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Supercritical Fluid Extraction of Nitramine-Based Gun Propellant: A Fluid Survey

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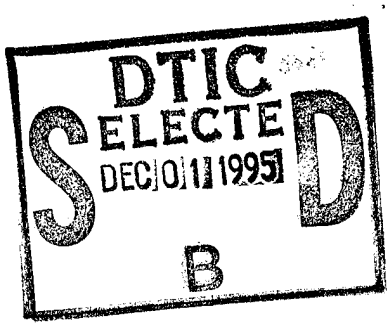

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13. ABSTRACT *(Maximum 200 words)*

A survey of the extraction of RDX from M43 solid gun propellant was conducted using 39 supercritical fluid systems, which included 36 carbon dioxide-based systems modified by the addition of small amounts of polar organic solvent. These fluids were ranked by quantification of the mass of RDX extracted per unit mass of fluid. Correlations between the physical and chemical properties of the solvent modifiers and the fluid extraction efficiences were sought through detailed analysis of the extraction data. Modifier dipole moment and RDX solubility in the neat solvent were found to be important factors in the interpretation of the experimental results. The most effective carbon dioxide modifers for the extraction of RDX were found to be dimethylsulfoxide, octanenitrile, 1-methyl-2-pyrrolidinone, dimethylformamide, butyrolactone, and acetonitrile.

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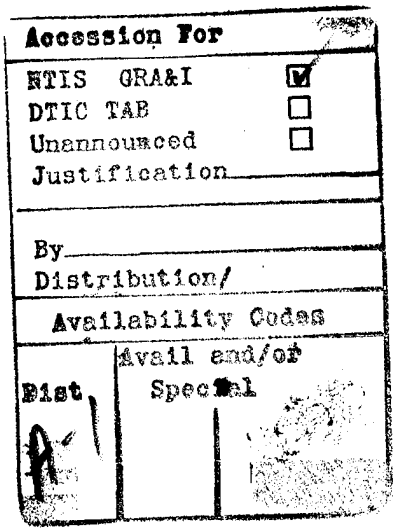

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1. INTRODUCTION

Environmental regulations have become more stringent over the last several years. The usual methods of handling excess energetic material–open burning and open detonation (OB/OD)—have come under scrutiny and may indeed be totally phased out in the near future. As a result of these regulations, a need for new environmentally sound technologies for dealing with excess and scrap propellants and explosives has arisen. One environmentally friendly method currently under consideration for dealing with these materials is supercritical fluid extraction (SFE). SFE offers the possibility for removal and recovery of the valuable energetic ingredients from propellants and explosives, as opposed to disposal of these materials through destructive OB/OD processes.

The physical state of any pure substance is determined by its temperature and pressure. Figure 1 shows a phase diagram for carbon dioxide (CO_2). This phase diagram displays two unique points. The triple point occurs at the intersection of the solid-liquid, solid-gas, and gas-liquid equilibrium curves and represents the unique temperature and pressure conditions where the solid, liquid, and gas phases coexist. The critical point occurs at the terminus of the liquid-gas equilibrium line. At temperatures and pressures exceeding the critical temperature (T_c) and critical pressure (P_c), there is no longer a demarcation between the liquid and gas phases and the substance is referred to as a supercritical fluid. Table 1 lists T_c and P_c for several fluids; more comprehensive tabulations of critical pressures and temperatures can be found in Murray et al. [1] and Weast [2]. Liquid-like densities, as well as gas-like viscosities and diffusivities, are characteristic of supercritical fluids and make them ideal mass transfer solvents for extraction and recovery processes [3].

Carbon dioxide is the most commonly used supercritical fluid for SFE. This choice is based on both its low cost and its easily accessed critical parameters (see Table 1). In addition, it is relatively inert and thus poses a negligible ozone-depleting potential and low toxicity. CO_2 is commercially prepared by recovery from industrial and natural sources [4]. Commercial CO_2 is used as a refrigerant (dry ice or cryogenic liquid), for carbonation of beverages, and as a fire suppression agent in fire extinguishers. In addition to these more conventional uses for CO_2, one of its first commercial uses in its supercritical state was for the decaffeination of coffee [5].

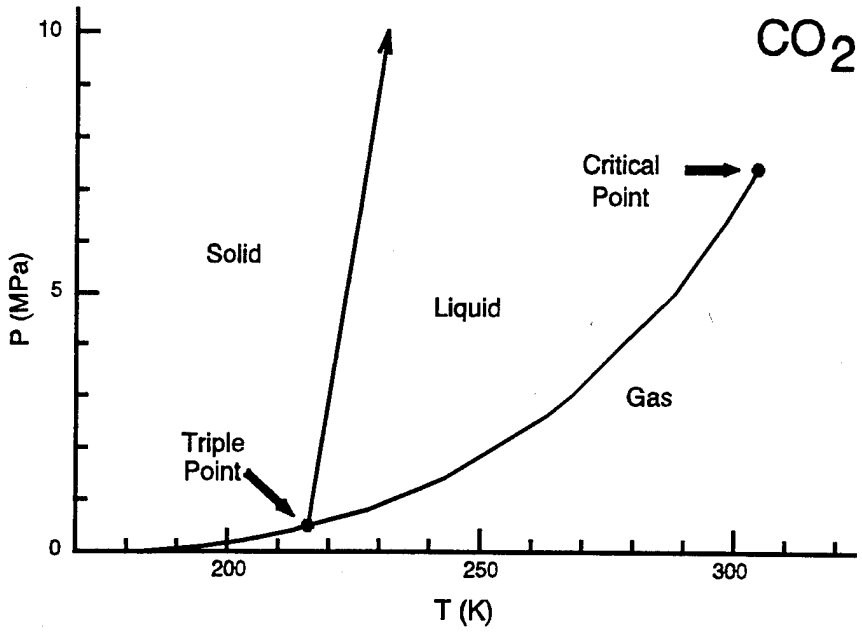

Figure 1. Phase diagram for CO_2.

Nitramines are a class of energetic materials which are often used in propellants and explosives. The two most commonly used nitramines are 1,3,5-trinitro-1,3,5-triazacyclohexane (RDX) and 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane (HMX). RDX and HMX are found in both commercial and military propellant and explosive formulations. In addition, HMX is typically found as an impurity in domestic RDX at the 2 to 10-weight-percent level. SFE and supercritical fluid chromatography (SFC) have been used extensively to study single base (e.g, nitrocellulose based) [6–9] and double base (e.g., nitrocellulose/nitroglycerine based) propellants [10,11]. In most cases, SFE/SFC was used for the extraction of plasticizer and stabilizer ingredients. A significant problem with the use of SFE for removing RDX and HMX from propellants and explosives is the limited solubility of nitramines in neat supercritical carbon dioxide [12]. One technology developed in the late 1980s is that of gas antisolvent (GAS) recrystalization, where a material which is dissolved in a conventional solvent can be forced to precipitate out by supersaturating the solution through the addition of a soluble gas, such as CO_2 [13–16]. Given the large amount of hazardous waste that would be generated from a conventional organic solvent-based extraction of formulated munitions, GAS recrystallization is not viewed as a primary nitramine recovery process, but it could have a large impact on the processing and separation of recovered RDX and

Table 1. Critical Parameters and Dipole Moments for Selected Fluids

Fluid	T_c		P_c		Dipole Moment (Debyes)	Comments
	K	°C	MPa	lb/in^2		
Carbon Dioxide	304.3	31.1	7.38	1,070	0.0	Nonpolar
Ethane	305.6	32.4	4.88	708	0.0	Nonpolar
Propane	370.0	96.8	4.25	616	0.0	Nonpolar T_c high
Xenon	289.9	16.7	5.84	847	0.0	Nonpolar Very Expensive
Sulfur Hexafluoride	318.9	45.7	3.76	545	0.0	Nonpolar
Monofluoromethane	315.2	42.0	5.60	812	1.8	Very Expensive
Fluoroform	299.5	26.3	4.86	705	1.6	Expensive
Nitrous Oxide	572.6	36.6	7.24	1,050	0.2	Strong Oxidizer
Water	647.6	374.4	22.11	3,208	1.0	T_c Too High Corrosive
Ammonia	405.6	132.4	11.35	1,646	1.5	T_c High Corrosive
Hydrogen Sulfide	373.4	100.2	8.94	1,297	0.9	T_c High Too toxic

HMX [15,16]. Two approaches to address the problem of nitramine insolubility in neat CO_2 can be taken. The first of these is to replace CO_2 with a polar supercritical fluid. Three promising polar fluids with easily accessed critical parameters are monofluoromethane, fluoroform (CHF_3), and nitrous oxide (N_2O) (see Table 1). One recent report on the SFE of caffeine indicates that N_2O can act as an oxidizer with explosive results [17]. Monofluoromethane is too expensive for further consideration. This leaves CHF_3 as one of the most likely polar fluid candidates. The second approach which can be taken to overcome the solubility problem of the nitramines is the use of small quantities of polar organic solvents (referred to as cosolvents, entrainers, or modifiers) to change the solubility parameters and solvation strength of CO_2-based supercritical fluids. Serious investigations of the use of modifiers for CO_2-based SFE have only begun over the last 5 years or so. Results from these studies are reviewed in a report by Schroeder et al. [18].

The goal of this work was to identify those supercritical fluids which show the most promise for use as mass transfer solvents for SFE-based nitramine recovery processes. A survey of 36 modified CO_2 supercritical fluids has been conducted. An additional three neat supercritical fluids were also included in the survey. The nitramine extraction potential for these fluids was evaluated by using them to extract RDX from M43 gun propellant. Chemical and physical properties of the cosolvents used were also examined to gain more insight into which factors are important in the selection of effective CO_2 modifiers.

2. EXPERIMENTAL

All extractions reported here were performed with a CCS Instrument Systems (CCSIS) SFE system, which consisted of a high-pressure pump (CCSIS model 392A) and a bench-scale SFE unit (CCSIS model 3100-100). The apparatus, shown in a block diagram in Figure 2, is capable of working at fluid pressures as great as 69 MPa (10,000 lb/in^2). Neat CO_2, N_2O, and CHF_3 were obtained from Matheson Gas Products. The CO_2 and N_2O were SFC grade, and the CHF_3 was 98.0% minimum purity. The organic modifiers used in this study were obtained from Aldrich Chemical Company and were used without further purification.

The SFE system used allows for both static and dynamic extractions (see Figure 3). In the case of static extraction, the sample is exposed to a nonflowing bath of fluid. Dynamic extraction refers to the situation where the fluid is allowed to flow continuously through the extraction cell. The primary purpose of static extraction is to allow the fluid to permeate the sample and to begin the mass transfer process of the target molecule(s) from the sample to the fluid phase. Dynamic extraction is then used to maximize the mass transfer process by providing to the sample a supply of fluid that is free of the extraction target solute. The extracted material is collected only during the dynamic extraction run.

A single grain of RDX-based composite gun propellant (M43) was placed in a 50-ml stainless steel SFE cell rated to 69 MPa (Keystone Scientific). Organic modifier was added directly to the SFE cell which was then back-filled with CO_2. The addition of 2 ml of organic solvent to the SFE cell resulted in an approximate modifier level of 4% by volume. For the present study, we chose not to use the modifier addition module (CCSIS model OM-300) which was included with our SFE apparatus. Contamination of the fluid transfer lines was an inherent problem with the frequent changing of modifiers. The direct addition of the modifier into the extraction vessel minimized this problem. The 2-hr static

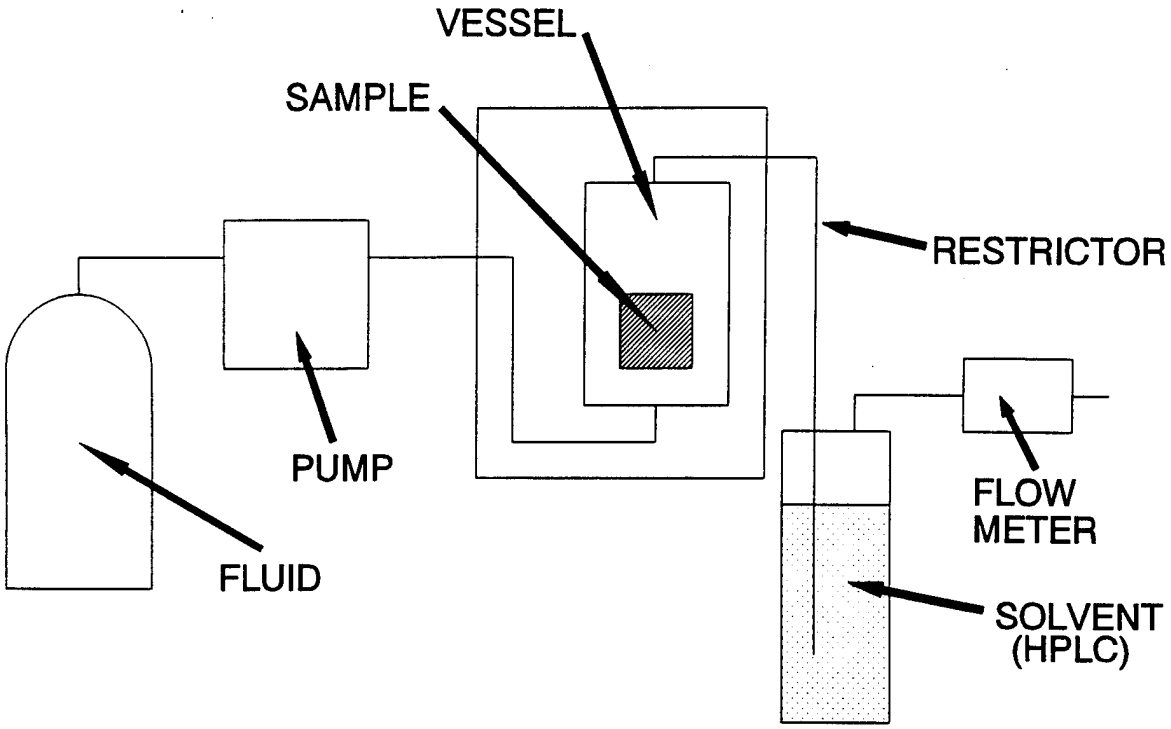

Figure 2. Block diagram of supercritical fluid extraction apparatus.

