

**APPLICATIONS OF SUPERCRITICAL FLUIDS TO THE EXTRACTION AND
ANALYSIS OF OLIGOMERS AND POLYMER ADDITIVES**

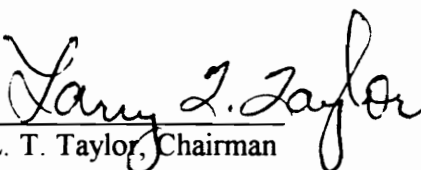
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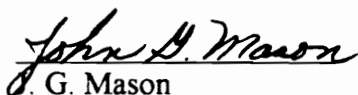
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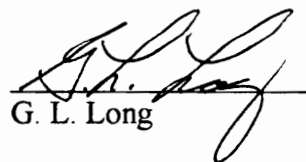
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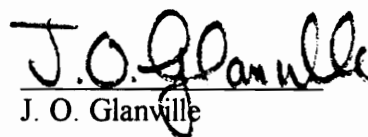
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APPLICATIONS OF SUPERCRITICAL FLUIDS TO THE EXTRACTION AND ANALYSIS OF OLIGOMERS AND POLYMER ADDITIVES

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Abstract

Supercritical fluids (SF)s have several physicochemical properties that can often make them superior to conventional liquid solvents. These characteristics include relatively high densities, low viscosities, zero surface tension and high diffusivities. This unique combination of properties allows them to have solvating strengths that can approach those of pure liquids while maintaining many of the advantageous transport qualities of gases. In the past decade SFs have seen increased use as solvents for both extraction (SFE) and chromatography (SFC). A particularly exciting area of applications has been in the field of polymeric materials. Since polymers are not discrete molecules, but, rather broad distributions of very similar compounds (oligomers), they can pose interesting challenges for the separation chemist. SFs are uniquely suited to meet these challenges. The goal of the work done in this laboratory over the past few years has been to use SFs to extract and characterize both oligomers and additives from polymeric materials.

A method for the post-polymerization fractionation of a low molecular weight, high density polyethylene wax using analytical scale SFE equipment was developed. Supercritical CO₂ was used to separate very narrow molecular weight distributions (MWD)s from the polyethylene feedstock. The resulting MWDs were characterized by SFC and high temperature gel permeation chromatography (GPC) and found to have polydispersities and molecular weights much lower than the parent wax. Supercritical

propane was used to fractionate higher MWDs from the feedstock, however its greater solvating strength for the polyethylene oligomers resulted in larger polydispersities. A dual pump SFE system was used to deliver a dynamic mixture of propane in CO₂. The resulting fractions were very similar to those achieved by pure CO₂, but the recoveries were much higher. Increasing the temperature appeared to have both a kinetic and thermodynamic contribution to oligomer extraction.

Supercritical CO₂ was also used to extract additives from an insoluble polymeric nitrocellulose (NC). The primary stabilizer additive (diphenylamine) and its nitrated derivatives were extracted from the propellant. The SF extracted stabilizer profile was characterized using liquid chromatography (LC), gas chromatography (GC) and SFC. SFC was shown to provide separations of propellant additives that were superior to the existing LC method while maintaining lower temperatures than GC. Extracts from propellants stored at elevated surveillance temperatures contained more highly nitrated stabilizer derivatives. However, some question was raised as to the actual validity of elevated temperature programs for propellant screening due to potential differences in reaction mechanisms.

A LC-thermospray mass spectrometry (MS) interface was modified for use with packed column SFC. The system was used as a chemical ionization (CI) source for the high CO₂ flow rates emanating from packed columns. Methane was used as a reagent gas (RG) for positive chemical ionization (PCI). The resulting CO₂ + CH₄ mixed RG was studied at CO₂ pump pressures typical of SFC pressure programming. The background ions varied widely with CO₂ partial pressure and source temperature, however, spectra of a propellant test mixture were relatively unaffected by changing RG. The system was also used to perform negative CI (NCI) using the mobile phase CO₂ as a RG. This method was found to be very useful for nitrated derivatives of diphenylamine. SFC-CH₄-PCI-MS

confirmed the intact elution of thermally labile *N*-nitroso compounds thought to exist in propellants. SFC-CI-MS, both NCI and PCI, was used to characterize the SF extracts of polymeric nitrocellulose and was demonstrated to have potential for the analysis of a wide range of compounds found in the propellant industry. SFC-CH₄-PCI was also determined to be compatible with methanol modified mobile phases. The mobile phases in this case were delivered from premixed cylinders. However, severe limitations regarding the reliability of premixed mobile phases in SFC were shown to exist.

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CHAPTER 1

Supercritical Fluid Extraction

Introduction

From analytical to process scale, separations can be a chemist's greatest challenge. Removing solvents, reactants and impurities; separating and isolating mixture components and extracting analytes from a variety of matrices are just a few of the problems encountered by all chemists. These processes are usually driven by a separation of phases. Because most substances have very low solubilities in gases, and vapor pressure derived separations (i.e. distillation) require some degree of volatility - liquids have evolved as the most common bulk phase used in the majority of separations. The level of differential partitioning into the liquid phase governs how efficient the separation can be. These liquid-liquid and liquid-solid (soxhlet) extraction methods have remained relatively unchanged since the turn of the century.

However, many separations can not be achieved using conventional methods. These situations may require solvent strengths not available to the solvent being used, or, they may be unable to fine tune the solvent strength to provide the necessary selectivity, or, it may be difficult to remove the solvent from the desired material once the separation is complete. Additionally, as a result of the Montreal Protocol, many traditional solvents are in the process of being banned by 1995 (1). Fortunately, the last decade has seen a veritable revolution in the use of supercritical fluids (SFs) to solve many difficult separation problems. While early emphasis was on the use of SFs (esp. CO₂) to perform highly efficient chromatographic separations of non-volatile mixtures - more recently, that emphasis has shifted to the use of SFs for analytical and bulk extractions. Recent SFE applications at Virginia Polytechnic Institute and State University have ranged from

the demilitarization of propellant stockpiles and fractionation of polymers to the removal of trace organics from soils and water (2-5). The application of SFs to the area of sample preparation represents the greatest advance in that field in decades. The United States Environmental Protection Agency (EPA) and the Food and Drug Administration (FDA) are in the process of developing SFE methods that will replace longtime liquid-based sample preparation methods. These new methods will cut down on solvent consumption, analysis time and the number of handling steps required for many long accepted methods.

Several instrument manufacturers have designed benchtop SFE systems that make the study of SF-based separations a relatively easy and inexpensive proposition. It is now possible to explore a variety of SFs with or without co-solvents, at various pressures and temperatures and flow-rates until the right conditions for the desired separation are achieved. These instruments, designed primarily with the analytical chemist in mind, can even provide the process chemist with the necessary tools to thoroughly study and optimize SF applications prior to expensive and timely scale-up. Some systems are readily adaptable to prep-scale operation, and in the cases where small quantities of material are desired (i.e. pharmaceuticals) they are even useful at the pilot-scale. There are many instances in which analytical SFE can be used to provide the industrial chemist with valuable information concerning potential process applications. SFs are finding applications in the process chemistry and analysis of foods, petrochemicals, polymers and explosives to name just a few.

Supercritical Fluid Characteristics

In a single component phase diagram such as the generic one seen in Figure 1, the latent heat and volume change associated with the liquid-vapor equilibrium boundary

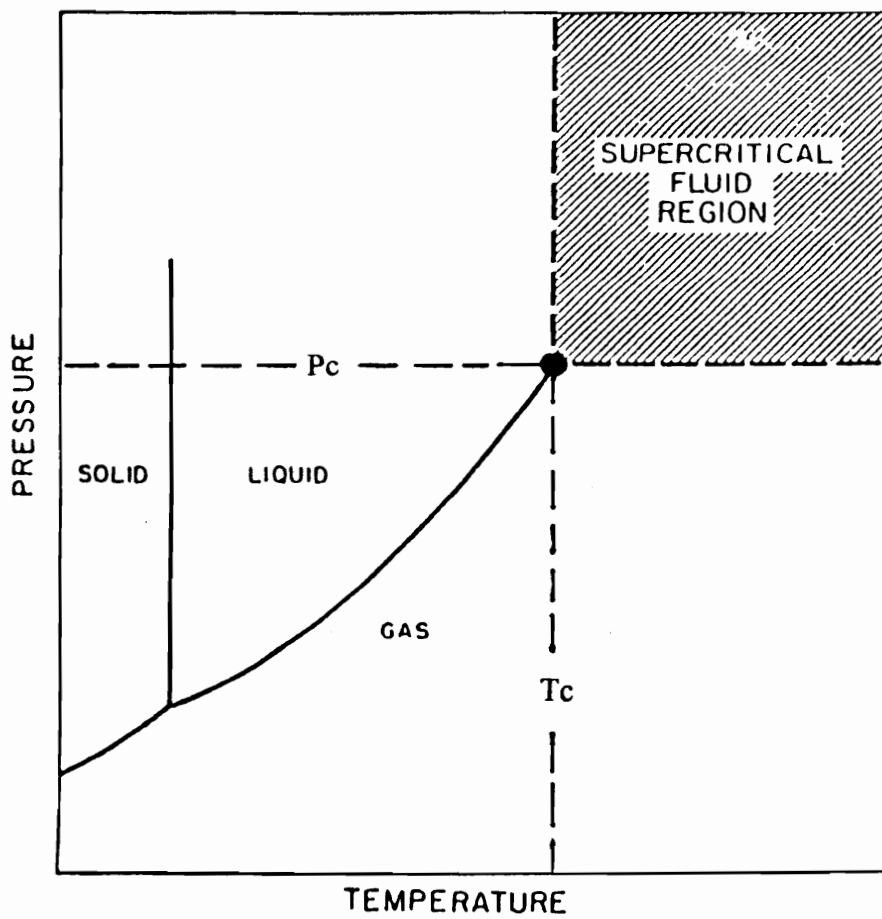


Figure 1. Single component phase diagram.

decreases with increasing temperature, until it ends abruptly at what is referred to as the critical point (Cp). This point defines the critical temperature (Tc) and critical pressure (Pc) for a substance. Table I shows the critical parameters and associated dipole moments for some common SFs (6). Note that the presence of a dipole moment in a molecule increases the magnitude of the critical parameters, often-times to levels that are impractical for instrumental applications (i.e. H₂O).

Hannay and Hogarth (7) first observed the unique solvent characteristics of a SF in 1879. They were studying the solubility of potassium iodide and cobalt chloride in gaseous ethanol and found that the two solutes could be dissolved by raising the pressure above the mixture's critical point. The degree of solubility in the SF was reported to be a function of pressure. Since then, SF phase behavior has been documented for a number of solute-SF systems (8-10).

To understand the principles by which a SF behaves, it is beneficial to first picture a gas as a solvent. As is well known, a gas can be used to perform separations based on vapor pressure. The gas is placed in contact with the sample at elevated temperatures and analytes dissolve into the gas as a function of their volatility. This is routinely done in the case of thermal desorption and gas chromatography. However, most materials, especially those of polymeric origin, do not exhibit sufficiently high vapor pressures to be separated by thermal methods. They, like most solids, show no appreciable solubility in a gas. Under such conditions, the enthalpy of dissolution requires a stronger interaction between analyte and solvent in order to overcome solute-solute or solute-matrix interactions. Additionally, increased temperatures often result in thermal decomposition of the sample. However, by increasing the pressure of the gas above the critical point, it is possible to impart it with liquid-like densities and solvating strengths. In the vicinity of the critical point the density of the gas will increase rapidly with increasing pressure.

Table I

Physical parameters of some supercritical fluids.

SF	Critical Temperature (°C)	Critical Pressure (atm)	Dipole Moment (D)
<i>Carbon Dioxide</i>	31.3	72.9	0
Nitrous Oxide	36.5	72.5	0.51
Ammonia	132.5	112.5	1.65
Propane	96.8	43.1	0
Xenon	16.6	58.4	0
Methanol	240.1	82.0	1.70
Freon	111.8	40.7	0.17
Water	374.4	224.1	1.80

At this point there is a dramatic rise in solubility for many compounds, with the observed solubility being several orders of magnitude greater than that predicted from classical thermodynamics of ideal gases. Figure 2 shows the actual and theoretical solubilities for naphthalene in SF ethylene (11). This deviation from classical predictions is the result of contributions from an imperfection coefficient that become very significant in the vicinity of the C_p . As the partial molar volume of the solute begins to decrease dramatically, the average distance between molecules decreases and non-ideal gas behavior begins to govern the interactions between the solvent and sample - accounting for the tremendous "enhancement" in solubility. Now, in addition to vapor pressure, the mechanisms of chemical interactions between the sample and the "high pressure" gas are available to the chemist to generate separations. In this supercritical region, shown as the shaded area in Figure 1, the solvating strength is a direct function of density - which in turn is dependent on system pressure (at constant temperature) or temperature (at constant pressure). Interestingly, there is no break in the continuity of solvent strength as the SF goes from a gas into the supercritical region. Thus, it is possible to finetune the solvating strength of the SF any where in the range from the ideal gas to nearly that of the pure liquid. Because of the non-compressibility of liquids, this phenomenon is peculiar to the SF. In this region, the chemist has more means to control solvent behavior than at any other time. It is even possible, by adding small quantities of co-solvents to the SF, to custom design a SF for a specific application.

In the SF region a substance has other characteristics that compliment its solvent properties. The physical properties of a SF tend to be intermediate between those of liquids and gases. Diffusivities are typically an order of magnitude higher than in the corresponding liquid; while viscosities are usually an order of magnitude lower. These factors, along with zero surface tension exhibited by the SF, allow it to have many of the

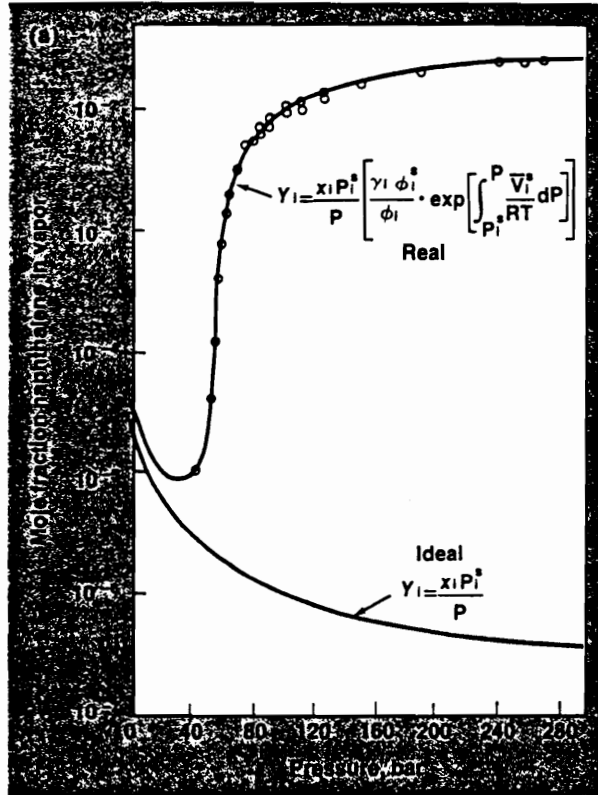


Figure 2. Real and predicted solubilities of naphthalene in CO₂ as a function of pressure (11).

advantageous mass transport characteristics of a gas while retaining liquid-like solvating strengths. Additionally most common SFs are gases under ambient conditions, and their complete removal or complete recirculation is simply a matter of decompression and/or recompression. And in the case of SF CO₂, its "detector transparency" for both flame and optical based detectors make it an ideal chromatographic mobile phase.

