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Paul H. Miyares

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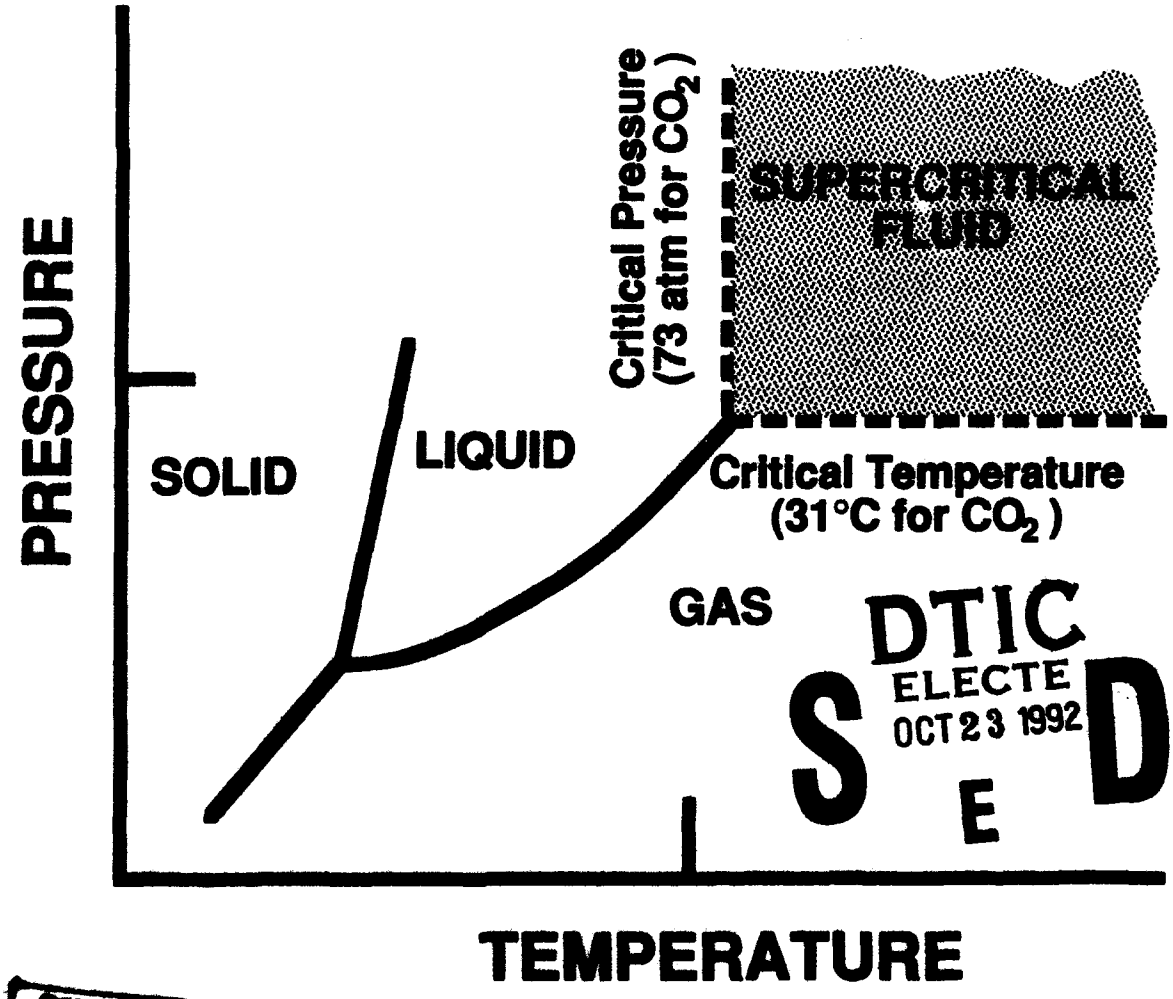

For conversion of SI metric units to U.S./British customary units of measurement consult ASTM Standard E380, Metric Practice Guide, *published by the American Society for Testing and Materials, 1916 Race St., Philadelphia, Pa. 19103.*

Cover: *Phase diagram for carbon dioxide.*

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U.S. Army Corps of Engineers
Cold Regions Research & Engineering Laboratory

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Prepared for
U.S. ARMY WATERWAYS EXPERIMENT STATION

PREFACE

This report was prepared by Paul H. Miyares, Research Chemist, Geochemical Sciences Branch, Research Division, U.S. Army Cold Regions Research and Engineering Laboratory. Funding for this research was provided by the U.S. Army Waterways Experiment Station, Vicksburg, Mississippi (Ann B. Strong, Project Monitor).

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Supercritical Fluid Chromatography for the Analysis of Nitroaromatics, Nitramines and Nitrate Esters

PAUL H. MIYARES

INTRODUCTION

Supercritical fluid chromatography (SFC) is a rapidly growing branch of chromatographic science offering a unique combination of chromatographic conditions similar to high-performance liquid chromatography (HPLC) with the high resolution of capillary columns and highly specific detectors similar to gas chromatography (GC).

The objective of this study was to examine the feasibility of SFC with a thermionic detector known as TID-2-H_2/air for the determination of nitroaromatics, nitramines and nitrate esters in environmental samples, using carbon dioxide (CO_2) as the carrier fluid. The specific analytes of interest are:

- 2,4,6-trinitrotoluene (TNT);
- 2,4-dinitrotoluene (2,4-DNT);
- 2,6-dinitrotoluene (2,6-DNT);
- hexahydro-1,3,5-trinitro-1,3,5-nitramine (RDX);
- octahydro-1,3,5,7-tetranitro-1,3,5,7-tetrazocine (HMX);
- nitroglycerine (NG);
- pentarythitol tetranitrate (PETN);
- methyl-2,4,6-trinitrophenylnitramine (tetryl);
- 2-amino-4,6-dinitrotoluene (2-Am-DNT);
- 4-amino-2,6-dinitrotoluene (4-Am-DNT);
- 1,3,5-trinitrobenzene (TNB); and
- 1,3-dinitrobenzene (DNB).

I evaluated the chromatography by testing various separations and comparing them with accepted HPLC separations. I also compared the detection capabilities of TID-2-H_2/air with those of the UV detector used with HPLC. The results of this study were used to determine whether an SFC-TID-2-H_2/air method for these analytes promises to be an improvement, both analytically and operationally, over accepted HPLC-UV technology.

BACKGROUND

History of SFC

"Supercritical" describes the state of a compound when it is above its critical temperature and critical pressure. A supercritical fluid is a substance in the supercritical state that exhibits both gaseous and liquid properties. A fluid in this state is similar to a gas, where the volume expands to fill the volume of the container, but it has densities and solvating properties that are similar to those of a liquid.