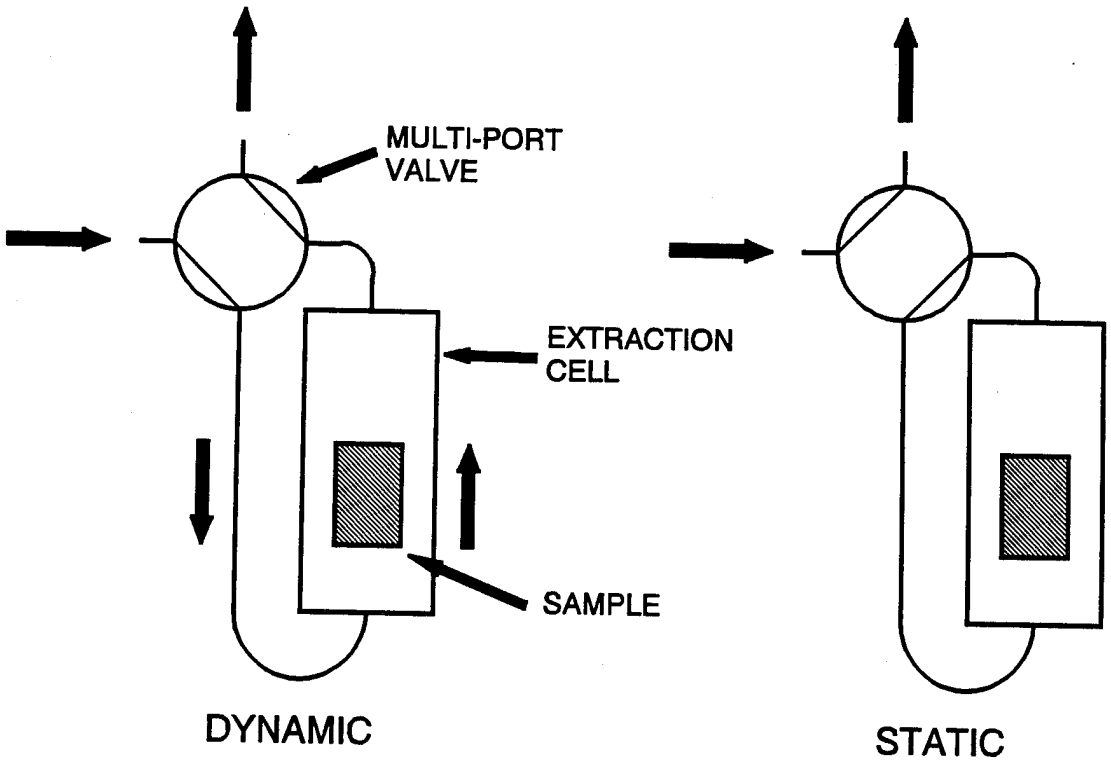

Figure 3. Dynamic-vs.-static supercritical fluid extraction.

extractions were performed at a pressure of 41 MPa (6,000 lb/in^2) and a temperature of 323.2 K (50° C). The extraction time was chosen to allow for adequate mixing of the modifier with the CO_2, as well as penetration of the fluid into the propellant grain. Collection of the extracted nitramine was accomplished by running the extractor in dynamic SFE mode, where the fluid was expanded through a flow restrictor into an acetonitrile solvent trap. The mass of CO_2 used was calculated by venting the solvent trap through a mass flow meter (MKS Instruments) and recording the CO_2 flow rate as a function of time. The CO_2 flow data were then integrated to yield the total volume, and the volume of gaseous CO_2 was converted into grams of CO_2 used in the extraction run. The total volume of supercritical CO_2 expanded through the restrictor was kept below the 50-ml volume of the vessel to ensure that only statically extracted material was collected. Extraction runs involving neat CO_2, N_2O, or CHF_3 as the extraction medium were performed using the same procedures as those used for the modified CO_2 runs. Since these runs involved the use of neat fluid, no modifier was added to the extraction cell.

The amount of RDX extracted was quantified using high-performance liquid chromatography (HPLC). The acetonitrile solvent trap was diluted to a 50-ml total volume, and HPLC peak areas were compared with those from a standard RDX solution. A C18 column (5-µm particle size, 4.6-mm inner diameter, 150-mm length, Alltech Associates) was used with a 75:25 water:methanol mobile phase and a flow rate of 1 ml/min. A 10-µl sample loop was used for injection onto the column. Quantitative detection of extracted RDX was performed using ultraviolet (UV) detection at 246 nm. ISCO HPLC equipment was used and included a model 2360 gradient programmer, a model 2350 pump, and a model V^4 absorbance detector. RDX extraction values were obtained by dividing the mass of RDX recovered by the total mass of CO_2 that was vented through the mass flow meter. Figure 4 shows an HPLC chromatogram of RDX (and HMX impurity) extracted from M43 gun propellant.

The composition of M43 gun propellant is as follows: 76% RDX, 16% polymer, and 8% plasticizer. The RDX particles were slightly oblong with a mean size of approximately 5 µm. The mass of a typical propellant grain was in the range of 1.2–1.4 g. The grains as received were coated with an exterior graphitic glaze and had 19 perforations running axially (see Figure 5). The surface area of the perforations accounts for approximately 40% of the total surface area of the propellant grain, with the remaining 60% of the surface area belonging to the grain exterior surfaces (cylinder side and ends). The propellant was used without size reduction or any other pretreatment.

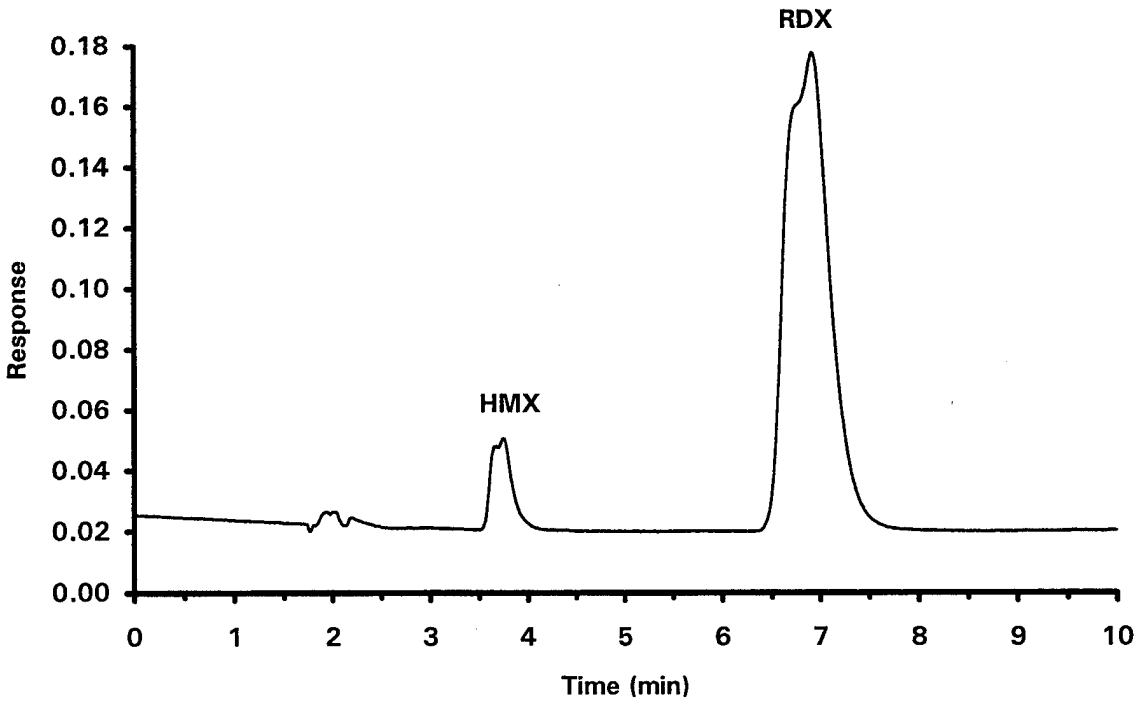

Figure 4. HPLC chromatogram of RDX and HMX extracted from M43 gun propellant using dimethylsulfoxide–modified CO_2.

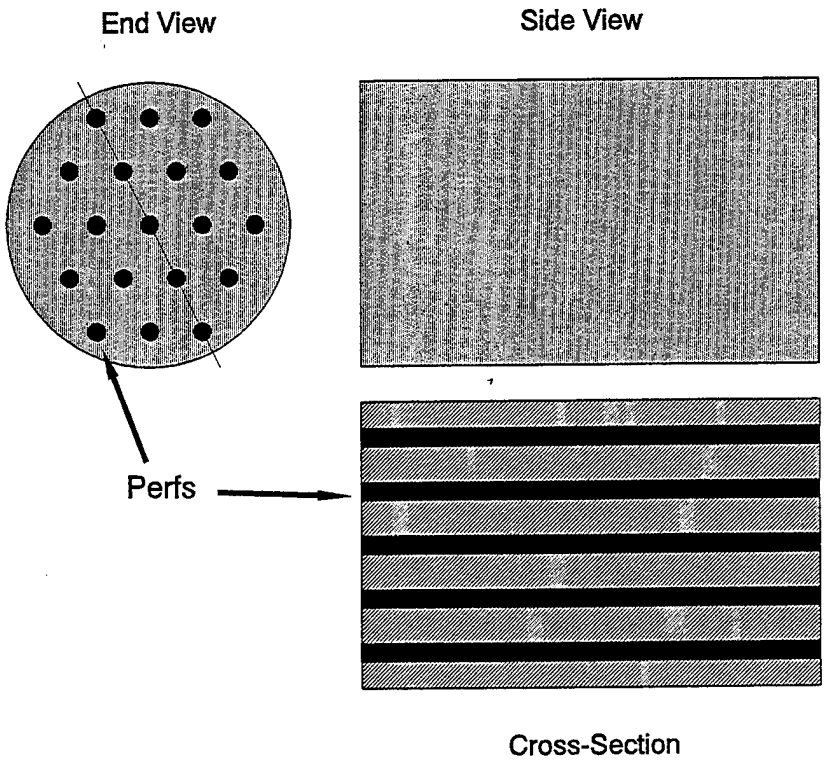

Figure 5. Approximate geometry of M43 gun propellant grain.

Each propellant grain was visually examined following the extraction process to assess its degree of swelling. In addition, a few of the grains were examined using either reflectance Fourier transform infrared microspectroscopy (FT-IR-mic) [19,20] or Fourier transform Raman (FT-Raman) spectroscopy [21]. For these spectroscopic investigations, the propellant grains were split lengthwise using a razor blade. Spectra were taken of the grain interiors, as well as of exterior surfaces where the graphitic glaze had come off during the extraction process. FT-IR-mic spectra were measured using a Spectra-Tech IR-Plan infrared microscope (MCT detector) coupled to a Mattson Instruments Polaris FT-IR spectrometer. Instrumental parameters involved coaddition of 32 scans at a resolution of 8 cm^{-1}. The microscope was operated in the reflectance mode. The spatial resolution of the microscope was set to 40 μm using an adjustable slit. All FT-IR-mic spectra were ratioed against an aluminum foil background. Kramers-Kronig transformations were performed to correct spectral distortions caused by changes in sample refractive index near absorption bands [22]. FT-Raman spectra were measured using a Bomem DA-8.02 Fourier transform spectrometer equipped with a CaF_2-quartz beamsplitter and a liquid-nitrogen-cooled InGaAs detector. Samples were irradiated with 1.06-μm laser radiation using a Quantronix Series 100 Nd:YAG laser. Instrumental parameters involved coaddition of 100 scans at a resolution of 4 cm^{-1} and a laser power of 500 mW.

3. RESULTS

The results of the 41-MPa, 50° C SFE survey for RDX-based composite gun propellant are reported in Tables 2 and 3. The results for extraction studies using neat CO_2, CHF_3, and N_2O are listed in Table 2. Table 3 lists the values for RDX extraction using modified CO_2. The data listed in Table 3 include the raw extraction values (milligram RDX/gram CO_2), the extraction enhancement factors relative to the use of neat CO_2, the approximate modifier mole-percent in the extraction mix, and the normalized extraction enhancement factors (NEEF) relative to a modifier level of 3 mole-percent. The moles of CO_2 and modifier (and thus the modifier mole-percent) in the 50-ml extraction vessel were calculated using the following equations:

$$\text{Moles modifier} = \frac{V_m \rho_m}{M_m}, \tag{1}$$

$$\text{Moles } CO_2 = \frac{V_{CO_2} \rho_{CO_2}}{M_{CO_2}}, \tag{2}$$

and

$$V_{CO_2} = 50\,ml - V_m, \tag{3}$$

where the V's, ρ's, and M's in equations 1 and 2 are the volumes, densities, and molar masses, respectively, of the modifier or of CO_2. An approximation to the volume for CO_2 was made in equation 3 by taking the 50-ml extraction vessel volume and subtracting the volume of modifier used. This approach for calculation of modifier mole-percent ignores any volume changes due to mixing of the CO_2 and the modifier, volume changes due to compression of the modifier at the 41-MPa and 50° C operating conditions, and the volume of the propellant grain; the overall error level for these assumptions is estimated to be approximately 10–15%. Each entry in Tables 2 and 3 represents a single SFE run, except for the entry for neat CO_2 which is an average of two runs. Neat CO_2 was found to extract 0.011-mg RDX/gram of CO_2 used. On a volume basis, the most effective modifier surveyed was dimethylsulfoxide; on a molar basis, octanenitrile was found to be the most effective modifier for extraction of RDX.

Table 2. Measured RDX Extraction Values and Assigned Swelling Index Values for CO_2, CHF_3, and N_2O for Static Extraction of M43 Gun Propellant at 41 MPa and 50° C

Neat Fluid	Extracted RDX (mg RDX/g Fluid)	M (g/mole)	Extracted RDX (mg RDX/mole Fluid)	Swelling Index
Carbon Dioxide	0.011	44.01	0.48	0
Fluoroform	0.004	70.01	0.28	0
Nitrous Oxide	0.002	44.01	0.09	1

In addition to quantifying the RDX extraction values for these fluids, each propellant grain was visually inspected following the extraction process. Even for the fluids with the largest enhancement factors, only a very small percentage of the initial mass of RDX was removed. A qualitative swelling index was set up by noting the condition of the perforations visible at each end of the propellant grain. A swelling index value was assigned based on the following criteria:

Swelling Index 0: all perforations were well defined on each end of the grain.

Swelling Index 1: perforations were well defined on only one end of the grain.

Swelling Index 2: perforations were slightly degraded or collapsed on both ends of the grain.

Swelling Index 3: perforations were totally collapsed on both ends of the grain.