ABCs of SFE

The enhanced solvent properties of SFs have only recently been explored to their potential by separation scientists. Drawing from the advances made in LC hardware during the 1970s, the 1980s saw a number of instrumental developments (primarily for analytical chemists) that make the use of SFs in a benchtop environment a relatively easy and inexpensive proposition. There are now several manufacturers with instruments devoted to both supercritical fluid chromatography (SFC) and supercritical fluid extraction (SFE). The typical benchtop SFE apparatus will consist of (A) a gas supply, (B) a pump and controller used to pressurize the gas, (C) a temperature controlled oven, (D) an extraction vessel, (E) a back pressure regulator and (F) a collection device.

For analytical SFE systems the gas supply is simply a laboratory sized cylinder from any number of manufacturers. Carbon dioxide, by virtue of its moderate critical parameters, high purity and low cost is the most common SF being used today - but many other potentially useful fluids are available (Table 1). Some gas suppliers will provide premixed fluids for applications where pure SF CO₂ is inadequate.

From the gas supply, the SF travels from the tank to the pump where it is pressurized to the desired value. Two major types of pumps are found in SFE instruments; syringe and piston. Syringe pumps have fixed volumes and any extraction in progress must be interrupted if the pump is emptied during the extraction. This

situation is becoming a serious disadvantage as extraction cells become larger so that more representative samples can be extracted. Piston pumps are only limited by the liquid volume of the gas supply cylinder. However it is necessary to cool the piston heads in some manner so that the non-compressible liquid phase is pumped. It appears that most new instruments now incorporate piston pumps in their design. The majority of manufacturers provide two pumps (usually as an option) with one delivering the primary fluid, while the other delivers the desired level of co-solvent. SFE pumps typically have maximum pressures between 6000 and 10,000 psi, and can provide liquid flowrates to several mLs per minute. The controller on many SFE instruments allows several extraction steps to be programmed into the method. This ability is particularly useful when fractionations are being performed.

From the pump the SF travels to an extraction vessel where the sample is contained. The extraction vessel is housed in an oven so that the desired temperature can be maintained. As more applications are explored, the need for higher extraction temperatures is being realized. Often the most difficult part of solubilizing an analyte is its initial desorption from the matrix. High temperatures can help overcome this energy threshold thereby allowing more complete extractions to take place. Ovens provided with analytical SFE instruments usually have maximum temperatures from 100 - 150 °C. The extraction vessels contained in the oven are usually stainless steel cartridges with volumes from a fraction of a mL to greater than 10 mL, although larger vessels are available. At least one manufacturer provides disposable cartridges of polymeric composition. All are sealed on both sides with frits (usually 0.5µm) to prevent the entrainment of particulates.

Back pressure in analytical SFE can be provided by a fixed restrictor (usually a narrow bore fused silica or stainless steel capillary). With a fixed restrictor the flow rate

cannot be controlled independently of the pressure. Thus, linear restrictors must be replaced with different diameters and/or lengths of tubing in order to maintain constant flowrates under different pressure conditions. Their narrow orifices can also be prone to plugging if a large amount of border-line soluble material is being extracted. Heating the restrictors helps to alleviate (not eliminate) plugging problems. High pressure micro-metering valves are becoming more popular. These backpressure regulators allow flowrates to be adjusted to constant levels at different pressures. They usually do not work well at low flow rates and their large dead volume can be difficult to rinse clean of extracted material - an especially undesirable characteristic for trace analysis. However, the valves are particularly useful to those wishing to model process methods.

During a typical SFE application the sample is placed in the high pressure extraction vessel and equilibrated to the desired temperature. The extraction fluid is then allowed to flow into the vessel and is pressurized to the desired value. At this point either a static, dynamic or combination static-dynamic extraction can be initiated. As analytes are dissolved in the SF they must be removed by the SF phase into a separate region. Normally, the analytes travel through the restrictor where the SF decompresses and the analytes deposit in some sort of trap. This is often a cooled liquid or solid support. In the case of solid supports, the analytes must be rinsed from the support in a separate step. In the past, poor SFE recoveries were often erroneously blamed on poor extraction efficiencies when the true culprit was incomplete trapping (or inadequate rinsing of the solid trap). Volatile materials typically pose the greatest difficulty in this respect. However, even non-volatile, polar samples extracted under certain circumstances can be problematic.

To trap the extract in a liquid, the restrictor end is usually immersed in the collection solvent. There the decompressed SF rises rapidly to the surface, hopefully

leaving the extracted analyte in the liquid. If a liquid trap is being used, high SF flow rates can result in violent bubbling and physical removal of the extract by the aerosol following decompression of the SF in the solvent. Also, if the extract exhibits poor solubility in the collection solvent, poor recoveries usually result. The best recoveries during liquid collection of the extract usually result from a combination of low-to-moderate SF flow rates in a solvent known to exhibit an affinity for the compounds of interest. It is important to immerse the restrictor as far below the surface of the collection solvent as possible. Capping and generating a slight back pressure in the collection vessel also appear to help improve recoveries. Sometimes dual trap solvents can help deal with difficult combinations of analytes (12).

In our laboratory we are frequently asked by industries to demonstrate the feasibility of the SFE or supercritical fluid fractionation (SFF) process prior to their commercial investment in the technique. We usually try to mimic the process that the sponsor would like to implement at the analytical level. In a case where it is desired to remove a specific impurity/analyte from a bulk material our efforts usually follow a routine. Preliminary studies are performed by spiking the analyte on an inert matrix. This is often sand or Celite, a form of diatomaceous earth. In this way, the analyte's solubility in various pure or modified SFs is investigated at several pressure and temperature combinations. Although these results are rarely directly transferable to the actual matrix, they do provide a good starting point. In particular these studies help optimize the conditions under which the analytes can be quantitatively recovered following removal by SFE.

To perform a fractionation, multiple extractions on the same sample under different conditions are performed. It is possible to fractionate materials on the basis of their solubility in the SF by varying the density, temperature or co-solvent concentration

of the extracting medium. The level of control afforded by a SF allows samples to be separated according to their molecular weight, composition, degree of crystallinity, degree of polymerization, etc. For instance, to fractionate a polymer into different molecular weight distributions (MWD)s, the sample can be extracted at different densities at constant temperature - taking advantage of the decrease in solubility most oligomers exhibit with increasing size. The first extraction is done under conditions of low density - the extract is collected then replaced with a fresh collection vessel. A second extraction, at a higher density is then performed, with the extract again being collected in a fresh vessel. This is done, consecutively until the fractionation is complete. Programmable SFE pumps and fraction collectors now make this a hands-off procedure. As long as differential solubility in the SF exists, some degree of fractionation can usually be generated.

CHAPTER 2

Supercritical Fluid Fractionation of Polyethylene Wax with CO₂

Introduction

Supercritical fluids (SFs) have already received a measure of acceptance among analytical chemists for their ability to provide characteristics that fill a niche between traditional liquid and gas chromatography as well as to provide a viable alternative to liquid-solid extraction techniques (13-16). They are also beginning to receive a great deal of attention in the area of polymer processing for the purification and/or fractionation of polymeric materials (11). Most industries, however, desire to see results at the analytical SFE level before they are willing to invest at the process scale. This work investigates the potential of supercritical CO₂ as a solvent for the fractionation of low molecular weight, high density polyethylene wax into narrow molecular weight distributions using analytical scale extractions.

It is often desirable to generate polymeric materials with molecular weight distributions (MWDs) narrower than can be achieved during polymerization reactions. This is particularly true for the manufacture of ultra-high purity materials and in the determination of optimum MWD for a specific polymeric application. Because it can be impossible to achieve such MWDs during polymerization reactions, post-polymerization fractionation is necessary. Conventional liquid-based separation techniques such as filtration, precipitation and distillation are the techniques most often used in the fractionation of polymeric materials. Due to the inability to make fine adjustments to the solvating power, liquids often fail to provide the necessary selectivity required to generate the narrowest molecular weight profiles. Supercritical fluids (SFs) have a number of characteristics that make them potential candidates for solving a variety of

separation problems associated with polymer processing. They have solute diffusivities an order of magnitude higher (10^{-4} -vs- 10^{-5} cm²/s) and viscosities an order of magnitude lower (10^{-4} -vs- 10^{-3} N s/m²) than most liquids. These characteristics along with their zero surface tension lend them mass transport qualities far superior to conventional liquid solvents. In addition, a SF's solvating strength is a function of its density, which is in turn a function of system pressure and temperature. Thus, the solubility parameter of a SF can be fine tuned over a wide range of values, ranging from near gas-like at low densities, to that of the liquid state at high densities. For instance, the Hildebrand solubility parameter (a qualitative measure of solvent strength) of CO₂ can be varied from 1.3 to 8.7 H at 100 °C by increasing the pressure from it's critical value of 73 atm to 600 atm. This means that separations can often be optimized to remove specific analytes or oligomer distributions from the matrix.

In a case where the polymer shows limited solubility in the SF it is possible to remove specific analytes from the matrix free of interferences. There are a number of applications at the analytical scale where additives have been selectively removed from the polymer for subsequent analysis and quantitation (17-20). If the polymer is soluble to some degree in the SF then it is often possible to perform post-polymerization fractionation, whereby several MWDs can often be removed from the parent polymer with a single SF by merely changing the system's pressure and/or temperature in succession. Publications by Schoslki (11) and Krukonis (14,21) review many situations in which supercritical fluids were successively employed to solve difficult separation problems related to polymer processing. These include among others, the removal of unreacted monomer following free radical polymerization, the fractionation of synthetic polymers, and the purification of very low vapor pressure oils. SF CO₂ was even used as

a reaction medium to control the degree of polymerization and as a means of generating finely divided polymer powders.

There are many fluids with different physicochemical properties and critical parameters available to the chemist or engineer for polymer processing applications. Supercritical CO₂ has been used extensively as a mobile phase for supercritical fluid chromatography (SFC) throughout the last decade. Its low critical parameters ($P_c=74.8$ atm, $T_c=31.1^\circ\text{C}$), nontoxicity, detector compatibility and relatively low cost have all contributed to its widespread use both for SFC and supercritical fluid extraction (SFE). It has been used with and without alcohol modifiers to separate both individual oligomers of Triton X-100® and low MW polystyrene on a packed silica gel column during SFC (22). The solubilities of several polymers in supercritical fluid (SF) CO₂ have been determined (23). In general, most polymers exhibit relatively poor solubility in CO₂. Only polymethacrylates, polydimethylsiloxanes and atactic polyolefins are soluble to any appreciable degree. Although low MW oligomers of many polymers are soluble in SF CO₂, separating polyethylene oligomers with SFC has proven problematic. The higher MW oligomers are prone to fall out of solution in the unheated injector and transfer lines. It is usually necessary to maintain the entire system (sample, syringe, injector, etc.) at constant temperature in order to achieve a successful separation. Rynaski (24) found it necessary to heat the injector, syringe and transfer lines of a capillary SFC system to 115 °C in order to elute the C-80 oligomer from a PE 740 standard. The relatively poor solvating capabilities that supercritical CO₂ exhibits toward polyethylene oligomers implies that it might be used as a solvent to generate PE fractions with very narrow MWDs.

In a typical polymer fractionation scheme with a SF, the sample will be contained in some sort of high pressure vessel. For analytical scale studies the vessel is usually a

commercially available extraction vessel ranging in volume from less than a mL to rarely more than 50 mL. In process scale operations the high pressure vessels are much larger, often capable of containing many metric tons of raw material. The SF, supplied by a pump capable of pressures greater than 5000 psi, is usually allowed to pass through the vessel in a dynamic fashion, dissolving oligomers, additives, and/or other material according to its solvating ability and depositing them in another region after some degree of decompression. For analytical scale studies the SF is normally decompressed in the region of an analyte trap and then vented into the atmosphere. The fractions removed during an isothermal fractionation are collected in a step-wise method, with each successive step being at a higher density (or co-solvent concentration) than the previous one. Thus, very narrow "slices" can potentially be removed from the raw polymer. The choice of a solvent for supercritical fluid fractionation (SFF) affects how narrow the slices can be. A solvent that exhibits high solvating strength for the polymer of interest even at low densities probably will be unable to exhibit the selectivity necessary to generate very narrow MW fractions from a material with an initially broad molecular weight distribution (MWD). Krukoni (14) described many of the fundamental principles and applications directed toward post-polymerization fractionation of impurities, residual solvents, and unreacted monomer and individual oligomers from a wide variety of polymers.

Experimental

Extraction. Three supercritical fluid extractors were used in the study. Initial extractions were performed on a Hewlett Packard 7680 (Avondale, PA) extractor, previously described in greater detail by Mulcahey et al. (25), and an Isco SFX 2-10 SFE system. The HP 7680 is a highly automated stand-alone off-line SFE system that allows

the operator to program various extraction parameters from a keyboard without having to physically intervene during the course of a multistep extraction. Both static and dynamic extractions or any combination of the two can be performed. After the CO₂ passes through the extraction vessel (1.5 or 7.0 mL) it decompresses through a variable restrictor which allows both flowrate and density to be simultaneously controlled. The decompressed SF no longer has any solvating strength so analytes are deposited on a solid phase trap - usually stainless steel beads or a chromatographic stationary phase. The user has control of the temperature of this trap for both the deposition step and subsequent rinse by a liquid solvent. Multiple density, temperature and rinse steps can be programmed into a single extraction, allowing a high degree of hands-off operation.

The Isco (Lincoln, NE) SFX 2-10 extractor was used only briefly during the study. It suffered excessive plugging from the dissolved wax at densities greater than 0.35 g/mL. The system employed unheated liquid collection which proved undesirable for this particular application. However, the Isco pumping system was modified into a "homebuilt extractor" that provided reasonably trouble-free operation throughout the density range of SF CO₂.