The unique properties of supercritical fluids were first observed by de la Tour in 1822 upon the disappearance of the meniscus between gaseous and liquid phases in a closed system at a critical temperature (referenced in Lee and Markides 1987). In 1879, Hannay and Hogarth noted that the solvating properties of a supercritical fluid were similar to a liquid when they observed similar absorption spectra for an inorganic salt in both a supercritical fluid and a liquid (referenced in Lee and Markides 1987).

Supercritical fluids were introduced to chromatography in 1962, when Klesper et al. published the first study employing supercritical Freons as the mobile phase for the separation of metal porphyrins. This work was followed by that of Giddings et al. (1966) on "dense gas chromatography" and others, who explored this new technology and laid the foundation for modern SFC. In 1966 and 1967, Sie et al. published a series of works that thoroughly discussed the theory and application of SFC. The advancement of SFC, though, was

hampered by inadequate instrumentation, and it was overshadowed by HPLC for many years (Lee and Markides 1987).

The resurgence of SFC in the early 1980s was led by growing interest in using supercritical fluids as extractants (Lee and Markides 1987). Advancements in instrumentation as well as in column technology also contributed. Novotny et al. (1981) published the results of a study using open tubular columns, while researchers at Hewlett-Packard studied the use of packed columns (Gere et al. 1982). At the same time, Hewlett-Packard marketed the first commercially available SFC system by modifying HPLC equipment. SFC is now an increasingly popular analytical technique. There are several commercially available systems, with numerous packed and capillary columns and a host of detectors, including electron capture detection (ECD), flame ionization detection (FID), thermal energy analysis (TEA), thermionic ionization detection (TID), ultraviolet (UV) and mass spectrometry (MS).

SFC for munitions

One of the military's most serious environmental problems has been soil and water contamination from munitions and munitions byproducts. Contamination has occurred through the disposal of wastewater from manufacturing and load-and-pack facilities, burning of off-specification munitions and detonation of out-of-date ordnance. Further contamination may also have occurred at military impact areas or artillery training facilities where large numbers of munitions are detonated. Many explosives and their byproducts incorporate three classes of organic compounds: nitroaromatics, nitramines and nitrate esters.

Because of monitoring requirements at disposal sites, methodology has been developed for the determination of these compounds. Several GC techniques have been developed using a variety of detectors, such as ECD (Douse 1981, Belkin et al. 1985, Richard and Junk 1986), TEA (Lafleur and Mills 1981, Douse 1983), FID (Jurinski et al. 1975), TID (Patterson 1986, West and Lee 1986) and MS (Pereira et al. 1979). Also, a number of HPLC methods have been developed using UV (Jenkins et al. 1986, 1989), TEA (Lafleur and Morriseau 1980), electrochemical detection (Maskarinec et al. 1984), ECD (Krull et al. 1981) and LC/MS (Voyksner and Yinon 1986). Methods employing direct colorimetric analysis (Jenkins and Walsh 1992), as well as thin-layer chromatography (Hoffsommer and McCullough 1968), have also been used. Although many of these methods are quite sensitive, each has its advantages and disadvantages. GC methods have demonstrated high sensitivity and selectivity, but problems have been encountered with compounds exhibiting low volatility and thermal lability. HPLC methods provide adequate chromatographic resolution and excellent analyte stability, but methods of detection, although sensitive, lack selectivity. Colorimetric and thin-layer chromatographic techniques also lack selectivity and are more appropriate for field use.

Only a few studies have been published using SFC to analyze for munitions (West and Lee 1986, Douse 1988, Griest et al. 1989, Ashraf-Khorassani and Taylor 1989a,b, Munder et al. 1991), and only three of these deal with any of the analytes of interest in this study. In 1988, Douse introduced SFC-TEA into forensic analysis as an alternative to GC-TEA or HPLC-TEA. He stated that capillary GC-TEA is restricted to the determination of thermally stable and highly volatile compounds, while HPLC-TEA is limited to the determination of nitrate esters and nitramines. To analyze for nitroaromatics, a photolytic reactor is required prior to the TEA pyrolysis unit. Additionally, HPLC-TEA requires a cryogenic trap to prevent solvent contamination of the detector. These additional units make an HPLC-TEA difficult to operate and maintain. Douse performed trace determinations of explosives using a 6.8-m × 0.05-mm-ID SB Octyl 50 Superbond cross-linked flexible silicon capillary and TEA detection. He worked with a number of munitions of interest, including TNT, RDX, NG, PETN and tetryl (Fig. 1). Previously these analytes could not be easily determined simultaneously by capillary GC due to thermal instability or low volatility or by HPLC due to detector limitations. Unfortunately Douse was unable to resolve tetryl and RDX. In addition, HMX had a poor peak shape. This is most likely due to poor solubility of HMX in CO_2. Schoenmaker and Uunk (1987) felt that CO_2 has a solvating power similar to that of methylene chloride and that it is not sufficiently polar to elute HMX (Yarbro and Gere 1987).

Griest et al. (1989) showed SFC to be complementary to GC and HPLC for the analysis of munitions. Using a Deltabond-cyano (5-μm particle size) 25- and 15-cm-long packed column separations and TID detection, Griest et al. successfully resolved seven high explosives: TNT, 2,4-DNT, 2,6-DNT, PETN, NG, tetryl, RDX and HMX. Acceptable resolution was achieved for all analytes except HMX in approximately 20 min (Fig. 2). Although

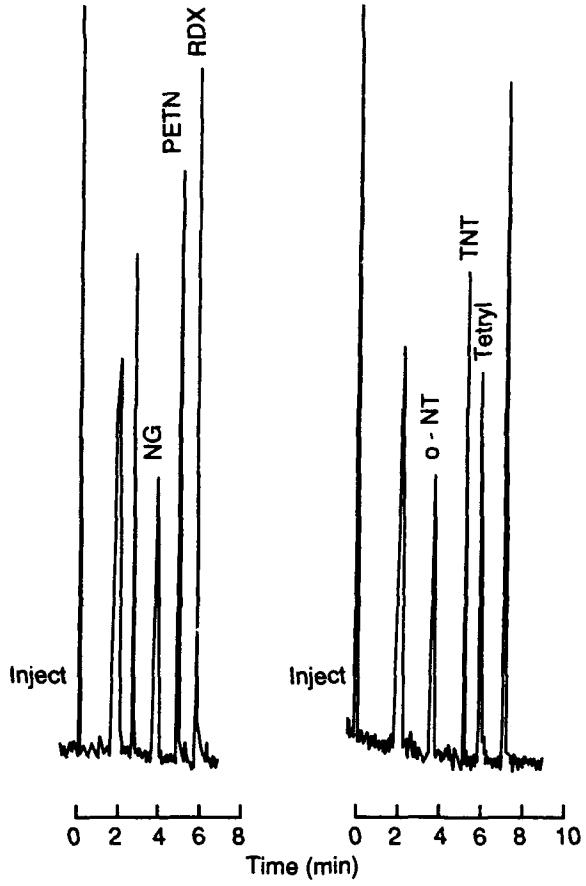

Figure 1. Separation of high explosives using an SB-Octyl 50 Superbond cross-linked flexible silicon capillary column (6.8 m x0.05 mm ID). (After Douse 1988.)

