Extraction of Nitroguanidine (NQ) From Triple-Base Gun Propellant

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20020328 037

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Abstract

Laboratory-scale solubility and extraction studies were carried out to investigate the feasibility for recovery of nitroguanidine (NQ) from M30 triple-base gun propellant. The recovery process that was investigated involved stripping nitroglycerine (NG) from M30 propellant using supercritical carbon dioxide (CO_2), followed by aqueous extraction of NQ. The solubilities of NQ and NG in supercritical CO_2 were investigated. NQ was found to be relatively insoluble. NG was found to be up to six orders of magnitude more soluble than NQ in supercritical CO_2. The solubility of NQ in water was investigated at atmospheric pressure. Data were taken over a range of temperatures from 28 °C to 75 °C. The solubility data were found to follow an exponential function of $1/T$ over a range of 0 °C to 100 °C. The solubility of NQ varies by almost two orders of magnitude over this temperature range. A significant matrix effect was observed for the extraction of NG from M30 propellant. Prior micromilling of the propellant considerably enhanced the extraction of NG using supercritical CO_2. NQ was readily extracted from NG-depleted M30 propellant using hot water. The bulk of the NQ was recovered by precipitation at 1 °C. A small amount of NQ remained unrecovered in the extraction solution.

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1. Introduction

This report describes laboratory-scale efforts on the recovery of nitroguanidine (NQ) from the triple-base gun propellant M30. The U.S. demilitarization stockpile includes close to 30M lb of triple-base gun propellant, representing a potential resource of almost 15M lb of NQ. The bulk composition of a typical M30 propellant is roughly 47% NQ, 29% nitrocellulose (NC), 22% nitroglycerine (NG), 1.6% ethyl centralite (EC), and 0.4% cryolite. Lieb (1987) has shown that the NQ used in the production of M30 consists of needle-like crystals that tend to align with the flow field upon extrusion, especially near friction surfaces such as extrusion die pins, pin plate feed holes, or the walls of the die itself. The extraction technologies examined in the report include supercritical fluid extraction (SFE) to strip the NG plasticizer from the propellant and aqueous extraction of the NQ.

2. Safety Considerations

Some comments regarding safety considerations are in order. Subjecting energetic materials to a supercritical fluid environment poses potential safety hazards in addition to those that are considered for conventional energetic materials handling. Vande Kieft and Hillstrom addressed these specific hazards in their report (Vande Kieft and Hillstrom 1997). The safety considerations and recommendations found in their report were directed towards a trinitrotoluene/ cyclotrimethylenetrinitramine (TNT/RDX) large-scale separations process, but many of the points raised are valid for laboratory-scale operations. SFE involves placing material in a sealed vessel, under pressure, and at a somewhat elevated temperature. Initiation of even a small amount of energetic material under these conditions could have serious consequences. Particular caution is required when sealing the extraction vessel to ensure that no energetic material is trapped between the threads of the vessel cap.

Neat NG is an extremely sensitive energetic material. The NG solubility studies described in this report were carried out using a less sensitive NG/β-lactose compound. Even so, the much greater solubility of NG relative to RDX in supercritical carbon dioxide (CO_2) warrants extra caution. The measurement of NG solubility in CO_2 as great as 20 weight-percent raises the possibility of concentrating NG to a hazardous level. To reduce the hazard associated with handling concentrated NG, this material was collected using an acetonitrile trap to dilute the extract.

3. Solubility Studies

Solubility studies were carried out on NG and NQ in supercritical CO_2, and NQ in liquid water. Supercritical CO_2 solubility studies were carried out in an extraction apparatus depicted schematically in Figure 1.
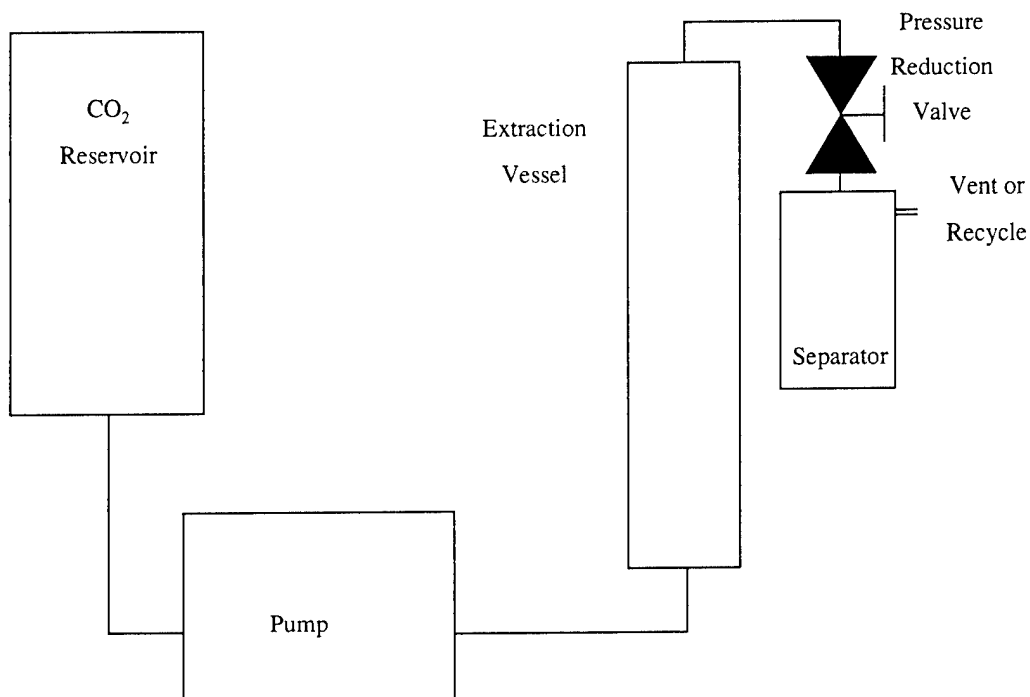
Figure 1. Schematic of SFE apparatus.