The third extraction scheme incorporated an Isco (Lincoln, NE) 260D syringe pump and a Fisher Isotemp 100 oven. High purity CO₂ (Scott Specialty Gases, Plumsteadville, PA) was routed from the pump to the oven where it entered a high pressure extraction vessel (Keystone Scientific, Bellefonte, PA). Just prior to the extraction vessel, 50 cm of the 0.70 mm i.d. stainless steel tubing was coiled and placed in the oven to insure that the SF had reached the desired extraction temperature before entering the extraction vessel. The outlet of the vessel was connected to a short piece of 25 μ m i.d. fused silica tubing. This tubing provided the necessary back pressure to generate the high pressures required during fractionation with supercritical CO₂. Unlike

the variable orifice restrictor of the HP 7680, the linear fused silica restrictor did not allow independent control of the density and flow rate. Additionally, the long decompression zone associated with a linear restrictor made it prone to plugging from cluster formation by non-volatile components (26a). The exit end of the fixed restrictor was placed near the bottom of a vial containing 6 -12 mL of o-dichlorobenzene (o-DCB). The vial was capped and the decompressed SF was allowed to escape through a short piece of stainless steel tubing that pierced the cap and septum. In order to help eliminate restrictor plugging, the collection vial was also positioned in the oven and maintained at the same temperature. As a result of the low vapor pressure of o-DCB, 45 minute extractions at temperatures of 100 °C could be performed with minimal (2-3 mL) evaporative loss of the collection solvent. As long as the entire extraction and collection apparatus was contained within the oven the fractionations could proceed relatively free of plugging.

Feedstock. The sample used for the fractionation was a low molecular weight ($\langle M_n \rangle = 800$), high density polyethylene wax with a polydispersity of 2.8 and a degree of crystallinity reported at 85%. The wax was available as irregular shaped flakes 3 - 7 mm in diameter and 0.5 mm thick, spherical pellets approximately 3 mm in diameter or a very fine powder. All of the extractions were performed on the flakes unless otherwise stated.

Extract Analysis. Extracts from the HP 7680 were analyzed by capillary supercritical fluid chromatography using a Lee Scientific Series 600 SFC (Lee Scientific, Inc., Salt Lake City, UT). Oligomers were separated on a 7m x 50 μm i.d. octyl column after a timed split injection of 0.03 second from a 0.5 μL loop. The oven was maintained at 75 °C while the pressure was ramped to 400 atm at 5 atm/min after an initial 5 minute hold

at 100 atm. Detection was by flame ionization with the signal integrated by a Hewlett Packard 3396 integrator. Extract samples and the injection syringe were stored in the oven prior to injection. All samples were dissolved in o-DCB. Peaks were identified using a wax standard (Supelco, Inc., Bellefonte, PA) and individual hydrocarbon standards. Peak molecular weight (MW) was determined to be the MW of the oligomer with the largest eluted peak area.

Extracts from the Isco 260D based system were analyzed by high temperature gel permeation chromatography (GPC) using a Waters ALC/GPC -150 (Millipore Corporation, Milford, MA). Size exclusion took place via three Column Resolution, Inc. (San Jose, CA) 30cm x 6.0mm i.d. Permagel columns (pore size = 100, 500 and 1000 Å) with HPLC grade o-DCB (Aldrich Chemical Co., Inc., Milwaukee, WI) at 130 °C as the mobile phase. The flow rate was set to 1.0 mL/min and detection was by differential refractometry. The GPC system was calibrated using five Polystyrene standards (Aldrich Chemical Co., Inc.) with peak MWs at 580, 950, 2950, 9200 and 22,000 amu). The resulting calibration curve had a linearity of $r = 0.998$. The refractometer signal was recorded and integrated with an HP 3396 Integrator. All molecular weights were recorded as polystyrene equivalents. Peak MWs were determined by comparison with retention time data of MW standards. Number average ($\langle M_n \rangle$) and weight average ($\langle M_w \rangle$) molecular weights were determined by manual digitization of the integrator trace (26b). The peak information provided by the integrator trace was processed by "in-house" software. The software rounded MWs to the nearest 100, but used 3-4 significant figures for the calculation of polydispersities. Thus, table values may appear to have some discrepancy.

Differential scanning calorimetry (DSC) was performed on a Perkin Elmer (Norwalk, CT) TGS-2 Thermogravimetric Analyzer. For DSC analysis the o-DCB was

evaporated from the extracts in a vacuum oven. The resulting polyethylene film (2 - 10 mg) was scraped from the walls of the collection vial and placed in a gravimetric pan for analysis. The samples were scanned at a rate of 10.00 °C per minute and peak maxima were determined for the as-received polyethylene, the collected fractions and resulting raffinate.

Results and Discussion

Initially supercritical fluid extractions were done with the HP 7680 using CO₂ and a cryocooled trap containing stainless steel beads. Two sets of extractions were performed at temperatures of 60 and 80 °C. For both extractions 300 mg of sample was subjected to successive extractions with CO₂ at progressively higher densities such that the raffinate from each extraction step became the feedstock for the succeeding one. At 60 °C fractions were collected at 0.25, 0.40, 0.60 and 0.85 g/mL; while at 80 °C, five fractions from 0.30 to 0.70 g/mL separated by increments of 0.10 g/mL were accumulated. For each extraction step a liquid CO₂ flow rate of 2 mL/min was maintained through the variable restrictor and the extraction time was adjusted at each density so that a constant 25 vessel volumes of supercritical CO₂ were flushed through the 1.5 mL extraction thimble. Extraction times ranged from 5 minutes at a density of 0.25 g/mL to 16 minutes at 0.80 g/mL. After deposition on the stainless steel beads at 5 °C, the temperature of the trap was raised to 80 °C while being rinsed with *o*-DCB. The extracts were then analyzed using capillary SFC. Figure 3 shows the capillary SFC chromatogram from the 60 °C, 0.60 g/mL fraction. The polar *o*-DCB elutes from the octyl column very slowly, generating a large solvent peak, thus restricting peak identification to C-18 and higher. For this fraction the oligomer distribution was centered around the C-26 oligomer. Figure 4 shows molecular weight distributions of the

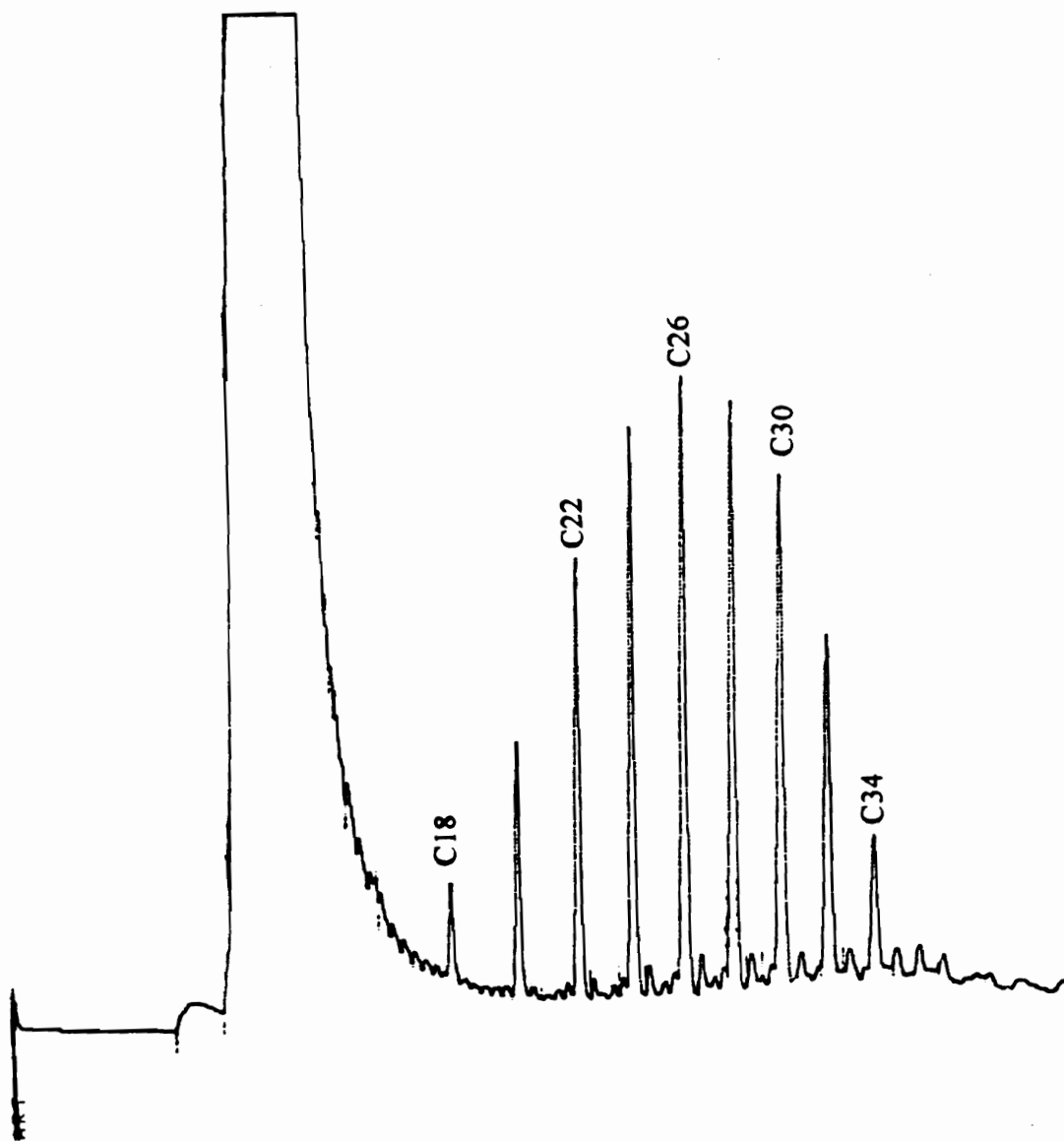


Figure 3. Capillary SFC-FID chromatogram of the 60 °C, 0.60 g/mL fraction collected from the HP 7680.

combined individual fractions arising from extractions done at 80 °C. The plot shows the SFC-FID peak area for each eluted oligomer plotted in such a manner as to graphically represent the molecular weight distribution for each fraction. In a quantitatively complete fractionation the individual fractions should "co-add" to produce a distribution identical to the initial polymer. The approximate peak MW appears to be centered around C-28 which has a MW of 394 - well below the polymer's known weight and number-average molecular weights. Figure 5 shows a plot of extract $\langle Mw \rangle$ as a function of the fractionation density at two different temperatures. The weight-averaged molecular weights were calculated taking in consideration the mass bias of the flame ionization detector (27). It illustrates the shift toward lower molecular weight distributions when the extraction temperature is reduced from 80 to 60 °C. The plot shows that at any given density the $\langle Mw \rangle$ is significantly higher at 80 °C than it is at 60 °C. The effect is even more pronounced in the higher density fractions from which the heaviest oligomers are expected to be extracted from the wax. Additionally, total recovery (measured gravimetrically) increased from 12 - 20% when the fractionation temperature was increased from 60 to 80 °C. Since the solvating strength of CO₂ does not increase much above the 0.85 g/mL shown in Figure 5, the role of increased temperature in generating higher MW distributions from the parent polymer is clearly important. Both thermodynamic and kinetic contributions are probably at work here. Polyethylene, due to its simple, regular and flexible chains can pack tightly into a highly crystalline structure. This degree of crystallinity and subsequent high heat of fusion can greatly influence dissolution phenomena. In the crystalline state, solute-solute interactions can be difficult for a solvent to overcome. While the individual oligomer may be soluble in the SF at a given pressure and temperature - removing it from the crystalline solid would certainly require more energetic conditions. For instance, atactic polypropylene is quite soluble

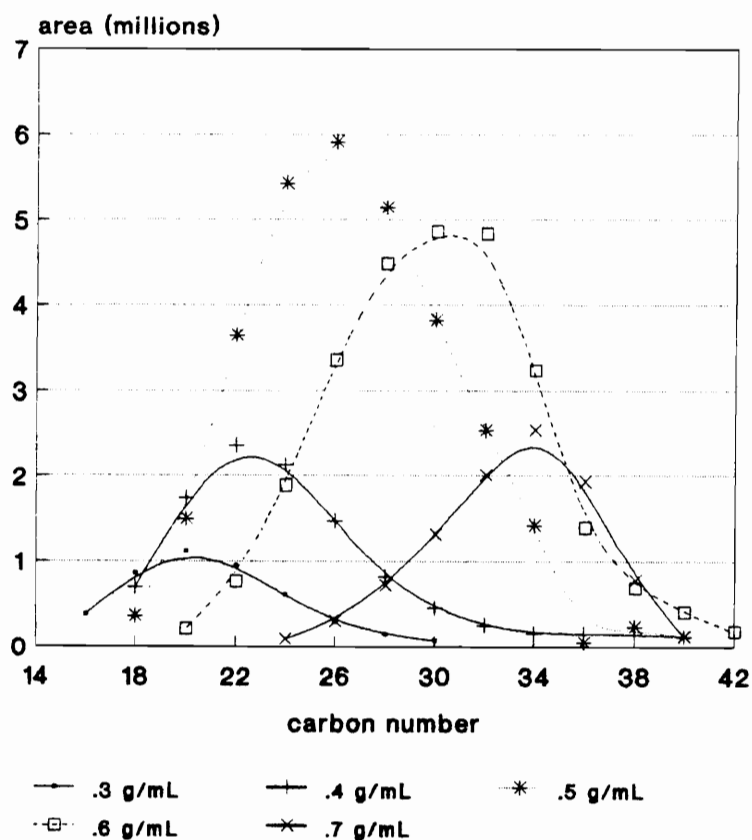


Figure 4. Molecular weight distributions from the 80 °C HP 7680 sequential extractions - determined by plotting the capillary SFC-FID peak areas for the eluted oligomers at each extraction density. All extractions were with 25 vessel volumes of SF CO₂ at a liquid flowrate of 2 mL/min.