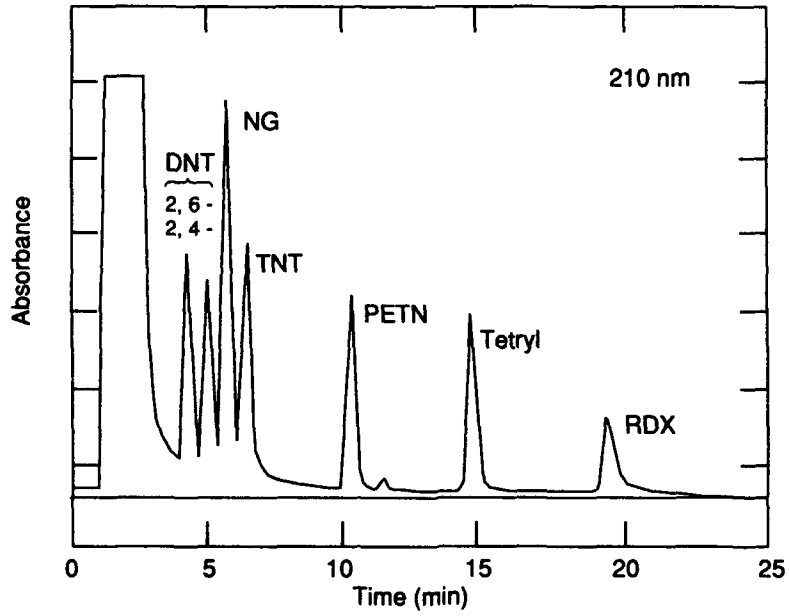

Figure 2. SFC separation of high explosives using a Deltabond-cyano packed column (2.5 m x 1 mm, with 5-μm particles). (After Griest et al. 1989.)

not shown, a tailing peak for HMX was observed after RDX eluted on a 15-cm column, again due to its low solubility in CO_2. The detection limits were estimated to be approximately 10 times higher than the reporting limits for the analogous HPLC-UV method developed by Jenkins et al. (1989).

In 1991, Munder et al. employed on-line supercritical fluid extraction (SFE) and SFC with triple detection (UV, ECD, FID) for the determination of explosives and propellants. They were successful in separating or partially separating a suite of 20 munitions compounds that included TNT, 2,4-DNT 2,6-DNT, NG, PETN, HMX, RDX and tetryl, as well as a number of nitrates, phthalates and phenylamines. Although complete resolution of all 20 compounds was not achieved, those analytes that are of interest in this study were resolved. The detection limits for this method were estimated to be 100 pg for some of the analytes for a 1.4-mg soil sample.

All three groups, though, had difficulty working with very polar compounds such as HMX, and all felt that the nonpolar characteristics of CO_2 were the source of the problem. The solvating power of CO_2 may be a limiting factor in the use of SFC for the determination of the munitions required by the military.

Other studies include two by Ashraf-Khorassani and Taylor (1989a,b), who used SFC/Fourier transform infrared (FT-IR) spectroscopy in a qualitative study to characterize double-base propellants and propellant stabilizers. Also, West and Lee (1986) evaluated the use of capillary SFC-TID for the analysis of polycyclic nitroaromatics. This study described the comparison of three modes of TID. They concluded that the TID-2-H_2/air mode was sensitive and highly selective to nitro-containing polycyclic aromatics. They found, though, that the detector limited the chromatography to density programming at low oven temperatures (40°C) because of sensitivity toward density change at high temperatures. They also found that this TID mode has a limited dynamic range.

EXPERIMENTAL METHODS

The analyses for this study were performed on a Lee Scientific Supercritical Fluid Chromatograph model 600 modular system consisting of an SFC pump, a GC/SFC programmable oven equipped with a high-speed pneumatic injection valve, a time split injector, a thermionic ionization detector from Detector Engineering Technologies, and a computerized system controller. Data were collected by a Hewlett-Packard model 3393 digital integrator.

The following Lee Scientific columns were used during the study:

SB-Methyl-100 (2.5 m × 0.05 mm ID)
SB-Biphenyl-30 (2.5 m × 0.05 mm ID)
SB-Cyanopropyl-50 (2.5 m × 0.05 mm ID)
SB-Cyanopropyl-25 (5.0 m × 0.05 mm ID)
SB-Smectic (2.5 m × 0.05 mm ID).

The supercritical fluids used as the mobile phase were SFC-grade CO_2, as well as CO_2 modified with 5 and 10% methanol and 5 and 10% acetone, obtained from Scott Specialty Gases. The analytes were Standard Analytical Reference Materials (SARMs) obtained from USATHAMA, except for 2-Am-DNT and 4-Am-DNT, which were reagent grade. Methanol, acetonitrile and acetone solvents (all HPLC grade) used to prepare the various standards and samples were from Baker, Mallinkrodt or Alltech.

The optimum separation for the suite of analytes of interest was experimentally determined. The separation was performed on an SB-Cyanopropyl-25 column eluted with 100% CO_2 and using the temperature and density conditions outlined in Table 1.

Samples were introduced using an LC-type syringe, overfilling the 0.50-µL sample loop. The valve was fired and the loop rotated to the in-line position for 2.5 s. Analytes were detected by the TID-2-H_2/air detector optimized with an H_2 flow rate of 4.2–4.5 mL/min and a source heating current of 2.7–2.8 A.

SFC COLUMNS

The first part of this study focused on determining whether an adequate separation was feasible for the analytes of interest. For SFC, as in GC, it is possible to use either packed or open tubular (capillary) columns. Packed SFC columns are very similar to LC columns. They have smaller inner diameter (ID) but similar particle-size (3, 5 or 10 µm) packing. These columns have a large number of theoretical plates per unit distance, which is advantageous for rapid analysis of simple mixtures but is not advantageous for a complex that contains a large number of analytes. A limitation of packed columns is that they require an eluent flow rate of 2–20 mL/min (Lee and Markides

Table 1. Temperature–density program for optimum separation using the SB-Cyanopropyl-25 column.

	Density program	*Temperature program*
Initial settings	0.150 g/mL	100°C
Injection time	2.5 s	—
Hold time A	5.0 min	5.0 min
Ramp A	0.1 g/mL·min	35°C/min
Final A	0.30 g/mL	150°C
Hold time B	1.2 min	5.0 min
Ramp B	0.05 g/mL·min	50°C/min
Final B	0.42 g/mL	175°C
Hold time C	5.0 min	19.0 min
Ramp D	0.50 g/mL·min	—
Final D	0.55 g/mL	—
Final hold	15.0 min	—

1987), which prohibits the use of many of the GC-like detectors unless the column effluent is split. For this study I was restricted to capillary columns because I chose to use a TID-2-H_2/air (GC-like) detector, which cannot operate under the high-flow-rate conditions of the packed columns.

