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ANALYTICAL METHODS FOR NITROGUANIDINE AND CHARACTERIZATION OF ITS DEGRADATION PRODUCTS

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The objectives of this research were (1) to develop an accurate and sensitive method of analysis for nitroguanidine alone and in the presence of other explosives, (2) to characterize the products resulting from the chemical degradation of nitroguanidine and (3) to determine the rates of degradation of nitroguanidine under acidic, basic and neutral conditions.

This study showed that nitroguanidine can be separated and identified in a mixture of other explosives by using either thin layer or high pressure liquid

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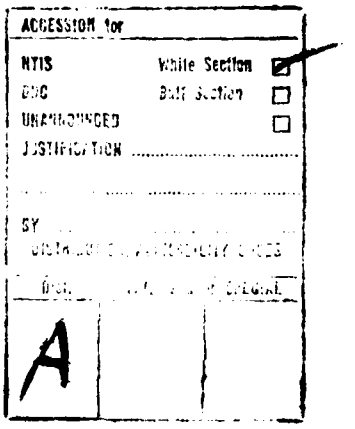
20. Abstract (cont'd)

chromatography. Quantitative analysis, based on high pressure liquid chromatography, can be carried out. Nitroguanidine was found to be stable in water and in dilute acid, but to decompose instantly in concentrated (>6N) acid to CO_2 and a nitrogen oxide. A kinetic study of hydrolysis by base, to give N_2O and NH_3, showed the reaction to be pseudo-first order. The reaction was found to be subject to specific base catalysis.

Preface

Currently nitroguanidine is used in various propellants formulated in this country. Because of the solubility of nitroguanidine in water a potential pollution problem is created during clean-up operations at various munitions plants. As a consequence the U.S. Army Medical Research and Development Command requested the Pollution Abatement Group under contract #IA05759 to develop a method to detect nitroguanidine in waste streams and to determine the amount of nitroguanidine present.



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Analytical Methods for Nitroguanidine and Characterization of Its Degradation Products

Introduction: Current interest in nitroguanidine stems from its use in various propellants now being formulated in this country. Since nitroguanidine imparts attractive properties to a propellant, such as, lower burning temperatures, increased thrust, reduced flash, and increased storage stability, its use in propellants will probably increase. However, because of the high solubility of nitroguanidine in water the potential for pollution of discharge streams also increases. The probable sources of this pollution are from waters used to clean cutting machine blades, and from periodic building washouts.

At Radford Army Ammunition Plant (RAAP), VA, where the triple-base propellant, M30, is produced, the estimated flow of water for cutting machines on one line is about 189 l/day. If this water is assumed 50 saturated with nitroguanidine approximately 4.5 kg/day of nitroguanidine could be discharged into the neighboring river. Thus it is important that analytical methods be developed for the rapid determination of nitroguanidine in small quantities in waste waters and in the presence of other explosives.

Objective: The objectives of this research were (1) to develop an accurate and sensitive method of analysis for nitroguanidine alone and in the presence of nitroglycerin and nitrocellulose as it exists in the M30 propellant,

(2) to characterize the products resulting from the chemical degradation of nitroguanidine and (3) to determine the rates of degradation of nitroguanidine under acidic, basic and neutral conditions.

Discussion: Nitroguanidine is a white crystalline material which exists in two crystalline forms, α and β. Originally these two forms were thought to have different chemical and physical properties, however, recent studies have shown that there is no difference between α and β nitroguanidine.[1]

The structure of nitroguanidine has been extensively discussed in the literature.[2] At present most evidence supports a nitroimine structure (A) being in equilibrium with the tautomeric form (B) in

(A) (B)

aqueous solutions. In acidic, neutral, or slightly basic media structure (A) predominates.

In the ultra-violet absorption spectrum of nitroguanidine in aqueous solutions only one band is observed over the pH range 2-12. The λ_{max} of this band is at 264 nm (ϵ_{max} = 13,000). In more alkaline solutions a

[1]E. Ripper, Chimie et Industrie, 103, 1763-1765 (1970).

[2]W. Kemula et al., Bull. Acad. Pol. Sci., Chem. Ser., XVIII, 455 (1970).

new band appears at λ_{max} 246 nm. As the solutions are made more alkaline, this band increases and the band at 264 nm decreases. This effect is supportive of a shift in the equilibrium towards structure (B) under the more alkaline conditions.