3.1 NQ in CO_2

For the NQ study, about 0.5 g of NQ powder was loaded into an extraction vessel that consisted of a thick-wall 6-mm outside diameter (O.D.) steel tube. End caps with sintered frits were used to contain the powder, while allowing the passage of supercritical CO_2 through the tube. The tube was heated to a temperature of 80 °C, and CO_2 at a pressure of 482 bar was passed through the bed of NQ. The extraction tube was periodically taken offline from the apparatus, carefully vented, and weighed to determine a mass loss due to extraction of NQ. The NQ gravimetric mass-loss profile is shown in Figure 2.
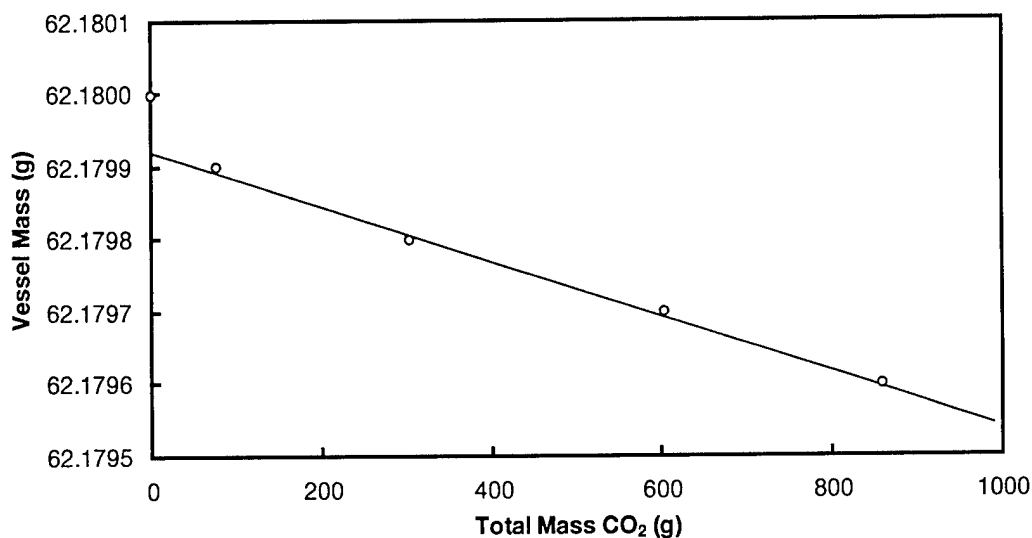
Figure 2. NQ mass loss vs. total mass of CO_2 at 80 °C and 482 bar.

The initial mass loss was attributed to stripping of residual processing solvent or water from the NQ. A linear regression fit was applied to the subsequent measurements to determine a solubility of 3.8×10^{-4} mg of NQ per gram of CO_2 at 80 °C and 482 bar. NQ is insoluble in dense CO_2, with a measured solubility about three orders of magnitude lower than that of RDX (Morris 1998).

3.2 NG in CO_2

A similar set of experiments was carried out for NG. Because NG was known to be extractable from propellant formulations using supercritical CO_2 (Melvin 1990), milder temperature and pressure conditions were employed relative to those for NQ. Because of the hazards of working with neat NG, a composition of 10 weight-percent NG on β-lactose was used (see section 2). A quantity of about 6 g of the NG/β-lactose composition, containing 600 mg of NG, was loaded into a 7.5-mL extraction vessel. Figure 3 shows the gravimetric extraction profile for the stripping of NG from the β-lactose using supercritical CO_2 at 40 °C and 103 bar. The last point shown in Figure 3 represents the stripping of all of the NG from β-lactose, with a corresponding 600-mg mass loss. A linear regression fit of the previous data points indicates a solubility of 13-mg NG per gram of CO_2 at 40 °C and 103 bar. Table 1 shows NG solubility data measured at a number of additional pressures.
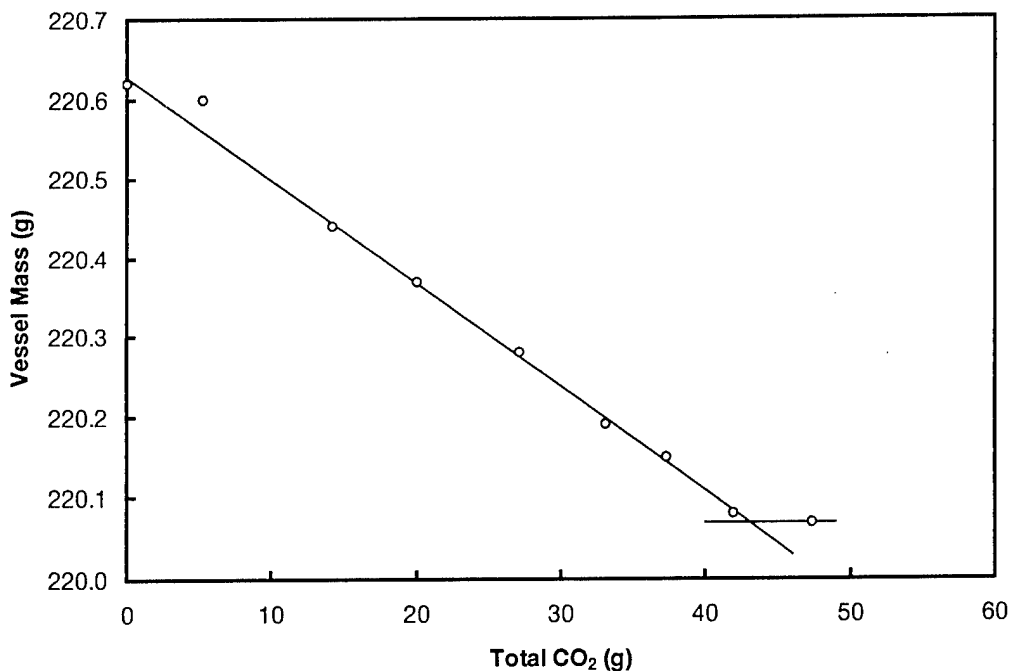
Figure 3. NG mass loss vs. total mass of CO_2 at 40 °C and 103 bar.

