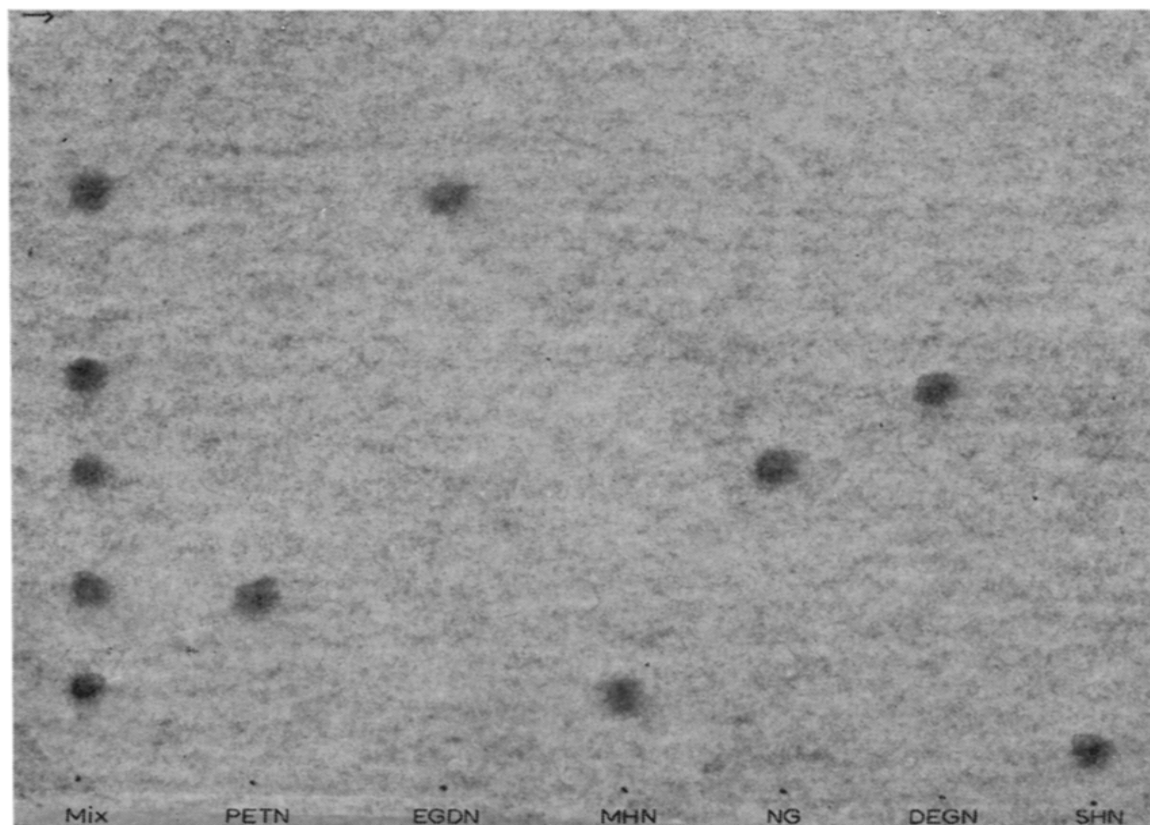


Fig. 2. Thin layer chromatogram showing the resolutions of five explosive nitrates from their mixture on alumina. Photograph taken under U.V. light after spraying with diphenylamine. Solvent: petroleum ether-ethylene dichloride (4:1); system: ascending.

<i>Magnesium silicate</i>				<i>Silica Gel G</i>			
<i>Compound</i>	<i>Mono-chloro-benzene</i>	<i>Xylene</i>	<i>Petroleum ether-ethylene dichloride (80:20)</i>	<i>Toluene</i>	<i>Mono-chloro-benzene</i>	<i>Xylene</i>	<i>Petroleum ether-ethylene dichloride (80:20)</i>
	0.61	0.48	0.29	0.55	0.49	0.54	0.00
	0.91	0.64	0.62	0.66	0.70	0.69	0.15
	0.53	0.36	0.21	0.42	0.33	0.39	0.00
	0.70	0.54	0.49	0.61	0.61	0.63	0.06
	0.57	0.42	0.35	0.40	0.41	0.39	0.05
	0.09	0.12	0.05	0.11	0.07	0.09	0.00

DEGN, NG, PETN and MHN. Nonpolar solvents are to be preferred to polar ones that produce tailing.

On alumina plates MHN was more strongly held than on Silica Gel G or magnesium silicate. The behaviour of NG on alumina was seen to be reverse to DEGN when compared with the movement on Silica Gel G and magnesium silicate. The adsorbant effect of alumina on NG and MHN may be due to complex formation. In NG, MHN and SHN vicinally active hydrogens are available for complex formation whereas in DEGN they are absent.

During quantitative estimations of these compounds a pink colour was produced after saponification and addition of the Griess-Romijn reagent. The colour of the solutions was stable and the compounds could be conveniently estimated to 2-4  $\mu\text{g}$ .

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## Detection of rearrangement reactions by silver nitrate thin-layer chromatography

The method of separation and determination of triglycerides according to unsaturation and isomeric configuration on thin layers of silver nitrate impregnated silica gel is a recent elegant analytical development. Since the time that DE VRIES<sup>1</sup> had effected the separation of the methyl esters of palmitic, oleic, elaidic and linoleic acids and triglycerides like elaidodipalmitin and oleodipalmitin on a silicic acid column impregnated with silver nitrate, many investigators extended this method to silica gel thin layers containing silver ions in order to elucidate the compositions of natural, synthetic and modified triglycerides. BARRETT *et al.*<sup>2</sup> later adapted the silver nitrate thin-layer chromatography to the separation and estimation of constituent triglycerides of lard, interesterified lard, cocoa butter, palm oil, peanut oil, soybean oil and cottonseed oil. Subsequently REISER *et al.*<sup>3</sup> and JURRIENS *et al.*<sup>4,6</sup> utilised the thin-layer technique for quantitative analyses of natural triglycerides. KAUFMANN AND WESSELS<sup>5</sup> separated the glycerides of sunflower oil by first fractionating on a silver nitrate impregnated silica gel layer and effecting further separation in a reversed phase system. PRIVETT *et al.*<sup>7</sup> by adopting this method determined quantitatively the component glycerides formed by the random rearrangement reaction of a synthetic

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