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# PREPARATION OF INSENSITIVE RDX FROM CRUDE RDX USING AN ANTISOLVENT PHASE SEPARATION PROCESS

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## ABSTRACT

This paper describes the separation of two of the most widely used explosive compounds, RDX (1,3,5-Trinitro-1,3,5-triazacyclohexane) and HMX (1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane). A simple antisolvent phase separation process to obtain >99% pure RDX from an explosive mixture consisting of RDX ( $\approx 90\%$ ) and HMX ( $\approx 10\%$ ) was developed. The process does not require modifications to the existing RDX manufacturing process, and only minimal amounts of new waste products and solvents are generated as there is no chemical reaction or complexation involved in this new process.

## 1. INTRODUCTION

Explosive compounds with Reduced Sensitivity (RS) for Insensitive Munitions (IM) are desired for reasons of safe load, assemble, and pack (LAP) operations and to meet the improved performance requirements of the energetics. The most common method of RDX manufacturing used in the United States is the continuous Bachmann process (Bachmann et al., 1949). The crude product formed during the process is filtered and recrystallized to form RDX. RDX produced by the Bachmann Process usually contains about 8-12% HMX as an acceptable byproduct. The sensitivity of the final explosive depends on the relative composition of RDX and HMX (Figure 1). The sensitivity of the crude RDX increases with increase in composition of HMX. HMX and solvent inclusions are the main impurities causing enhanced sensitivity (Borne and Ritter, 2006; Nock and Doherty, 2004).

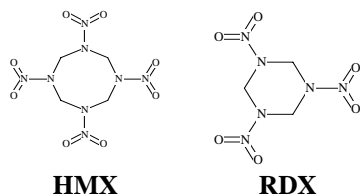


Fig 1. Chemical structures of RDX and HMX.

## 2. EXPERIMENTAL

Separation of the two energetic compounds RDX and HMX from their mixture using techniques such as recrystallization, selective adsorption, membrane separation, and phase separation by the addition of hydrophilic solvent have been attempted in our laboratory. Among these attempts, the solubilization of crude RDX in a suitable solvent and phase separation by adding water as an antisolvent was found to be effective in enriching the RDX composition. The resulting precipitate yielded a product with RDX composition >99%. Experimental details of the antisolvent phase separation are briefly presented here.

### 2.1 Materials

Crude RDX (a mixture of RDX and HMX), obtained from U.S. Army Armament Research Development and Engineering Center, Picatinny Arsenal, NJ 07806, USA, was used as received. Acetonitrile (ACS reagent grade) was purchased from Aldrich Chemicals, USA. The standards required for the determination of RDX and HMX were supplied by Accustandard, New Haven, CT, USA.

### 2.2 Analytical Methods

RDX and HMX concentrations were measured using the HPLC with a UVD170U and an Acclaim E1 Explosive column (Dionex ICS-3000). Chromatographic data were analyzed using Chromeleon® software. The critical step in the analysis of RDX by HPLC/UV is separation of the sample on a reverse-phase column, which provides good selectivity without risk of thermal breakdown of the analyte (Jenkins et al., 1986). The method is simple, quick, and reproducible. Sensitivity is in the low- to mid-ppb range, with very good recovery and excellent precision. The solutions were diluted appropriately prior to analysis.

## 2.3 Solubility of RDX and HMX

The solubility of RDX and HMX in water and acetonitrile was measured at room temperatures by adding an excess amount of the solid compound to sealed glass flasks containing deionized water and acetonitrile. Experiments were conducted in a shaker water bath (Julabo SW 23), and the temperature was controlled within  $\pm 0.5^\circ\text{C}$ . The flasks were stirred at 150 rpm for about 36 hours. Once thermal equilibrium was established at a given temperature, three 2-mL samples were withdrawn with a syringe, centrifuged for 10 minutes at 2000 rpm, and immediately diluted with appropriate solvent to avoid precipitation. To overcome adsorption losses on the glassware during experimentation, all the glassware was soaked in the solution of RDX and HMX for about 24 hours and rinsed with deionized water several times to remove excess solutes. The concentration of RDX and HMX was determined as detailed above.

## 2.4 Solubility modification

A homogenous stock solution was prepared by dissolving about 40 grams of crude RDX (a mixture of RDX and HMX, as received from an Army Ammunition plant) in 1000 mL of acetonitrile. The solution was analyzed using a chromatograph equipped with an UV detector. The analysis showed that the crude RDX contains 91.4% of RDX and 8.6% of HMX. To 50 mL of RDX stock solution in capped bottles, different volumes (25, 50, 100, 150, 200, 250 mL) of water were added and stirred for about 30 minutes on a magnetic stirrer. A precipitate formation was observed. The system was kept at room temperature ( $23 \pm 0.5^\circ\text{C}$ ) for about 2 hours. Then the precipitate was separated by filtration using Whatman filter paper. The precipitate was allowed to dry in air for about 48 hours and the weight of the precipitate was recorded. A small amount of the precipitate was analyzed for its composition, again by dissolving it in acetonitrile and injecting it into the chromatograph system. The concentration of RDX and HMX in the precipitate was determined with different amounts of added water. Table 1 lists the results.