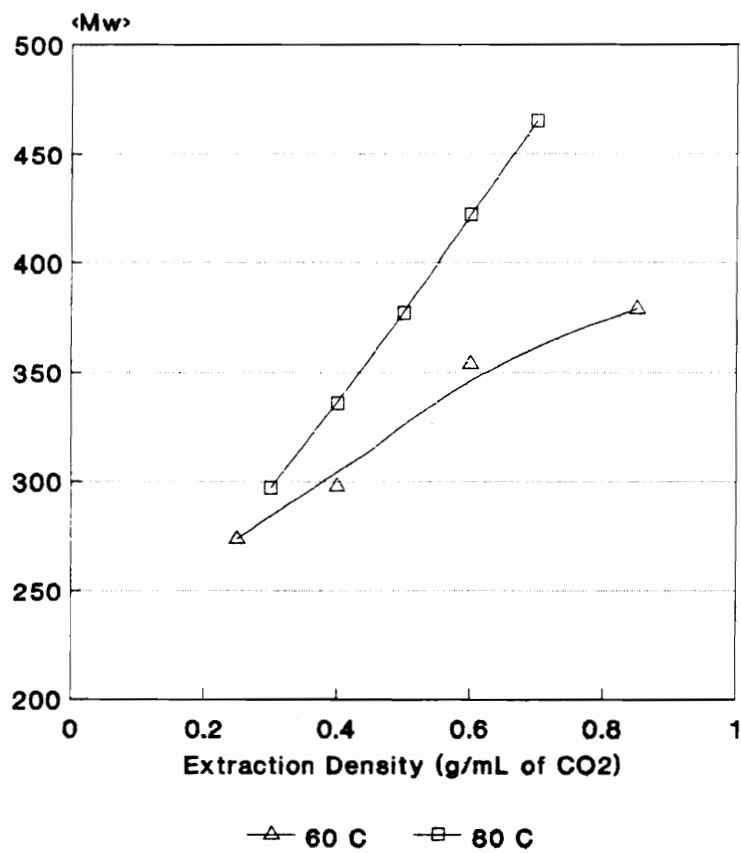


Figure 5. Graph of weight-averaged molecular weights (determined by capillary SFC) plotted as a function of extraction density at 60 and 80 °C.

in CO₂ while the more crystalline isotactic polypropylene is practically insoluble (23). Factors that usually reduce crystallinity in a polymer (i.e short chain branching in PE) tend to increase its solubility in a SF. Thus, the increase in peak MW with temperature at constant density could be a result of traversing molecular weight dependent melting transitions. With each increase in temperature, higher MW oligomers pass from the crystalline to molten state allowing their extraction by the SF CO₂. However, it was later determined that increasing the extraction temperature much above 100 °C resulted in the PE wax melting and moving *en masse* through the restrictor where it was prone to "plugging" as the CO₂ decompressed.

There might also be a kinetic contribution from increased extraction temperature. Oligomer extractability in a SF is both solubility and diffusion controlled (28). This model says that if oligomer solubility in the SF is high and the flow rate is such that its concentration in the mobile phase is nearly zero, then the extraction will be diffusion controlled. Diffusion of longer chain oligomers within the polymer matrix will always be more limited than for those with shorter chain lengths. Thus, increasing the temperature at a constant density will allow more of the heavier components that are soluble at that CO₂ density to escape the matrix and be solvated by the SF, thereby shifting the MWD to a higher value.

Although the HP SFE system with solid phase trapping was able to achieve polymer fractionation, it was unable to reach the desired MWs and there was also great difficulty in moving the extracted wax through the transfer lines from the extraction thimble to the trap - especially at higher densities. The reason for this problem was because the transfer line and switching valve between the extraction vessel and solid phase trap (~30cm) was unheated and the resulting "cold spot" was very prone to plugging. The situation was exaggerated even further when the powder, with a much

greater surface area, was used as the feedstock. In general, there was difficulty with plugging when any of our commercial SFE systems were used to extract the wax. The additional valving and transfer lines that help provide user-friendly features for many SFE applications serve as "trouble spots" for oligomers exhibiting borderline solubility.

Additionally, the MWDs of the extracted fractions were much lower than initially hoped for. This may in part be due to the fact that the highest temperature available for extraction and subsequent trap rinse was 80 °C. The results we previously acquired at 80 °C compared to those at 60 °C, along with findings in other laboratories (28,29) indicated that temperatures greater than 80 °C might significantly improve extraction capabilities. We were also concerned that the heaviest oligomers extracted and trapped during a fractionation step might not be sufficiently dissolved by the o-DCB rinse solvent at 80 °C.

In order to eliminate these concerns, the "homebuilt" extractor described previously was employed. The new system minimized transfer line distances and allowed us to explore higher extraction temperatures than were allowable with our commercial instruments. Thus, all components of the system could be kept at the same temperature and the movement of dissolved wax restricted to only the extraction vessel exit frit and the restrictor. With the new system the fractionations could be performed without the persistent plugging that plagued our earlier, more complex commercial systems. Analysis of all extracts generated by the "homebuilt" system was by high temperature GPC using o-DCB at 130 °C as the mobile phase rather than SFC.

In order to determine the optimum temperature for fractionation, a series of extractions were performed at four different temperatures (60, 80, 100, 120 °C). GPC was performed on the 0.60 g/mL fraction. Figure 6 demonstrates the relationship between peak MWs and the extraction temperature for the 0.60 g/mL cut. At this density

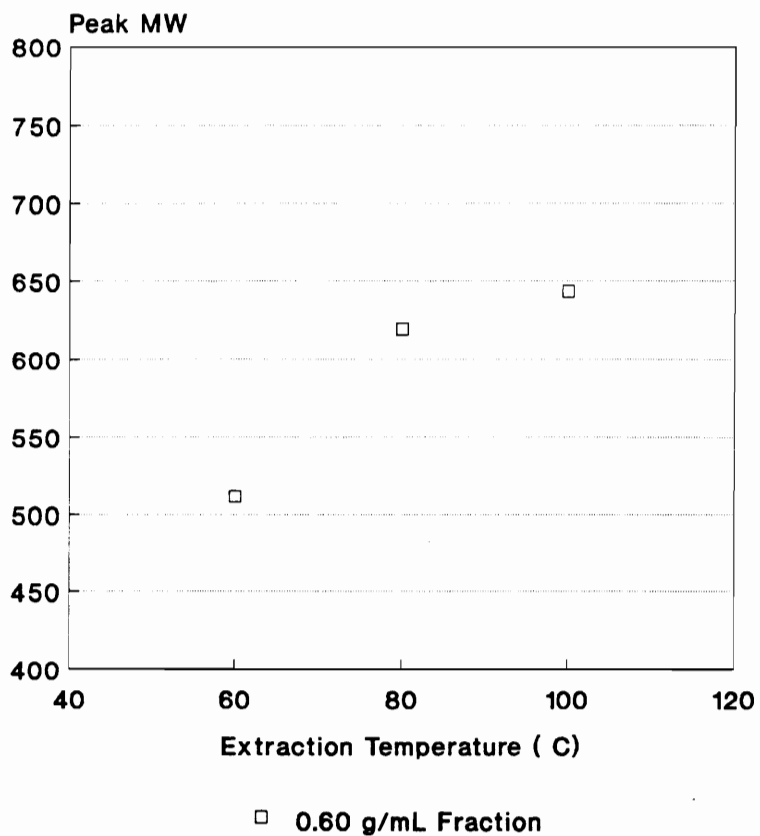


Figure 6. Effect of extraction temperature on MW distribution at constant density. Points depict peak MWs of the 0.60 g/mL fraction extracted at three different temperatures (60, 80 and 100 °C).

the MW distribution shifted toward higher values with increasing temperature as would be expected based on the HP extraction results (Figure 5). There were limitations, however, to this temperature enhancement. When the temperature of the extraction vessel was increased to 120 °C, the viscosity of the polyethylene was reduced to the point where it could be entrained by the supercritical CO₂ and mechanically moved through the restrictor to the trap. Thus, 100 °C was chosen as the best temperature to fractionate the particular sample in our possession. Operating in this range meant that the SF would be interacting with the PE in a semi-molten state. The final T_m for the PE sample was 125 °C. As a general reference point, C-70, with a MW of 984 has a T_m of 105.3 °C (30). At a fractionation temperature of 100 °C a high percentage of oligomers from the amorphous regimes of the polymer would be expected to be in the liquid state. Additionally, polymer T_m values are known to be depressed in the presence of a high pressure gas - increasing the likelihood of having a liquid-SF boundary in the extraction vessel (14).

The first complete series of extractions performed using the Isco based system was done at densities ranging from 0.20 g/mL of CO₂ up to 0.78 g/mL at 0.10 g/mL increments. Each of the seven fractions was collected after a 30 minute extraction. Peak MWs ranged from 300 for the 0.20 g/mL cut to 1500 for the 0.78 g/mL fraction. The Figure 7 shows the GPC-RI trace for the 0.50 g/mL fraction. This fraction had a bimodal distribution with peak MW maxima at 421 and 272. The presence of two maxima indicated that at 100 °C and a CO₂ density of 0.40 g/mL (i.e. the extraction prior to 0.50 g/mL) the 30 minute extraction time employed was inadequate to remove all the components that were soluble at this density. Thus, the 0.40 g/mL fraction was also present in the 0.50 and as we found later, the 0.60 g/mL fraction.

The ratio of $\langle M_w \rangle$ to $\langle M_n \rangle$ is a measure of the "narrowness" of a polymer's molecular weight distribution and is referred to as polydispersity. Before extraction the

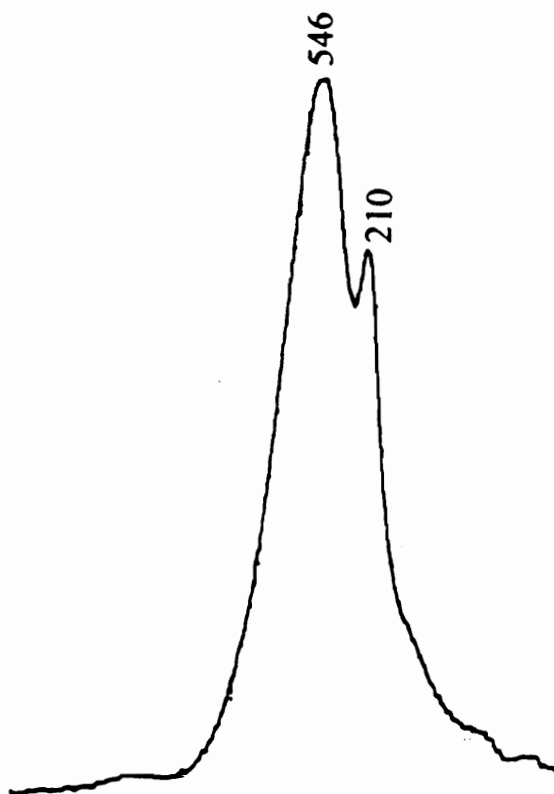


Figure 7. GPC-RI trace for the 0.50 g/mL fraction generated from the 0.10 g/mL fractionation increments. The chromatogram depicts a bimodal distribution with peak MWs at 546 and 210.

wax had a $\langle M_w \rangle$ of 2240 and a polydispersity of 2.8. The polydispersity for all fractions collected here employing 0.10 g/mL increments was between 1.2 and 1.3. The MW distribution for the raffinate was noticeably skewed toward the heavier fractions since the lower molecular weight oligomers had been removed by SFE. The raffinate from this fractionation had a $\langle M_w \rangle$ of 6300 and a polydispersity of 1.84.

For our work, bimodal distributions and polydispersities greater than 1.20 were undesirable. In hopes of eliminating these undesirable qualities, a second complete fractionation was performed, but this time the increment between extractions was reduced to 0.05 g/mL and the extraction time was increased from 30 to 45 minutes. The result of this modification to the resulting fractions was the elimination of bimodal distributions, an increase in the number of fractions produced, and a substantial reduction in polydispersity. Figure 8 shows overlapping GPC-RI traces for the 0.20 through 0.78 g/mL fractions from the 0.05 g/mL fractionation. Note the narrow, symmetric peaks and the steady trend toward higher MW distributions (shorter GPC retention times) with increasing density. These results were very much in line with our goals for polydispersity and MW range. Table II shows the molecular weight distributions for these GPC traces in terms of peak MW, $\langle M_n \rangle$, $\langle M_w \rangle$ and polydispersities. The typical polydispersity for these fractions was lowered to 1.07 as a result of reducing the increment between successive fractions from 0.10 to 0.05 g/mL. The 0.25 g/mL fraction was apparently not securely capped before being placed in the hi-temp GPC oven and evaporated prior to analysis. Figure 9 reveals that peak MW varies smoothly and predictably as a function of extraction density. Thus, once such a plot is generated for a raw polymer, it should be possible to extrapolate the density required to generate a desired MW distribution. Figure 10 shows a plot of peak endotherms in °C versus CO₂ density for the 0.50, 0.60, 0.70 and 0.78 g/mL fractions as determined by DSC. All collected fractions had endotherms

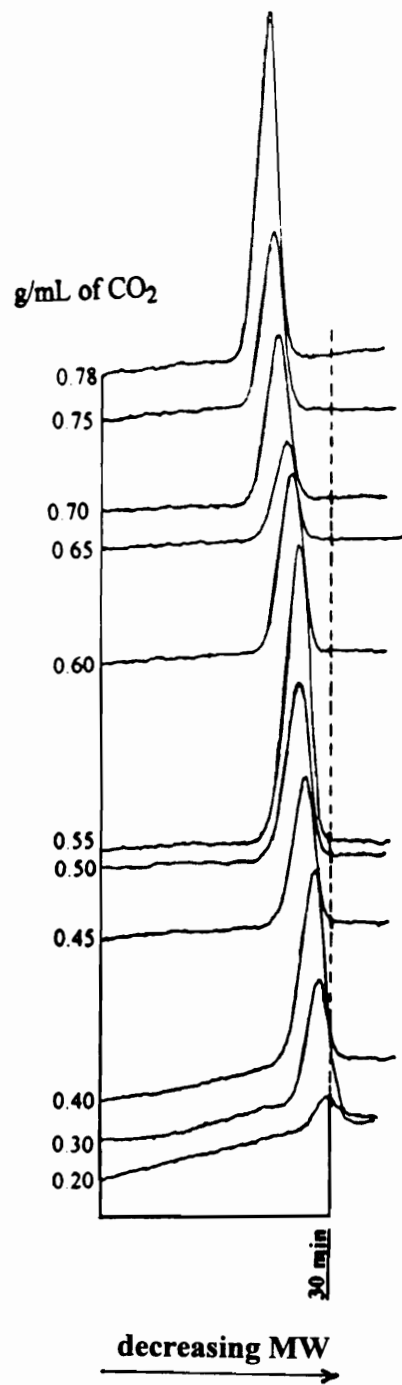


Figure 8. GPC-RI traces for each density fraction collected at the 0.50 g/mL increment.

Table II
Molecular weight distribution information for the fractions collected at 0.05 g/mL increments.

1	2	3	4	5	6	7
Fraction #	Pressure (atm)	Density (g/mL)	Peak MW	<Mw>	<Mn>	<Mw>/<Mn>
1	103.1	0.20	323	300	300	1.07
2	137.1	0.30	336	300	300	1.07
3	153.7	0.35	377	400	300	1.08
4	170.8	0.40	422	400	400	1.07
5	188.7	0.45	511	500	400	1.08
6	207.9	0.50	552	600	500	1.09
7	229.1	0.55	596	600	500	1.08
8	254.5	0.60	643	700	600	1.07
9	285.2	0.65	841	800	700	1.07
10	328.5	0.70	907	1000	900	1.07
11	389.5	0.75	1018	1100	1000	1.07
12	430.7	0.78	1382	1400	1300	1.06

* Columns 5 and 6 (weight and number-averaged MWs) were rounded to the nearest one-hundred by the software, while the unrounded values were used to calculate polydispersities. Peak MW (column 7) was determined as the polystyrene MW of the retention time for each fraction.