Table 3. Measured Fluid Enhancement Factors, Modifier Mole-Percents, NEEFs at 3 Mole-Percent, and Assigned Swelling Index Values for Static Extraction of M43 Gun Propellant at 41 MPa and 50° C

Modifier	Extracted RDX (mg RDX/g CO_2)	Enhancement Factor	Modifier Mole-Percent	NEEF @ 3 Mole-Percent	Swelling Index
Dimethylsulfoxide	0.76	68	3.38	60	2
1-Methyl-2-Pyrrolidinone	0.49	44	2.42	54	2
Octanenitrile	0.38	34	1.46	70	0
Dimethyl formamide	0.34	31	2.72	34	2
Acetonitrile	0.28	25	3.99	19	2
Butyrolactone	0.20	17	2.62	20	3
2-Nitropropane	0.16	14	2.58	16	3
Nitrobenzene	0.13	12	2.06	18	2
Benzonitrile	0.12	11	2.08	16	2
Pyridine	0.12	10	2.73	11	3
Nitromethane	0.11	9.8	3.85	7.6	2
Nitroethane	0.11	9.7	2.93	9.9	2
2-Hexanone	0.09	8.0	1.81	13	3
Denatured Ethanol	0.08	6.7	3.24	6.2	0
1-Nitrobutane	0.08	6.7	2.00	10	2
1-Propanol	0.07	6.2	3.08	6.0	0
1-Nitropropane	0.07	5.9	2.37	7.5	3
2,4-Pentanedione	0.06	5.3	2.07	7.7	3
Pyrrole	0.06	5.0	3.03	5.0	0
Acetone	0.04	3.8	3.27	3.5	3
Tetrahydrofuran	0.04	3.7	2.24	5.0	3
1-Nitropentane	0.04	3.3	2.37	4.2	0
1-Hexanol	0.02	2.1	1.78	3.5	0
Propanol	0.02	2.1	2.92	2.2	3
2-Methyl-2-Nitropropane	0.02	1.8	2.05	2.6	0
Hexanal	0.02	1.8	1.94	2.8	0
Butyronitrile	0.02	1.8	2.21	2.4	3
1-Nitrohexane	0.02	1.6	1.60	3.0	0
Aniline	0.02	1.5	2.11	2.1	1
Methanol	0.02	1.4	5.54	0.8	1
2,2,2-Trifluoro Ethanol	0.01	1.1	3.02	1.1	0
1,1,1,5,5,5-Hexefluoro-2-4 pentanedione	< 0.01	0.4	2.07	0.6	0
Propylamine	< 0.01	0.3	2.57	0.4	3[a]
Triethylamine	< 0.01	0.2	1.60	0.4	0
2-Propanol	< 0.01	0.2	2.88	0.2	1
Hexylamine	< 0.01	0.2	1.62	0.4	3[a]

[a]Extensive crumbling and discoloration of propellant grain were observed.

A large variation in grain appearance was observed across the range of the swelling index values. Quite often, it was possible for a grain with an assigned index value of 0 to transmit light through the length of the perforations. For a grain with an assigned index value of 3, it was usually difficult, if not impossible, to determine where the perforations were. Assigned swelling index values are listed in Tables 2 and 3.

Infrared microscopy can be used for a qualitative examination of the RDX extraction gradient in the propellant grains following the SFE process. Figure 6 shows FT-IR-mic spectra of a propellant grain which had been extracted using CO_2 modified with dimethylformamide. The upper spectrum shows the interior of the grain at a profile depth of 0–40 μm from the exterior surface. The lower spectrum is of the exterior surface. In Figure 6, infrared transitions are identified for four propellant ingredients: the binder polymers cellulose acetate/butyrate (CAB) and nitrocellulose (NC), RDX, and the plasticizer (P). The observed infrared transitions are approximately as follows: CAB ~ 1,740 cm^{-1}, NC ~ 1,670 cm^{-1}, RDX ~ 1,600 cm^{-1}, and P ~ 1,570 cm^{-1}. RDX is also responsible for most of the infrared activity shown in Figures 6 and 7 at reciprocal wavelengths lower than 1,570 cm^{-1}. It can be seen that RDX and plasticizer are observed in the spectrum profiled to a depth of 40 μm but are missing from the spectrum of the grain's exterior. The evanescent wave penetration depth of the infrared beam into the propellant sample is on the order of a few micrometers; apparently, the RDX is totally removed from the surface of the grain to at least this depth.

FT-IR-mic spectra were also used to profile the interior of the cross-sectioned grain to a depth of 200 μm below the grain's exterior (see Figure 7). While the spectra in Figure 7 have not been normalized, the peak heights for CAB in each of the spectra indicate that they are on approximately the same vertical scale; polymeric binder ingredients such as CAB are fairly insoluble in the supercritical fluids used in this study. The RDX and plasticizer peak heights are seen to decrease as the profile moves from the bulk interior (160–200-μm depth) toward the exterior (0–40 μm) of the grain. These variations in the amounts of RDX and plasticizer detected as a function of grain depth can be interpreted as extraction gradients which were frozen into the grain structure when the supercritical fluid was vented from the extraction cell. Spectroscopically, one can see significant extraction of RDX and plasticizer from the propellant grain at depths of up to 80 μm.

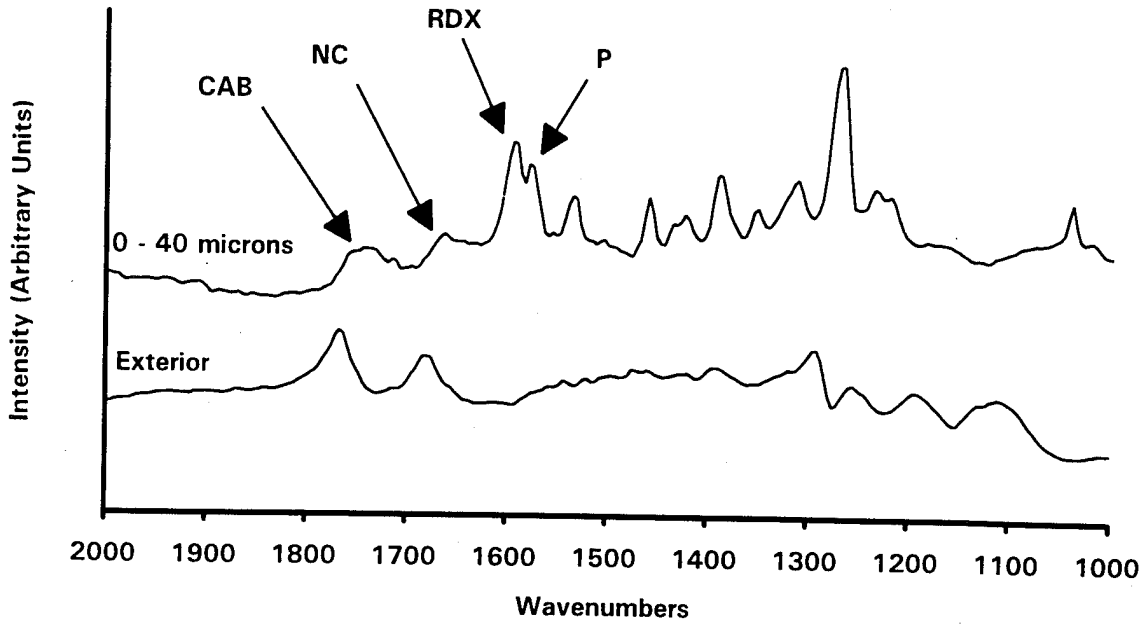

Figure 6. FT-IR-mic spectra of M43 propellant grain following extraction using dimethylformamide-modified CO_2. Upper spectrum: grain interior at a profile depth of 0–40 μm. Lower spectrum: grain exterior.

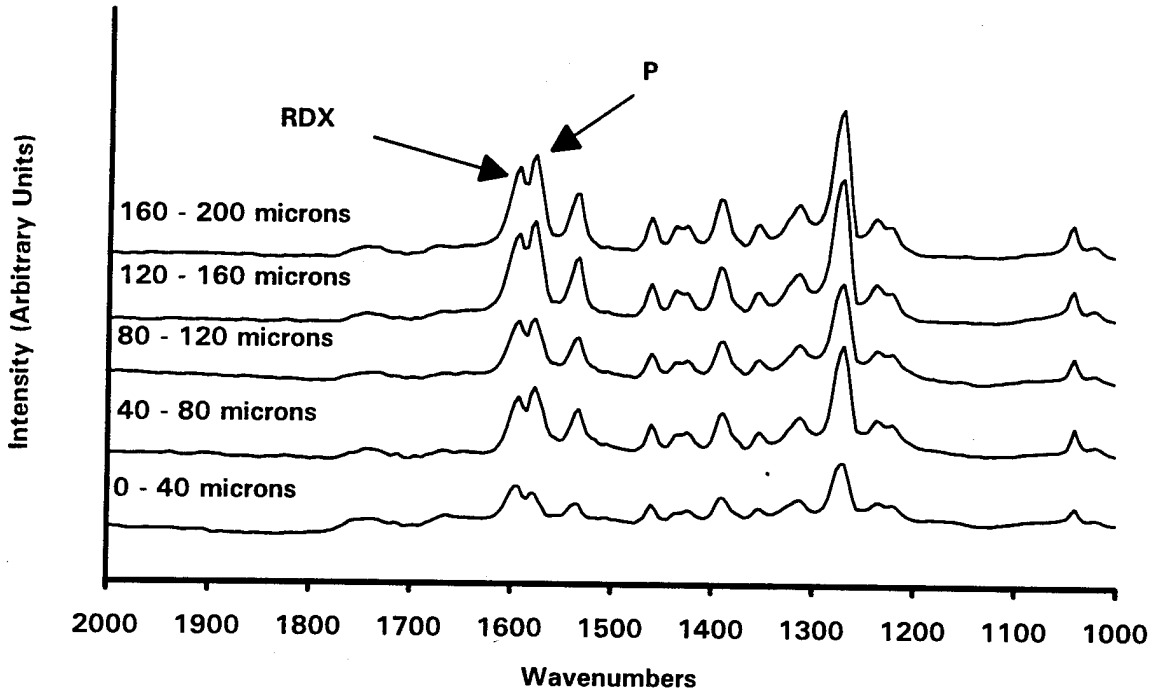

Figure 7. FT-IR-mic spectra of M43 grain following extraction using dimethylformamide-modified CO_2. Profile of grain interior at 40-μm spatial resolution up to a depth of 200 μm from the exterior of the grain.

FT-Raman spectroscopy was also used to examine a single grain of M43 following extraction. Raman spectra of the bulk interior of an unextracted M43 propellant grain and the exterior of a grain which was extracted using acetonitrile-modified CO_2 are shown in Figure 8. The extracted grain was stored in a sealed vial for 2 days following extraction prior to this spectroscopic investigation. The small peak seen at approximately 2,250 cm^{-1} in the lower spectrum of Figure 8 indicates the presence of acetonitrile trapped in the propellant grain residue following extraction. Additional Raman spectra were taken of the interior of the extracted propellant grain, which indicated lesser amounts of trapped acetonitrile than that which was observed at the grain's surface. One explanation of the presence of modifier in the propellant grain is that the modified CO_2 penetrated the grain during the extraction process. When the pressure was released upon venting of the extraction cell, the CO_2 quickly gasified and escaped, leaving the acetonitrile behind in the grain.

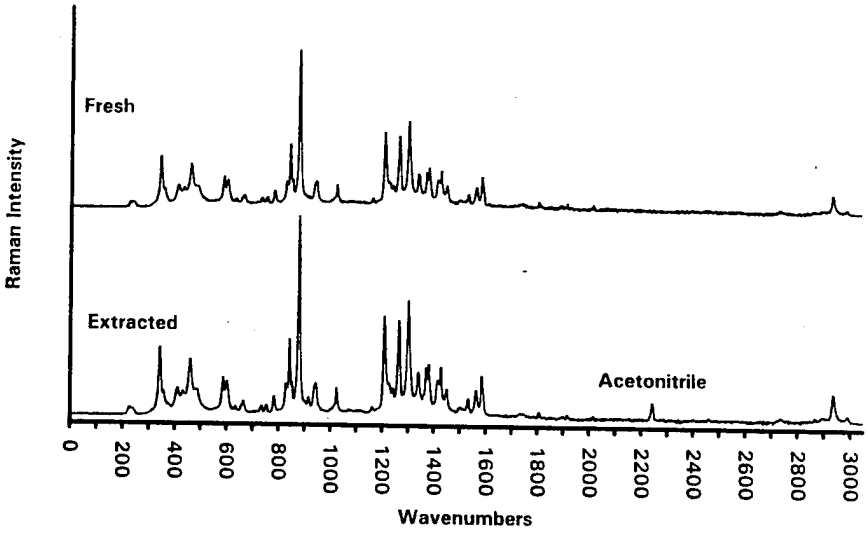

Figure 8. Raman spectra of (top) fresh M43 gun propellant and (bottom) propellant residue following SFE with acetonitrile-modified CO_2.

In addition to these spectroscopic investigations, two grains were cleaved and inspected visually. These grains were extracted using CO_2 modified with either dimethylformamide or acetonitrile. The cross-sectioned grains revealed some degree of bleaching of the propellant bulk interior. Instead of the normal beige color of the cured propellant, a pure white color was observed in the bleached regions. This bleaching started at the exterior surface and extended in for about 2–4 mm from the exterior surfaces. It appears that these bleaching distances correspond to the penetration depths of the fluids used, although

this issue is somewhat clouded by the presence of the grain perforations. The bleaching of the grains extends well beyond the thickness from which we see significant removal of plasticizer (around 80 μm) in Figure 7, eliminating the possibility that plasticizer is responsible for the bleaching. At this time, it is suspected that the bleaching is caused by the extraction of stabilizer.

4. DISCUSSION

4.1 Mass Transfer Considerations. A distinction should be made between terms such as *solubility limit* and other terms such as *mass transfer rate* or *kinetic rate of dissolution.* Solubility limit is defined as the mass of a particular solute which is dissolved in a mass of solvent when the solvent-solute system, or solution, has reached thermodynamic equilibrium. Mass transfer rate and kinetic rate of dissolution refer to nonequilibrium processes governed by diffusion kinetics. The solubility limit, referring to a state at thermodynamic equilibrium, occurs at a minimum in free energy and is usually reached by a mass transfer process occurring at the interface between two different phases, such as solid and liquid (or solution) phases. The mass transfer rate ultimately determines how quickly thermodynamic equilibrium is reached and is itself driven by diffusion kinetics.

