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Identification of Explosives Containing Alkylammonium Nitrates by Thin-Layer Chromatography

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ABSTRACT: The alkylammonium nitrate sensitizers contained in Du Pont and Hercules water gel explosives can be uniquely identified by utilizing the three thin-layer chromatography (TLC) systems discussed in this paper. These TLC methods also identify the presence of other explosive ingredients and contaminants commonly found in debris from bombings.

KEYWORDS: criminalistics, explosives, chromatographic analyses, chemical analyses

The identification of explosive residue in evidentiary samples from bombings has been complicated by the proliferation of dynamite substitutes. Explosives sensitized with nitrostarch, nitrocellulose, ethylene glycol mononitrate, aluminum, and alkylammonium nitrates are displacing explosives sensitized with nitroglycerin and nitroglycol (traditional dynamites). For example, in the middle 1970s E. I. du Pont de Nemours & Co. discontinued the manufacture of explosives containing nitroglycerin in favor of water gels [*1*].

Unlike most other ingredients in commercial explosives, these modern sensitizers are often unique to explosives produced by one manufacturer, for example, methylammonium nitrate (monomethylamine nitrate or MMAN) used by Du Pont; ethanolammonium nitrate (monoethanolamine nitrate or MEAN) used by Hercules; Inc., and nitrostarch used by Trojan.[3] Thus, the type of explosive and its manufacturer can be identified if these sensitizers are detected.

This paper describes thin-layer chromatography (TLC) systems by which the currently used alkylammonium nitrate sensitizers, MMAN and MEAN, can be uniquely identified.

Materials and Methods

The materials utilized in this study are shown in Table 1. Solutions of the amine sensitizers used were prepared in the following manner: for MMAN, 0.1 g of recrystallized MMAN was

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[3]Private communication, Acrospace Corp., 1977.

TABLE 1—*Materials.*

Products	Source
Methyammonium nitrate (recrystallized from water and methanol)	Du Pont's Potomac River Development Laboratory (as water slurry) [*1*]
Ethanolamine dihydrochloride	Aldrich Chemical Co.
Amine hydrochlorides	Aldrich Chemical Co.
7,7,8,8-tetracyanoquinodimethan (TCNQ)	Eastman Kodak Co.
Lithium iodide	Alpha Division, Ventron Corp.
Fluorescamine (4-phenylspiro(furan-2(3H),1'-phthalan)-3,3'-dione)	Sigma Chemical Co.
Amino acids standard mixture	Sigma Chemical Co.
Ninhydrin	Matheson, Coleman & Bell
Diphenylamine	Matheson, Coleman & Bell
Boric acid	Mallinckrodt, Inc.
Sodium hydroxide (0.100*N*)	Ricca Chemical Co.
Solvents (certified ACS, reagent quality) chloroform methanol	Fisher Scientific
Ethanol	U.S. Industrial Chemicals Co.
Glass capillary tubes (32 by 0.8 mm, 0.1-mm wall)	Drummond Scientific Co.
5- by 20-cm glass TLC plates (cellulose [K2] and silica gel [K5]	Whatman, Ltd.

dissolved in 2 mL of an aqueous solution containing 0.3 g/mL of ammonium nitrate and 0.2 g/mL of sodium nitrate (ASN). The MEAN solution, a mixture of the chloride and the nitrate, was prepared by adding solid ethanolamine hydrochloride to an equimolar quantity of 4*M* nitric acid and diluting this eightfold with ASN. Other amine nitrate solutions were prepared by adding the amine hydrochloride to an equimolar quantity of 4*M* nitric acid and diluting this eightfold with ASN. Amino acid solutions were prepared by dissolving (not always completely) 20 to 30 mg of the amino acid in 2 mL of ASN.

The test solutions were applied with glass capillary tubes 1.5 to 2 cm from the bottom of the TLC plate and 1.5 cm from adjacent spots. The solution volume spotted was 0.5 μL. The plates were developed in closed TLC tanks with the level of appropriate development solvent reaching about halfway to the origin (Fig. 1). The solvent front was allowed to migrate to within 1 cm of the top of the plate with Systems I and III. System II was allowed to migrate only 10 cm from the origin (see Table 2). The plates were allowed to air-dry before spraying or visualizing. Three separate TLC systems were utilized for the complete separation and identification of the amine sensitizers.

The following paragraphs describe the preparation and use of sprays for visualizing the spots on the TLC plates. Primary amines and amino acids were detected by spraying the plates with a solution of 0.2% ninhydrin in 0.1*M* citric acid, adjusted to pH 5 with 2.0*N* sodium hydroxide [*2*]. Plates sprayed with ninhydrin were heated at 100°C for 7 to 10 min to develop the color. When Systems I and III were sprayed with ninhydrin, the limits of detection for MMAN and MEAN were about 0.5 μg.