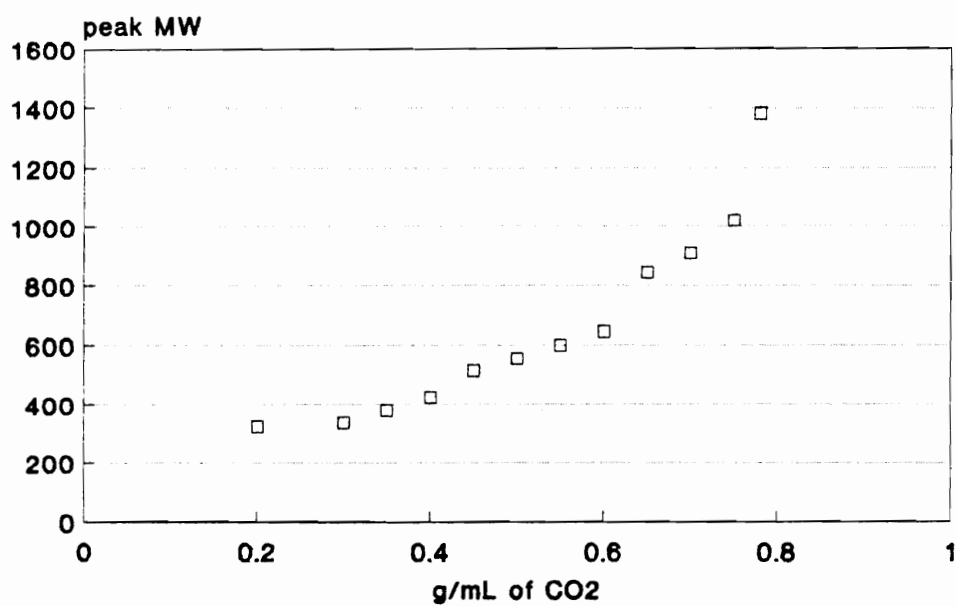


Figure 9. Plot of peak MWs as a function of extraction density with the fractions being collected at 0.05 g/mL intervals. Extraction time was 45 minutes for each fraction.

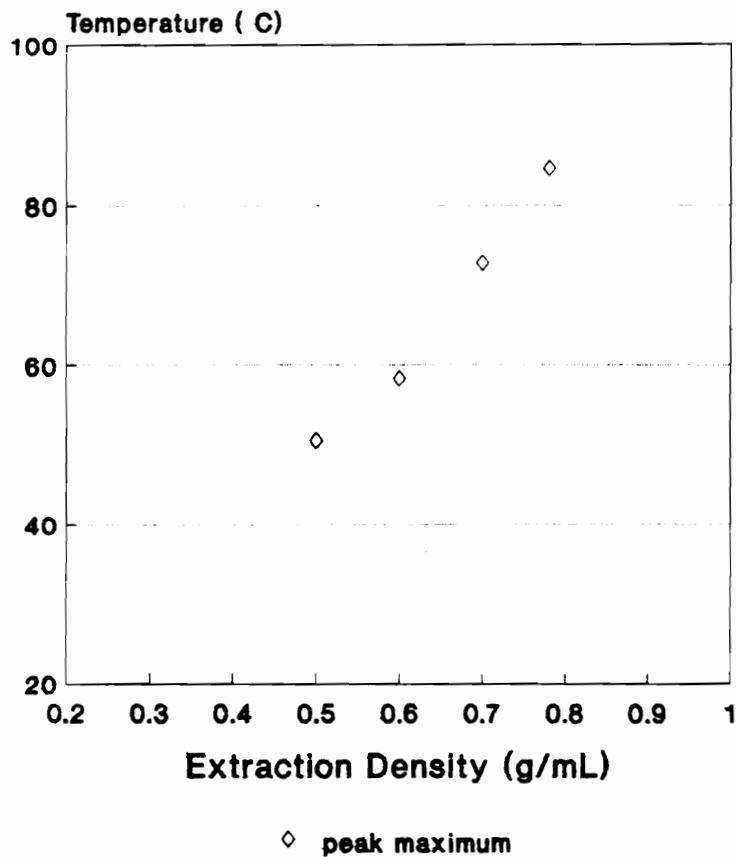


Figure 10. Peak maxima (°C) as determined by DSC and plotted against the density the fraction was collected at. The unextracted wax had a value of 114.9 °C while the raffinate peaked at 120.2 °C.

below that of the unextracted polyethylene, while the endotherm of the raffinate was higher than that of the initial wax. The DSC results, like those from the GPC, indicated that there was a predictable trend toward higher polymer MW distributions with increasing extraction density. Total recovery (measured gravimetrically) for the fractionation using 0.05 g/mL increments at 100 °C was 30%. In order to determine the percent recovery for individual fractions, the same fractionation was carried out a second time. This time the extracts were collected in dry and pre-weighed culture tubes. During the extractions the collection tubes were cryocooled to prevent loss of extracted material. Cryocooling within the oven was achieved by wrapping the base of collection vessel with stainless steel capillary tubing and allowing cryo-grade CO₂ to decompress inside the tubing. This provided a substantial cooling effect near the base of the collection vessel. Table III shows the recoveries for each fraction. The sum of the individual recoveries (156.7 mg) matches well with the total recovery (159.0 mg), determined by weighing the extraction vessel before and after the fractionation.

The polydispersities can be reduced even further by again reducing the increment between subsequent extractions. When the interval between successive extractions was further reduced to 0.025 g/mL, the polydispersities were lowered to 1.02. This indicated that "monodisperse" distributions might be achieved with supercritical CO₂ if the density increment can be sufficiently reduced. Even though there were twice as many fractions collected than there were at the 0.05 g/mL increments, total recoveries did not differ significantly (33% per 0.025 g/mL -vs- 30% per 0.050 g/mL). The recoveries for individual fractions collected at the 0.025 g/mL intervals were approximately one-half those of the corresponding fractions collected at 0.05 g/mL increments. Thus, it appeared that at a fixed temperature, there was a maximum depth from which oligomers could diffuse from the polymer particle during a 45 minute extraction. The result of this

Table III

Individual recoveries for fractions collected at 0.05 g/mL CO₂ intervals.

Fraction (density of cut)	mass of extract (mg)	percent of extract
0.20	0.6	0.4
0.25	2.6	1.7
0.30	4.6	2.9
0.35	8.9	5.7
0.40	13.0	8.3
0.45	18.6	11.9
0.50	18.8	12.0
0.55	19.4	12.4
0.60	17.6	11.2
0.65	17.2	11.0
0.70	16.3	10.4
0.75	10.1	6.4
0.78	9.0	5.7
13 Fractions	156.7 mg	98.9

situation is that at any given density there is a limited population of oligomers that are both soluble and capable of diffusing out of the matrix. Decreasing the extraction density interval in such circumstances results in narrower MWDs but has little effect on total recovery.

Conclusions

The high selectivity afforded by supercritical carbon dioxide can be used to generate very narrow MW fractions from the polyethylene feedstock. However, the resulting fractions are limited in peak MWs to less than 2000. Temperature was found to play an important role in the design of a trouble free extraction system as well as exerting a strong influence on the amount and size of oligomers removed at any given density. In order to improve recoveries and increase the MW range available to CO₂, it will probably be necessary to modify the SF with short chain alkanes (i.e. propane, butane) that exert a greater solvating strength for linear polyethylenes.

It may also be possible to improve recoveries and MW range by designing extraction systems better capable of dealing with low viscosity samples. This would allow the use of extraction temperatures that are above the melting point of polyethylene. The extraction of oligomers could then proceed free of crystalline interactions. This is particularly important for the more highly crystalline linear, high density polyethylenes. Additionally, it has recently come to our attention that melting the wax in an extraction vessel filled with sand or some other inert material, and allowing it to cool as a thin surface on these particles prior to SFE, can dramatically improve the diffusion of some oligomers into the SF.

CHAPTER 3

SFF of Polyethylene Wax with Propane and CO₂ Modified Propane

Introduction

Supercritical carbon dioxide was shown to be a relatively weak solvent for high density polyethylene. As such, it was able to generate very narrow MWDs. However, its MW range was severely limited (<2000) - at least in the case of the experimental arrangement discussed in Chapter 2. The use of a stronger solvent may extend the potential of SFs for the fractionation of polyethylenes. It is the purpose of this study to examine SF propane as a solvent for fractionating the same wax sample previously studied in Chapter 2.

Propane, with critical parameters of 43.1 atm and 96.8 °C, is another SF that can be used without difficulty in analytical SFE instrumentation. As early as 1963, it was shown to have powerful solvating ability for high MW oligomers of polyethylene when raised above its critical temperature and pressure (31), and more recently, Condo et al. (32) used propane at 118 °C and 640 bar to dissolve linear polyethylenes with MWs as high as 120,000. Watkins et al. (33) used supercritical and near-supercritical propane to fractionate a high density polyethylene into fourteen fractions of reasonably low polydispersity in the liquid-SF region. However, they were unable to achieve comparable results in the solid-SF region - presumably due to the higher MW and level of crystallinity within their sample.

This work investigates the use of supercritical propane and a mixture of propane in carbon dioxide (20 % (v/v) in CO₂) to fractionate a sample of the low MW high density PE wax into several "cuts" with different and narrower MWDs than the original polymer. In order to evaluate feasibility, we assembled a simple, analytical scale

benchtop SFE system that operated at constant temperature while the pressure was increased in a stepwise fashion to provide a solvent with a slightly higher solubility parameter for each successive extraction. The results reported here should be useful when contemplating transitions to preparative or pilot scale SFF operations.

Experimental

Extraction. High density polyethylene flakes with a $\langle Mn \rangle$ equal to 800 (determined by GPC) were fractionated using three different SFs. The flakes were wedge shaped and approximately 3 - 4 mm in diameter. The initial PE feedstock had a polydispersity of 2.8. Total short chain branching for the sample was less than 0.5 % and the degree of crystallinity (determined by DSC) was reported at 85 %. The final melting temperature for the polyethylene was determined to be 125 °C. In this study, supercritical CO₂, propane and propane modified CO₂ were delivered to the extraction vessel via two Isco syringe pumps (Lincoln, NE). The 260D and 100D were operated from a single controller. The instrument grade (99.5 % purity) propane (Scott Specialty Gases, Plumsteadville, PA) was shipped at 100 psi inside the tank, so it was necessary to cool the pump head in order to ensure an adequate fill. A cooling jacket was placed on the pump cylinder and cryo grade CO₂ was allowed to decompress inside the sleeve on the pump head. The pump reservoir and inlet tubing were rapidly cooled by the decompressing CO₂ such that the propane was then delivered in the form of a liquid. This technique allowed propane fills of greater than 70 % of total pump volume to be achieved. SFC grade CO₂ (Scott Specialty Gases) with helium headspace was used in the Isco 260D. It was not necessary to cool the pump when filling with CO₂. When used to provide mixed fluids, the outlet of the 100D was connected to the outlet line of the larger volume 260D using a mixing tee (provided by Isco). This configuration in conjunction

with the dual controller allowed v/v ratios up to 50% of the two fluids to be delivered to the mixing tee. From the mixing tee, the extraction fluid was routed to an oven containing a 3.5 mL extraction vessel (Keystone Scientific, Bellefonte, PA) capped at both ends by 0.5 μm frits. The vessel was oriented vertically in the oven with the SF entering from the top. Just prior to the extraction vessel, 50 cm of 0.70 mm i.d. stainless steel tubing was coiled and placed in the oven to ensure that the SF had reached the desired temperature before entering the vessel. The outlet of the extraction vessel was connected to a 20 cm x 25 μm i.d. fused silica restrictor (Polymicro Technologies Inc., Phoenix, AZ). The exit end of the restrictor was placed near the bottom of a vial containing 12 mL of ortho-dichlorobenzene (o-DCB). The vial was capped and the decompressed SF was allowed to escape through a piece of stainless steel tubing that pierced the cap and septum. The collection vial was positioned in the oven and the vent line from the trap was routed to a hood for removal of the flammable propane gas. All extractions were performed in the dynamic mode and after the allotted time (45 min.) the collection vial of o-DCB was removed from the oven and diluted back to the original 12 mL. Normally only 2 - 3 mL of solvent were lost to evaporation during each 45 min. extraction. Liquid flow rates were determined by measuring the volume of fluid leaving the pump over a five minute period at the controller. When extracting with modified fluid the total flow is a combination of the primary and modifier fluid flow rates.

Extract Analysis. Extracts were analyzed by high temperature gel permeation chromatography (GPC) using a Waters ALC/GPC-150 (Millipore Corporation, Milford, MA). Size exclusion took place through a single 30 cm x 7.5 mm, 5 μm , 500 Å polystyrene gel column (Polymer Laboratories, Amherst, MA) with HPLC grade o-DCB (Aldrich Chemical Co., Inc., Milwaukee, WI) as the mobile phase. The flow rate was set

to 1 mL/min and detection was by differential refractometry. The GPC system was calibrated for molecular weight determination using four polystyrene standards with MWs at 580, 950, 2950 and 22,000. The resulting calibration curve was linear over this range. The refractometer signal was recorded and integrated with an HP 3396 integrator. All calculated molecular weight values were polystyrene equivalent MWs. Peak MWs were determined by comparing the retention times of the calibrated molecular weight standards with the retention times of the various fractions. Number-averaged ($\langle M_n \rangle$) and weight-averaged ($\langle M_w \rangle$) molecular weights were determined by manual digitization of the integrator trace and rounded to the nearest 100 (except during the calculation of polydispersities - where the unrounded values were used).