There are two primary considerations in the interpretation of the present experimental survey of fluid systems. The first consideration is whether the supercritical fluid solution has reached the solubility limit. For the present work, a 2-hr extraction using a single whole propellant grain (in 50 ml of solvent) may not allow sufficient time for the solution to reach equilibrium. The second consideration involves the existence of equilibrium interactions, which can take place when multiple components are involved in the system. As an example, consider the situation involved with SFE of coffee [5]. The caffeine content of most coffees is about 1 weight-percent. If the caffeine in coffee were to dissolve to the same extent as does neat caffeine, decaffeination would require 5.0 g of CO_2 per gram of coffee, which would be equivalent to a caffeine solubility of approximately 2 mg of caffeine per gram of CO_2. In actuality, 150 g of CO_2 are required per gram of coffee to reduce the caffeine content by 95%. These figures are equivalent to 0.06 mg of caffeine being extracted per gram of CO_2. This figure can be compared to the 0.76 mg of RDX extracted per gram of CO_2 from unground M43 gun propellant using dimethylsulfoxide modifier (see Table 3). For coffee, it has been suggested that the chemical binding between the caffeine and the coffee substrate decreases the activity of the caffeine so that it does not dissolve to the same level as neat caffeine. It is not clear that this same type of interaction applies to SFE of gun propellant. The

ratio of target solute to substrate for RDX in M43 gun propellant is much larger than that for caffeine in coffee. In addition, the morphology of the coffee bean is vastly different from that of the M43 propellant grain. While caffeine would be distributed throughout the coffee biomass, RDX is localized as crystals in the propellant grain. Only the outermost layers of the RDX crystal would be expected to interact with the propellant binder (polymer plus plasticizer). For a 5-μm-diameter RDX crystal, only 1 molecule in about 800 would be in direct contact with the binder. While RDX is much less soluble in neat CO_2 than is caffeine in the same solvent, it is likely that in a formulated propellant extraction of RDX will be much less affected by binder interactions than is the case with caffeine in the coffee bean biomass.

4.2 Swelling Considerations. Swelling of the propellant grain is another issue that may become important when selecting a suitable supercritical fluid. A fluid that causes a large degree of propellant grain swelling may also penetrate the grain to a high degree, since increased penetration of the grain would expose more RDX for mass transfer to the supercritical fluid. However, this correlation has not yet been confirmed, and one should not draw any conclusions regarding the ultimate RDX solubility level from the ability of the fluid to swell the grain. Grain swelling is probably a result of solvation ("wetting") interactions with the binder's polymeric components rather than the result of dissolution of RDX particles.

Tables 2 and 3 list assigned perforation swelling index values along with RDX extraction results for the various supercritical fluids studied. One should be able to evaluate the relative potential for a supercritical fluid to both penetrate and extract RDX from the entire propellant grain by treating these two properties as independent variables. As an example, the systems using octanenitrile and dimethylformamide as modifiers for CO_2 display roughly the same amounts of RDX extracted per gram of CO_2. The use of the dimethylformamide modifier results in much greater swelling of the grain than does the use of the octane nitrile modifier. It is possible that the increased swelling resulting from the use of dimethylformamide vs. octanenitrile as a modifier for CO_2 may result in an increased RDX-removal efficiency from deep within the propellant grain on the basis of fluid penetration. Swelling considerations become less important if size reduction of the propellant grain is ultimately required for rapid removal of the RDX. Crushing of the propellant would result in a much larger overall surface area and much smaller required penetration distances. In any case, the most effective fluid surveyed, CO_2 modified with dimethylsulfoxide, exhibits a significant degree of grain swelling.

4.3 Modifier Considerations. It is interesting to look at the RDX extraction efficiencies (NEEF at 3 mole-percent from Table 3) in terms of the chemical and physical properties of the modifiers used as cosolvents for CO_2. Some of the properties which can be used to interpret the extraction results are polarizability, permanent dipole moment, and molar mass. Acid/base properties may be used for consideration of phase separation behavior of the binary supercritical fluid mixture. Scaling of Hammett σ values [23] can also form the basis for consideration of modifier inductive effects and molecular structure. Table 4 is a compilation of several modifier chemical and physical properties.

4.3.1 Basicity, Miscibility, and Phase Separation. It is important to consider the miscibility of the modifier compounds with CO_2. This issue has been addressed by several authors including Francis [24] and Dandge, Heller, and Wilson [25]. Breakdown of Francis' data (for liquid CO_2) according to chemical class reveals general miscibility between CO_2 and compounds with aldehyde, ketone, and nitrile groups. Nitro groups tend to decrease solubility, especially if more than one is present. No detailed studies on chain length for nitroaliphatics have been made, but these compounds are miscible with CO_2 for carbon chain homologs up to nitropropane. Aliphatic alcohols were found to be miscible for carbon chains up to six atoms in length (hexanol), with decreasing solubilities for longer chains. Alkyl-substituted amides such as dimethylformamide, diethylformamide, and diethylacetamide were found to be miscible with CO_2; however, formamide was found to display limited solubility in CO_2. Many of the modifiers used in the present work were reported to be miscible with CO_2. Of concern is the use of amine compounds with CO_2. N-alkyl substitution was found to increase amine solubility relative to the unsubstituted form of the amine. Amine-like bases weaker than ammonia were reported to have at least some limited solubility in CO_2. Pyridine was reported to be miscible with CO_2, while aniline has a reported solubility of 3 weight-percent.

Amine compounds are known to react with liquid CO_2. It is also known that ammonia reacts with CO_2 to form urea [12]. One possible mechanism for the reaction of CO_2 with amines is as follows:

$$RNH_2 + CO_2 \rightarrow RNH\text{–}COOH. \quad (4)$$

$$RNH\text{–}COOH + RNH_2 \rightarrow RNH\text{–}CO\text{–}HNR + H_2O. \quad (5)$$

Table 4. Physical and Chemical Properties of Surveyed Modifiers

Modifier	Polarizability Volume[a] (10^{-24} cm^3)	Dipole Moment[b] (Debyes)	M (g/mole)	Basicity[c] pK_b
Dimethylsulfoxide	8.0	3.69	78.13	14.0
1-Methyl-2-pyrrolidinone	—	4.09	99.13	—
Octanenitrile	—	—	125.22	—
Dimethylformamide	7.9	3.82	73.10	—
Acetronitrile	4.4	3.92	41.05	24.1
Butyrolactone	—	4.12	86.09	—
2-Nitropropane	—	3.73	89.09	—
Nitrobenzene	12.9	4.22	123.11	25.3
Benzonitrile	12.5	4.18	103.12	24.5
Pyridine	9.6	2.19	79.10	8.7
Nitromethane	5.0	3.46	61.04	25.9
Nitroethane	9.6	3.65	75.07	—
2-Hexanone	—	2.68	100.16	—
Denatured Ethanol[d]	5.1	1.69	46.07	16.4
1-Nitobutane	10.4	3.59	103.12	—
1-Propanol	6.7	1.68	60.10	—
1-Nitropropane	8.5	3.66	89.09	—
2,4 Pentanedione	10.5	3.03	100.12	—
Pyrrole	—	1.84	67.09	—
Acetone	6.4	2.88	58.08	21.2
Tetrahydrofuran	—	1.63	72.11	—
1-Nitropentane	—	—	117.15	—
1-Hexanol	12.5	1.55	102.18	—
Propanol	6.5	2.52	58.08	—
2-Methyl-2-Nitropropane	10.3	3.71	103.12	—
Hexanal	—	—	100.16	—
Butyronitrile	8.4	4.07	69.11	—
1-Nitrohexane	—	—	131.18	—
Aniline	12.1	1.53	93.13	9.4
Methanol	3.3	1.70	32.04	16.2
2,2,2-Trifluoro Ethanol	—	2.03	100.04	—
1,1,1,5,5,5-Hexafluoro-2, 4-pentanedione	—	—	208.06	—
Propylamine	9.2	1.17	59.11	3.3
Triethylamine	13.1	0.66	101.19	4.2
2-Propanol	7.0	1.66	60.10	17.2
Hexylamine	—	—	101.16	—

[a]Sources of polarizability data: references [26] and [27]
[b]Sources of dipole moment data: references [27–29]
[c]Aqueous pK_b values are derived from corresponding pK_a values. Sources of pK_a values: references [30] and [31]
[d]Values in this table are for neat ethanol. The denatured ethanol used as a modifier consisted of 90% ethanol, 5% methanol, and 5% 2-propanol.

The reactions in equations 4 and 5 would also account for the formation of urea from ammonia (R = H). Carbamic acids (RNH-COOH) are known to be somewhat unstable and readily lose CO_2 in the reverse reaction of equation 4 [32]. One can make an argument on the basis of LeChatelier's principle in favor of the reactions in equations 4 and 5 given the elevated pressures involved with supercritical fluid processes. The increased solubility of higher order N-alkyl-substituted amines might be explained by a reduction of N-H insertion sites for CO_2, particularly for tertiary amines such as triethylamine.

Apparently, the basicity of the modifier plays a role in its solubility in CO_2. Acidity and basicity can be assessed for compounds dissolved in aqueous solutions in terms of K_a and K_b, respectively. These quantities are defined as follows for basic species:

$$HB^+ \rightleftharpoons H^+ + B \qquad K_a = \frac{[H^+][B]}{[HB^+]}, \tag{6}$$

$$B + H_2O \rightleftharpoons HB^+ + OH^- \qquad K_b = \frac{[HB^+][OH^-]}{[B][H_2O]}, \tag{7}$$

where B stands for a neutrally charged base which is capable of accepting a proton in the Brönsted-Lowry formalization of acids and bases (e.g., ammonia). The addition of equations 6 and 7 results in water auto-dissociation reaction:

$$H_2O \rightleftharpoons H^+ + OH^- \qquad K_W = K_a\, K_b. \tag{8}$$

It is useful to use pK_a and pK_b. The "p" operator is defined as taking the negative of the base 10 logarithm of the argument:

$$pK_a = -\log_{10} K_a. \tag{9}$$

The "p" operator can be applied to the equilibrium constant in equation 8 to yield the relationship between pK_a and pK_b:

$$pK_a + pK_b = pK_W = 14. \tag{10}$$

Table 4 lists pK_b values for several of the modifiers used in the present work. These aqueous pK_b values were calculated from tabulated pK_a values for the protonated form of the modifier according to equation 10. The smaller the pK_b value, the more basic the compound. For nonaqueous solvents, such as CO_2, the Lewis formalism for acids and bases should be used; however, corresponding pK_a/pK_b values are generally not known for Lewis acids and bases and are not available for protonated solvent other than water. The assumption is made that these Brönsted-Lowry pK_b values can be used to give some general indication of the relative ordering of Lewis bases. It follows that primary and secondary amine bases with aqueous pK_b values smaller than that of ammonia ($pK_b = 4.8$) are insoluble in CO_2 due to reactions such as those proposed in equations 4 and 5. The pK_b values from Table 4 indicate that propylamine might tend to react with CO_2. While there is no pK_b value tabulated for hexylamine, it would also be expected to react with CO_2. These basicity considerations lead to the conclusion that reactions such as those shown in equations 4 and 5 may have occurred when using propylamine and hexylamine modifiers in this study. Such reactions may have been the source of the observed crumbling and discolorations noted with the use of these two modifiers (see Table 3).

For those compounds which display limited solubility in CO_2, such as aniline, it is possible to exceed the solubility limit when adding modifier to the extraction vessel. This situation would result in a phase separation between a pure solvent phase and a modified CO_2 phase. The aniline level of 2.11 mole-percent reported in Table 3 of this report is in excess of 4 weight-percent, exceeding the 3 weight-percent solubility limit reported by Francis. Some phase separation may have occurred when using this particular modifier in this study.

4.3.2 Dipole Moment and Polarizability Considerations. The permanent dipole moment of a molecule is a vector which is determined by the average (static) charge distribution within the molecule; tabulations of dipole moments give the magnitude of these vectors. Polarizability is a measure of the ability of the electron cloud of a molecule to be distorted by an electric field, resulting in an induced transient dipole. Polarizability is normally expressed as a volume in the centimeter-gram-second (cgs) units of cubic centimeter (cm^3) rather than in the International System of Units (SI) of coulomb•square meters/volt ($C•m^2/V$). Conversion from the units of $C•m^2/V$ to a unit of volume is accomplished by division by $4\pi\varepsilon_o$, where ε_o is the permittivity of free space. While tabulations of permanent dipole moments are fairly extensive, those for polarizability are much more sparse. This is evident by the large number of gaps in Table 4. Examination of the polarizability and molar mass data compiled in Table 4 reveals a rough

correlation between these two properties. Figure 9 shows a plot of polarizability vs. mass. The line in this plot is a linear regression fit forced through the origin; the slope of the line is 11.3%. While there is some scatter about this line, the general correlation between polarizability and molar mass is apparent.

The effect of the modifier permanent dipole moment on the RDX extraction efficiency can be assessed by plotting the normalized extraction enhancement factors at a 3-mole-percent modifier level (see Table 3) against the modifier dipole moments (see Table 4). Such a plot is shown in Figure 10. Examination of this plot suggests that a large dipole moment is a necessary, but not sufficient, requirement for an effective polar modifier. A dipole moment threshold of approximately 3.5 Debyes is observed for NEEF greater than 20; for enhancement factors of less than 20, the modifier dipole moments span a large range of values, from a low of about 0.7 Debye to a high of about 4.1 Debyes. Any polarizability effects can be assessed in a similar fashion by plotting the NEEF vs. the modifier molar mass; this plot is shown in Figure 11. A threshold of about 70 mass units appears to be a necessary, but not sufficient, requirement for normalized enhancement factors greater than 20; this mass threshold corresponds to a polarizability of about 8×10^{-24} cm^3. The fact that acetonitrile has an NEEF of approximately 20 (see Table 3), but a molar mass of much less than 70 (see Table 4) may indicate the existence of factors other than these inductive interactions. Alternate mechanisms for extraction enhancement, such as complex formation, should be considered on a case-by-case basis for individual chemical classes of functionality. However, the dependence of the enhancement factor on modifier polarizability and especially dipole moment thresholds may be useful in the future if additional modifiers are sought. Many ineffective modifiers may be quickly eliminated.

Note Added in Proof: The extraction data listed in Table 3 was recently re-examined as a function of dielectric constant; correlation results from this analysis are found in Appendix A.