Table 1. Solubility of NG in supercritical CO_2 at 40 °C.

Pressure (bar)	No. Data Points	Milligrams NG per gram CO_2
103	6	13.0
138	4	40.2
172	2	69.5
207	1	125
276	1	238

The Peng-Robinson equation-of-state (EOS) is often used to model solubility in supercritical fluids:

$$P = (RT / (\underline{V} - b)) - (a / [\underline{V}(\underline{V} + b) - b(\underline{V} - b)]), \tag{1}$$

where equation P is pressure, T is temperature, $\underline{V}$ is molar volume, R is the ideal gas constant, and the parameters a and b account for intermolecular interactions and molecular size (covolume), respectively. McHugh and Krukonis (1994)

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outline procedures—including FORTRAN source code—for thermodynamic modeling of solubility in supercritical fluids using the Peng-Robinson EOS.

Adaptation of these FORTRAN codes to model NG solubility was carried out in collaboration with Professor McHugh's research group (Kuntz et al. 1998). The initial modeling effort used the existing NG data published by Nauflett and Farncomb (1992) and measured under contract to the Naval Surface Warfare Center by Rancourt et al. (1992). Modeling of a multiphase system using the Peng-Robinson EOS requires the use of mixing rules to determine the effective a and b parameters for the binary component system. Calculation of these parameters requires a number of the physical properties for each of the system components be known—in particular, the critical temperature (T_c), critical pressure (P_c), and the molecular acentric factor, ω. While these parameters are well known for CO_2, they had to be calculated or estimated for NG (Kuntz et al. 1998). Fitting of the solubility data also requires the use of two adjustable binary interaction parameters k_{ij} and η_{ij}.

Once the critical points and acentric factors were established, solubility isotherms were calculated using the FORTRAN Peng-Robinson EOS codes. The parameters k_{ij} and η_{ij} were adjusted using iterations to provide the best agreement with the experimental data.

The measurement of the data presented in Table 1 was prompted by the facts that the existing data set was not published in tabular form (values for fitting had to be measured from graphs) and that the solubility data were measured up to only a moderate pressure of about 160 bar. The new NG solubility data from Table 1 were refit using the FORTRAN Peng-Robinson EOS codes, resulting in refined values for k_{ij} and η_{ij}. Figure 4 shows the resulting Peng-Robinson EOS solubility isotherm plotted along with both sets of NG solubility data. The parameters that were used to generate the solubility isotherm are listed in Table 2.

Examination of Figure 4 reveals a significant deviation from the Peng-Robinson solubility isotherm for the point in each data set measured at the highest pressure (159 bar and 276 bar, respectively). The initial attempts to fit the NG solubility data of Rancourt et al. (1992) (Nauflett and Farncomb 1992) also showed a substantial deviation for the measurement at a pressure of 159 bar, which could not be accounted for at the time (Kuntz et al. 1998). In light of the new data, this solubility measurement is concluded to be low by at least 50%.

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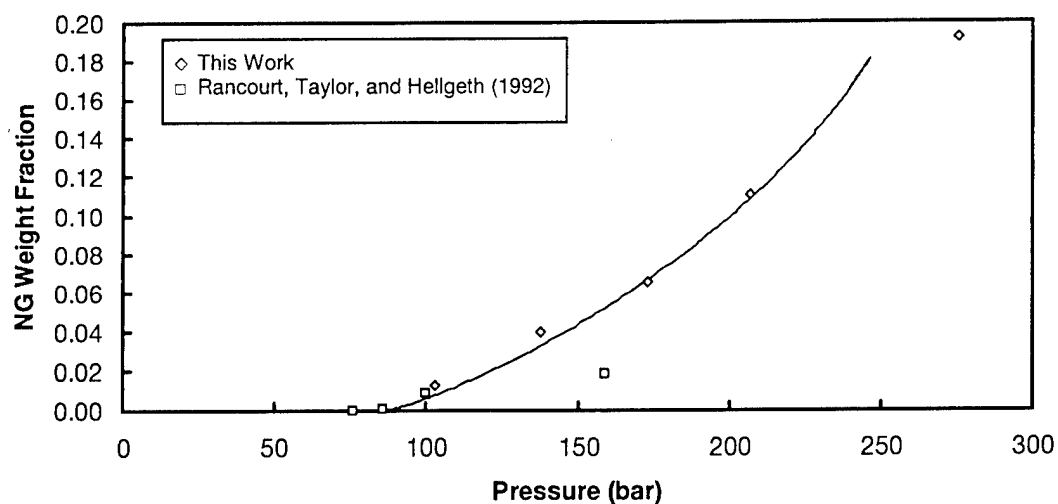
Figure 4. Peng-Robinson EOS fit of NG solubility data in supercritical CO_2 at 40 °C; $k_{ij} = 0.028$, $\eta_{ij} = 0.040$.

Table 2. NG-CO_2 solubility modeling parameters, 40 °C.

Property	NG	CO_2
M (g/mol)	227.1	44.0
T_c (K)	689.7[a]	304.2
P_c (bar)	30.0[a]	73.8
ω	1.10[a]	0.239
k_{ij}	0.028	
η_{ij}	0.04	

[a]From Kuntz et al. (1998).

The new solubility measurement at a pressure of 276 bar was based on a single mass-loss measurement (Table 1). This deviation can be accounted for by the finite time required to initially saturate the CO_2 stream passing through the bed of NG/β-lactose in the extraction vessel. If the initial flow of CO_2 passing through the vessel were not saturated, the gravimetric determination of mass loss would have resulted in a low NG solubility measurement. This situation

was expected to be a significant problem only at the higher pressures. Given the greater NG solubility at higher pressure, less CO_2 could be passed through the extraction vessel before stripping of all the NG. At the lower pressures (i.e., conditions of lower solubility), longer saturation runs were possible, minimizing the effect of initially unsaturated CO_2.

