

CHROM. 8187

## Note

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### Separation and identification of minor components in smokeless powders by thin-layer chromatography

ALAN W. ARCHER

*Research Section, Division of Analytical Laboratories, P.O. Box 162, Lidcombe, N.S.W. 2141 (Australia)*

(Received January 15th, 1975)

Smokeless powders contain, in addition to the major explosive components, small quantities of other compounds to improve the performance and stability. Thin-layer chromatography (TLC) has been used for the separation of the explosive components such as aliphatic nitrate esters<sup>1</sup>, nitramines<sup>2</sup> and aromatic nitro compounds<sup>3-5</sup>, but little has been published on the separation and identification of the other additives. Diphenylamine and its nitro and nitroso derivatives, produced in explosive compositions on long storage, have been examined by TLC<sup>6</sup> and the UV light absorbing compounds present in smokeless powders were separated and used to characterise various makes of ammunition<sup>7</sup>. This note describes solvent systems and spray reagents for the separation and identification of compounds used as additives and stabilisers in smokeless powders.

#### EXPERIMENTAL

TLC was carried out on 20 × 20 cm or 20 × 10 cm glass plates coated with a 0.25-mm thick layer of silica gel GF<sub>254</sub> (Merck, Darmstadt, G.F.R.). Before use the plates were heated at 120° for 30 min and allowed to cool. The following solvent systems were used: (A) benzene; (B) benzene-light petroleum (b.p. 40-60°)-ethyl acetate (12:12:1); (C) benzene-light petroleum (b.p. 40-60°) (1:1); (D) benzene-chloroform (1:1); (E) chloroform; (F) benzene-methanol (4:1).

#### *Spray reagents*

Four spray reagents were used. The preparation of the reagents was as follows:

Reagent I. Dissolve 1 g vanillin in 50 ml glacial acetic acid and add 5 ml orthophosphoric acid (85%). This solution is stable for at least two weeks.

Reagent II. Prepare a fresh mixture of ethanol (20 ml), acetone (20 ml) and 25% tetramethylammonium hydroxide solution (5 ml). This mixture is stable for one day.

Reagent III. Dissolve 0.25 g sulphanilic acid and 0.1 g 1-naphthylamine in 100 ml 50% (v/v) acetic acid. Although this reagent gradually turns pink, it is usable for at least one week.

Reagent IV. Dissolve 1 g potassium dichromate in 80 ml water and add 20 ml concentrated sulphuric acid. This mixture is usable for at least one week.

### Detection

Compounds showing a positive reaction to any of the following six detection methods used are marked + in Table I.

(1) *Daylight*. Yellow spots visible in daylight.

(2) *Ultraviolet light*. Dark spots on a fluorescent background when examined under ultraviolet (UV) light (wavelength 254 nm). Compounds marked F in Table I appear as fluorescent spots when examined under UV light (wavelength 350 nm).

(3) *Reaction with Reagent I*. Diphenylamine: immediate yellow, remains yellow on heating. N-Nitrosodiphenylamine: immediate blue, turns green on heating. Carbazole: violet on heating. Triphenylamine: blue-violet on heating. Glyceryl trinitrate and ethylene glycol dinitrate: orange-brown on heating. N-Phenylurea: pale yellow on heating. 1,1-Diphenylurea and ethyl N-phenyl carbamate: pale yellow-brown on heating.

(4) *Reaction with Reagent II*. Glyceryl trinitrate and ethylene glycol dinitrate: pale yellow-brown becoming darker on heating. 2,4-Dinitrodiphenylamine: red-brown, becoming darker on heating. 2,4-Dinitrotoluene: immediate blue, becoming darker on heating. 2,4,6-Trinitrotoluene: red-brown, becoming darker on heating. 4-Nitrotoluene: no reaction cold, faint purple on heating.

(5) *Reaction with Reagent III*. Glyceryl trinitrate and ethylene glycol dinitrate: immediate purple (if large amounts are present the spot becomes yellowish with a purple halo).

(6) *Reaction with Reagent IV*. 1,3-Dimethyl-1,3-diphenyl- and 1,3-diethyl-1,3-diphenylurea: immediate red. Diphenylamine and N-nitrosodiphenylamine: immediate blue. Triphenylamine: immediate dark greenish blue. Carbazole: immediate blue-green. 1,1-Diphenylurea: no reaction cold, bluish black on heating. All coloured spots turn brown on prolonged heating.

### Procedure

Add sufficient dichloromethane to just cover a few grains of powder sample (about 10 mg of sample and 0.1 ml of dichloromethane) in a small test tube and allow to stand for 5–10 min. This procedure will normally extract sufficient material for TLC, but if the sample is a single powder grain, remove the first extract, repeat the extraction with a second quantity of dichloromethane, combine the two extracts and evaporate to low volume before applying to the silica gel. For fired but unburnt powder grains on cloth, remove the grains from the cloth before extraction with dichloromethane, as extracts from some cloth samples contain interfering fluorescent substances.

Spot about 5  $\mu$ l of the extract onto each of two plates and run both plates in the benzene–light petroleum–ethyl acetate solvent. When the solvent front has travelled 13–15 cm, remove the plates from the tank, mark the position of the solvent front and allow the plates to dry. Note the position of any yellow spots visible in daylight, examine the plate under UV light (254 nm) and mark the position of any UV light absorbing compounds. Note also any fluorescent compounds when examined under long-wave UV light. Spray one plate with the vanillin reagent, note any colours produced in the cold and heat the plate at 120° for 5–10 min. Note the position and colour of any spots that appear. Spray the second plate with the alkaline acetone reagent and note the position and immediate colour of any spots that appear. Heat

the plate at 120° for 10 min, allow to cool, spray with the sulphanilic acid reagent and note the position and colour of any spots.