Capillary SFC columns are similar to GC capillaries but typically have smaller inner diameters (0.05 or 0.10 mm ID vs 0.325 mm ID). Theory and practice have shown that capillary SFC columns must be less than 0.10 mm ID to achieve acceptable efficiencies (> 3000 plates per m) (Peaden and Lee 1983, Fields et al. 1984). A typical SFC capillary (20 m × 0.05 mm) can produce 100,000 theoretical plates with a supercritical CO_2 mobile phase (Lee and Markides 1987). Capillary columns typically require a 1- to 10-mL/min flow rate, which is sufficiently slow for most GC- and LC-like detectors, including mass spectrometry. However, the sample capacity of these columns is limited. Although no published data were available, the manufacturer (Lee Scientific) warns against overloading certain columns with specific classes of compounds. For example, the SB-Methyl-100 is easily overloaded by strongly polar and hydrogen-bonding materials, and the SB-Cyanopropyl-50 can be easily overloaded by aliphatic hydrocarbons. This suggests that the selection of stationary phases is highly dependent on the analytes of interest.

In my search for a suitable separation, I tested many capillary columns. The first of these was an SB-Biphenyl-30 (Lee Scientific). This column was reported to resolve 2,4-DNT and 2,6-DNT, as well as TNT and TNB. I encountered a major problem, however. HMX and the isomers of DNT did not elute with satisfactory peak shapes for quantitation (Fig. 3). The peak shape of HMX is likely due to the poor solubility of HMX in CO_2. The poor peak shapes of the DNT isomers were determined experimentally to be a temperature-dependency problem. At a set density and temperature, one isomer would elute with a suitable peak shape and the other would not. I was unable to determine a density–temperature combination for which both isomers would elute with satisfactory peak shapes.

I next turned to an SB-Octyl-50 column (Lee Scientific), as suggested by Douse (1988). Douse found that RDX and tetryl have similar retention times (Fig. 2). I attempted to resolve this problem while retaining satisfactory separation of the analytes of interest by modifying the density–temperature program. Unfortunately I was unable to find conditions yielding a separation that was adequate for quantitative work. I went on to test an SB-Smectic column (Lee Scientific), which separates compounds on the basis of size and shape, and an SB-Methyl-100 column (Lee Scientific), a non-polar phase. The SB-Smectic and SB-Methyl-100 showed limited abilities to separate isomers or similar compounds such as TNT and TNB (Fig. 4, 5). Also, retention of the smaller analytes on the SB-Smectic and the less-polar analytes on the SB-Methyl-100 was so poor that peaks were not sufficiently resolved.

Having had only limited success with published capillary separations, I re-examined the work of Griest et al. (1988), who adequately resolved a suite of common munitions using a Deltabond-cyano packed column in a 20-min analysis. An SFC study by Ashraf-Khorassani and Taylor (1989b), as well as HPLC studies by Jenkins and Walsh (1987), Jenkins et al. (1988, 1989) and Jenkins

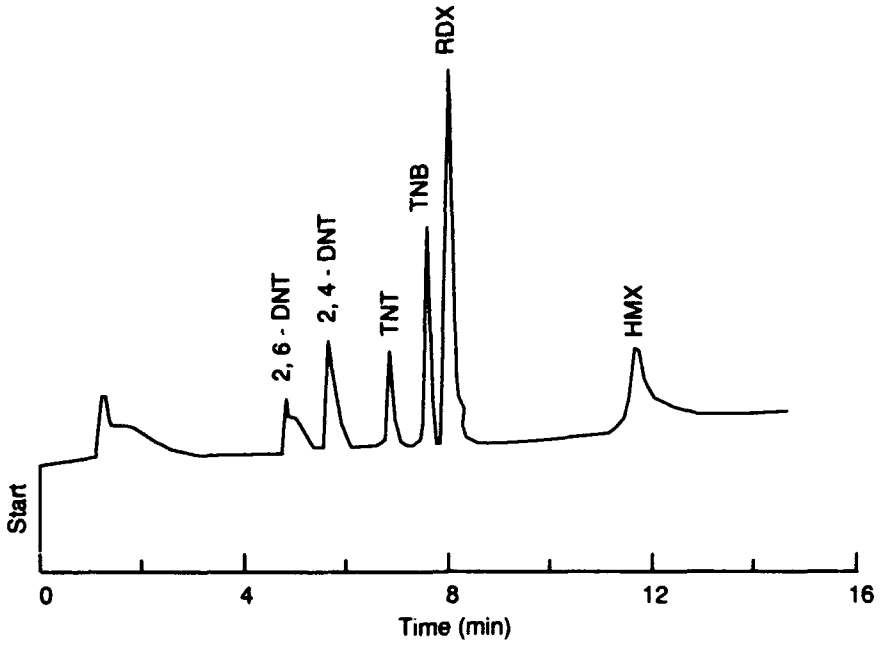

Figure 3. SFC separation of high explosives using an SB-Biphenyl-30 capillary column (2.5 m × 0.05 mm).

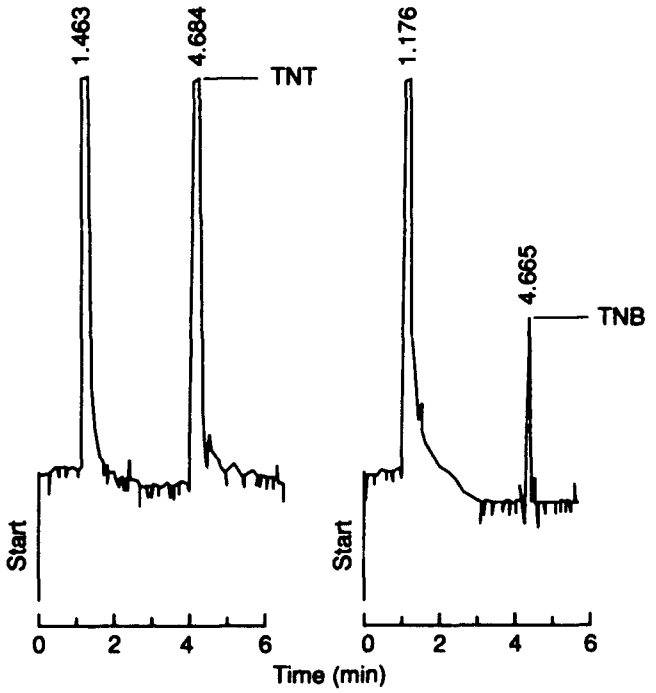

Figure 4. SFC chromatogram of TNT and TNB using an SB-Smectic capillary column (2.5 m × 0.05 mm).