Excluding the NG solubility data taken at pressures of 159 bar and 276 bar, it is apparent that the Peng-Robinson EOS modeling approach provided a reasonable representation for both sets of NG solubility data. However, one caveat regarding this particular application of the EOS modeling is warranted. The NG solubility data was modeled as a two-component system consisting of NG and CO_2. In actuality, both sets of experimental data involved three-component systems. In addition to NG and CO_2, a β-lactose substrate was also present. Although β-lactose is not soluble in CO_2, NG may partition between the fluid (CO_2) and solid (β-lactose) phases, resulting in a lower equilibrium solubility value than would be encountered with a true two-component system.

3.3   NQ in Water

Solubility data for NQ in water at 0 °C, 25 °C, and 100 °C can be found in the Johns Hopkins University Chemical Propulsion Information Agency (CPIA) manual M3 (CPIA 1982). Additional solubility data for NQ in water were measured as a function of temperature in the temperature range between 25 °C and 100 °C. All aqueous NQ solubility measurements were carried out at atmospheric pressure.

The apparatus used to measure the solubility of NQ in water is shown schematically in Figure 5. A continuously stirred solution of NQ was prepared by dissolving NQ in an excess of hot water. The beam from a helium-neon (HeNe) laser was passed through the solution, with the laser beam output being directed onto a large surface-area photodiode. The photodiode output was amplified and recorded as a function of temperature as the solution cooled. As the temperature of the system dropped, the solution reached its saturation point and NQ began to precipitate. Upon cooling through the saturation temperature, the NQ precipitate was rapidly formed. Figure 6 shows a representative plot of amplified photodiode current as a function of temperature in the laser scattering experiment. Scattering of the HeNe laser beam from the precipitated NQ resulted in an attenuation of the signal from the photodiode as the system transitioned from an optically clear solution to a solids-filled slurry. The saturation temperature was assigned at the midpoint photodiode current for this transition. For the data displayed in Figure 6, this transition occurred at a temperature of 56 ± 0.5 °C.
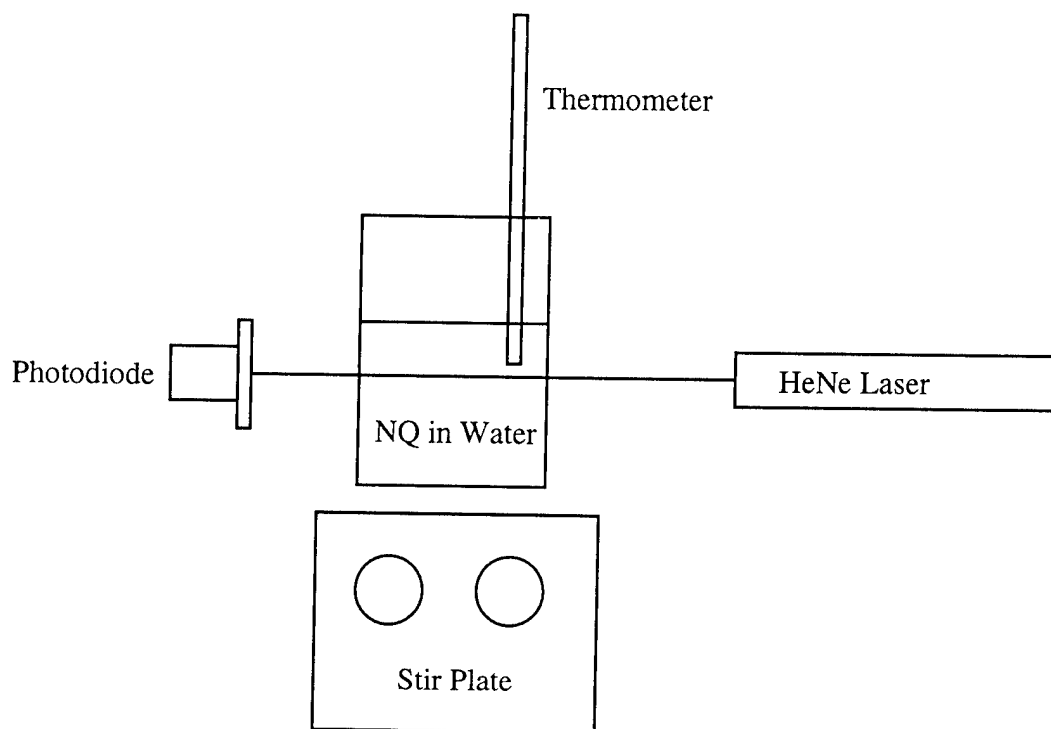
Figure 5. Schematic of NQ solubility apparatus.
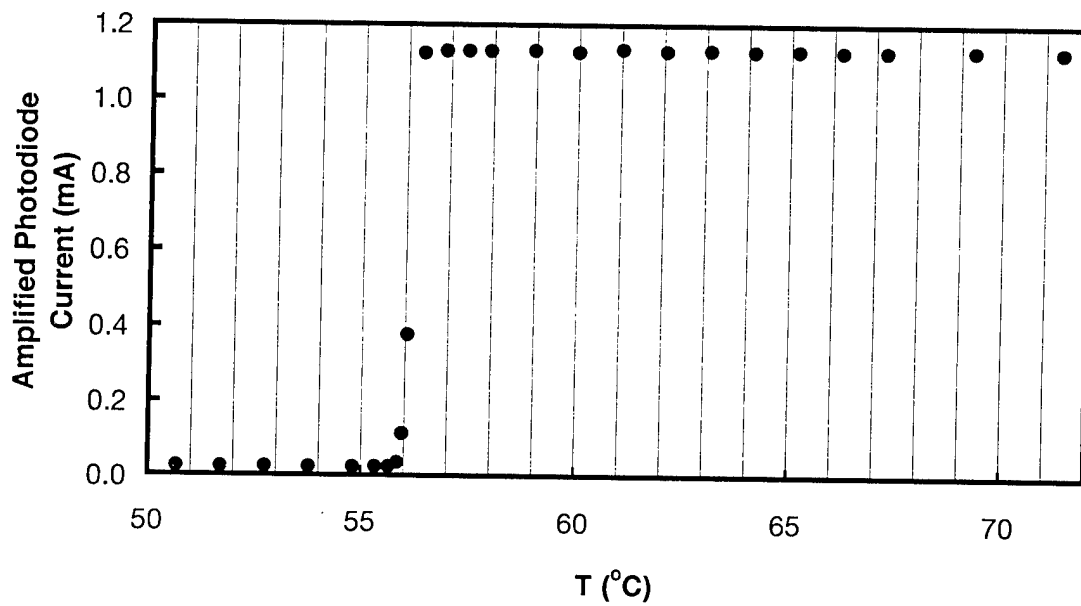
Figure 6. HeNe laser scattering raw data for cooling of 1.63-g NQ in 95.26-g water.

