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Analysis of Explosives and Explosive Residues. Part 3: Monomethylamine Nitrate

The E. I. du Pont de Nemours & Co., Inc. has recently announced that it is discontinuing the manufacturing of nitroglycerin-based dynamites and is replacing them with formulations whose primary ingredients are ammonium nitrate (AN) and monomethylamine nitrate (MMAN). The forensic chemist is thus confronted with the need to be able to analyze residues for the possible use of this type of explosive.

In Parts 1 and 2 [*1,2*], chemical spot tests and thin-layer chromatographic (TLC) techniques have been presented for the analysis of explosives and explosive residues. In this paper procedures are given for the qualitative determination of MMAN. Also presented are some of its physical and chemical properties.

The monomethylamine nitrate used in this study was obtained as a water slurry through the courtesy of du Pont's Potomac River Development Laboratory. The substance was recrystallized from water and methanol before use in order to improve its purity.

Physical Properties

MMAN is the salt of monomethylamine and nitric acid [*3*]. The compound is a white crystalline solid at room temperature with a melting point of 110 ± 2°C. Under crossed Nicol prisms, a crystalline phase transition is observed at 82°C. Both this phase transition and the melting point are seen as endothermic peaks in the differential thermal analysis (DTA) curve (Fig. 1) along with a strong exothermic peak starting at approximately 250°C with its maximum at approximately 285°C. The DTA was obtained with a du Pont Model 900 Thermal Analyzer.

Approximate solubilities of MMAN in various solvents are given in Table 1. In acetone MMAN shows definite signs of decomposition, turning yellow-brown. Therefore, the use of acetone as a solvent should be avoided in working with MMAN.

The infrared (IR) spectrum is given in Fig. 2. The IR spectrum was obtained from a KBr disk using a Perkin-Elmer infrared spectrophotometer, Model 457.

Chemical Tests

Table 2 lists the results of various spot tests for MMAN. Except for the dithiocarbamate test, the reagents and procedures for these tests are given in Part 1.

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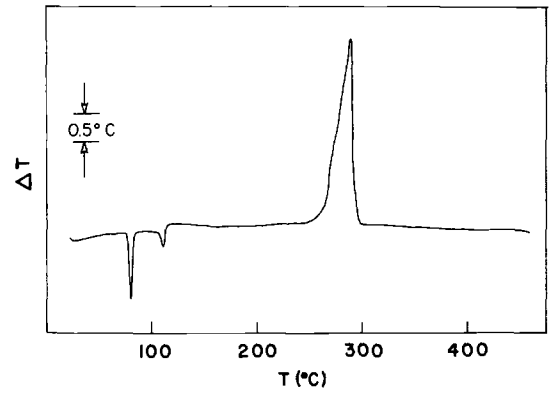

FIG. 1—*Differential thermal analysis (DTA) thermogram of MMAN. Temperature measured with chromel/alumel thermocouples. Heating rate of 20°C/min.*

TABLE 1—*Approximate solubilities of MMAN in various solvents at 20°C.*

Solvent	Solubility, g/l of solution
Water	965
Methanol	481
Acetone[a]	390
Ether	0.9

[a] MMAN showed evidence of decomposition in acetone.