4.3.3 Molecular Structure and Inductive Effects. Hammett studied the electronic inductive effects of various functional groups attached to a benzene ring by studying the reactions of a second functional group also attached to the ring [23]. By changing the first functional group, Hammett was able to assess the electron donating or withdrawing characteristics of that group as it modified the rates or shifted the equilibria for reactions on the second group. As an example, consider the dissociation reaction of benzoic acid in aqueous media as different functional groups are substituted at the para-position on the benzene ring. An electron-withdrawing group (such as nitro) would couple through the polarizable benzene

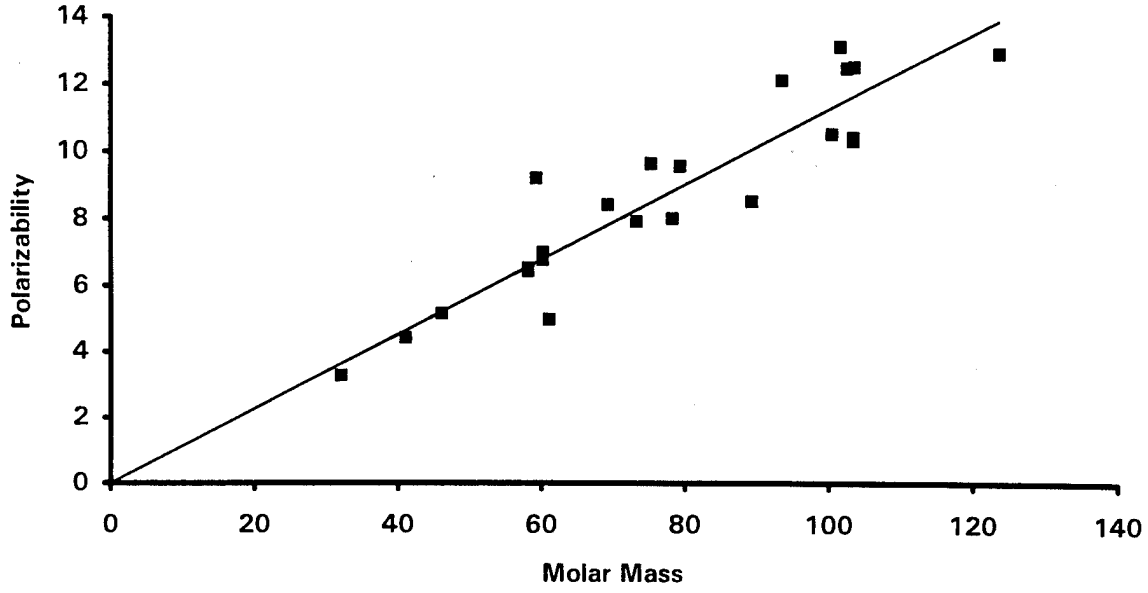

Figure 9. Plot of polarizability ($\times 10^{-24}$ cm^3) vs. molar mass for several of the modifiers used in this survey.

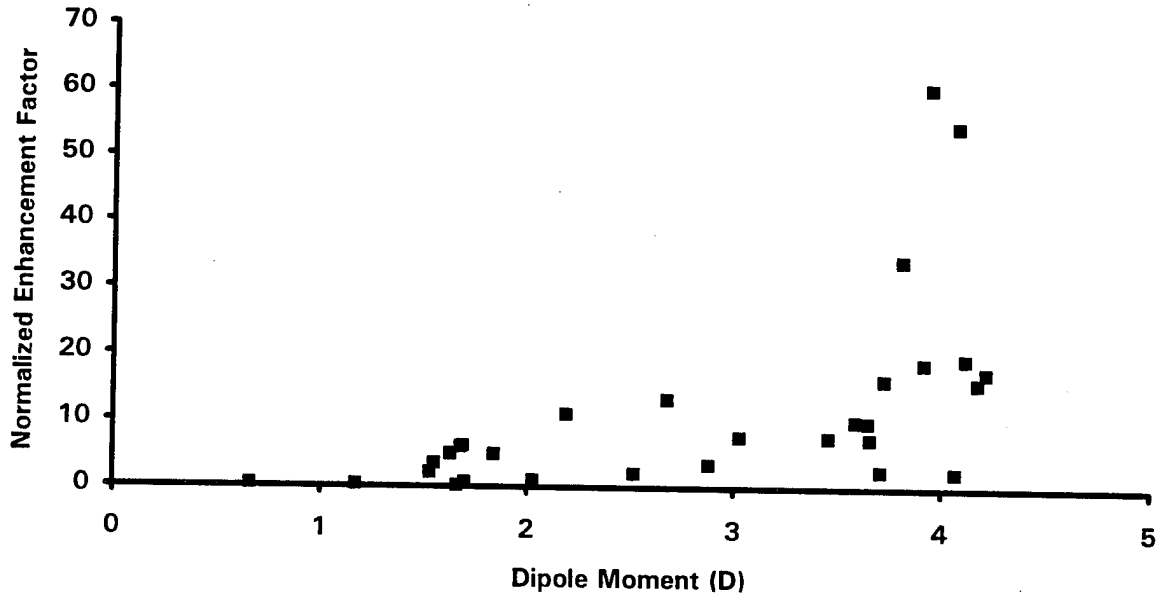

Figure 10. Plot of NEEF vs. permanent dipole moment for several of the modifiers used in this survey.

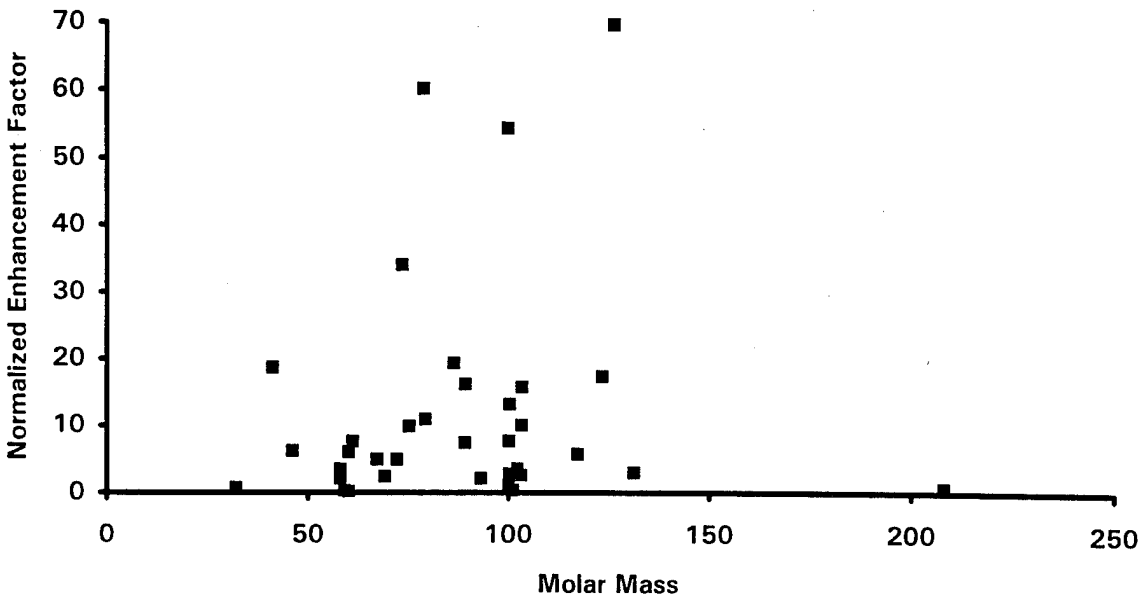

Figure 11. Plot of NEEF vs. molar mass for several of the modifiers used in this survey.

π-system to increase the strength of the acid, while an electron-donating group (such as amine) would weaken the strength of the acid. Hammett set up a linear free-energy relationship to describe the electron-withdrawing or -donating characteristics of various functional groups. Each functional group was assigned a factor, σ, which was used to scale the free-energy shift for substitution of that group on the benzene ring. The σ values were also sensitive to their position of the benzene ring relative to the second substituent; substitution in the para-position coupled into the π-system differently than substitution in the meta-position on the ring. An approximate ordering of Hammett σ values is shown in Table 5. Functional groups with σ values less than zero exhibit electron-donating characteristics while those with σ greater than zero exhibit electron-withdrawing characteristics.

It is interesting to note that the ordering of functional groups according to their Hammett σ values is in good correspondence with other measures of the inductive effect, such as permanent dipole moment. Consider the compilation of dipole moments in Table 4. The modifiers with nitrile and nitro functional groups have the largest dipole moments as well as having the largest Hammett σ values (see Table 5). The amine and alcohol groups have the smallest dipole moments and Hammett σ values, with the ketones and aldehydes falling in the middle of both scales.

It is worthwhile to examine how the chemical structure of the modifiers affects the ability of the modified fluid to extract RDX. The data in Table 6 compare the RDX extraction factors for placement

Table 5. Relative Ordering of Hammett σ Values[a]

Functional Group	σ_p (para-substituted)
$-N(CH_3)_2$	-0.83
$-NH_2$	-0.66
-OH	-0.37
$-OCH_3$	-0.27
$-CH_3$	-0.17
$-C_6H_5$	-0.01
-F	0.06
-CHO	0.22
-Cl	0.23
-Br	0.23
-I	0.28
$-CO_2CH_3$	0.39
$-CO_2H$	0.43
$-CO_2CH_2CH_3$	0.45
$-COCH_2CH_3$	0.48
$-SOCH_3$	0.49
$-COCH_3$	0.50
$-CF_3$	0.54
-CN	0.66
$-NO_2$	0.78

[a]Source: Reference [33].

Table 6. Comparison of NEEF at 3 Mole-Percent for Propyl (C3) and Hexyl (C6) Modifiers With the Functional Group Located on Carbon 1 or Carbon 2

Modifier	NEEF @ 3 Mole-Percent	
	Functional Group on Carbon 1	Functional Group on Carbon 2
C3 Alcohol	6.0	0.2
C3 Carbonyl	2.2	3.5
C3 Nitro	7.7	16.0
C6 Carbonyl	2.8	13.0

of the functional group on the end carbon vs. the second carbon of propyl and hexyl carbon chains. The pairs of modifiers being compared are: 1-propanol and 2-propanol; propanal and acetone (2-propanone); 1-nitropropane and 2-nitropropane; and hexanal and 2-hexanone. It is interesting to note that placing the

functional group on the second carbon atom in the aliphatic chain results in a larger NEEF for the carbonyl and nitro compounds, while the observed ordering is reversed for the propanols. This reversal may be the result of changing from an electron-donating group (alcohol: σ less than 0) to electron-withdrawing groups (nitro, carbonyl: σ greater than 0).

It is useful to consider the effects of the individual functional groups on a case-by-case basis. Tables 7–11 show the molar mass, dipole moment, and NEEF for modifiers with the nitro, nitrile, carbonyl, alcohol, and amine groups. No clear tendencies are observed as a function of aliphatic chain length. In general, but with several individual exceptions, the nitro and nitrile modifiers display significant RDX extraction enhancement factors, while the carbonyls and alcohols are less effective. Amine compounds are also ineffective as modifiers. In addition, significant decomposition, beyond simple swelling, of the grain was observed when using the propylamine and hexylamine modifiers (see Table 3). This decomposition is not surprising if one considers the reported reactivity of ammonia with energetic binder ingredients such as nitrocellulose and nitroglycerine [34]. Amine-nitramine incompatibilities are discussed in further detail on p. 26 of this report.

Abel, Marinkas, and Bulusu [35] is a bibliography on complex formation in RDX, HMX, TNT, and some related compounds. Among other things, this bibliography mentions literature references to complexes involving nitramines. The following is a quotation from Abel, Marinkas, and Bulusu [35]:

> "RDX and HMX can be considered to be mildly acidic in the sense that they can be titrated in nonaqueous solution, and show three or four inflection points respectively, according to the number of nitramine groups in the molecule. The majority of the compounds with which HMX forms complexes are mild Brönsted bases (many of them are N-heterocyclic compounds with nonbonding electrons which can participate in charge-transfer reactions, making them basic in the Lewis sense also). Thus, HMX complexes are also acid-base pairs."

Reference 35 also indicates that an equivalent set of RDX-base pairs does not exist—that is to say that RDX does not form complexes with most of the compounds with which HMX does. Suggestions that charge-transfer forces are important factors in the binding of RDX and HMX crystals are made in the bibliography. While this bibliography indicates that there is no clear understanding of the nature of the intermolecular forces involved in the complexes of RDX and HMX, a strong indication is made that charge-transfer may be at least partially responsible. Clearly, complexing phenomena need to be considered when discussing the role of modifiers for the extraction of nitramine materials such as RDX.

Table 7. Molar Mass, Dipole Moment, and NEEF at 3 Mole-Percent for Nitro Modifiers

Modifier	M (g/mole)	Dipole Moment (Debyes)	NEEF @ 3 Mole- Percent
Nitromethane	61.04	3.46	7.6
Nitroethane	75.07	3.65	9.9
1-Nitropropane	89.09	3.66	7.5
2-Nitropropane	89.09	3.73	16.0
1-Nitrobutane	103.12	3.59	10.0
2-Methyl-2-nitropropane	103.12	3.71	2.6
1-Nitropentane	117.15	—	5.7
1-Nitrohexane	131.18	—	3.0
Nitrobenzene	123.11	4.22	18.0

Table 8. Molar Mass, Dipole Moment, and NEEF at 3 Mole-Percent for Nitrile Modifiers

Modifier	M (g/mole)	Dipole Moment (Debyes)	NEEF @ 3 Mole-Percent
Acetonitrile	41.05	3.92	19.0
Butyronitrile	69.11	4.07	2.4
Octanenitrile	125.22	—	70.0
Benzonitrile	103.12	4.18	16.0

Table 9. Molar Mass, Dipole Moment, and NEEF at 3 Mole-Percent for Carbonyl Modifiers

Modifier	M (g/mole)	Dipole Moment (Debyes)	NEEF @ 3 Mole-Percent
Propanol	58.08	2.52	2.2
Acetone	58.08	2.88	3.5
Hexanal	100.16	—	2.8
2-Hexanone	100.16	2.68	13.0

Table 10. Molar Mass, Dipole Moment, and NEEF at 3 Mole-Percent for Alcohol Modifiers

Modifier	M (g/mole)	Dipole Moment (Debyes)	NEEF @ 3 Mole-Percent
Methanol	32.04	1.70	0.8
Ethanol	46.07	1.69	6.2
1-Propanol	60.10	1.68	6.0
2-Propanol	60.10	1.66	0.2
1-Hexanol	102.18	1.55	3.5

Table 11. Molar Mass, Dipole Moment, and NEEF at 3 Mole-Percent for Amine Modifiers

Modifier	M (g/mole)	Dipole Moment (Debyes)	NEEF @ 3 Mole-Percent
Propylamine	59.11	1.17	0.4
Hexylamine	101.16	—	0.4
Triethylamine	101.19	0.66	0.4
Aniline	93.13	1.53	2.1

The ability of amines to sensitize nitro-containing compounds is fairly well documented in the literature [36–40]. It is currently believed that sensitization is due to the formation of a complex between the amine and the nitro-containing compound [39,40]. Diphenylamine, a commonly used stabilizer for nitrocellulose, is also known to decompose nitroglycerin as well as higher nitrated aromatic compounds [41]. Nitramines such as RDX and HMX are known to be subject to chemical degradation by ammonia and simple amines such as methylamine [34,42]. The fact that no sensitization effect was found for RDX when exposed to diethylene triamine [39] can be explained by the relative inability, when compared to that of HMX, for RDX to form complexes with Lewis bases such as amines [35]. The uncertainty regarding the miscibility of the amines with CO_2, along with their reactivity and ineffectiveness as modifiers for the extraction of RDX, eliminates them as potential modifier candidates.