Table 3 shows the results for four concentrations of NQ in water. Figures 7 and 8 show plots of the combined NQ solubility data, which include the new data (Table 3) and the data found in the CPIA M3 manual (CPIA 1982). In Figure 7, the combined data are plotted as $-\log(x_{NQ})$ vs. 1000/T, where x_{NQ} is the NQ mole fraction and T is the absolute temperature converted to the Kelvin scale. When plotted in this fashion, the NQ solubility data are found to display a linear relationship. The slope of the line plotted in Figure 7 is proportional to the enthalpy of phase change for NQ going from its crystalline lattice into solution.

Table 3. Solubility of NQ in water at atmospheric pressure.

System Composition		Solubility	
NQ (g)	Water (g)	Grams NQ per 100-g Water	Temperature (°C)
0.50	99.05	0.50	28.2 ± 2.0
1.63	95.26	1.71	56.0 ± 0.5
2.17	97.60	2.22	66.5 ± 0.5
2.97	79.58	3.73	75.5 ± 0.5
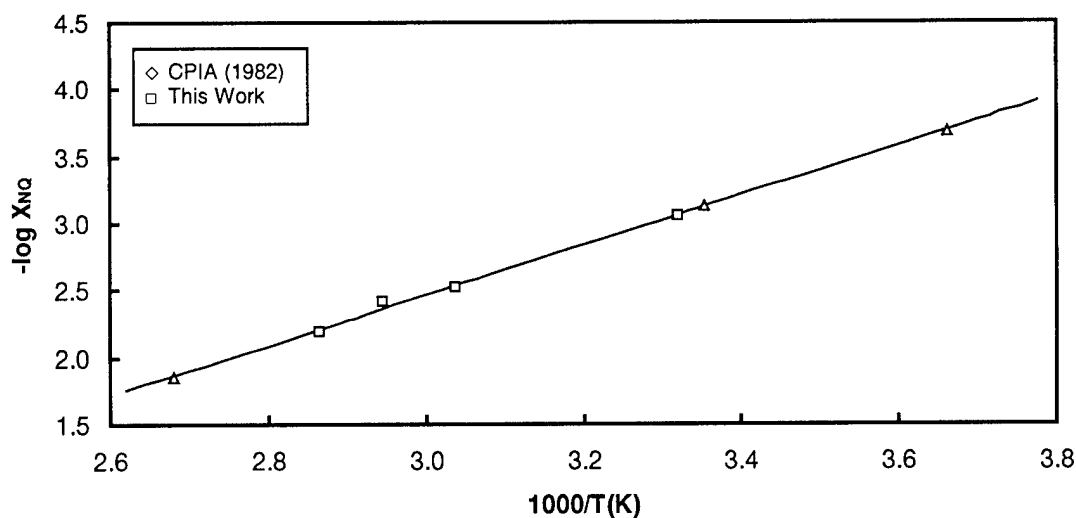
Figure 7. Log plot of mole fraction vs. 1000/T(K) for NQ in water.
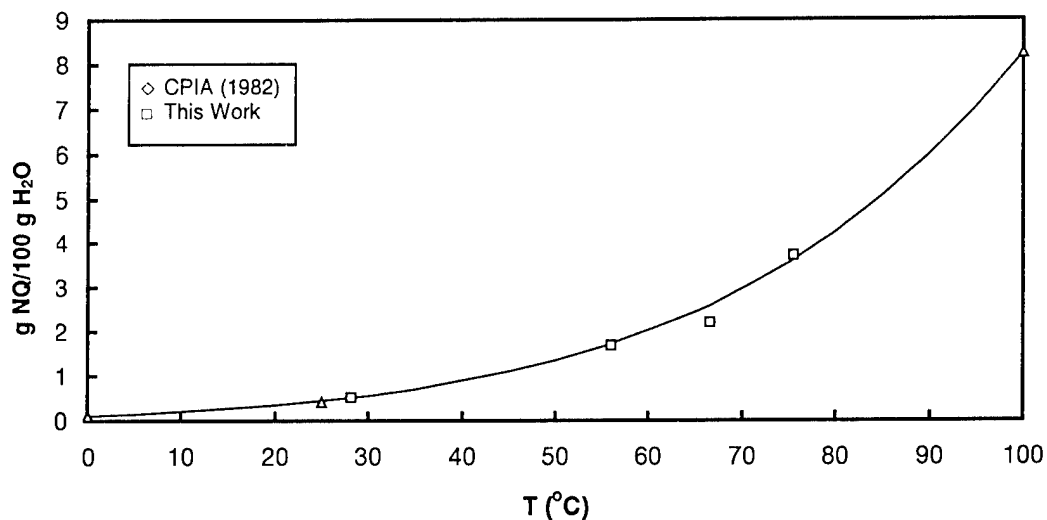
Figure 8. Linear plot of NQ mass solubility vs. T(°C) in water.