Results and Discussion

Propane. A temperature of 100 °C was also used for the fractionation using propane as the supercritical fluid. A total of eight successive extractions were performed with supercritical propane. The temperature (100 °C) that proved to be near optimum for the CO₂ extractions is very close to the critical temperature of propane (96.8 °C). Near the T_c of a substance, small changes in pressure can result in large changes in density. Subsequently, the pump must be capable of delivering minute changes in pressure if fine fractionation is to take place in this region. Figure 11 shows a graph of Hildebrand solubility parameters (34) for the three supercritical fluids used in this study, plotted as a function of pressure at 100 °C. Based on solubility parameter alone, it can be assumed that supercritical propane would be a much stronger solvent at lower pressures than CO₂ or propane-modified CO₂. There would be a gradual leveling out of each fluid's

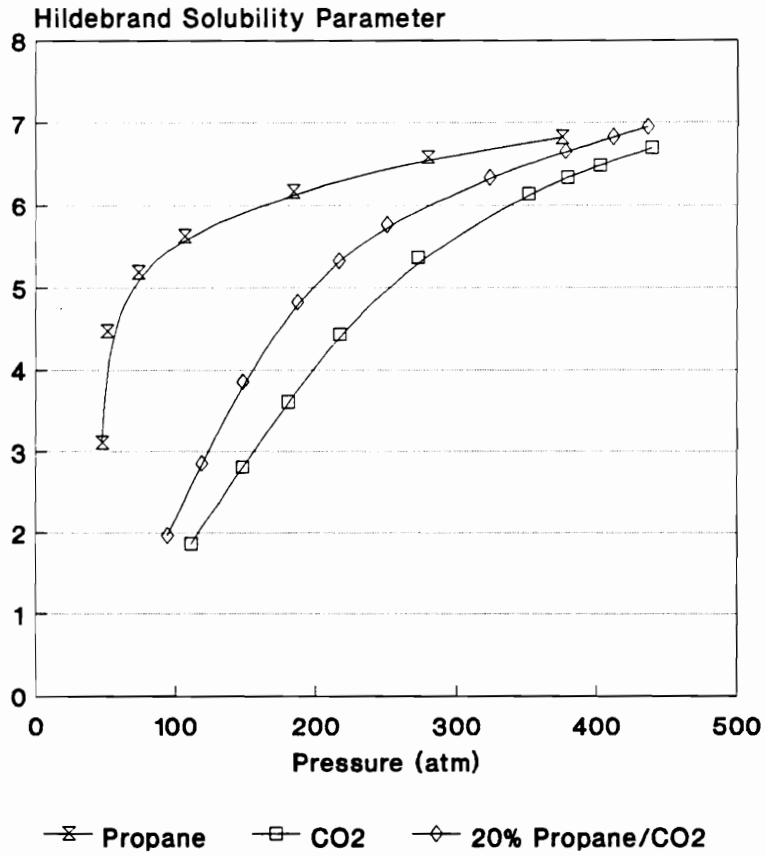


Figure 11. Graph showing Hildebrand solubility parameters at 100 °C for each of the supercritical fluids used in the study plotted as a function of pump pressure (34).

solvating ability at higher pressures where the solubility parameters appear to converge. Given a comparable fractionation scheme it would be assumed that at any given pressure the fraction generated by propane would have the highest MW followed by propane-modified CO₂ and then pure CO₂. Since the Hildebrand values appear to converge at high pressures for all three SFs, the difference between the resulting MWDs would be expected to be small at pressures greater than 400 atm. However, supercritical n-alkanes are known to be powerful solvents for waxes, and Hildebrand solubility values might not be a suitable way to compare supercritical propane with a dissimilar SF such as CO₂.

For the SFF using propane, a 300 mg sample of the wax (flakes) was placed in an extraction vessel half filled with Celite (diatomaceous earth) and was subjected to successive extractions at progressively higher densities such that the raffinate from the previous extraction became the feedstock for the succeeding one. Mixing the polymer with an inert matrix reduced the rate at which dissolved oligomers entered the frit and restrictor and thus helped prevent system plugging. It also kept the wax from consolidating inside the vessel thereby improving diffusion into and out of the matrix by maintaining surface area at a maximum. Liquid flowrates measured at the cylinder head exit ranged between 90 and 400 $\mu\text{L}/\text{min}$ in the pressure range of 47.0 to 256.0 atm. This pressure range is significantly lower than that required for SF CO₂; an important consideration for potential scale-up. The enhanced solubility of the oligomers in supercritical propane compared to CO₂ also allowed the fractionation to proceed free of the plugging that occasionally plagued the CO₂ based fractionations at higher densities.

Table IV shows the pressure and density used during each step of the fractionation and the resulting molecular weight data from each extract. Fraction number 2 failed to

Table IV

Density and pressure at which each fraction was extracted using supercritical propane.
Columns 4 - 7 denote MWD information determined from the GPC-RI traces.

1	2	3	4	5	6	7
Fraction #	Pressure (atm)	Density (g/mL)	Peak MW	<Mw>	<Mn>	<Mw>/<Mn>
1	47.3	0.22	738	800	700	1.21
2	48.1	0.24				
3	49.1	0.27	738	1000	800	1.24
4	49.7	0.29	878	1200	900	1.31
5	51.1	0.32	1045	1500	1100	1.38
6	72.7	0.37	1532	1600	1200	1.30
7	137.9	0.42	2001	2400	1700	1.39
8	276.1	0.47	2466	4100	2800	1.46

* Columns 5 and 6 (weight and number-averaged MWs) were rounded to the nearest one-hundred by the software, while the unrounded values were used to calculate polydispersities. Peak MW (column 7) was determined as the polystyrene MW of the retention time for each fraction.

register a response on the GPC-RI trace. This may be due to an inability of the supercritical propane to remove any additional oligomers from the wax with a pressure difference of only 0.70 atm (or 0.02 g/mL) between the two fractions, or, a failure of the pump to provide an actual increase in pressure over such a small range. Delivering such minute steps in density may also prove a difficulty for compressors at the process scale. At a density of 0.27 g/mL, fraction number 3 still had a peak MW of 738, but the $\langle M_w \rangle$ and $\langle M_n \rangle$ were slightly increased. Beginning with fraction number 4, the next five extracts showed a steady and predictable increase in peak MWs. Interestingly, the relationship between extract density and peak MW of the fraction proved to be linear in this range. Figure 12 shows overlapping GPC traces for fractions 1, 5 and 8 as well as that for the parent material. The GPC traces depict a general increase in MW (decreasing GPC retention times) and a broadening of the MWDs with increasing density as characterized by the trend in polydispersity (Column 7 in Table 4). Polydispersities at densities below 0.35 g/mL may be difficult to further reduce using supercritical propane due to limitations in accurately changing pump pressures. Above the 0.35 g/mL level at 100 °C the slope of the pressure/density curve is less severe, thus requiring greater increases in pressure to give rise to a small change in density. After eight 45 minute extractions at the densities shown in Table IV, 96% of the original wax had been removed. This was approximately three times the total recovery achieved by CO₂. Figure 13 shows scanning electron micrographs of the surface of unextracted PE, the raffinate from pure CO₂ extractions and the raffinate from the pure propane extractions. The propane extracted PE is clearly more pitted than the CO₂ extracted PE indicating a much higher degree of surface attack from the supercritical propane. Measurements of the particle diameter of PE pellets following static extraction at 300 atm and 100 °C

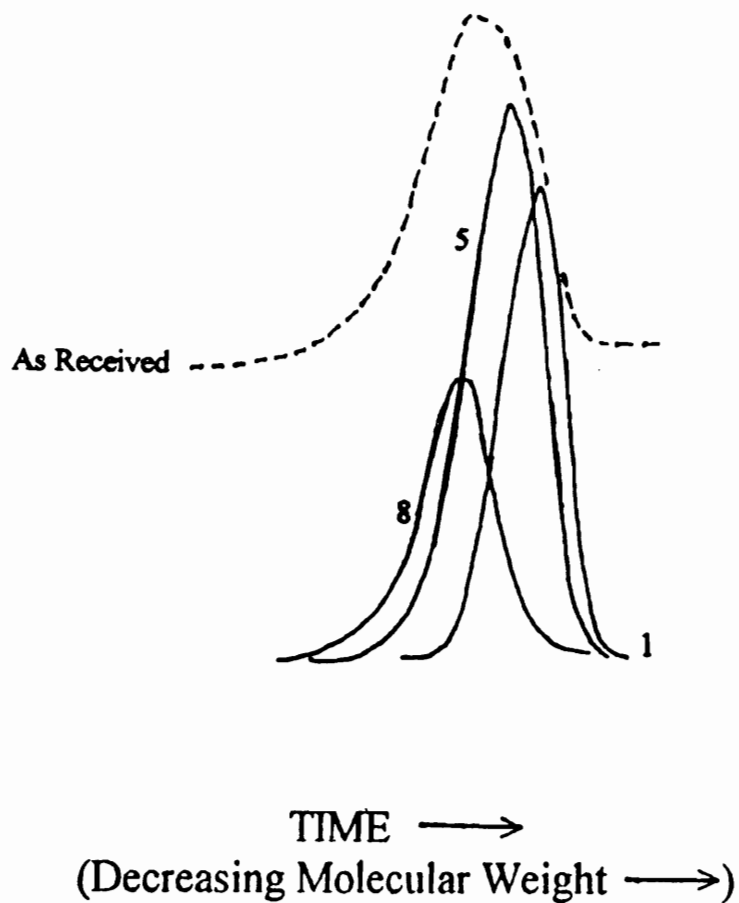
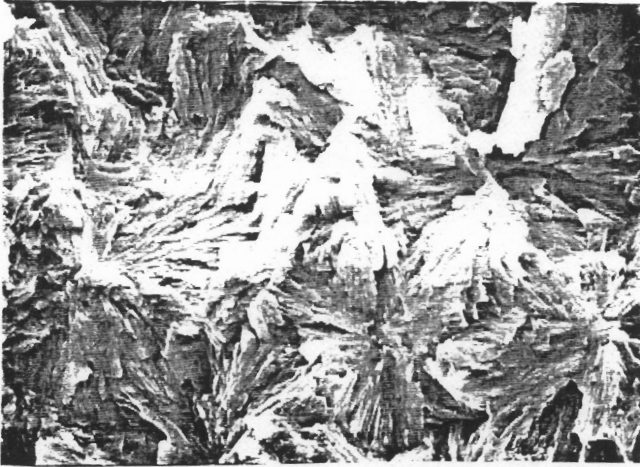
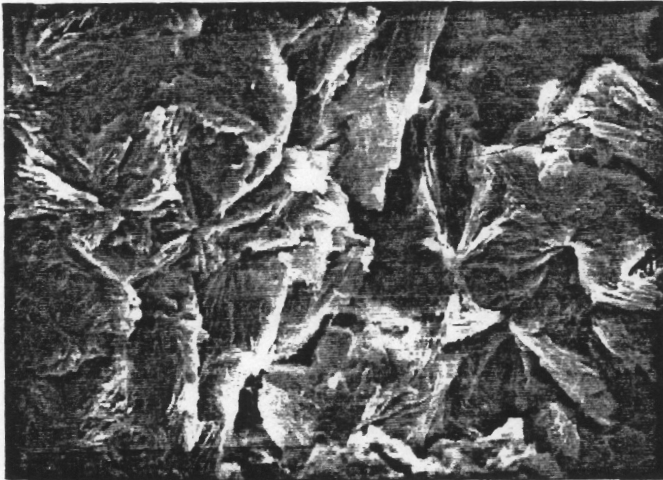


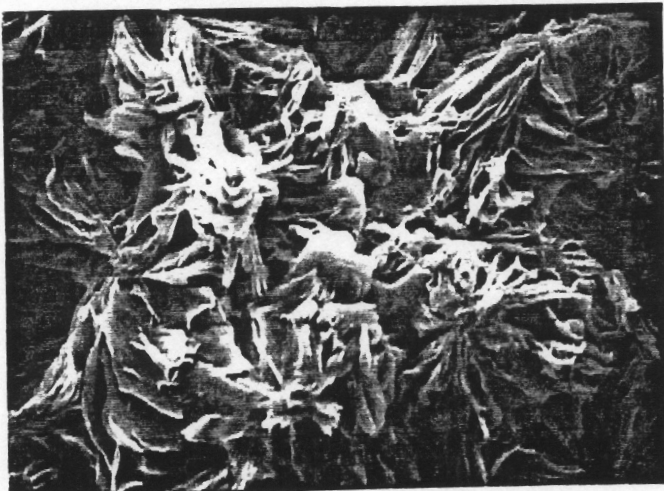
Figure 12. Overlapping GPC-RI traces for the polyethylene wax (as received) and fractions collected at the beginning (# 1), middle (# 5) and the end (# 8) of a SFF using pure propane.



As Received
1.00 kx



100 % CO₂
1.00 kx



100 % C₃H₈
1.00kx

Figure 13. Scanning electron micrographs of the surface of the wax as it was received and after it was fractionated with 100% CO₂ and 100% propane.

Table V

Density and pressure at which each fraction was extracted using supercritical propane-modified CO₂ (20% v/v). Columns 4 - 7 denote MWD information determined from the GPC-RI traces.

1	2	3	4	5	6	7
Fraction	Pressure	Density	Peak MW	<Mw>	<Mn>	<Mw>/<Mn>
#	(atm)	(g/mL)				
1	147.6	0.40	438	500	400	1.10
2	164.6	0.45				
3	186.1	0.50	491	600	500	1.11
4	199.1	0.53	521	500	500	1.08
5	230.2	0.58	546	600	500	1.10
6	275.8	0.63	688	700	700	1.05
7	309.1	0.66	878	1000	900	1.09
8	346.2	0.68	986	1100	1000	1.08
9	389.9	0.70	1303	1400	1300	1.12
10	428.8	0.72	1446	1600	1500	1.07

* Columns 5 and 6 (weight and number-averaged MWs) were rounded to the nearest one-hundred by the software, while the unrounded values were used to calculate polydispersities. Peak MW (column 7) was determined as the polystyrene MW of the retention time for each fraction.

with both propane and CO₂ revealed no noticeable swelling with either SF. However, measurements of particle mass immediately after contact with the SFs indicated that propane was more effectively penetrating the wax relative to SF CO₂. Additionally, much higher MW fractions are extracted using propane at comparable pressures than CO₂. However, the reduced solubility of the polyethylene oligomers in CO₂ allows much narrower molecular weight distributions to be extracted from the original wax than when using supercritical propane.

Propane Modified CO₂. The dual pump extraction system allowed mixtures of fluids to be used for extractions. In order to study the effect of propane when used as a modifier in supercritical CO₂ the Isco 100D was filled with propane and the 260D was filled with CO₂. The controller was programmed to deliver a propane:CO₂ v/v ratio of 20%. This was equivalent to 12 mole percent propane because of the lower liquid density of propane relative to CO₂. Supercritical fluid fractionation was then performed using the mixed fluid. It was expected that the mixture would produce fractions of intermediate composition to those acquired by pure propane and CO₂. However, the results shown in Table V indicate that there was very little difference between the MWs and polydispersities of the fractions collected with propane modified CO₂ and those collected with pure carbon dioxide. Figure 14 shows a plot of peak molecular weight as a function of extraction density for the SFFs using pure CO₂, pure propane and 20% propane in CO₂. The propane modified CO₂ fractions have molecular weights comparable to those achieved by CO₂ up to a density of 0.65 g/mL. Above this density there was a shift to higher MWDs with 20% propane. Pure propane provided a final fraction with a peak MW of 2500 from a pump pressure of only 256 atm compared to a final fraction of approximately 1400 from CO₂ and propane- modified CO₂ at 430 atm.