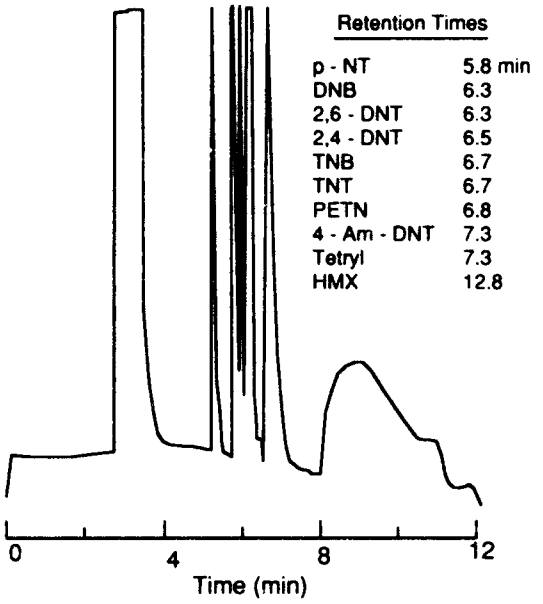

Figure 5. SFC separation of high explosives using an SB-Methyl-100 capillary column (2.5 m × 0.05 mm).

(1989), also indicated the utility of using the cyanopropyl stationary phase to resolve munitions compounds. Jenkins (1989) noted that a specific interaction exists between the polar nitroaromatics and nitramines and the -CN portion of the stationary phase that accounts for the unique separation and retention order of these compounds on an LC-CN phase column.

An SB-Cyanopropyl-50 (Lee Scientific) 2.5-m column showed great promise for a suitable separation (Fig. 6). The nitroaromatics and nitrate esters eluted between 8 and 11 minutes, with the RDX and HMX being retained to 16 and 24 min, respectively. With this long retention time, however, the HMX peak was broad and would be hard to quantitate, particularly at trace concentrations.

I then switched to an SB-Cyanopropyl-25 (Lee Scientific) 5.0-m column since the reduced polarity should shorten the HMX and RDX retention times. The combination of reduced polarity, longer column and slight modifications in the density–temperature program improved the separation for the nitroaromatics and nitrate esters over the SB-Cyanopropyl-50 column and shortened the elution time for RDX and HMX to 12 and 20 min, respectively (Fig. 7). The SB-Cyanopropyl-25 column was able to resolve the majority of the analytes of interest, although DNB, 2,4-DNT and NG were not resolved enough to be separately quantitated. Also, I was unable to develop a secondary separation adequate for confirmation, which is often required when analyzing environmental samples.

The currently accepted HPLC-UV methods for the determination of munitions (Jenkins et al. 1989, Miyares and Jenkins 1991) each report a primary and a confirmatory separation. Jenkins et al. employed an LC-18 (25 cm × 4.6 mm, 5 µm) column for primary analysis and have reported resolution of 11 munitions and munitions byproducts, including HMX, RDX, TNB, DNB, tetryl, TNT, 2,4-

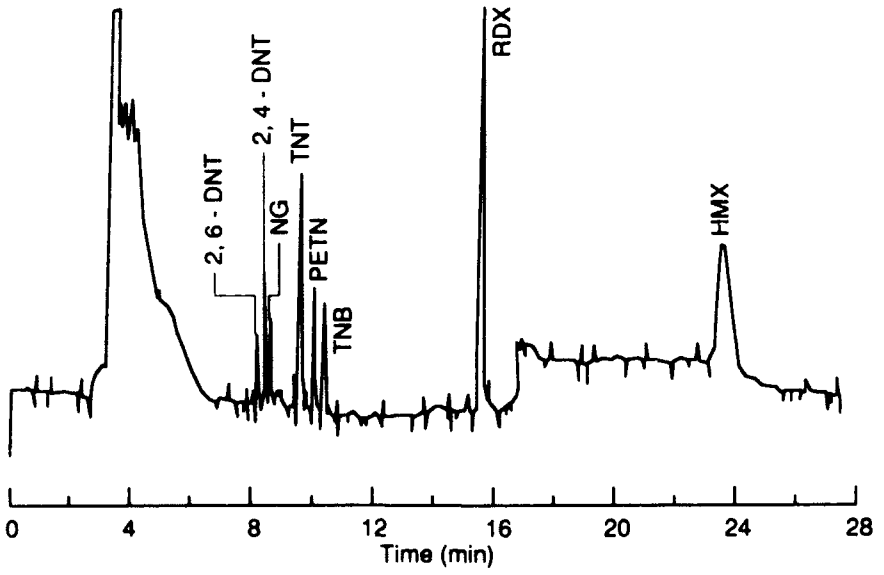

Figure 6. SFC separation of high explosives using an SB-Cyanopropyl-50 capillary column (2.5 m × 0.05 mm).

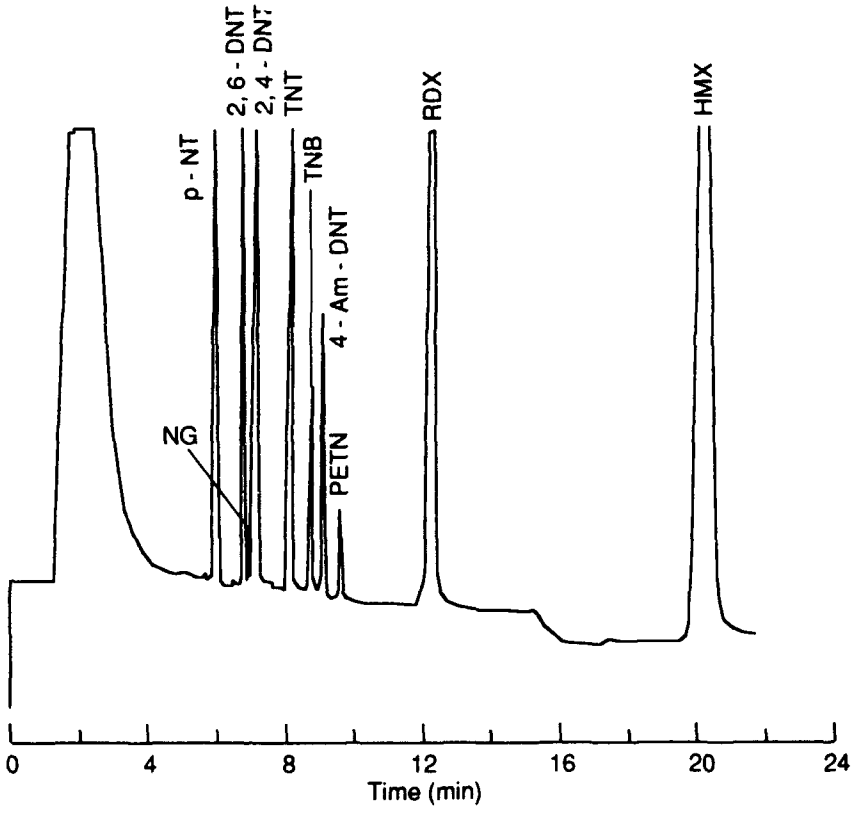

Figure 7. SFC separation of high explosives using an SB-Cyanopropyl-25 capillary column (5.0 m × 0.05 mm).