In Figure 8, the solubility data have been plotted on a linear scale in units of NQ mass solubility (grams NQ per 100-g water) vs. temperature. The data were fit to the following equation:

$$\text{Solubility}_{NQ} = 10^{-(1885/T(K) - 5.967)} \text{ (grams NQ per 100-g water).} \quad (2)$$

The fit in Figure 8 (i.e., equation 2) was based on a logarithmic treatment of the NQ solubility data in an analogous manner to Figure 7, where mass solubility was used in place of mole fraction. As was the case with Figure 7, equation 2 employs absolute temperature. It should be noted that the datum at 66.5 °C (339.6 K) was excluded from the regression used to generate equation 2. Inclusion of this point in the regression resulted in a 2.7% average error between the remaining experimental data and the predicted fit. When this point was excluded, the average error was reduced to 2.0%.

4. Extraction Studies

4.1 NG

Extraction of NG from M30 propellant was carried out using supercritical CO_2. The apparatus used for extraction of NG from M30 propellant was the same as that used in the NG solubility studies (Figure 1). Approximately 1 to 2 g of M30 propellant were placed in a 7.5-mL extraction vessel. Gravimetric extraction profiles of the propellant samples were generated using the same procedures as for the NG solubility studies (see section 2.2). Based on the relatively high

solubility of NG in supercritical CO_2 at 40 °C and 276 bar, these temperature and pressure conditions were used for the majority of the studies. Extractions were carried out using 0.25-in-diameter solid stick (no perfs) and ground M30. Unlike many propellants, the M30 sample did not have an exterior graphite coating. The propellant was ground using a micromill and was separated into two distributions using a 300-μm sieve. The two distributions were designated as coarse (>300 μm) and fine (<300 μm).

Ethyl centralite (EC) and NG are the only M30 components extractable with CO_2. Cryolite (AlF_6Na_3) is a mineral that is not expected to be soluble in CO_2. Figure 9 shows mass-loss profiles for the extraction of M30 gun propellant from the stick, coarse ground, and fine ground forms. The quantities of CO_2-extractable components are found in Table 4.
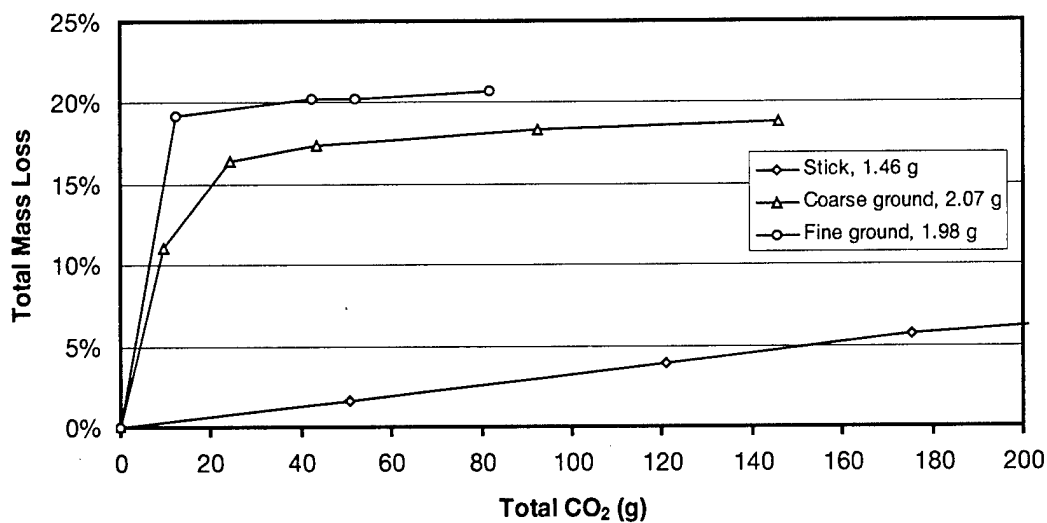
Figure 9. Mass-loss profiles for supercritical CO_2 extraction of M30 gun propellant at 40 °C and 276 bar.

Table 4. Quantities of extractable NG and EC from stick, coarse-ground, and fine-ground M30 samples.

Sample	M30 Mass (g)	NG Mass at 22 weight-percent (mg)	EC Mass at 1.6 weight-percent (mg)	Total Extractables (mg)
Stick	1.46	321	23	345
Coarse Ground	2.07	455	33	489
Fine Ground	1.98	436	32	467

As can be seen in Figure 9, the efficacy of extraction is highly dependent on the sample particle size. Dependence of extraction rate on particle size is well known, and has been previously observed for other energetic materials, such as the extraction of RDX from low-vulnerability ammunition (LOVA) gun propellant (Morris 1999). Initial extraction values corresponding to the first (non-zero) point in the mass-loss profiles of Figure 9 have been calculated for each of the three M30 extraction samples and are displayed in Table 5. Nitroglycerine composes the majority of the CO_2-extractable material in M30 (Table 4). A comparison of the initial extraction data for M30 propellant (Table 5) with the solubility data for NG in CO_2 at 40 °C and 276 bar (Table 1) reveals an order of magnitude difference between the extraction of NG from ground M30 and its extraction from β-lactose (i.e., solubility). When the solubility value of 238-mg NG per gram CO_2 is compared against NG extraction from M30 stick, the difference is close to 3 orders of magnitude.

Table 5. Initial mass-loss for supercritical CO_2 extraction of M30 gun propellant at 40 °C and 276 bar.

Sample	Total Extractables (mg)	Mass CO_2 (g)	Mass Loss (mg)	Initial Extraction Ratio[a] (milligrams per gram CO_2)	Extractables Removed (%)
Stick	345	50.7	25.9	0.51	8
Coarse Ground	489	9.6	230	24	47
Fine Ground	467	12.2	380	31	81

[a]Mass loss per gram CO_2 for first measurement.