A significant decrease in RDX extraction enhancement factor is noted in going from the 1-nitrobutane (n-nitrobutane) modifier to the 2-methyl-2-nitropropane (t-nitrobutane) modifier. One possible explanation is that n-nitrobutane can form an aci tautomer while t-nitrobutane cannot (see Figure 12). The formation of even a small amount of aci-n-nitrobutane would allow the formation of a hydrogen bond between the nitrobutane modifier and one of the RDX oxygen atoms. It should be kept in mind that several factors, such as dipole moment and polarizability, are expected to contribute to the modifier efficiency for extraction of RDX. If hydrogen bonding was a dominant factor in modifier performance, then methanol would be expected to have a much larger RDX extraction enhancement factor than was observed (see Table 3).

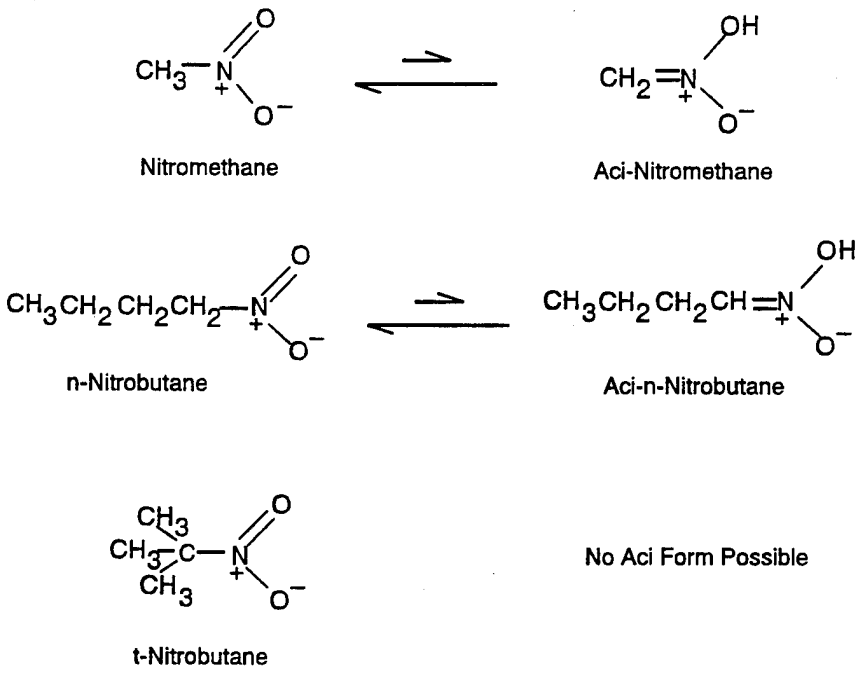

Figure 12. Aci tautomers for nitromethane and n-nitrobutane. No aci tautomer is possible for t-nitrobutane.

With the exception of butyronitrile, the observed RDX extraction enhancement factors for the nitriles are at least as large as those of the nitro compounds. The nitriles are ideal candidates to participate in charge transfer reactions with RDX. The lone pair of electrons is about as sterically unhindered as possible, being spatially separated from the majority of the aliphatic carbon chain (or aromatic ring) by the nitrogen and carbon atoms of the nitrile functionality. As was the case with the nitro modifiers, it appears that several factors need to combine to make an effective modifier.

One possible explanation of the poor performance of butyronitrile relative to the smaller acetonitrile and larger octanenitrile modifiers would be a change in modifier "mechanism" between the short and long aliphatic modifier chains. In such a case, butyronitrile may be caught in the transition between mechanisms. As conjecture, a mechanism for the long-chain modifiers would involve a complexation interaction (e.g., charge transfer) between the polar functionality at one end of the modifier with the RDX solute while the nonpolar end of the aliphatic chain could interact effectively with CO_2. There is no real evidence in the data supporting—or refuting—such a mechanism since octanenitrile is the only modifier examined with an aliphatic chain length as long as eight carbon atoms. Finally, a small molecule such as acetonitrile may be predominantly enhancing RDX solubility through dipole moment and charge transfer interactions; for an intermediate chain length such as encountered with butyronitrile, the "floppiness" of the carbon chain may interfere with some aspect of the short-chain mechanism, but the chain length is not great enough to effectively interact with CO_2.

A rough ordering of modifier functionality effectiveness can be made by making comparisons of the RDX extraction enhancement factor for different functional groups using the same aliphatic chain length or benzene substitution. The effectiveness of modifier functionality is as follows: 2-nitro > 1-nitro ~ 1-nitrile > ketone ~ 1-alcohol > aldehyde > 1-amine > 2-alcohol. This ordering is reported as a general trend; some variation to this listing is expected on a case-by-case basis. It is interesting to note that there is a general correspondence between the ordering of modifier functionality effectiveness and the Hammett σ values (see Table 5).

Table 12 shows the effect of fluorine atom substitution on 2,4-pentanedione and ethanol modifiers. In both cases, the addition of fluorine atoms to the modifier results in a significant decrease in RDX extraction enhancement factor. The explanation for this behavior probably lies in acidity and electronegativity considerations. In the case of the hexafluoropentanedione modifier, the addition of six fluorine atoms would raise the acidity of the two remaining hydrogen atoms which are bonded to the middle carbon. For protic modifiers, such as alcohols or carboxylic acids, the labile hydrogens would tend to become more acidic on addition of fluorine. This would make them more likely to hydrogen-bond to the nitros of RDX. However, acidification of the modifier molecule may tend to decrease complexation interactions with RDX, which is mildly acidic itself [35]. An unfavorable electrostatic interaction between the $-CF_3$ local dipole and the total dipole moment of RDX or that of the nitro group nearest to the modifier molecule would tend to reduce the stabilization energy associated with hydrogen bonding. Also, any complexation between RDX and trifluoroethanol or hexafluoropentanedione would tend to leave the

$-CF_3$ groups facing towards the exterior of the complex. These exposed fluorine atoms could have destabilizing interations with the CO_2 oxygen atoms.

Table 12. Effect of Fluorine Substitution

Modifier	M (g/mole)	Dipole Moment (Debyes)	NEEF @ 3 Mole-Percent
2,4-Pentanedione	100.12	3.03	7.7
1,1,1,5,5,5-Hexafluoro-2,4-pentanedione	208.06	—	0.6
Ethanol	46.07	1.69	6.2
2,2,2-Triflouroethanol	100.04	2.03	1.1

Table 13 lists the remaining nonaliphatic/nonaromatic modifiers looked at in this study. Aniline is included in this table for comparison to pyrrole and pyridine. Structures of the cyclic modifiers listed in Table 13 are shown in Figure 13.

Table 13. Molar Mass, Dipole Moment, and NEEF at 3 Mole- Percent for Nonaliphatic Modifiers

Modifier	M (g/mole)	Dipole Moment (Debyes)	NEEF @ 3 Mole-Percent
Dimethylsulfoxide	78.13	3.96	60.0
Dimethylformamide	73.10	3.82	34.0
1-Methyl-2-pyrrolidinone	99.13	4.09	54.0
Butyrolactone	86.09	4.12	20.0
Tetrahydrofuran	72.11	1.63	5.0
Pyrrole	67.09	1.84	5.0
Pyridine	79.10	2.19	11.0
Aniline	93.13	1.53	2.1

As seen in Figure 13, methyl-pyrrolidinone, butyrolactone, tetrahydrofuran, and pyrrole are all five-membered cyclic compounds. The presence of the carbonyl group in the methyl-pyrrolidinone and the butyrolactone result in significant increases (>2x) in dipole moment relative to pyrrole and tetrahydrofuran. The RDX extraction enhancement factors are substantially larger for butyrolactone and methyl-pyrrolidinone as compared to those for pyrrole and tetrahydrofuran.

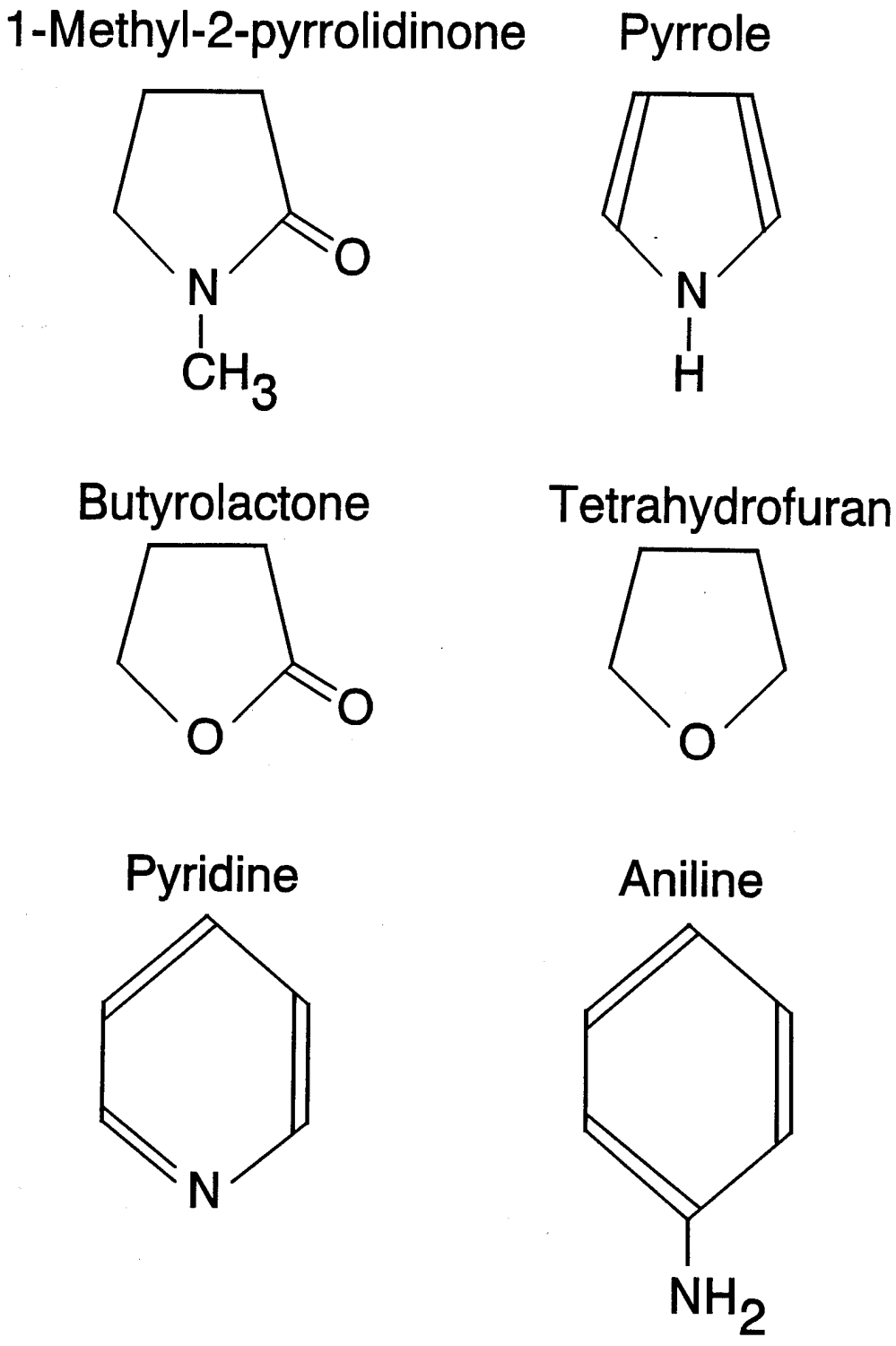

Figure 13. Structures of several cyclic modifiers used in this survey.

A comparison of the RDX extraction enhancement factors for pyrrole, pyridine, and aniline is of interest. The dipole moment of pyridine is roughly 25% larger than that of pyrrole and roughly 40% larger than that of aniline. The nitrogen heteroatoms of pyrrole and pyridine are embedded in the polarizable electron π-ring structure; such is not the case with aniline. These dipole moment and polarizability factors may account for the ordering of the modifier efficiencies for these molecules; pyridine has a RDX extraction enhancement factor twice that of pyrrole and five times larger than that of aniline.

4.4 Solubility Correlations. Filliben [43] contains several tables summarizing the solubility of RDX in a variety of solvents. The data in these tables are listed as grams RDX per 100 g of solvent, grams RDX per 100 ml of solvent, grams RDX per 100 g of solution, or grams RDX per 100 ml of solution. These data were compiled and converted into values with units of grams RDX per 100 g of solvent; this compilation is shown in Table 14. Solubility unit conversion was generally a straightforward process. For the conversion from grams RDX per 100-ml solution, a gross approximation was made by setting the volume of solvent to be equal to the total volume of solution; the greatest solubility value converted in this case was 7-g RDX per 100-ml solution. Solvent density was required for conversion of solvent volume to solvent mass. In addition, many of the values listed in Table 14 were interpolated between reported values at 20° C, 25° C, 30° C, or 40° C in order to get a more complete set of values at 25° C or 30° C. Entries in Table 14 with more than one value correspond to listings in multiple tables in Filliben [43].