Degradation of Nitroguanidine Under Neutral, Acidic, and Basic Conditions: Nitroguanidine (obtained from RAAP) was dissolved in water and the solution heated under reflux conditions for 24 hours. During this time no noticeable change of the nitroguanidine could be detected by UV, IR, tlc or hplc. Even after heating for several days no change had occurred under neutral conditions.

Where nitroguanidine was heated at 100°C for 24 hours in dilute hydrochloric acid solutions (0.1 M, 0.5 M, and 1.0 M) no detectable change took place. The acid solutions were neutralized with base and evaporated to dryness. The residual solids gave the same UV's and IR's as the starting material. Decomposition of nitroguanidine under acidic conditions does not occur unless there is a large excess of acid. With H_2SO_4 it was found that a ratio of approximately 2500 moles of acid to 1 mole of nitroguanidine was needed to cause degradation.

Solutions of nitroguanidine in NaOH or NH_4OH are readily hydrolysed at a pH above 10. When nitroguanidine is heated to 55°C in 0.5 M NaOH (pH 12) complete hydrolysis occurs in 2 hours as indicated by the loss of the absorption peak in the UV at 264 nm. In 1 M NH_4OH (pH 10.5) at 55°C it takes 4 hours for complete hydrolysis.

Only gaseous products were found after base hydrolysis of nitroguanidine. These materials were shown to be N_2O and NH_3 by gas chromatography using a Porapak Q column at room temperature. Identification was made by comparison with known samples and by mass spectroscopy.

Rates of Degradation of Nitroguanidine in Base: The rate of decomposition of a 6.7×10^{-5} M solution of nitroguanidine was followed by observing the decrease of the UV λ_{max} at 265 nm with time at constant temperature and constant pH (Fig. 1). Plots of log (A_0-A_t) vs. time at the temperatures and pH's studied gave straight lines which were consistent with first order or pseudo-first-order reactions (Fig. 2). From the slopes of these plots the following rates were determined:

pH	Temp.	Rate k
12.6	42°C	3.7×10^{-3}/min
9.9	66°C	4.6×10^{-4}/min

At temperatures above approximately 60°C and at a pH above 11.5 these plots are no longer linear, but instead, show a downward curvature. Plotting c^{-1} vs. t (second order) shows a greater deviation from linearity.

A series of 5 reactions were run wherein the pH was held at 9.9 and the temperature at 66°C but the concentration of buffer was changed in a systematic fashion. Under these conditions no change in the rate was observed. Therefore, the process seems to be subject to specific base catalysis.