Nitrates were detected by spraying the plates with a solution of 5% diphenylamine (DPA) in 95% ethanol followed by 10-min exposure to ultraviolet light and then spraying the plates with concentrated sulfuric acid [*1,3*]. When System I was sprayed with diphenylamine/sulfuric acid combination, the limits of detection for MMAN and MEAN were about 1.0 μg. It should be noted that even when a TLC plate had been run in System I and sprayed with ninhydrin, a subsequent spraying of the plate with the diphenylamine/sulfuric acid combination still revealed the presence of nitrates.

Primary amines and amino acids form intensely fluorescent substances when reacted with

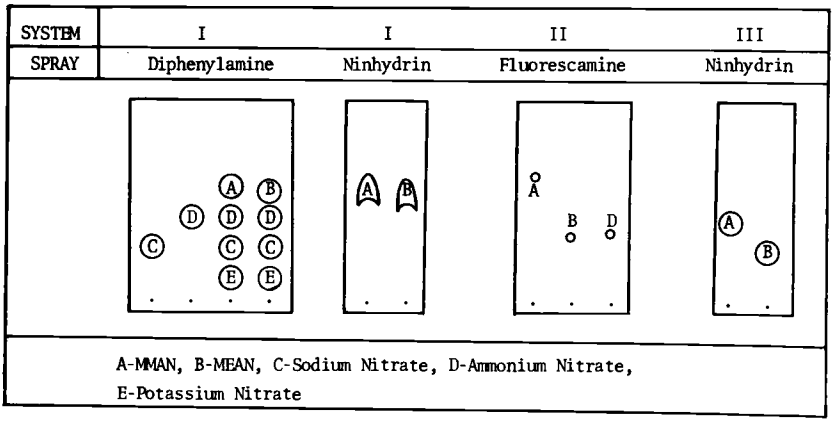

FIG. 1—*Plates were developed in closed TLC tanks with the level of appropriate development solvent reaching about halfway to the origin.*

TABLE 2—*Solutions used for Systems I, II, and III in Fig. 1.*

System	Development Solution	Plate	Sprays
I	chloroform/methanol/water (100:90:14)	K2	diphenylamine or ninhydrin
II	chloroform/methanol (7:3)	K5	fluorescamine visualization
III	chloroform/100% ethanol/water/HCl (conc.) (100:90:5:3.5)	K5	ninhydrin

fluorescamine. This reaction proceeds rapidly at room temperature at pH 9. A solution of fluorescamine was prepared by dissolving 50 mg of fluorescamine in 100 mL of acetone. A 0.2*M* borate buffer solution was prepared by dissolving 1.24 g of boric acid in 100 mL of distilled water. The pH of this solution was adjusted to 9.0 by titration with 0.1*N* sodium hydroxide [*4*]. A drop of the MMAN and MEAN solutions was placed into separate wells of a porcelain spot plate. Into each of these wells, two drops of the borate buffer solution were added followed by one drop of the fluorescamine solution. Upon completion of the reaction, the solution were examined under ultraviolet light to observe the fluorescence. Those solutions that reacted positively were spotted on K5 TLC plates and developed utilizing System II. Visualization of the amines was made under ultraviolet light. The limit of detection for MMAN and MEAN was about 2.0 μg.

Inorganic cations were detected by spraying K2 plates, developed in System I, with a solution of 0.5% lithium tetracyanoquinodimethanide (Li TCNQ) in 50% ethanol. This solution was prepared immediately before spraying the TLC plate [*5*]. Li TCNQ was synthesized from TCNQ and lithium iodide according to Melby et al [*6*]. See Table 3.

Results and Discussion

When visual and microscopic examinations of evidentiary debris from explosions fail to reveal the presence of an explosive, this laboratory extracts the debris first with distilled water and secondly with acetone or methanol. The extracts are filtered and evaporated to dryness. The water extract is redissolved in a small quantity of water for chemical spot tests [*2*]. If the presence of nitrite or nitrate ions is detected with the Griess spot test, the water and methanol

TABLE 3—R_fs *(as %) and spot colors of MMAN and various inorganic nitrates and chlorides chromatographed on K2 plates in System I.*

Compound	R_f[a]	Li TCNQ Color
Potassium nitrate	14	blue-green
Ammonium nitrate	31-46	brown-black
Sodium nitrate	17-32	brown-black
MMAN	40-56	light blue
Aluminum chloride	0-41	yellow
Strontium nitrate	22-41	pale green
Barium nitrate	17-22	green
Calcium nitrate	0-51	gray-green

[a] R_fs are recorded as the R_f of the tail and the R_f of the leading edge.

extracts may contain MMAN or MEAN. These extracts are then prepared for TLC analysis by adding a few drops of the extracting solvent to the respective extract to redissolve and concentrate the residue.

Screening for alkylammonium nitrates and confirming the presence of ammonium, sodium, and potassium ions is performed using TLC System I. The nitrates are visualized using the diphenylamine/sulfuric acid spray combination [*1,3*]. Amines are visualized by spraying with ninhydrin. Spraying for the visualization of amines must be conducted before spraying with the diphenylamine/sulfuric acid spray combination or on a separate TLC plate. Because of interferences in this TLC system from some compounds (notably calcium salts from soil or explosives), and uncertainty in distinguishing MMAN and MEAN from each other and a few other compounds, it is necessary to also use other TLC systems for the confirmation of MMAN and MEAN.