Surface area and size play major roles in the extraction of NG from M30 propellant. The fine-ground and coarse-ground samples can be thought of as having nominal particle size distributions of ~300 μm. For the same bulk volume of material, a collection of 300-μm cubes will have about 30 times greater surface area than a 0.25-in-diameter cylinder. For actual ground samples, it would not be correct to assume a regular smooth shape, such as a cube or sphere, for the particles that make up the sample. The inclusion of surface roughness on the particles can increase the actual surface area by at least a factor of 2. When comparing the extraction between the stick and ground forms of the propellant, it is reasonable to expect the actual difference in sample surface area to be about two orders of magnitude. Extraction of NG occurs primarily at the interfacial surface between the fluid (CO_2) and solid (propellant) phases. The increased surface area of the ground propellant is directly reflected in the initial extraction data shown in Table 5, which displays about a 2 order of magnitude increase

between the stick propellant and the ground samples. This tendency is also observed when comparing the coarse-ground and fine-ground propellant, with the finer materials having a slightly greater surface area. The mass of NG initially available for extraction at the solid-fluid interface increases in proportion to the sample surface area.

Although not shown in Figure 9, the extraction of the stick propellant was continued using a total solvent mass greater than 1200 g of CO_2, with the extraction of about 0.2-g NG, or 13.6% of the initial sample mass. Similar extraction levels using less than 20 g of CO_2 were achieved for both of the ground samples. The reduction in the physical dimension of the ground-propellant sample resulted in a decreased path length from the center of the particle to the solid-fluid interface. In addition to increasing the surface area of the sample, grinding of the propellant samples reduced the mass-transfer requirements for migration of the NG from the bulk interior of the propellant to the extraction interface.

4.2 NQ

Aqueous extraction of NQ from NG-depleted M30 propellant was carried out using the apparatus shown schematically in Figure 10. A sample of 1 to 2 g of ground NG-depleted M30 was placed in a 2.5-mL steel extraction vessel. The vessel was placed in a 95 °C constant temperature water bath. The solution of extracted NQ in hot water was collected in a plastic vessel. The vessel was cooled at a temperature of 1 °C for at least 90 min to precipitate the NQ. Extracted NQ was recovered using vacuum filtration and was weighed after drying.

Figure 11 shows a gravimetric profile for the extraction of NQ from a 1.28-g sample of NG-depleted fine-ground M30 gun propellant. The NQ content of this sample was ~0.79 g. Five fractions were collected in this experiment, with the recovery of 0.68 g (86%) of the NQ. An average water flowrate of 0.8 g/min was used for these five fractions. The mass of unrecovered NQ (0.11 g) is consistent with its solubility at 1 °C (0.12-g NQ/100-g water). NQ was recovered from the first four fractions, using a total of 67.3 g water. No precipitate was recovered from the fifth fraction, indicating NQ depletion from the propellant sample. A much higher recovery yield would be expected by reusing the water for subsequent extractions, since this water would already be saturated for NQ at 1 °C.

No attempts were made to extract NQ directly from bulk M30 propellant. While NG is nominally insoluble in water, it might be extracted to some extent at the elevated temperatures required to extract NQ. As the temperature is lowered, some of the NG may separate from the solution. Sensitive crystalline NG may
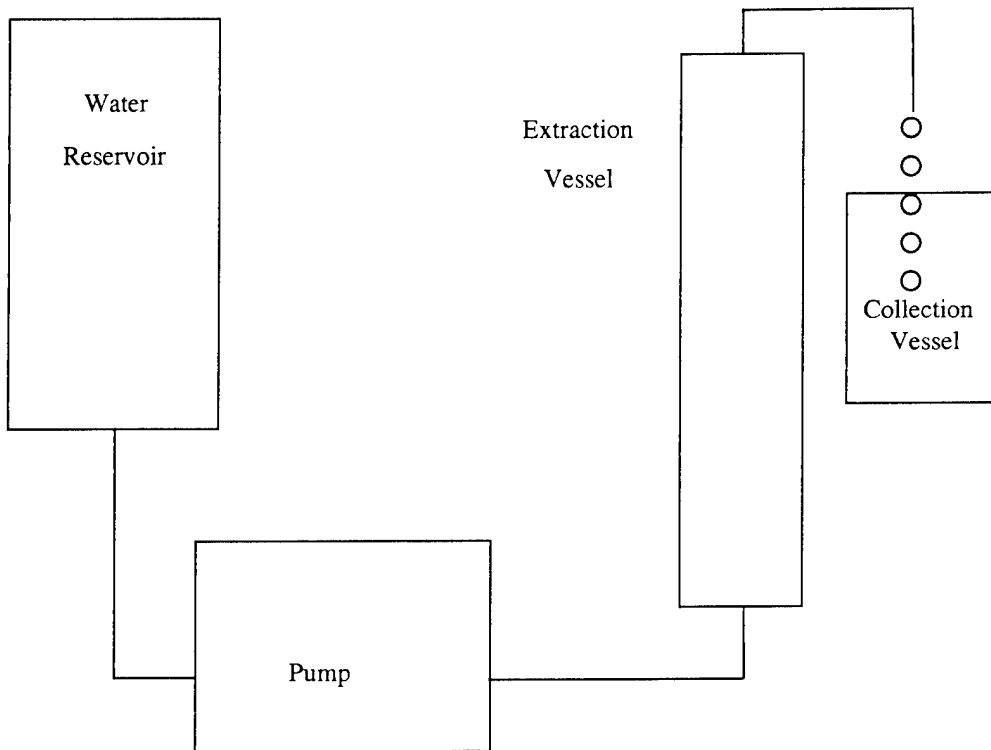
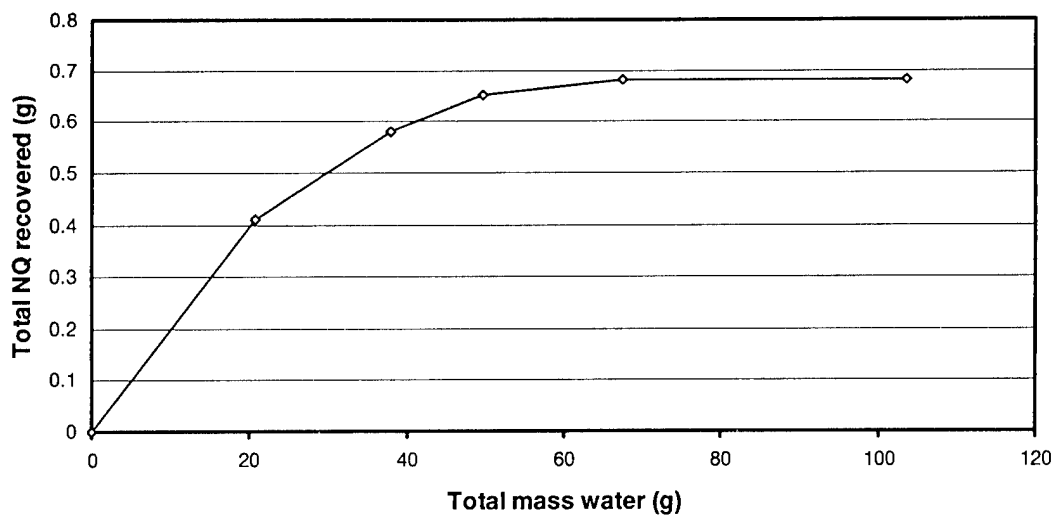Figure 10. Schematic of aqueous extraction apparatus.