The solubility data listed in Table 14 can be plotted against the RDX extraction enhancement factors to look for any correlation in solvating strength between the molecule as a neat solvent and as a CO_2 modifier. Such a plot is shown in Figure 14. A general correlation between the neat solvent and modifier solvating strengths of a given molecule is apparent. In addition to the RDX solubility values from the literature, Table 14 also contains the NEEF from Table 3 as well as calculated modifier solubilities. It should be kept in mind that these "solubilities" are based on extraction of RDX from M43 gun propellant and are expected to be somewhat lower than values based on true RDX solubilities. The modifier solubilities indicate the mass of RDX which would be extracted per 100 g of solvent when used as a modifier for CO_2 at the mole-percent levels indicated in Table 3. These values are generally an order of magnitude below the corresponding neat solvent solubilities for RDX. Certainly the underlying fundamental physical and chemical properties which result in high RDX solubilities for a given solvent

Table 14. RDX Solubilities[a]

Modifier	RDX Solubility (g RDX/100 g Solvent)		RDX NEEF @ 3 Mole-Percent	Modifier Solubility (g RDX/100 g Modifier in CO_2)
	25° C	30° C		
Dimethylsulfoxide	41.0, 41.8	44.3	60.0	1.2
1-Methyl-2-pyrrolidinone	40.0	42.3, 71.3	54.0	0.9
Dimethylformamide	35.9, 37.0	36.0, 37.6, 39.7	34.0	0.7
Butyrolactone	14.0	14.3	20.0	0.4
Acetone	8.2, 8.2	8.7, 9.2, 9.5	3.5	0.1
Acetonitrile	5.5	6.6, 8.9, 13.6	19.0	0.7
Nitromethane	—	4.4	7.6	0.2
Nitroethane	—	2.9	9.9	0.2
1-Nitropropane	—	2.0	7.5	0.1
2-Nitropropane,	—	2.0	16.0	0.3
Aniline	1.9	—	2.1	< 0.1
Methanol	0.3	0.3	0.8	< 0.1
Ethanol	0.1	0.2	6.2	0.2

[a]Compiled from data in reference 43.

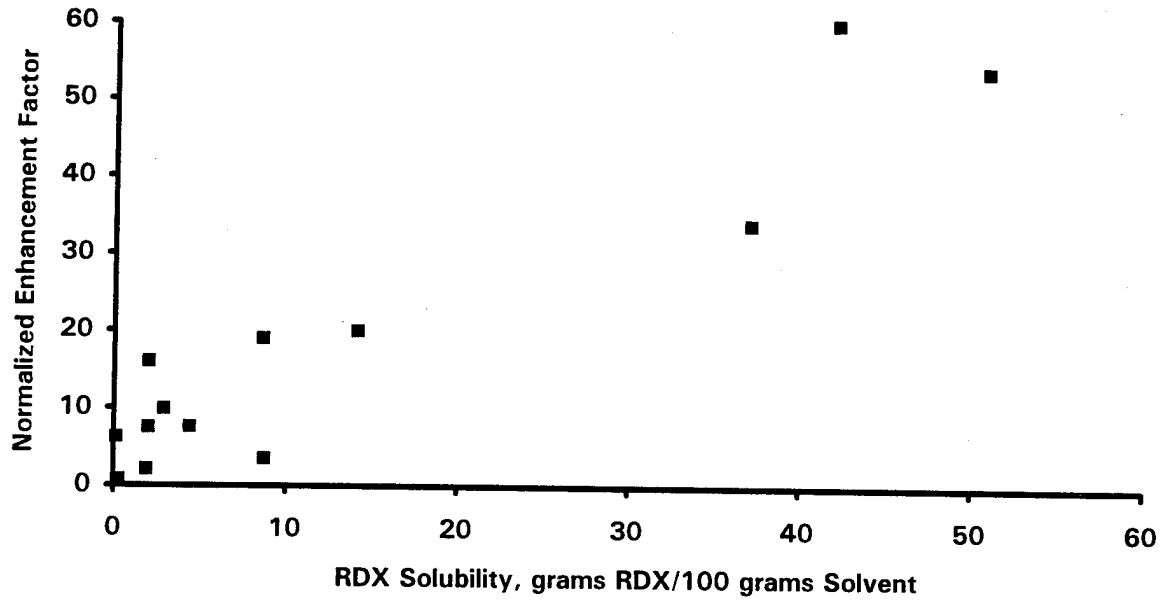

Figure 14. Plot of NEEF vs. average RDX solubility at 25° C to 30° C for several of the modifiers used in this survey.

still apply when the solvent is used as a modifier for CO_2. As is indicated in Table 14, those modifiers which display the largest RDX extraction enhancement factors—dimethylsulfoxide, dimethylformamide, 1-methyl-2-pyrrolidinone, and butyrolactone—also possess significant solubilities as neat solvents for RDX.

5. SUMMARY AND CONCLUSIONS

A survey of supercritical fluid extraction using 39 fluid systems, including 36 CO_2-based fluids using polar modifiers at the 4 volume-percent level, was conducted to evaluate the potential for extraction of RDX from nitramine-based propellants. A common set of conditions (50° C and 41 MPa) was chosen to perform a quantitative comparison of these different fluids. The extraction data were quantified in terms of milligrams RDX extracted per gram of CO_2, as well as by defining an RDX extraction enhancement factor. This RDX extraction enhancement factor was defined as the mass of RDX extracted using a given fluid normalized to that extracted using neat CO_2. The RDX extraction enhancement factors were themselves normalized on a molar basis to a modifier level of 3 mole-percent in the supercritical fluid mix. It was these normalized RDX extraction enhancement factors which were used to perform the majority of the quantitative comparisons of the modified CO_2-based supercritical fluids.

The most efficient fluid systems found were CO_2 modified with dimethylsulfoxide (volume basis) or octanenitrile (molar basis). At a level of 4 volume-percent, the dimethylsulfoxide-modified CO_2 fluid was found to be 68 times more efficient than unmodified CO_2. At a normalized 3% molar level, the octanenitrile-modified CO_2 fluid was found to be 70 times more effective than unmodified CO_2. On this molar basis, dimethylsulfoxide was the second most effective modifier with an RDX NEEF of 60.

Visual inspection of propellant grains subsequent to the SFE process was used to define a swelling index for the fluids. About half of the fluids resulted in significant swelling of the propellant grains, with assigned swelling index values of 2 or 3. While most of the fluids that exhibited RDX extraction enhancement factors of 10 or greater were assigned swelling index values of 2 or 3, no correlation can be made between the mass of RDX extracted per gram of fluid and the swelling index values. Rather, these two properties should be treated as independent variables when selecting a mass transfer fluid.

Infrared microscopy was used to qualitatively probe the RDX extraction gradient of a propellant grain extracted with dimethylformamide-modified CO_2. The RDX was totally removed from the surface of the

grain. Significant removal of RDX could be observed to penetration depths as great as 80 μm. If this removal depth is determined by kinetic parameters such as mass transfer rates rather than thermodynamic solubility limits, there is an implication that size reduction will be required for time-effective removal of RDX from propellant and explosive materials.

Examination of modifier dipole moments as a function of RDX extraction enhancement factor revealed an apparent dipole moment threshold of approximately 3.5 Debyes for the fluids which had normalized enhancement factor of greater than 20. Polarizability effects were assessed through the use of modifier molar mass. As in the case of dipole moment, an apparent threshold was observed for the fluids which displayed normalized enhancement factors of greater than 20. This threshold of about 70 mass units corresponds to a polarizability volume of about 8×10^{-24} cm^3. Both the dipole moment and polarizability thresholds appeared to be necessary, but not sufficient, requirements for large extraction enhancement factors. No good correlations were found which involved both permanent dipole moment and polarizability.

Note Added in Proof: Analysis of the extraction data as a function of dielectric constant in the Appendix indicates a significant correlation between NEEF and the product of modifier dipole moment and dielectric constant.

A rough correlation was found between the mass solubility of RDX in the neat modifier and the extraction enhancement factor—the best solvents for RDX (where data were available) were also the among the best CO_2 modifiers for extraction of RDX.

An analysis of the extraction data for aliphatic and monosubstituted benzene modifiers was done to determine the effects of chemical functionality on the extraction of RDX. In general, modifiers with the most electron-withdrawing character, such as the nitros and nitriles, were the most effective modifiers. The effectiveness of these modifiers was ordered roughly in the same manner as their Hammett σ values, with the amines displaying the least effectiveness as modifiers for CO_2. The nature of the ineffectiveness of the amines was not fully resolved since amine miscibility problems with CO_2 were pointed out. More importantly, the primary aliphatic amines looked at as potential modifiers, propylamine and hexylamine, caused significant degradation of the propellant ingredients under the experimental conditions used for this survey. Given the incompatibility between amines in general and nitro-containing molecules, the use of amines as modifiers for the extraction of RDX is strongly recommended against. Modifiers which

included sulfur (dimethylsulfoxide) or multifunctional amide (dimethylformamide, 1-methyl-2-pyrrolidinone) or ester (butyrolactone) groups were found to have RDX extraction enhancement factors much greater than the majority of the monosubstituted aliphatic compounds studied.

Fluorine substitution on ethanol and 2,4-pentanedione adversely affected the RDX extraction enhancement factors; this decrease in extraction efficiency may be due to an increase in modifier acidity upon substitution of several highly electronegative fluorine atoms. Fluorine atom substitution does not increase modifier extraction enhancement factor through increasing dipole moment or polarizability.

Several modifiers were found which exceeded the extraction enhancement levels which would be expected based on comparison with structurally similar compounds or which could be explained by dipole moment, polarizability, or solubility arguments. Compounds such as acetonitrile, octanenitrile, and perhaps even pyridine may exhibit some level of charge-transfer interaction with RDX. The large difference in extraction efficiency observed between t-nitrobutane and n-nitrobutane may be due to hydrogen bonding between aci-n-nitrobutane and RDX; the formation of an aci tautomer is not possible with t-nitrobutane.

In conclusion, several physical and chemical properties which may be useful for the rapid screening and selection of additional modifiers for CO_2, if required in the future, have been identified. These properties include large dipole moments, polarizabilities, and neat solvent solubilities for RDX. While the work in this report focused on RDX, many of the results and correlations uncovered would be expected to carry over as general trends for supercritical fluid extraction of other nitramine materials, such as HMX.

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6. REFERENCES

1. Murray J. S., P. Lane, T. Brinck, K. Paulsen, M. E. Grice, and P. Politizer. "Relationships of Critical Constants and Boiling Points to Computed Molecular Surface Properties." Journal of Physical Chemistry, vol. 97, pp. 9369–9373, 1994.

2. Weast R. C., ed. CRC Handbook of Chemistry and Physics, 58th Edition. West Palm Beach, FL: CRC Press, 1977.

3. Eckart M. P., J. F. Brennecke, and C. A. Eckert. "Molecular Analysis of Phase Equilibria in Supercritical Fluids." Supercritical Fluid Technology: Reviews in Modern Theory and Application, Boca Raton, FL: CRC Press, 1991.

4. Braker, W., and A. L. Mossman. Matheson Gas Data Book. 6th Edition, Matheson, Lyndhurst, NJ, pp. 120–129, 1980.

5. McHugh, M., and V. Krukonis. Supercritical Fluid Extraction. Principles and Practice. Butterworths, Boston, pp. 182–188, 1986.

6. Via, J., and L. T. Taylor. "Chromatographic Behavior of N-Nitrosodiphenylamine and Diphenylamine." Proceedings of 1990 JANNAF Propellant Development and Characterization Subcommittee Meeting, CPIA Pub. 545, pp. 225–234, November 1990.

7. Thomas, B. P. "Quantitative Extraction of Gun Propellant Using Supercritical Carbon Dioxide." Proceedings of 1992 JANNAF Propellant Development and Characterization Subcommittee Meeting, CPIA Pub. 578, pp. 149–158, April 1992.

8. Gallagher, P. M., and V. J. Krukonis. "Supercritical Fluid Processing of a Single Base Propellant and a Nitramine Base Munition." Final report, contract no. DAAH01-90-C-0732, Phasex Corp., Defense Advanced Research Projects Agency, January 1992.

9. Farncomb, R. E., and G. W. Nauflett. "Supercritical Fluid Extraction of Depleted Stabilizers from Single-Base Propellant and Adding New Stabilizers." Proceedings of 1993 JANNAF Safety and Environmental Protection Subcommittee Meeting, CPIA Pub. 600, pp. 305–309, August 1993.

10. Ashraf-Khorassani, M., and L. T. Taylor. "Coupled Supercritical Fluid Chromatography and Supercritical Fluid Extraction of Nonpolymeric Ingredients in Double-Base Propellants." Proceedings of 1988 JANNAF Propellant Characterization Subcommittee Meeting, CPIA Pub. 497, pp. 105–112, November 1988.

11. Farncomb, R. E., and G. W. Nauflett. "Removal of Lead and Copper from a Double-Base Propellant." Proceedings of 1993 JANNAF Safety and Environmental Protection Subcommittee Meeting, CPIA Pub. 600, p. 297–304, August 1993.

12. Matson, D. W., B. W. Wright, R. D. Smith, W. S. Melvin, and J. F. Graham. "Applications of Supercritical Fluid Systems to Solid Rocket Propellants." Proceedings of 1987 JANNAF Propulsion Meeting, CPIA Pub. 480, vol. 3, pp. 401–408, December 1987.

13. Gallagher, P. M., M. P. Coffey, V. J. Krukonis, and N. Klasutis." Gas Antisolvent Recrystallization: New Process to Recrystallize Compounds Insoluble in Supercritical Fluids." (ACS Symposium Series No. 406). American Chemical Society, pp. 334–354, 1988.

14. Krukonis, V. J., and P. M. Gallagher. "Exploratory Development on a New Nitroguanidine Recrystallization Process: Gas Anti-Solvent Recrystallization." Phasex Corporation Final Report to U.S. Air Force Armaments Technology Laboratory, Contract F08635-87-C-0346, April 1988.

15. Krukonis, V. J., M. P. Coffey, and P. M. Gallagher. "Exploratory Development on a New Process to Produce Improved RDX Crystals: Supercritical Fluid Antisolvent Recrystallization." Phasex Corporation Final Report to U.S. Army Ballistic Research Laboratory, Contract DAAA15-86-C-0079, Aberdeen Proving Ground, MD, May 1988. (Also published as Krukonis, V. J., M. P. Coffey, and P. M. Gallagher. "Exploratory Development on a New Process to Produce Improved RDX Crystals: Supercritical Fluid Antisolvent Recrystallization." Contract Report BRL-CR-606, U.S. Army Ballistic Research Laboratory, Aberdeen Proving Ground, MD, January 1989.)

16. Gallagher, P. M., V. J. Krukonis, and L. J. Vandekieft. "Gas Anti-solvent Recrystallization: Application to the Separation and Subsequent Processing of RDX and HMX." Proceedings of the 2nd International Symposium on Supercritical Fluids, Phasex Corporation, Boston, MA, May 1991.

17. Raynie, D. E. "Warning Concerning the Use of Nitrous Oxide in Supercritical Fluid Extractions." Analytical Chemistry, vol. 65, pp. 3127–3128, 1993.