If screening by System I indicates the presence of MMAN or MEAN, then fluorescamine derivatized amines are separated using System II. The water and methanol extracts are prepared for System II by adding a few drops of distilled water to the evaporated extracts. A few drops of the redissolved extract solution are then placed onto a well of a porcelain spot plate for derivatization as described previously. This system gives an excellent separation of MMAN from MEAN. While MEAN and ammonia produce spots having similar R_fs with this system, they can be distinguished from one another by using System III.

System III, although slow, separates MMAN from MEAN with no interference from ammonia. Plates developed using this system are sprayed with ninhydrin. The developing solution must be prepared using 100% ethanol and concentrated hydrochloric acid since this system is sensitive to the concentration of water. The loss of hydrochloric acid and the uptake of water reduce the efficiency of this solvent in three or four weeks. This system is especially useful when MMAN or MEAN are in very low concentrations in the extract and may fail to be detected with System II. While high concentrations of amino acids streak in System III and can obscure the presence of MMAN and MEAN, amino acids remain at the origin in System II, thus eliminating their interference with MMAN and MEAN. Data for these three systems are presented in Table 4. All compounds were run in the presence of ammonium, sodium, and potassium nitrate.

The presence of most inorganic cations contained in an explosive can be confirmed by spraying a Li TCNQ solution on K2 plates developed in System I. Ammonium chloride, iron (II) sulfate, magnesium chloride, potassium perchlorate, calcium salts, and strontium salts can change the R_f of MMAN, MEAN, ammonium nitrate, sodium nitrate, and potassium nitrate in TLC System I. The presence of these interferences can cause streaking which may result in (1) the presence of MMAN and MEAN being masked as the interferences migrate past

TABLE 4—R_fs (as %).

Solvent System	System I	System II	System III
TLC Plate	K2	K5	K5
MMAN	40-56	60	31-37
MEAN	33-47	39	18-28
Ammonium nitrate	31-46	40	...
Sodium nitrate	17-31	...	...
Potassium nitrate	10-14	...	...
n-Ethylammonium NO_3	61-72	...	37-38
n-Propylammonium NO_3	66-72	73	41-51
n-Amylammonium NO_3	77-88	69	48-66
Iso-propylammonium NO_3	26-29	...	41-55
Iso-butylammonium NO_3	69-82	...	...
1-amino-2-propanol NO_3	52-61	54	36-38
2-amino-1-propanol NO_3	41-56	42	41-43
2-amino-1-butanol NO_3	55-68	53	41-45
Anthranalic acid	95-97	...	95-97
Phenylalanine	44-67	0	5
3,4-Dihydroxylphenylalanine	1	0	49
Tryptophan	0-28	0	50
Tyrosine	0	0	50
Norvaline	40-61	0	50
Ethionine	47-61	0	49
Isoleucine	52-63	0	49
Leucine	47-78	0	50
Methionine	4-54	0	50
Alanine	14-27	0	41
Arginine	0	0	24-3
Asparagine	0	0	19-24
Aspartic acid	0	0	49
Citruiline	0	0	3-38
Cystine	0	0	25-28
Glutamine	5-14	0	49
Glycine	1	0	28-41
Histidine	0	0	16-23
Lysine	1	0	14
Norleucine	61-75	0	50
Proline	33-42	0	50
Serine	10	0	38-43
Threonine	0-22	0	...
Valine	36-61	0	50
3-Phenyl-1-propylamine	...	...	69-76
2-Amino-1-phenylethanol	...	...	69-76
Phenethylamine	...	...	69-74
Methamphetamine	...	...	70-75
Dextroamphetamine	...	...	65-70

[a] R_fs are recorded as the R_f of the tail and the R_f of the leading edge. Tert amines, secondary amines, aniline, guanidine, hexamine, hydroxylamine, diphenylamine, urea, uric acid, and so forth do not react with ninhydrin.

the R_fs of MMAN and MEAN or (2) the nitrate salts migrate to R_fs indistinguishable from MMAN or MEAN. Li TCNQ is quite helpful with identifying these interferences as well as some of the cations contained in fireworks and commercial explosives.

The use of these three TLC systems provides the necessary data for the unique identification of MMAN and MEAN. Ninhydrin and fluorescamine react with only primary amines. The diphenylamine/sulfuric acid spray combination and Griess spot test identify the presence of nitrate ions [2, 7]. The use of three different TLC systems increases specificity. In Systems I

and III, compounds larger than ethanolamine nitrate and nitrates of alkylamines, alkylamine alcohols, and arylamines have greater R_f values than MMAN or MEAN. System II provides the separation of MMAN and MEAN from amino acids that remain at the origin.

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