Table 1. Composition of RDX and HMX in the precipitate and the precipitate yield.

Vol. of RDX+HMX in acetonitrile, (ml)	Vol. of H <sub>2</sub> O, (ml)	Yield of precipitate* (%)	Precipitated solid (%)	
			RDX	HMX
50	25	42.4	100	0
50	50	72.7	99.2	0.8
50	100	98.8	93.1	6.9
50	150	98.7	92.6	7.4
50	200	100	91.4	8.6

\*% Yield = [Weight of precipitate/(Amount of RDX + HMX in Original solution)] X 100.

## 2.5 Fourier Transformer Infrared Spectroscopy

Fourier Transform Infrared spectra of crude RDX and enriched RDX were recorded on Jasco FTIR Spectrophotometer (Jasco FT/IR-4100) in the range of  $4000 - 400\text{ cm}^{-1}$ .

## 2.6 X-Ray Diffraction Spectroscopy

XRD analysis was done on a Siemens D5000 unit with a ceramic Cu tube, graphite monochromator, computer-controlled theta-compensating slit and automated 40 sample changer equipped with the Diffrac Plus software and Powder Diffrac File 2002 database. Scans were collected from 4 to 80 degrees 2-theta, 2 second counts at 0.020 degrees steps. All samples were mounted and analyzed in the X-Ray Microanalysis Laboratory at University of Illinois, Champaign, IL, USA.

## 2.7 RESULTS AND DISCUSSION

The proposed process is based on the difference in solubility of RDX and HMX in acetonitrile and modification of solubility of RDX in a solvent mixture. It is also important that the maximum solubility of RDX is high in acetonitrile, the selected solvent. The solubility of RDX in water and acetonitrile at room temperature ( $23^\circ\text{C}$ ) was 45.9 mg/L and 48.7 g/L respectively, while the solubility for HMX are 3.49 mg/L and 17.15 g/L, respectively. Acetonitrile was chosen as a solvent to dissolve crude RDX (RDX and HMX mixture). Acetonitrile is also selected because it has the desirable transport properties of viscosity and diffusivity, and its relatively low and has normal boiling point of  $81.6^\circ\text{C}$  with an enthalpy of vaporization of 31.3 kJ/mol. The composition of RDX and HMX in the precipitate was determined for different amounts of added water to the solution. Table 1 lists the results.

To understand the structure and crystalline nature of the air dried precipitate of RDX, the Fourier Transform Infrared (FTIR), Nuclear Magnetic Resonance (NMR) spectra and X-ray diffraction (XRD) patterns were recorded. Figures 2 and 3 show the corresponding XRD patterns for crude and enriched RDX. Results of the  $^1\text{H}$  NMR spectra and FTIR spectra of crude RDX and the enriched precipitate were analyzed. Analysis of the separation process and spectral information show that relatively pure RDX can be obtained from the crude RDX following the simple phase separation process. As shown in Table 1, RDX with purity greater than 99% can be obtained with an yield greater than 70%.

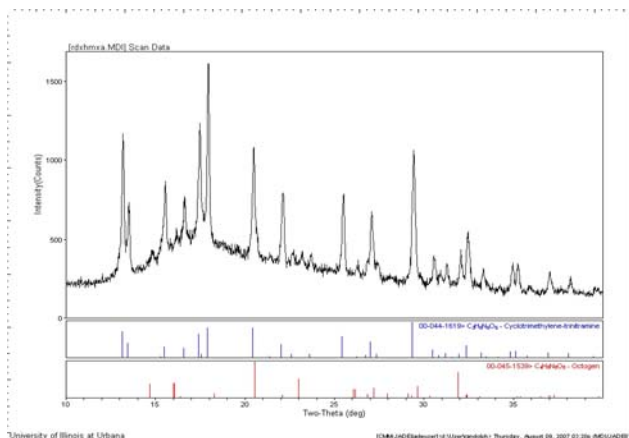


Fig. 1. XRD spectrum of crude RDX.

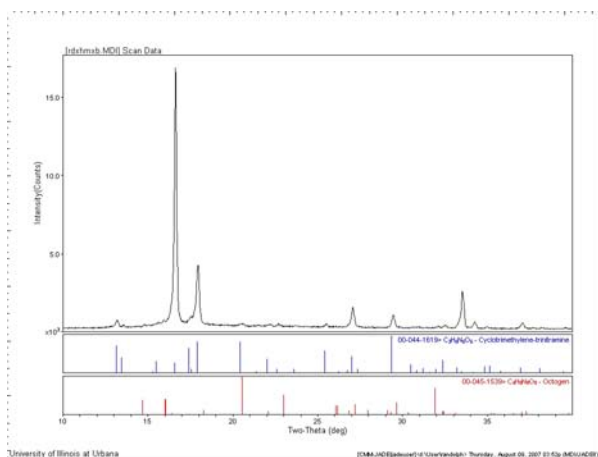


Fig. 2. XRD spectrum of the enriched RDX.

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