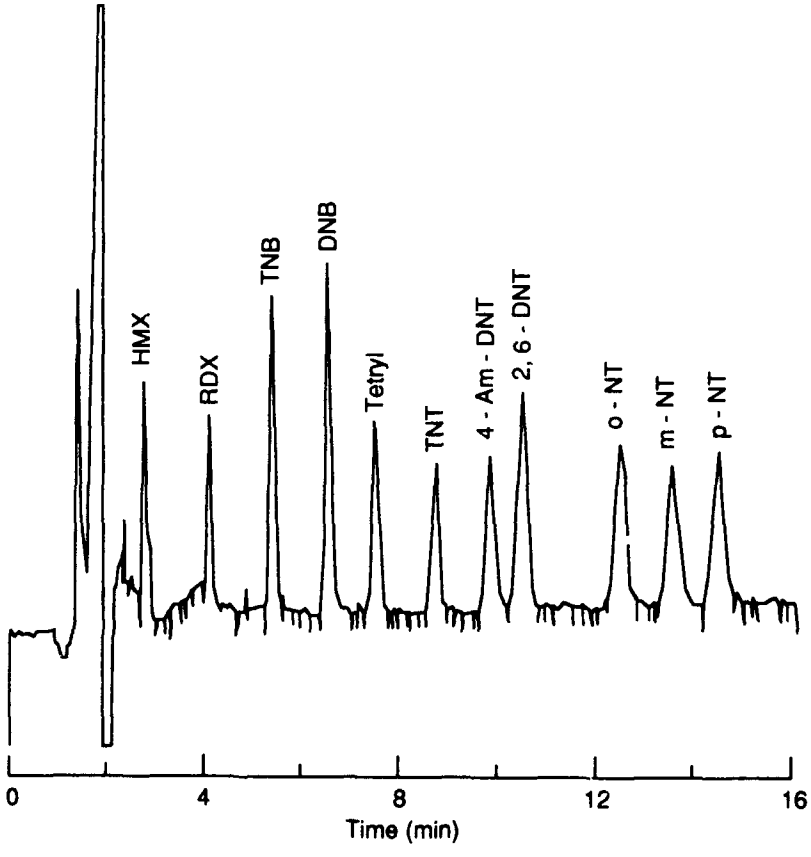

Figure 8. HPLC separation of high explosives using an LC-18 packed column (25 cm × 4.6 mm, with 5-μm particles, 50/50 [v/v] MeOH/H_2O at 1.5 mL/min). (After Jenkins and Walsh 1987, Jenkins et al. 1988, 1989.)

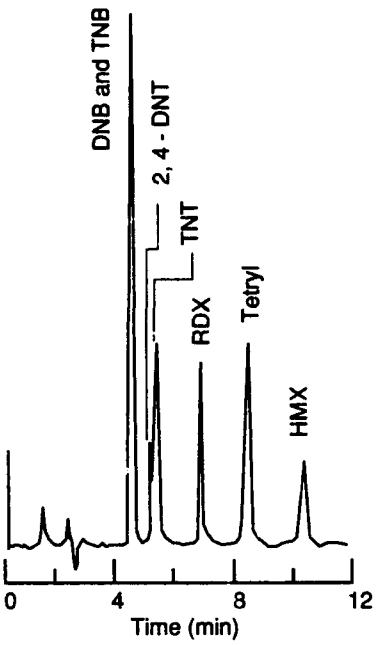

Figure 9. HPLC separation of high explosives using an LC-CN packed column (25 cm ×4.6 mm, with 5-µm particles, 50/50 MeOH/H_2O [v/v] eluent at 1.5 mL/min). (After Jenkins and Walsh 1987, Jenkins et al. 1988, 1989.)

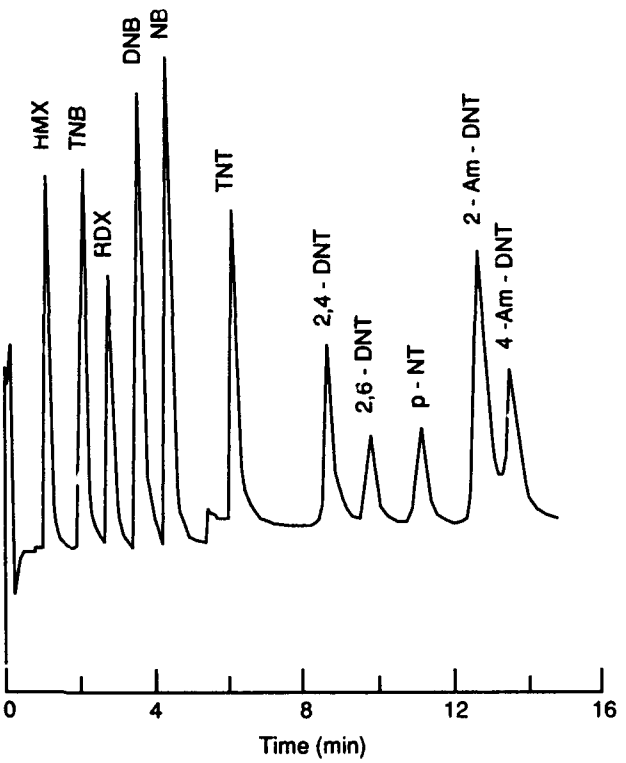

Figure 10. HPLC separation of high explosives using an LC-8 packed column (7.5 cm ×4.6 mm, with 3-µm particles, 70.7/27.8/1.5 H_2O/MeOH/THF [v/v/v] eluent at 2.0 mL/min). (From Miyares and Jenkins 1991.)

DNT, 2,6-DNT, 2-Am-DNT, 4-Am-DNT and the three isomers of mono-nitrotoluene (ortho, meta, para) (Fig. 8). They also reported an adequate confirmation separation employing an LC-CN column (25 cm × 4.6 mm, 5 µm) (Fig. 9). Miyares and Jenkins (1991) reported a primary separation using an LC-8 column (7.5 cm × 4.6 mm, 3 µm), which resolved HMX, RDX, TNB, DNB, NB, TNT, 2,4-DNT, 2,6-DNT, 2-Am-DNT and 4-Am-DNT sufficiently for quantitation (Fig. 10). They also reported a confirmation separation using an LC-8 column (3.3 cm × 4.6 mm, 3 µm) in series with an LC-CN (3.3 cm × 4.6 mm, 3 µm) (Fig. 11). Both methods reported by Jenkins et al. and Miyares and Jenkins are carried out under isocratic conditions and at room temperature. In contrast the SFC separation developed for this study is carried out under an intricate combination of temperature and density ramps (Table 1). Therefore, I see no evidence that chromatography for munitions by SFC has any overwhelming advantages over chromatography by HPLC.