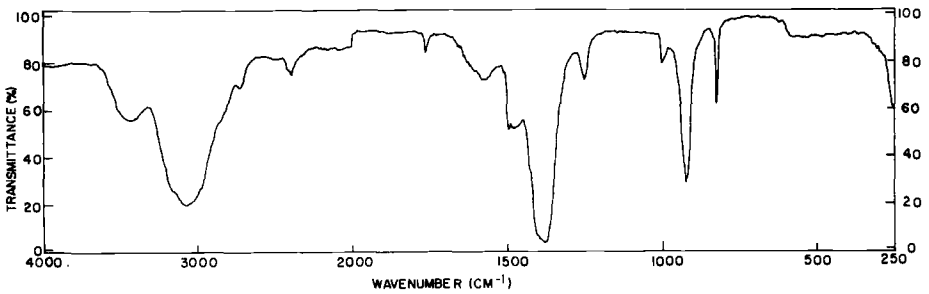

FIG. 2—*Infrared spectra of MMAN, obtained as a KBr disk.*

TABLE 2—*Results of various spot tests on MMAN.*

Test Reagent	Result
Aniline sulfate	dirty light yellow
Barium chloride	NR
Brucine	deep red, turns orange
Cupric tetrapyridine	NR
Diphenylamine	deep blue
Dithiocarbamate test	brown-gray to black precipitate
Griess	red
J-acid	dirty green, turns brown
Methylene blue	NR
Nessler	white precipitate
Nitron	white precipitate
Silver nitrate	NR
Sulfuric acid	NR

NR = no reaction.

The dithiocarbamate test is a modification of a test given in Feigl [*4*] for primary and secondary amines. It consists of two solutions: Solution A, 1:1 solution of CS_2/EtOH and Solution B, 5% $AgNO_3$ in 50% NH_4OH. The solid sample or methanol extract is put into a white spot plate. Since any methanol interferes with the test, the extract must be air evaporated to dryness. To the spot plate add 2 drops of Solution A. Then add 4 to 6 drops of Solution B. Depending upon concentration, MMAN gives a brown-gray to a black precipitate around the edge of the liquid. Upon standing, the reagent blank gives a slight gray precipitate around the edge of the liquid. Always compare the test of the unknown against a reagent blank. The limit of detection is approximately 20 μg. None of the compounds tested in Part 1 gives similar results. Ammonium nitrate and other inorganic nitrates do not appear to interfere.

The results from thin-layer chromatography (TLC) are given in Table 3. The table

TABLE 3—*TLC* R_f *values and color development.*

		Compound		
Compound	R_f	Stage 1, Diphenylamine	Stage 2, UV Light	Stage 3, Sulfuric Acid
Ammonium nitrate (AN)	0.5	NCD	dirty yellow [a]	dark blue
2,4-Dinitrotoluene (2,4-DNT)	1	yellow	yellow	color fades
2,6-Dinitrotoluene (2,6-DNT)	1	yellow	yellow	color fades
Ethyleneglycol dinitrate (EGDN)	0.9	NCD	dirty yellow	dark blue
Monomethylamine nitrate (MMAN)	0.6	NCD	dirty yellow	dark blue
Nitrocellulose (NC)	0	NCD	dirty yellow	green-black
Nitroglycerin (NG)	0.9	NCD	dirty yellow	dark blue
Nitrostarch (NS)	1	NCD	dirty yellow	green-black
Pentaerythrityl tetranitrate (PETN)	1	NCD	gray-green	blue to blue-gray
Potassium nitrite	0.2	NCD	NCD	dark blue
2,4,6-Trinitrophenylmethylnitramine (Tetryl)	1	brown-red	brown-red	blue-green, yellow
2,4,6-Trinitrotoluene (TNT)	1	brown-yellow	brown-yellow	color fades
Cyclotrimethylenetrinitramine (RDX)	1	NCD	light gray	blue

NCD = no color development

[a] Turns blue to blue-green on prolonged standing (> 12 hours).

gives the R_f values and color development for MMAN and several other explosives. The compounds were migrated on glass plates coated with 250-μm Avicel® (Analtech, Inc.). The plates were initially activated at 100°C for one hour. The eluent consisted of $CHCL_3$, CH_3OH, H_2O (100:90:14). The color development follows that given in Part 2. The limit of detection exceeds 0.5 μg.

Conclusion

The chemical spot tests offer good screening tests for distinguishing other explosives from MMAN. However, in an explosive containing both MMAN and ammonium nitrate, the white precipitate for MMAN given by the Nessler reagent is obscured by the brown precipitate for ammonia. Of the methods discussed here, TLC appears to be the method of choice for the confirmation of MMAN.

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