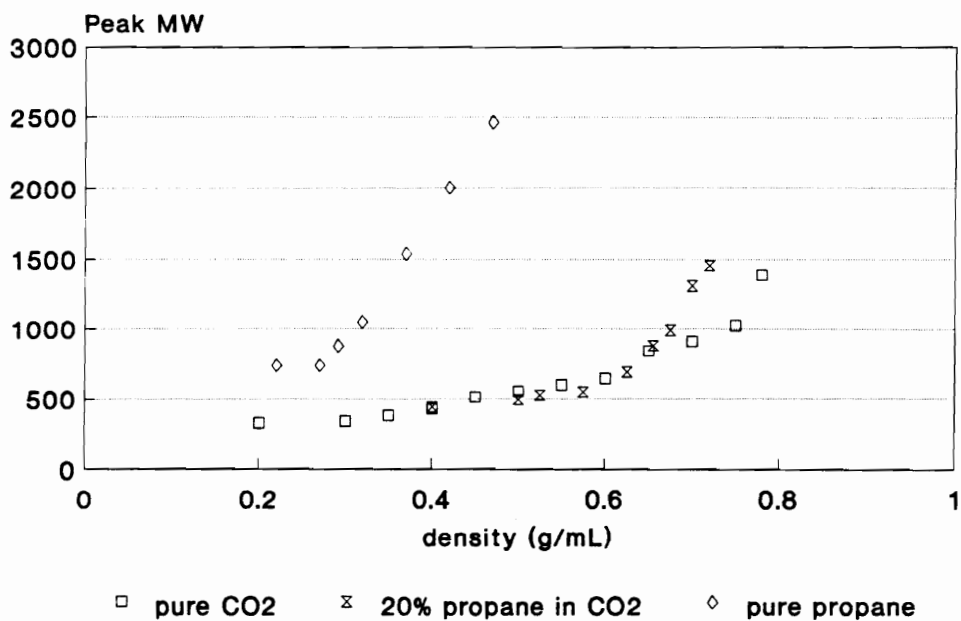


Figure 14. Graph showing the peak MWs for each extract determined from calibrated retention times and plotted as a function of the extraction density for each of the three SFs.

Table VI

Total recoveries determined gravimetrically for SFFs using CO₂, propane-modified CO₂ and propane. Flow rates are liquid flow rates determined at the pump controller. Extraction time is 45 minutes per fraction collected. All extractions were at 100 °C.

SF	Flow rates ($\mu\text{L}/\text{min}$)	Ext. Time (min)	# of fractions collected	Total Rec. (%)
CO ₂	100 - 400	45	13	30
20 % v/v propane in CO ₂	250 - 450	45	10	54
propane	90 - 400	45	8	96

Although Figure 14 showed that adding 20% propane to CO₂ only had minor effects on the resulting MWDs of the extracts, there was a rather substantial increase in total recovery as a result of modifying CO₂ with propane. Table 6 shows that the modified CO₂ resulted in approximately an 80% increase in yield over that provided by pure CO₂. The improved recovery was probably a result of enhanced surface attack by propane while overall solvent strength changed little from that of pure CO₂ below 0.65 g/mL. However, above 0.65 g/mL, as a result of much greater flow rates through the fixed restrictor, the total mass of propane in the extraction vessel was apparently great enough to begin influencing the ability of the overall fluid to solvate heavier oligomers. This situation resulted in shifting the resulting MWs to higher values than those acquired from pure CO₂. Measurements of particle dimensions (and mass) before and after static extraction with supercritical CO₂ indicated it was probably only able to penetrate the outermost region of the polymer flake. Propane, already seen to be a better solvent for the wax, probably allowed a greater percentage of oligomers to be "loosened" from this region and then extracted from the vessel. Thus, it is assumed that the presence of propane (at least at the 12 mole percent level) in CO₂ allowed for improved recovery of oligomers out of the matrix without substantially changing the solvating strength of the overall SF. This indicated that it may be possible to improve recoveries while maintaining the narrow MWDs provided from pure CO₂ by using propane as a modifier - but only by using higher concentrations of propane in the CO₂ would fractions with substantially higher MWDs likely be achieved.

Conclusions

Both CO₂ (Chapter 2) and propane proved able to fractionate the low MW PE sample into numerous cuts of progressively higher MWs. Whether to use supercritical

CO₂, propane or a combination of the two would depend on the desired product. For very fine cuts of almost "monodisperse" distributions in the sub 2000 MW range, CO₂ would be the most desirable supercritical solvent. However, pure CO₂ resulted in total recoveries of ~33% and required pressures greater than 6000 PSI to generate fractions at the high end of its range. Modifying the CO₂ with propane (at least 20 % v/v) appeared to be a means of improving recoveries without sacrificing the "narrowness" of the MW distribution. It might also be possible to improve extraction yields by using feedstock of a smaller particle size and/or operating in the liquid-SF region. Another unexplored alternative might be the use of *n*-butane as a modifier. It would be expected to be a stronger solvent for the heavier oligomers and the resulting CO₂/*n*-butane mixtures would have much lower critical temperatures (< 90 °C) than pure *n*-butane (T_c = 155.2 °C).

In order to generate MW fractions higher than 1500, and/or to do so at much reduced pressures, supercritical propane would probably be the solvent of choice. With pure propane, generating consistently good fractions below 1000 MW may depend on the pump's ability to accurately render minute changes in pressure (unless a higher temperature is used). There was also a broadening of MWDs when using supercritical propane for the fractionation. This situation could probably be mitigated at densities above 0.35 g/mL (100 °C) by reducing the increment between successive extractions, although it may never be possible to reduce polydispersities to the range available to pure CO₂.

CHAPTER 4

Supercritical Fluid Extraction and Chromatography of Polymeric Additives

Introduction

In the previous two chapters SFs were used to selectively remove oligomers of different molecular weight distributions from the parent polymer. In such cases the polymer must show some degree of solubility in the supercritical fluid. But there are many instances where certain polymers show no appreciable solubility in the SF. This situation often affords a unique opportunity for the analyst to use SFs to extract additives from the polymer for subsequent qualitative and/or quantitative analysis without interferences from co-extracted oligomers. Most liquid solvents lack the kind of selectivity necessary to remove specific analytes while leaving the bulk of matrix undisturbed. SFs have proven ideal for extracting antioxidants, plasticizers, etc. from insoluble polymers (35-37). Additionally, the advantageous solvating and transport characteristics of SFs, as well as their superior detector compatibility, make SFC an excellent choice for separating these moderately polar and often thermally labile polymeric additives. In this chapter, the application of SF carbon dioxide to the extraction and separation of polymer additives from U.S. military explosives is investigated.

Single base propellant, which contains nitrocellulose (Figure 15) as the only energetic component, has been known for more than 100 years. The smokeless powder first prepared by Volkmann in Austria burned so fast that it damaged or burst open cannons (38). In 1884, Vielle of France invented the first smokeless progressive-burning powder using a form of nitrocellulose that was soluble in a mixture of ether and alcohol

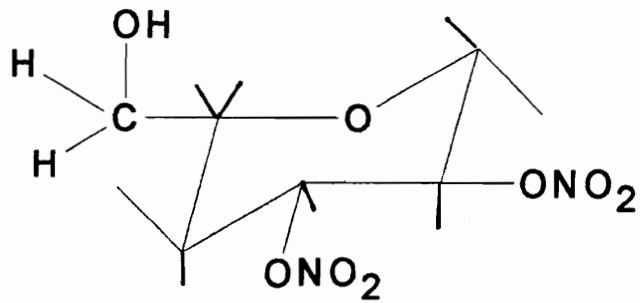
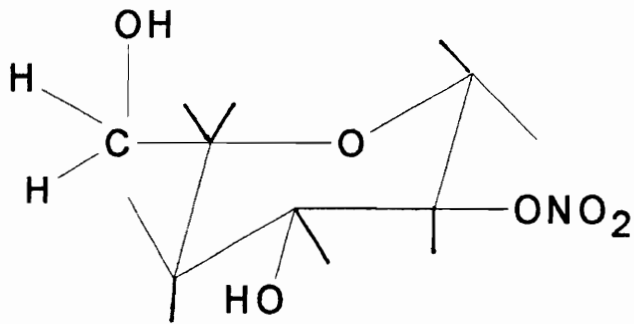


Figure 15. Structures of a 2-monosubstituted (A) and a 2,3-disubstituted (B) anhydroglucose units of cellulose. There are eight possible substitutions.

termed "pyrocellulose". Not surprisingly, nitrocellulose is inherently unstable and as it ages it releases NO_2 . The presence of NO_2 radicals in the propellant can autocatalyze further thermolysis of the propellant. If nitric ester decomposition continues unabated, excess heat generation in the propellant can result in an "explosive incident".

In Germany, diphenylamine (DPA) was used as a stabilizer to bind NC decomposition products, significantly reducing autocatalysis rates, as early as 1896 (39). The original United States "pyro" single base propellant that was first used in 1897 by the Navy contained no stabilizer until 1909, when 0.5% DPA was incorporated. Older pyrocellulose powder containing only nitrocellulose (99%, 12.6% nitrogen) and DPA (1%) was very hard and hygroscopic, which made solvent removal difficult. The introduction of gelatinizers of comparatively low energy such as 2,4-dinitrotoluene (2,4-DNT) and di-n-butylphthalate (DBP) made the removal of residual solvent much easier, and the working properties of the mixtures were made more suitable to the operations of manufacture.

The chemical stability of single base propellant is determined by examining its behavior at elevated temperature. Recently, an excellent review of stability test methods for gun propellants has appeared (40). The current method employed by the U.S. Navy and Army is a propellant life continuous surveillance test at 65.5 °C (41). In this regard, many attempts have been made to correlate the stability of single base propellants with stabilizer content (42). It is well known that DPA stabilizes by binding nitrocellulose decomposition products and converting them into stable compounds. The main reaction products of NO_2 and DPA are 2-nitrodiphenylamine (2-NDPA), 4-nitrodiphenylamine (4-NDPA) and *N*-nitrosodiphenylamine (*N*NODPA). More highly nitrated di, tri and tetra-nitrated derivatives are also expected through the natural aging of DPA stabilized

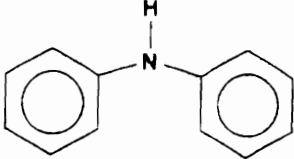
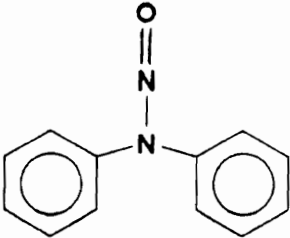
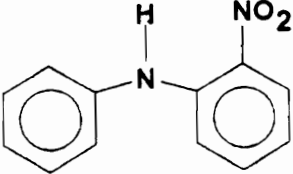
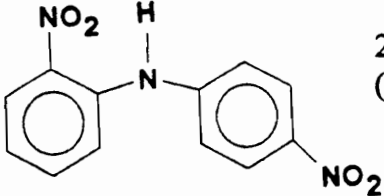
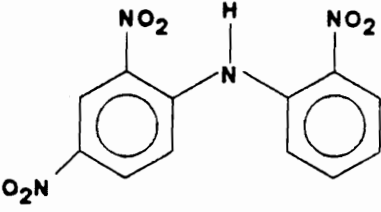
	Diphenylamine (DPA)	Primary Stabilizer
	N-Nitrosodiphenylamine (NODPA)	Stabilizer Derivative
	2-Nitrodiphenylamine (2-NDPA)	Stabilizer Derivative
	2,4' - diNitrodiphenylamine (2,4' - diNDPA)	Stabilizer Derivative
	2,2',4' - triNitrodiphenylamine (2,2',4' - triNDPA)	Stabilizer derivative

Figure 16. Structures of diphenylamine and its derivatives found in the NC gun propellants.

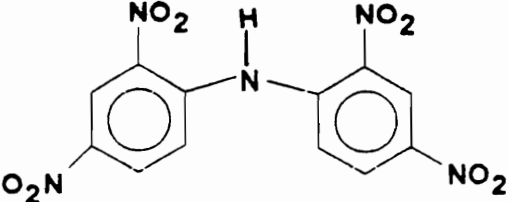
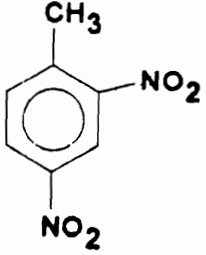
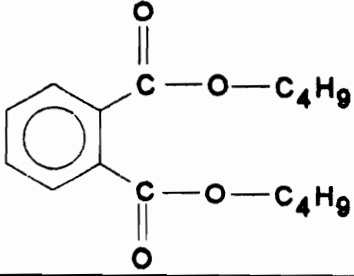
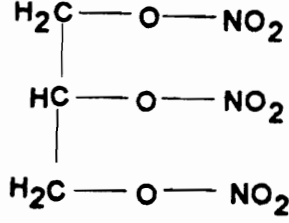
	<p>2,2',4,4' - tetraNitroDPA (2,2',4,4' - tetraNDPA)</p>	<p>Stabilizer Derivative</p>
	<p>2,4 - Dinitrotoluene (2,4-DNT)</p>	<p>Plasticizer</p>
	<p>Dibutylphthalate (DBP)</p>	<p>Plasticizer</p>
	<p>Nitroglycerine (NG)</p>	<p>Base</p>

Figure 17. Structures of some NC additives and a highly nitrated (tetra) derivative of DPA.

smokeless powders. Figures 16 and 17 show the structures of several of the most common stabilizer derivatives and additives found in NC gun propellant extracts. The actual mechanism for nitration is not well understood. There appears to be evidence for both direct nitration of the ring as well as indirect nitration through the formation *N*-nitroso intermediates. In the indirect method, the *N*-NO group rearranges via an intramolecular Fisher-Hepp mechanism and then oxidizes to NO₂ (43). Additionally, the capacity that these nitrated products have for further stabilizing activity is heavily debated nowadays. It is well known that the less highly nitrated derivatives of DPA have excellent NC stabilizing characteristics. *MNODPA* is thought to be the primary intermediate before the nitro derivatives are formed. Linus Pauling identified *MNODPA* as a valid stabilizer in 1946 (44) even though the stabilizing mechanism is apparently a two step process. Currently, the Navy considers it as a NC stabilizer, while the Army ignores its role. It is our contention that any molecule possessing the ability to bind NC decomposition products, whether directly or indirectly, can be thought to have stabilizing qualities. This subject has been the source of much debate among the propellant community throughout the past decade (45-48).

The most important methods currently used to evaluate the change in stabilizer content are volumetric bromination, GC and more recently, LC methods with largely nonspecific detectors (i.e. flame ionization (FID) and ultraviolet (UV) (45-48). Sample preparation has usually consisted of liquid-solid soxhlet extraction using large volumes of methylene chloride at ambient or elevated temperatures for 36 hours - followed by concentration of the resulting solution. SFE is a viable alternative to this type of sample preparation, offering both greater speed, ease of operation, and reductions in chlorinated solvents. SFC is currently an alternative separation method to both high-performance liquid chromatography (LC) and GC (49a). This method offers attractive features, which

make it suitable for the separation of moderately polar, thermally labile or nonvolatile compounds. It also has the ability to be interfaced with a wide array of GC and LC detectors, and appears to be more amenable to spectrometric detection (both infrared and mass spectrometry) than LC. Additionally, it offers greater speed and ease of method development than LC.