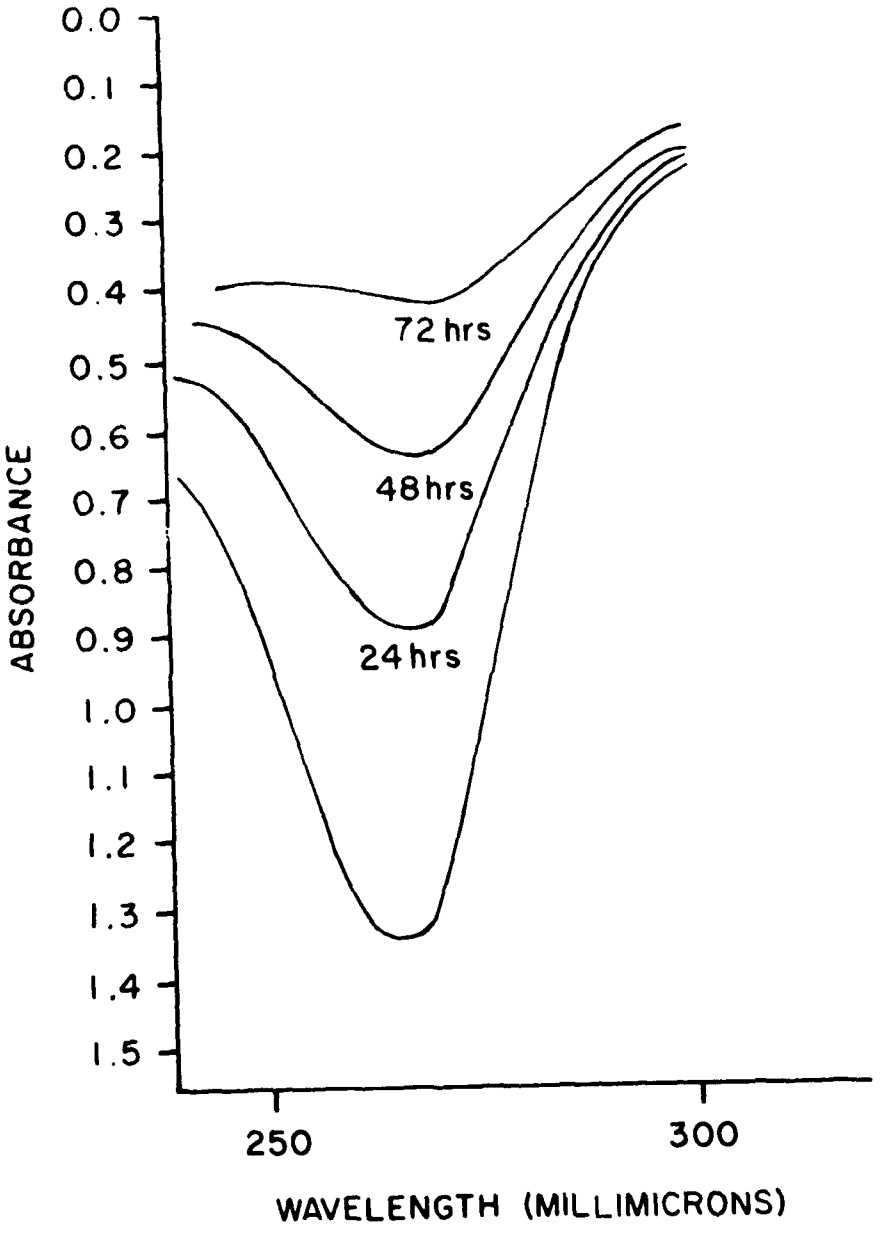

Fig. 1. Variation of absorbance of nitroguanidine with base.