Figure 11. Gravimetric profile for the 95 °C aqueous extraction of NQ from 1.28 g of NG-depleted fine-ground M30 propellant.

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form at the even lower temperatures used to fully precipitate the NQ. Farncomb et al. (1995) have shown that nitrate esters like NG can be extracted from water using supercritical CO_2. If direct aqueous extraction of NQ were to be implemented, supercritical CO_2 extraction of any residual NG from the solution may be advisable prior to low-temperature recovery of NQ.

5. Summary

Laboratory-scale solubility and extraction studies were carried out to investigate the feasibility for recovery of NQ from M30 triple-base gun propellant. The recovery process investigated involved stripping NG from M30 propellant using supercritical CO_2, followed by aqueous extraction of NQ. As a preliminary step, solubility studies were carried out on NQ and NG.

The solubility of NQ in supercritical CO_2 was investigated at conditions of 80 °C and 482 bar. Under these conditions, NQ was found to be insoluble, with a measured solubility of 3.8×10^{-4} mg NQ per gram of CO_2. The solubility of NG was also investigated using supercritical CO_2. NG was found to be up to 6 orders of magnitude more soluble than NQ under much more modest conditions of 40 °C and 103–276 bar. Solubility considerations indicate that NQ and NG can be separated using supercritical CO_2.

The solubility of NQ in water was also studied at atmospheric pressure. Data were taken over a range of temperatures of 28 °C to 75 °C. These data were compared with existing data at 0 °C, 25 °C, and 100 °C. The NQ solubility data were found to follow an exponential function of $1/T$ over a range of 0°–100 °C. The solubility of NQ varies by almost two orders of magnitude over this temperature range.

A significant matrix effect was observed for the extraction of NG from M30 propellant. Micromilling the propellant prior to extraction considerably enhanced the extraction of NG using supercritical CO_2. This step would probably not be practical for a large quantity of propellant.

NQ was readily extracted from NG-depleted M30 propellant using hot water. The bulk of the NQ was recovered by precipitation at 1 °C. A small amount of NQ remained in the extraction solution. Reusing the solution for subsequent extractions could minimize the loss of NQ to the extraction solvent. Direct aqueous extraction of NQ from bulk propellant would require further evaluation and hazards assessment regarding the fate of any co-extracted NG.

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REPORT DOCUMENTATION PAGE

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project(0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)	2. REPORT DATE	3. REPORT TYPE AND DATES COVERED
	February 2002	Final, October 1996 – September 1999

4. TITLE AND SUBTITLE
Extraction of Nitroguanidine (NQ) From Triple-Base Gun Propellant

5. FUNDING NUMBERS
622618.H80

6. AUTHOR(S)
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8. PERFORMING ORGANIZATION REPORT NUMBER
ARL-TR-2669

9. SPONSORING/MONITORING AGENCY NAMES(S) AND ADDRESS(ES)
EQBRD, Industrial Ecology Center, TACOM ARDEC
ATTN: AMSTA-AR-WET
Picatinny Arsenal, NJ 07806-5000

10. SPONSORING/MONITORING AGENCY REPORT NUMBER

11. SUPPLEMENTARY NOTES

12a. DISTRIBUTION/AVAILABILITY STATEMENT
Approved for public release; distribution is unlimited.

12b. DISTRIBUTION CODE

13. ABSTRACT(Maximum 200 words)

Laboratory-scale solubility and extraction studies were carried out to investigate the feasibility for recovery of nitroguanidine (NQ) from M30 triple-base gun propellant. The recovery process that was investigated involved stripping nitroglycerine (NG) from M30 propellant using supercritical carbon dioxide (CO_2), followed by aqueous extraction of NQ. The solubilities of NQ and NG in supercritical CO_2 were investigated. NQ was found to be relatively insoluble. NG was found to be up to six orders of magnitude more soluble than NQ in supercritical CO_2. The solubility of NQ in water was investigated at atmospheric pressure. Data were taken over a range of temperatures from 28 °C to 75 °C. The solubility data were found to follow an exponential function of $1/T$ over a range of 0 °C to 100 °C. The solubility of NQ varies by almost two orders of magnitude over this temperature range. A significant matrix effect was observed for the extraction of NG from M30 propellant. Prior micromilling of the propellant considerably enhanced the extraction of NG using supercritical CO_2. NQ was readily extracted from NG-depleted M30 propellant using hot water. The bulk of the NQ was recovered by precipitation at 1 °C. A small amount of NQ remained unrecovered in the extraction solution.

14. SUBJECT TERMS
extraction, nitroglycerine, nitroguanidine, M30

15. NUMBER OF PAGES
28

16. PRICE CODE

17. SECURITY CLASSIFICATION OF REPORT	18. SECURITY CLASSIFICATION OF THIS PAGE	19. SECURITY CLASSIFICATION OF ABSTRACT	20. LIMITATION OF ABSTRACT
UNCLASSIFIED	UNCLASSIFIED	UNCLASSIFIED	UL

NSN 7540-01-280-5500

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