18. Schroeder, M. A., R. A. Fifer, and J. B. Morris. "The Relationship of Chemical Structure to Supercritical-Fluid Solubility and to Cosolvent-Modifier Properties: A Literature Review." Technical report, U.S. Army Research Laboratory, Aberdeen Proving Ground, MD, to be published.

19. Bergin, F. J. "Some Novel Applications of an Infrared Microscope." Applied Spectroscopy, vol. 43, pp. 511–515, 1989.

20. Pesce-Rodriguez, R. A., C. S. Miser, K. L. McNesby, R. A. Fifer, S. Kessel, and B. D. Strauss. "Characterization of Solid Propellant and Its Connection to Aging Phenomena." Applied Spectroscopy, vol. 46, pp. 1143–1148, 1992.

21. McNesby, K. L., J. E. Wolfe, J. B. Morris, and R. A. Pesce-Rodriguez. "Fourier Transform Raman Spectroscopy of Some Energetic Materials and Propellant Formulations." J. Raman Spectroscopy, vol. 25, pp. 75–87, 1994.

22. Hadni, A. Essentials of Modern Physics Applied to the Study of the Infrared. Elmsford, NY: Pergamon Press, pp. 428–435, 1967.

23. Lowry, T. H., and K. S. Richardson. Mechanism and Theory in Organic Chemistry. New York: Harper & Row, pp. 60–61, 1976.

24. Francis, A. W. "Ternary Systems of Liquid Carbon Dioxide." Journal of Physical Chemistry, vol. 58, pp. 1099–1114, 1954.

25. Dandge, D. K., J. P. Heller, and K. V. Wilson. "Structure Solubility Correlations: Organic Compounds and Dense Carbon Dioxide Binary Systems." Ind. Eng. Prod. Res. Dev., vol. 24, pp. 162–166, 1985.

26. Weast, R. C., M. J. Astle, and W. H. Beyer, eds. CRC Handbook of Chemistry and Physics, 66th Edition. Boca Raton, FL: CRC Press, Boca Raton, pp. E69–E74, 1985.

27. Lowry, T. H., and K. S. Richardson. Mechanism and Theory in Organic Chemistry. New York: Harper & Row, pp. 86–87, 1976.

28. Weast, R. C., M. J. Astle, and W. H. Beyer, eds., CRC Handbook of Chemistry and Physics, 66th Edition, Boca Raton: CRC Press, pp. E58–E61, 1985.

29. Dean, J. A., ed. Handbook of Organic Chemistry, New York: McGraw-Hill, pp. 4-46–4-79, 1987.

30. Streitwieser, A., Jr., and C. H. Heathcock. Introduction to Organic Chemistry. New York: Macmillan Publishing Co., Appendix IV, 1976.

31. Peters, D. G., J. M. Hayes, and G. M. Hieftje. A Brief Introduction to Modern Chemical Analysis. Philadelphia: W. B. Saunders Co., Appendix 2, 1976.

32. Streitwieser, Jr., A., and C. H. Heathcock. Introduction to Organic Chemistry. New York: Macmillan Publishing Co., p. 495, 1976.

33. Dean, J. A., ed. Handbook of Organic Chemistry. New York: McGraw-Hill, pp. 7-2–7-7, 1978.

34. Melvin, W. S. "Critical Fluid Demilitarization and Ingredient Reclamation Technology." Proceedings of 1992 JANNAF Safety and Environmental Protection Subcommittee Meeting, CPIA Pub. 588, pp. 297–312, August 1992.

35. Abel, J. E., P. L. Marinkas, and S. Bulusu. "Complex Formation in RDX, HMX, TNT, and Some Related Compounds: A Bibliography." ARLCD-SP-77005, U.S. Army Armament Research and Development Command, Large Caliber Weapon Systems Laboratory, Dover, NJ, December 1977.

36. Engelke, R., W. L. Earl, and C. M. Rohlfing. "Production of the Nitromethane Aci-Ion by UV Irradiation: Its Effect on Detonation Sensitivity." Journal of Physical Chemistry, vol. 90(4), p. 545, 1986.

37. Engelke, R., W. L. Earl, and C. M. Rohlfing. "The Importance of Enolate Anions in the High Pressure Kinetics of Nitroalkanes and Nitroaromatics." International Journal of Chemical Kinetics, vol. 18, p. 1205, 1986.

38. Engelke, R., W. L. Earl, and C. M. Rohlfing. "Microscopic Evidence that the Nitromethane Aci-Ion is a Rate Controlling Species in the Detonation of Liquid Nitromethane." Journal of Chemical Physics, vol. 84(1), p. 142, 1986.

39. Cook, M. D., and P. J. Haskins. "Decomposition Mechanisms and Chemical Sensitization in Nitro, Nitramine, and Nitrate Explosives." Proceedings of Ninth Symposium (International) on Detonation, OCNR 113291-7, pp. 1027–1031. Office of the Chief of Naval Research, Portland, OR, 1989.

40. Constantinou, C. P., T. Mukundan, and M. M. Chaudhri. "Sensitization of Nitrocompounds by Amines." Energetic Materials, J. E. Field and P. Gray, eds., The Royal Society, London, pp. 403–417, 1992.

41. Urbanski, T., Chemistry and Technology of Explosives. Vol. III, Oxford: Pergamon Press, pp. 559–563, 1967.

42. Melvin, W. S., and W. W. Wharton. "Nitric Oxide Catalysis in Minimum Signature Propellants." Proceedings of JANNAF 1984 Propulsion Meeting, February 7–9, CPIA Pub. 390, Vol. III, pp. 77–85, New Orleans, LA, February 1984.

43. Filliben, J. D., ed. CPIA/M3 Solid Propellant Ingredients Manual. unit 16, The Johns Hopkins University, Chemical Propulsion Information Agency, Columbia, MD, June 1990.

APPENDIX:

DEPENDENCE OF NEEF ON DIELECTRIC CONSTANT

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At the suggestion of Professor Mark McHugh of the Johns Hopkins University Department of Chemical Engineering, we recently re-analyzed our extraction results as a function of modifier dielectric constant. Dipole moment and dielectric constant data are listed in Table A-1. Where possible, we used condensed-phase dipole moment data for this analysis.

Table A-1. Experimental Results From M43 SFE Study and Selected Modifier Properties

Modifier	Normalized Extraction Enhancement Factor (NEEF) at 3 Mole-Percent	Dipole Moment[a]	Dielectric Constant[b]
Octanenitrile	70		13.90 (25)
Dimethylsulfoxide	60	3.9 (B)	48.9 (20)
Methylpyrrolidinone	54	4.09 (B)	32.0 (25)
Dimethylformamide	34	3.86 (B)	38.3 (20)
Butyrolactone	20	4.12 (B)	20.3 (21)
Acetonitrile	19	3.47 (B)	37.5 (20)
Nitrobenzene	18	3.96 (B)	34.82 (25)
2-Nitropropane	16	3.76 (g)	25.52 (30)
Benzonitrile	16	3.9 (B)	26.5 (20)
2-Hexanone	13	2.68 (B)	14.6 (15)
Pyridine	11	2.20 (B)	12.3 (25)
Nitroethane	9.9	3.61 (g)	28.06 (30)
2,4-Pentanedione	7.7	2.5 (B)	25.7 (20)
Nitromethane	7.6	3.46 (g)	35.87 (30)
1-Nitropropane	7.5	3.60 (g)	23.24 (30)
Ethanol	6.2	1.71 (B)	25.00 (20)
1-Propanol	6.0	1.75 (B)	22.2 (20)
Pyrrole	5.0	1.80 (B)	7.48 (18)
Tetrahydrofuran	5.0	1.75 (B)	7.58 (25)
Acetone	3.5	2.77 (B)	20.7 (25)
1-Hexanol	3.5	1.55 (B)	13.3 (25)
Butyronitrile	2.4	3.6 (B)	20.3 (21)
Propanal	2.2	2.57 (B)	18.5 (17)
Aniline	2.1	1.53 (B)	6.89 (20)
Methanol	0.8	1.68 (B)	33.62 (20)
Propylamine	0.4	1.36 (B)	5.31 (20)
Triethylamine	0.4	0.9 (B)	2.42 (25)
2-Propanol	0.2	1.66 (B)	18.3 (25)

[a]Letters in parentheses refer to determination as follows: g - gas phase; B - benzene solution; C - cyclohexane solution. Dipole moment data are found in reference 29.

[b]Numbers in parentheses refer to temperature (°C) at which dielectric constant was determined. Dielectric constant data are found in reference 29.

[c]Dipole moment data from reference 28.

The RDX extraction data were plotted versus the dielectric constant (ε) or the product of the dielectric constant and dipole moment (μ x ε). Linear regression analysis was done on these plots using the Excel spreadsheet, and the linearity of the plot was assessed using the reported regression coefficient. In addition to linear plots, the square root function was also used to improve the linear regression fits for the extraction data. These square root plots were found to result in slightly better regression coefficients. The results of these plots are summarized in Table A-2.

Table A-2. Linear Regression Analysis of RDX SFE Data

Dependent Variable[a]	Independent Variable[b]	Multiple R[c]
Sqrt(NEEF)	μ x ε	0.80791
NEEF	μ x ε	0.78091
Sqrt(NEEF)	ε	0.52252
NEEF	ε	0.44296

[a]NEEF = normalized extraction enhancement factor, Sqrt(NEEF) = square root of NEEF.
[b]μ = dipole moment, ε = dielectric constant.
[c]Multiple R = Excel regression coefficient.

The dielectric constant is essentially a measure of ability of a medium to become polarized in the presence of an electric field. Our interest in the dielectric constant lies in the ability of the electric field associated with permanent dipole moments to polarize the supercritical fluid medium. Figures A-1 and A-2 show the plots of square root of NEEF vs. ε and μ x ε, respectively. While much scatter is evident in these plots, rough correlations between square root of NEEF and ε or μ x ε are apparent.

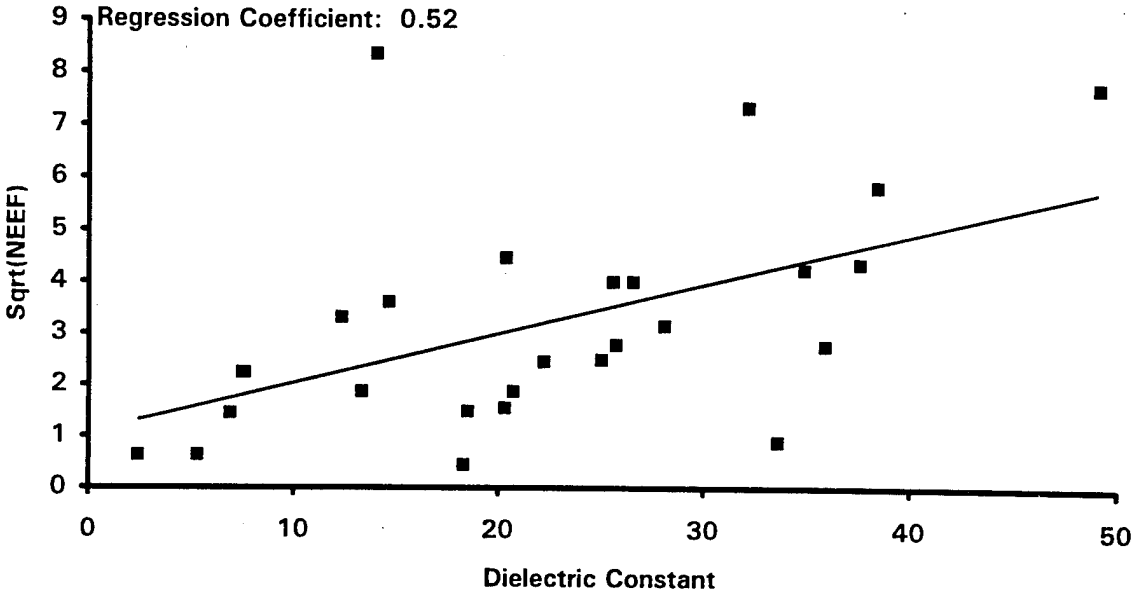

Figure A-1. Plot of the square root of the NEEF vs. modifier dielectric constant.

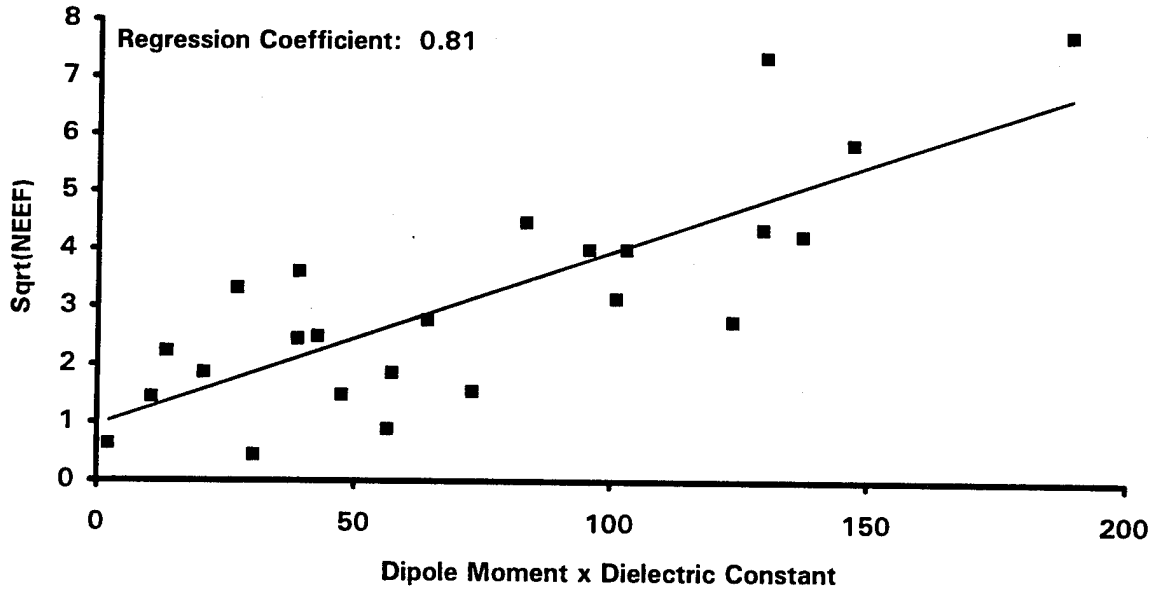

Figure A-2. Plot of the square root of the NEEF vs. product modifier dipole moment and dielectric constant.

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