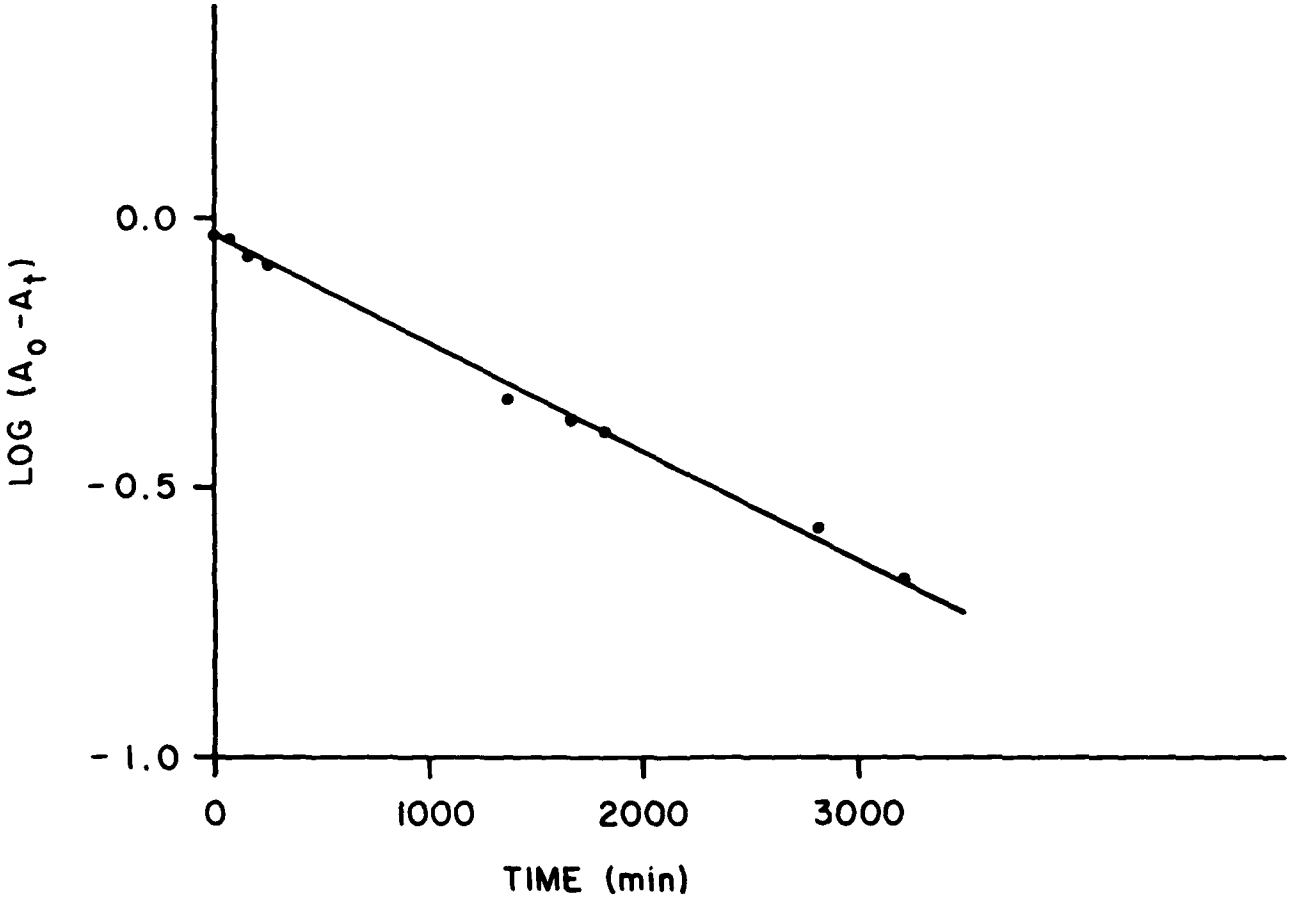

Fig. 2. Log (A_o-A_t) of nitroguanidine vs. time at pH 9.9 and 66°C.

The Arrhenius activation energy, E_a, was calculated at pH 11.8 from a linear plot of the following rate data:

Temp ^{o}K	k	
316	2.0×10^{-3}/min	$\ln k = -E_a/RT + Z$
326	5.3×10^{-3}/min	$E_a = 22.5$ kcal
336	1.8×10^{-2}/min	$Z = 29.5$/min

Analytical Methods for the Detection of Nitroguanidine: Two methods for the rapid separation and detection of nitroguanidine in the presence of other explosives were investigated. The first was thin layer chromatography (tlc). In this method 10 cm glass plates coated with either alumina or silica gel were used. With the proper choice of solvent, both coatings were found to be effective. The solvent system with alumina plates was 2% aqueous tetrahydrofuran, and with silica gel plates the developing solvent was benzene/nitromethane 2/1. Since nitroguanidine has UV absorption, UV light could be used as the detecting agent. There are several chemical agents which are also suitable for the detection of nitro- and nitramine compounds, the most general one being 1% diphenylamine in ethanol.[3] When plates containing nitro compounds are sprayed with this reagent and then exposed to UV light, various colored spots develop depending on the type of nitro function present. Although tlc is fast, it is difficult to use for quantitative analysis.

The second technique, which is more amenable to quantitative analysis of mixtures, was high pressure liquid chromatography (hplc).

[3]B. B. Coldwell, Analyst 84, 665-7 (1959).

Using this method it was possible to separate nitroguanidine from other common explosives (Fig. 3). The separation of compounds is such that the individual components can be easily collected and identified by other means (i.e., IR, UV, NMR, etc.).

In this study two different column materials and three different solvent systems were used. One column was packed with neutral alumina, and 2% aqueous tetrahydrofuran was used as eluting solvent. When a standard mixture of α-TNT, RDX, HMX, and nitroguanidine was fractionated with this system, the nitroguanidine was separated from the other materials but the HMX and RDX were not separated.

The second system investigated employed a μ-porasil column; the eluting solvent was 25% isopropanol/75% hexane, or 10% isopropanol/90% $CHCl_3$. The results obtained are summarized below:

	αTNT	RDX	HMX	Nitroguan.
Isopropyl/hex.	1.4 min	3.5	8.6	5.0
Isopropyl/$CHCl_3$	1.2	2.3	6.5	7.5

The elution times are relative to the time of injection.

A representative sample of washings from the M30 propellant was analyzed by hplc, using a μ-porasil column and 10% isopropanol/90% chloroform as eluting solvent. Using two UV detectors, one set at 254 nm for nitroguanidine and one at 220 nm for nitroglycerin, both compounds were easily detected. Nitroglycerin was eluted in 1.8 min and nitroguanidine in 7.2 min. Even at a level of 0.8 ppm, nitroguanidine was easily detected.