SFC DETECTORS

The second part of this study concentrated on detection. A wide range of GC-like and HPLC-like detectors have been used in conjunction with SFC. These include ECD, FID, TEA, TID, UV, MS and FT-IR. Many of these have been employed in studies for the analysis of munitions by SFC. For this study the TID-2-H_2/air detector was chosen because of its selectivity toward nitrogen-containing compounds. A schematic of the TID-2-H_2/air detector is shown in Figure 12. In this detector a highly reactive flame-like gaseous layer surrounds a hot ceramic surface that contains cesium. Compounds introduced into the boundary layer are chemically decomposed by active gas-phase chemistry. Electronegative products of the decomposition are selectively ionized at the surface of the thermionic source (Patterson 1986). Nitrogen- or phosphorous-containing compounds are ionized with especially high efficiency by this process. Patterson (1986) reported that typical GC detec-

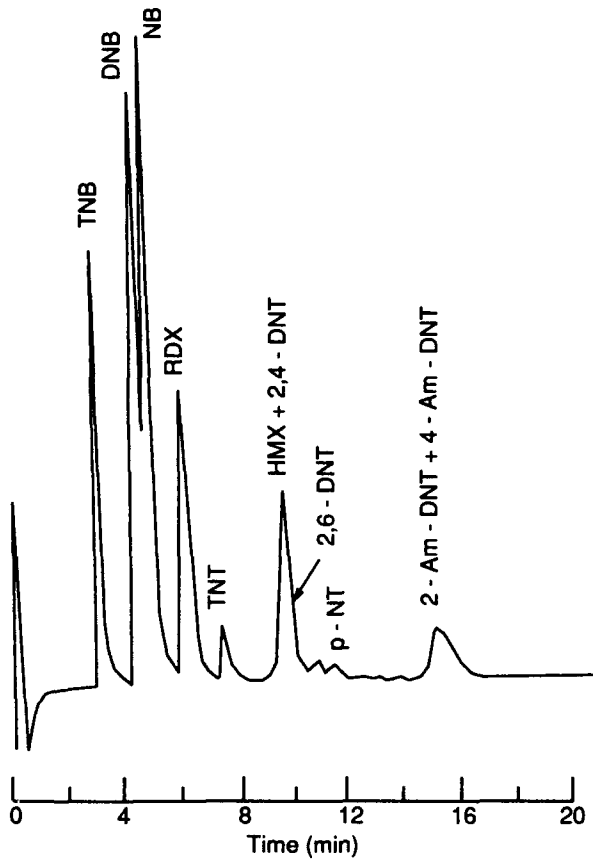

Figure 11. HPLC separation of high explosives using LC-8 and LC-CN columns in series (both 3.3 cm ×4.6 mm, with 3-μm particles, 70.7/27.3/1.5 H_2O/MeOH/THF [v/v/v] eluent at 1.5 mL/min). (From Miyares and Jenkins 1991.)

tion capabilities for this detector are 1–20 pg injected, and the specificity with respect to hydrocarbons is 104–105. For SFC-TID the data are far less favorable. West and Lee (1986) reported a detectable range of 0.4–8 ng injected for a series of nitrated polycyclic aromatics (S/N = 3) using SFC-TID-2-H_2/air. They also reported that the linear range was limited to 10–100 ng injected. Based on the 500-nL injection that our SFC can deliver, these figures correspond to 0.8–16 mg/L in solution and 4.0–16 mg/g based on a 10.0-mL extraction of 2.0 g of soil.

The sensitivity of the TID-2-H_2/air depends on the concentration of H_2 gas in the boundary layer, which is controlled by the flow rate of H_2 gas and the temperature of the thermionic source, which in turn is controlled by the current applied. The required flow rate of H_2 ranges from 3 to 6 mL/min, with approximately 4 mL/min being optimum for nitrogen analyses. The optimum current will vary with the condition of the individual thermionic source. The current should be high enough to produce a boundary layer but not so high as to produce a flame. West and Lee (1986) used an H_2 flow rate of 5.3 mL/min and a current of 3.3 A. With these settings they reported a low selectivity (~10^3 over a hydrocarbon) and a large dependency on increasing density of fluid. Such density changes cause severe baseline drifting, which greatly hampers the ability to perform any chromatography.

My procedure for optimizing detector response was based on the response of TNT. I began by setting the current and H_2 flow rate in accordance

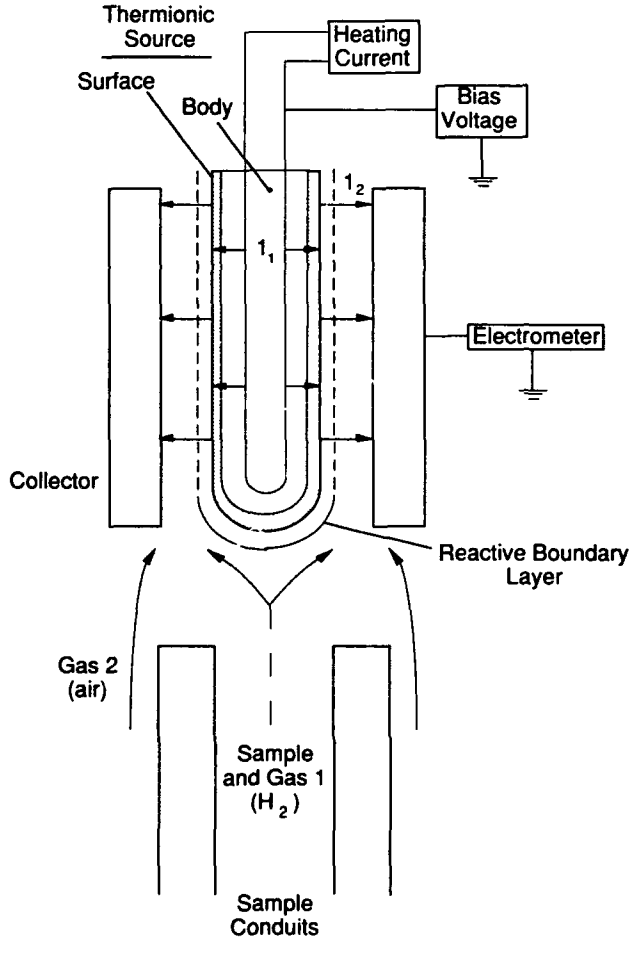

Figure 12. Schematic of the TID-2-H_2/air detector. (After Patterson 1986.)

with the manufacturer's recommendations (~2.7 A and ~4.0 mL/min). I then adjusted the current and flow rate and noted the subsequent effects on the signal-to-noise ratio. I found that a current range of 2.65–2.80 A combined with an H_2 flow rate of ~3.7–4.2 mL/min resulted in the highest achievable signal-to-noise ratio for this system. Outside of these ranges I observed either reductions in signal levels or drastic increases in both signal and noise levels. At these lower settings I did not observe the baseline drift with density change reported by West and Lee (1986).