From the results obtained, further plates can be spotted and run in appropriate solvents to confirm the presence of suspected compounds. If UV absorbing compounds with  $R_F$  values in the range 0–0.2 are present, they may be further separated by running a freshly spotted plate in benzene–chloroform. Further separation of slow moving compounds can be obtained with chloroform as solvent. Glyceryl trinitrate and ethylene glycol dinitrate can be differentiated in the benzene–light petroleum solvent.

If nitroguanidine is thought to be present, the sample can be extracted with water as described by Jenkins and Yallop<sup>5</sup> and run in the benzene–methanol solvent.

## RESULTS AND DISCUSSION

The compounds examined, together with their  $R_F$  values in the solvent systems used, and their reactions to the spray reagents are shown in Table I. N-Phenylurea,

TABLE I

### $R_F$ VALUES AND METHODS OF DETECTION

For solvent systems and detection methods, see text.

No.	Compound	Solvent system						Detection						
		A	B	C	D	E	F	1	2	3	4	5	6	
1	Diphenylamine	0.63	0.66	0.54	0.74	0.85			+	+				+
2	N-Nitrosodiphenylamine	0.44	0.60	0.23	0.72	0.85			+	+				+
3	2-Nitrodiphenylamine	0.55	0.70	0.46	0.77	0.88		+	+					
4	4-Nitrodiphenylamine	0.27	0.28	0.05	0.48	0.73		+	+					
5	2,4-Dinitrodiphenylamine	0.40	0.50	0.13	0.68	0.80		+	+			+		
6	N,N-Diphenylbenzamide	0.08	0.12	0	0.34	0.66	0.82		+					
7	N-Phenylurea	0	0	0	0	0.02	0.41		+	+				
8	1,1-Diphenylurea	0	0	0	0.02	0.19	0.54		+	+				+
9	1,3-Diphenylurea	0.02	0.03	0.02	0.10	0.33	0.64		+					
10	1,3-Diethyl-1,3-diphenylurea	0.02	0.07	0.02	0.26	0.56			+					+
11	1,3-Dimethyl-1,3-diphenylurea	0.02	0.05	0.02	0.18	0.48			+					+
12	Ethyl N-phenyl carbamate	0.17	0.26	0.04	0.44	0.66			+	+				
13	Ethyl N,N-diphenyl carbamate	0.13	0.31	0.08	0.58	0.74			+					
14	Triphenylamine	0.73	0.80	0.75	0.78	0.87		+	F	+				+
15	Carbazole	0.57	0.46	0.37	0.69	0.72		+	F	+				+
16	Glyceryl trinitrate	0.50	0.43	0.24	0.65	0.78				+	+	+		
17	Ethylene glycol dinitrate	0.56	0.49	0.31	0.68	0.82					+	+	+	
18	1-Nitroguanidine	0	0	0	0	0	0.25		+					
19	4-Nitrotoluene	0.61	0.70	0.42	0.75	0.78			+					
20	2,4-Dinitrotoluene	0.48	0.55	0.23	0.70	0.78			+			+		
21	2,4,6-Trinitrotoluene	0.54	0.70	0.25	0.73	0.80			+			+		

1,3-diphenylurea and 1,1-diphenylurea are not well resolved in the benzene-chloroform solvent but these three compounds may be separated with chloroform as the liquid phase. Nitroguanidine may be differentiated from N-phenylurea and the diphenylureas with benzene-methanol as liquid phase.

The spray reagents are reasonably sensitive. Reagent I gives a definite colour with 1  $\mu\text{g}$  diphenylamine or N-nitrosodiphenylamine and Reagent II is reported<sup>8</sup> to detect 2  $\mu\text{g}$  2,4-dinitrotoluene and 1  $\mu\text{g}$  2,4,6-trinitrotoluene. Subsequent treatment with Reagent III, as described by Lloyd<sup>9</sup>, will detect 1  $\mu\text{g}$  glyceryl trinitrate. The acid dichromate reagent is reported<sup>4</sup> to detect about 1  $\mu\text{g}$  diphenylamine and N-nitrosodiphenylamine and about 0.3  $\mu\text{g}$  of the 1,3-dialkyl-1,3-diphenylureas.

A range of 42 samples of smokeless powders from various manufacturers was examined by the procedure described. The most commonly used stabiliser was diphenylamine and this appeared to be always associated with N-nitroso- and 2- and 4-nitrodiphenylamine. The polynitrodiphenylamines appear to occur only in old samples of nitrocellulose powders<sup>6,10</sup> and were not found in the samples examined. Glyceryl trinitrate, 2,4-dinitrotoluene and the 1,3-dialkyl-1,3-diphenylureas were also present in the majority of the samples examined. Similar chromatograms were obtained when extracts from powders were compared with extracts from the corresponding unburnt powder grains, after firing at close range (20 cm) into cloth.

#### ACKNOWLEDGEMENTS

The author is grateful to the New South Wales Mines Department and the Ballistics Section, New South Wales Police Department, for provision of samples and assistance, and acknowledgement is made to the Director and Government Analyst and the New South Wales Health Commission for permission to publish this paper.

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