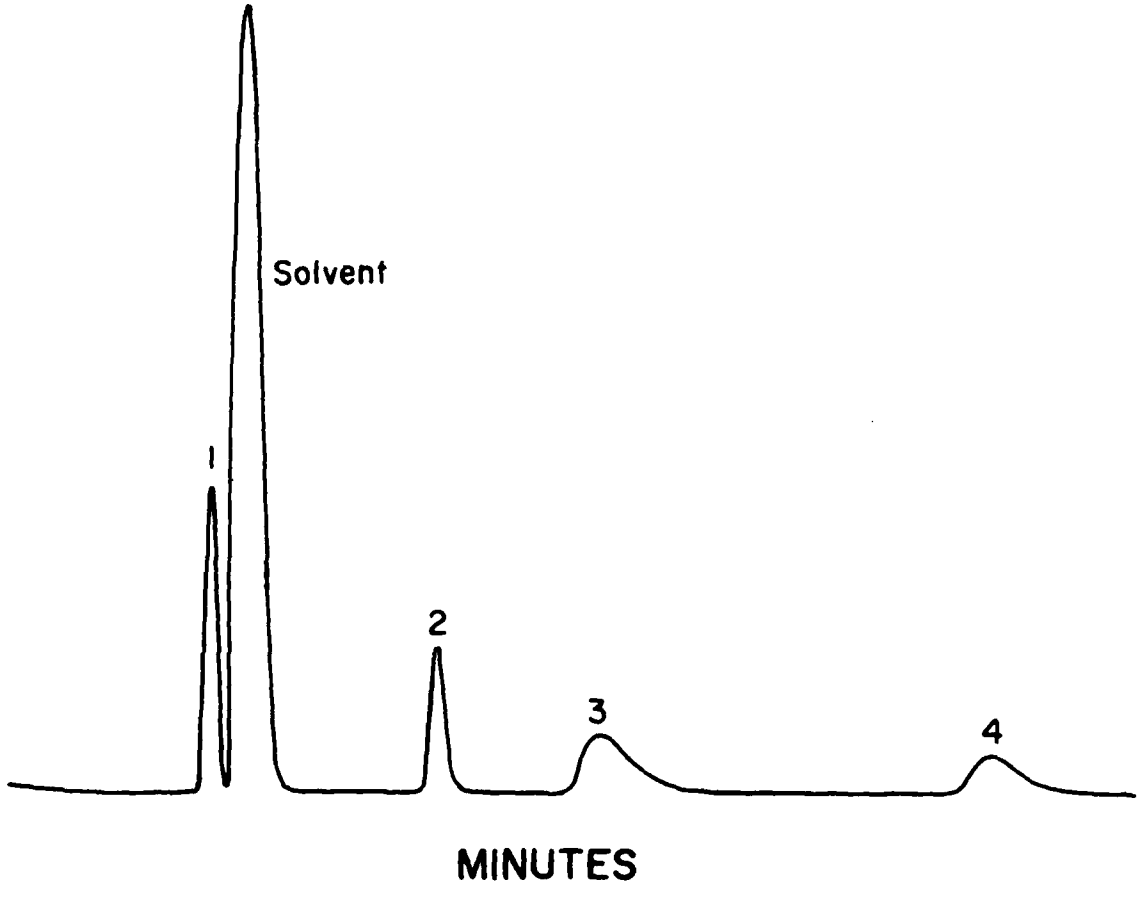

Fig. 3. Separation of α-TNT (1), RDX (2), NITROGUANIDINE (3), and HMX (4) using hplc. Column material -μ-porasil; length - 12"; flow rate - 3 ml/min; chart speed - 1"/min; solvent system - 25% isopropanol/75% hexane; detector - U.V. at 254 nm.

Conclusion: It has been demonstrated that nitroguanidine can be detected and separated easily and rapidly from other explosives using hplc. In less than 10 minutes a mixture of αTNT, RDX, HMX, and nitroguanidine can be separated with detectability of nitroguanidine as low as 0.8 ppm.

Nitroguanidine is only very slowly degraded in water and dilute acid. A reasonable rate of degradation can be effected by using base with a pH of 10 or above.