Using the flow and current settings specified above, some preliminary analyses of munitions standards were carried out. The results showed that some of the analytes could not be detected even at concentrations as high as 1.0 g/L.* For the analytes that could be detected, the detection capabilities were consistent with the limits reported by West and Lee (1986). These limits were significantly higher than the certified reporting limits reported by Jenkins et al. (1989) for the HPLC-UV methods. Because of these results I felt that a certified reporting limit test was not warranted.

SFC OPERATIONS

The third part of this study dealt with the basic operations of an SFC system compared to GC and HPLC. Operating an SFC system is very similar to operating a GC system with a few hints of HPLC tossed in. The Dionex SFC system evaluated in this study was operated only with capillary columns. These columns, as in GC, require precision cutting of the ends with sapphire-tipped cutting tools, and they require precise positioning within the injector and detector for optimum performance. They are only 195 µm in diameter, compared to 325 µm for GC. Being smaller and more flexible than GC columns, SFC columns are much harder to install. HPLC columns can be installed or removed in less than 1 minute, but SFC columns can take 15 minutes or longer to install, depending on experience.

The introduction of samples is very simple. The high-speed pneumatic valve is analogous to the Rheodyne valves used in many HPLC systems. One major drawback for capillary SFC, though, is the limitation on injection size. The injection loop for our system is only 0.50 µL in total volume versus 1.0–2.0 µL for GC and 10–1100 µL for HPLC. This limits the detection capabilities for the instrument, and for trace analysis it requires sample preparation procedures that include a preconcentration step.

Analyzing samples under routine conditions using an established method requires comparable steps for both SFC and HPLC once the systems are up and running. Both HPLC and SFC systems can be equipped with auto-injection and sophisticated data-handling systems for analyses requiring extended (overnight) times. However, operators of HPLC systems may require one to two days of training on a specific instrument, while SFC operators may require three to five days of instruction.

Developing separations is more difficult in SFC than in HPLC. Jenkins (1989) noted that reversed-phased (RP)-HPLC separations are based on solvophobic behavior, where retention times are strongly correlated to octanol–water partition coefficients (K_{ow}). McDuffie (1981) showed that this relationship was so predictable that K_{ow} values could be used to predict capacity factors and thus retention times for an RP-HPLC separation. In SFC the partitioning of analytes between the mobile and stationary phases is part of the mechanism for separation, but the mechanism may also include specific effects from density, temperature, linear velocity and volatility of analytes or a combination of these effects. Consequently it is a much more difficult process to understand and interpret, and thus a more difficult system for which to predict the proper chromatographic conditions.

In SFC one needs to determine the proper fluid, the proper temperature–density–pressure combination for that fluid, and the proper stationary phase to achieve adequate separations. In HPLC the strength of the eluent for a given stationary phase needs to be determined. Although the two requirements seem to be analogous, determining the temperature–density–pressure combination is far more time consuming than determining the proper ratio of two or three solvents in an eluent. The temperature, density and pressure of supercritical fluids are interrelated in such a way that for a given density, there are many temperature and pressure combinations. Also, at low pres-

*Figures 3–7 indicate a significant response for all analytes, but here the detector was set at an excessively high H_2 flow rate and source current to achieve a response to establish retention times and resolutions. Unfortunately, as discussed earlier, high H_2 flow rates and high currents eliminate selectivity by reducing the detector to a pseudo-FID, and they also cause excessive drifting in the baseline with changing density.

sures the relationship between density and temperature is not linear, where at high pressures they appear to have a linear relationship. Due to the complex interrelationships of these effects, the conditions for separation are often some combination of temperature varying at constant density, density varying at constant temperature and temperature varying with varying density. In contrast, developing an isocratic or gradient elution HPLC separation requires a systematic varying of the percentage of each component of solvents in the eluent until the desired resolution is achieved. For both techniques, choosing a column will be specific to the analytes of interest and may require testing of more than one column before the separation is adequate.

SFC WITH MODIFIED FLUIDS

During this study I examined the effects of using solvent-modified CO_2 as the carrier fluid. The solvents tested were methanol and acetone, each at 5 and 10% concentration, by volume. Both solvents showed potential for a slight to moderate positive effect on the chromatography. Retention times decreased slightly with resolution being maintained. The greatest effects were seen with acetone over methanol-modified fluid. Unfortunately the use of the modifiers had an adverse effect on the detector, causing baseline drifting and inconsistencies in analyte responses.

CONCLUSION

The use of SFC with GC-like selective detectors has been shown by many to be an excellent technique to fill in the analytical gaps between GC, where thermal lability and volatility are the limiting factors, and HPLC, where available detectors limit selectivity. Some papers have shown that SFC is an adequate technique for some specific munitions applications. For routine environmental monitoring and site characterization required by the military, though, SFC does not offer advantages over the accepted HPLC-UV methods. Although separations are possible for some combinations of munitions compounds, separations were not adequate for quantitation of all the analytes of interest in this study. Also, the possibility of a confirmatory separation is meager because of the limited number of stationary phases available for capillary columns. The sensitivity of the SFC-TID-2-H_2/air is significantly less than that for HPLC-UV. The basic operations and the understanding of the science of SFC are more difficult than that of HPLC.

In conclusion, SFC-TID-2-H_2/air is selective, and there exists the potential capability of analyzing the three class of compounds of interest to the military, but the limited detection capabilities, the column limitations and the difficulty of basic use and understanding of the instrumentation far outweigh its potential capabilities.

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A supercritical fluid chromatographic (SFC) system equipped with a capillary column and a thermionic ionization detector (TID) was evaluated as a potential analytical tool for the simultaneous determination of nitroaromatics, nitramines and nitrate esters. Examination of several stationary phases and modified fluids was carried out while determining optimal conditions for a suitable separation. The results indicate that a cyanopropyl stationary phase is best suited for these analytes, but the available percentages of cyanopropyl in the phase (i.e. 25% and 50%) do not give total resolution. The performance and usability of the TID was evaluated. Detection limits are estimated to be several times greater than those for standard HPLC and GC methods. Also, the usability and performance of the SFC were compared with HPLC and GC. SFC-TID can be used for the simultaneous determination of nitroaromatic, nitramines and nitrate esters, but current column and detection capability limitations greatly reduce its potential.

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