The work in this chapter describes the use of SFs for both the extraction (SFE) and subsequent separation (SFC) of propellant additives and stabilizer derivatives from military explosives. These preliminary studies are qualitative in nature and designed to demonstrate potential feasibility relative to conventional methods. The U.S. military is interested in SFs from a variety of perspectives. They are concerned with upgrading current propellant surveillance procedures - in hopes of reducing the number of "incidents" in an aging arsenal. Many of the additives and decomposition products are also serious environmental pollutants and it is important to have good analytical protocols to monitor their movements through soils and waters. Additionally, methods to "fingerprint" explosive residues are important to aid in forensic investigations of terrorist bombings. They are even hopeful that SF methods that can remove stabilizer for analysis might also be able to reintroduce stabilizer into highly destabilized propellants rendering them safe to handle.

Experimental

Nitrated derivatives of both DPA and MNODPA were prepared by Steroids LTD (Chicago, IL). Standards and extracts were dissolved in either methylene chloride (J.T. Baker) or methanol (Fisher Scientific). Propellant samples that had undergone accelerated aging were made available to us by George Naufflett, Naval Ordnance Station, Indian Head, MD.

A Nicolet LC/9560 ternary gradient system was used for LC separations. The detector was a variable wavelength UV (Spectroflow 757) by Kratos normally set at 254 nm. A Rheodyne injector with a 10- μ L loop supplied the 250 x 4.6 mm IBM C-18 column with sample. All chromatograms were recorded on a Hewlett-Packard (HP) (Avondale, PA) 3394A integrator.

An HP 5890 Series II GC equipped with cool-on-column and split-splitless injection was used. The system was controlled by an HP Vectra Chem Station, employing an HP 7673 autoinjector with an output to an HP Deskjet Plus printer. An HP-5 (25m x 200 μ m, 200 μ m i.d. and $df=0.33\mu$ m) column with a maximum temperature rating of 320 °C was used with helium (AIRCO) as the carrier gas. Injections were 1 μ L splitless with the injector at 350 °C and 65 °C for cool-on-column with FID. For additional GC confirmation, an HP 5970 mass selective detector (MSD) was used in both scanning and selected ion monitoring (SIM) modes.

A Suprex 200A (Pittsburgh, PA) was employed for SFC with both open-tubular and microbore packed columns. It is high pressure syringe pump system capable of delivering linear or asymptotic pressure and density gradients. A Valco (Houston, TX) electronic injector with a 0.1 μ L internal loop was used for sample injection. An HP 3394A integrator converted the SFC-FID signal to a chromatogram. The Suprex MPS 225, a slight variation of the 200A, was used for on-line SFE-SFC.

A Hewlett-Packard 7680 extractor was used for separating components from single base propellant. High purity carbon dioxide was provided by Scott Specialty Gases (Plumsteadville, PA). It would have been beneficial to grind the single base samples prior to SFE, however, we were reluctant to do this for safety reasons. Instead, razor sliced propellant strips (300 mg) were loaded in a 7 mL extraction vessel. The flow of liquid CO₂ was 2 mL/min for 30 min. The vessel was maintained at 60 °C and

385 atm, thereby yielding a supercritical fluid of 0.85 g/mL density. Extracted material was trapped on stainless-steel beads (100 μm) at 5 $^{\circ}\text{C}$, then removed from the trap with 1.5 mL of CH_2Cl_2 .

Results and Discussion

The goals of this research were to evaluate the usefulness of SFE and SFC for single base propellant surveillance and to identify propellant decomposition products produced via accelerated aging protocols. Five single base propellant samples manufactured in 1942-1943, originally containing approximately 1% DPA stabilizer were heated for 1-5 years at 65.5 $^{\circ}\text{C}$ to "simulate" aging. SFE using pure CO_2 was employed in order to isolate and concentrate nonpolymeric components in each of the aged propellants as well as the control sample. Unfortunately, propellants with identical histories could not be located. The control propellant had aged at room temperature since 1943. Three of the heated samples (310, 1230 and 1500 days) that had also been prepared in the early 1940s contained nitrocellulose derived from cotton linter, while in two samples (615 and 915 days) wood pulp served as the cellulose source. The percent cellulose nitration was the same ($\sim 13.16\%$) in all samples.

Figure 18 shows the GC-FID trace of the propellant control extract. Numerous components have been extracted even though single base propellant is supposed to initially contain only nitrocellulose (NC-energetic component at $\sim 85\%$), 2,4-dinitrotoluene (DNT-plasticizer at $\sim 10\%$), dibutylphthalate (DBT-plasticizer at $\sim 4\%$) and diphenylamine (DPA-stabilizer at $\sim 1\%$). Peak assignments were based upon (A) retention time comparisons with known compounds and (B) the mass spectrum of

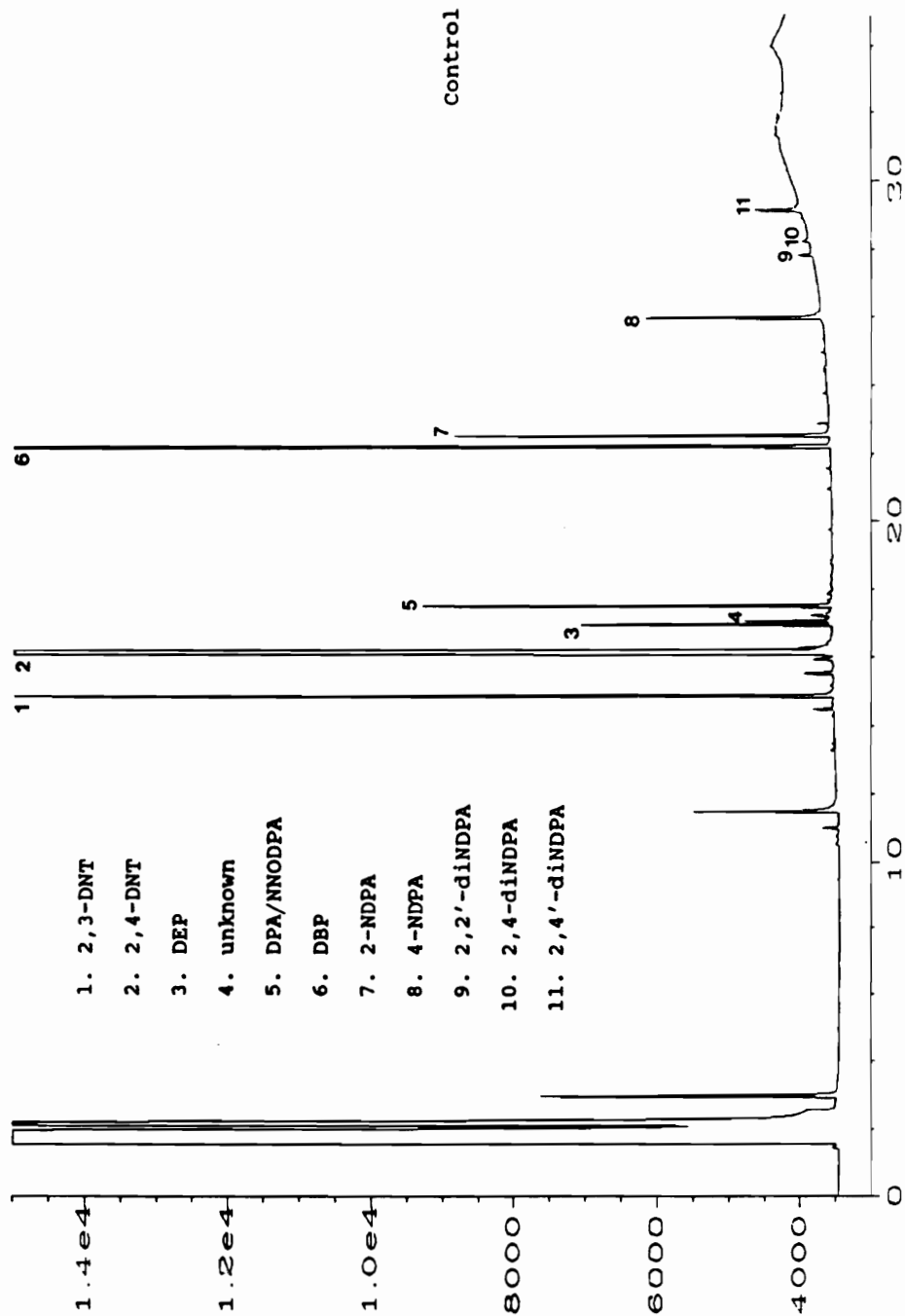


Figure 18. GC-FID separation of a SF₆ extract of a DPA stabilized NC propellant manufactured in 1943 (control).

each eluted component. Obviously, certain ingredients must not have been pure during the manufacturing step, as suggested by the presence of 2,3-DNT along with 2,4-DNT, and the presence of both DBP and diethylphthalate (DEP). Furthermore, reaction of the stabilizer has already commenced as evidenced by the presence of several nitrated DPAs (peaks 7-11). Surprisingly, there was still some DPA and/or NNODPA present in the 50 year old propellant.

Extract analysis via GC-FID of the sample heated 315 days (Figure 19) suggested a buildup of dinitrated DPAs (2,2'-diNDPA, 2,4-diNDPA and 2,4'-diNDPA) at the expense of DPA and its *N*-nitroso derivative - which are now almost completely absent from the chromatogram. Also, relative concentrations of 2-NDPA and 4-NDPA appeared to decrease following storage at 65.5 °C for 315 days. Peak number 4 may also be an undetermined stabilizer derivative as evidenced by its large increase in peak area in the "aged" extract. After 915 days at 65.5 °C, no mononitrated DPA was present and at the end of 1500 days even all traces of dinitrated DPA had disappeared (Table VII). Based on the two chromatograms, SFE may indeed serve as the sample preparation step for the design of a practical method to monitor single base propellants.

Although we did not do any specific comparisons with soxhlet extractions, we were told by the project sponsors that SFE with pure CO₂ removed the same additives and stabilizer derivatives from the NC as would be expected from liquid-solid extraction (36 hours) (49b). Supercritical fluid extracts were also much "cleaner" than liquid extracts. Liquid (i.e. methylene chloride or acetonitrile) extracts also dissolve some NC oligomers, particularly from older, more decomposed explosives. This material must then be filtered from the extract prior to LC analysis. SFE samples required no filtering.

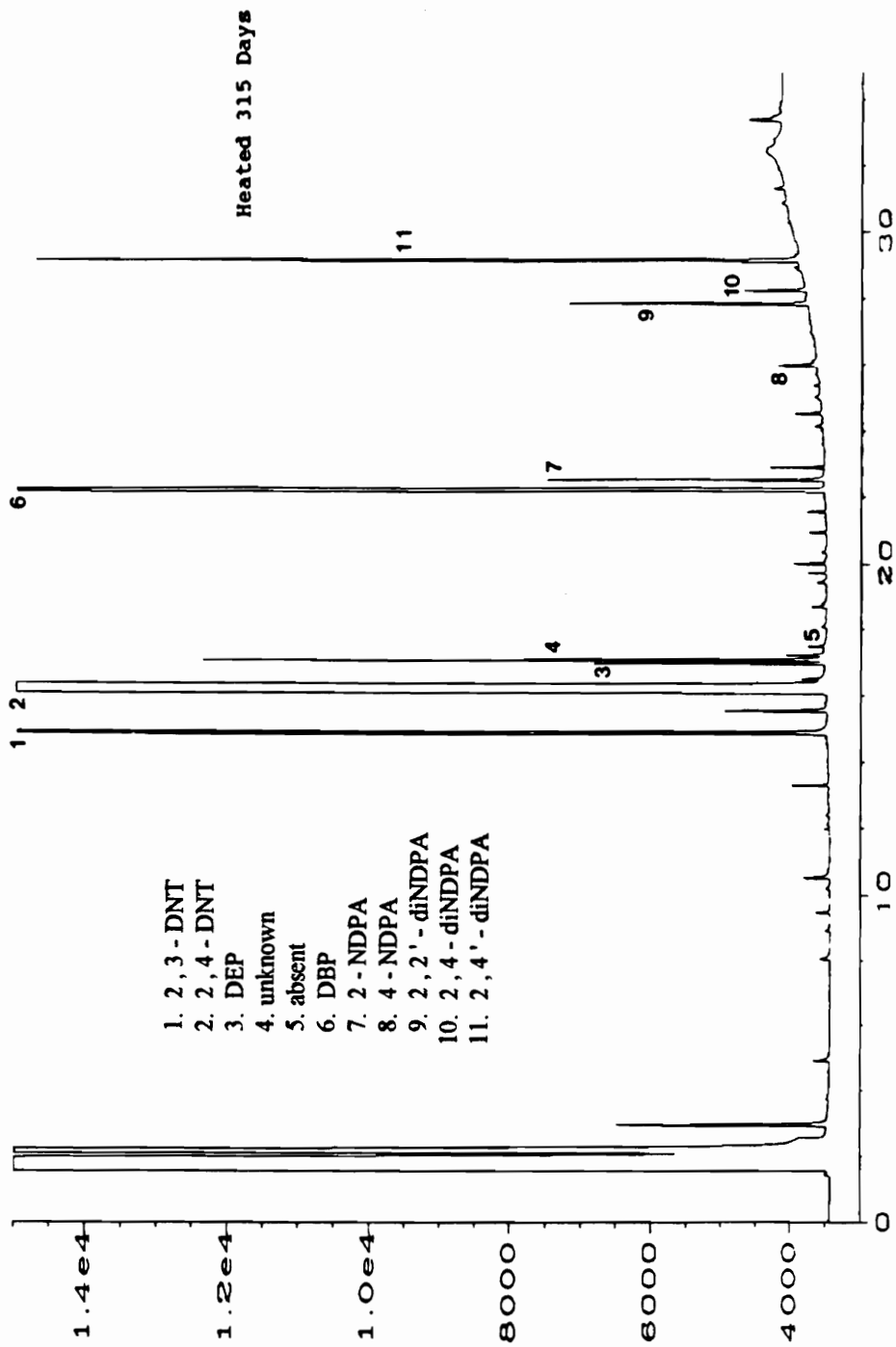


Figure 19. GC-FID separation of a SF₆ CO₂ extract of DPA stabilized NC propellant manufactured in 1943 and stored at 65.5 °C for 315 day

Table VII.

Fate of stabilizer in DPA stabilized single base propellant following storage at 65.5 °C for 315 - 1500 days.

Prepared Control	Control 50 Yrs Later	315 Days	615 Days	915 Days	1235 Days	1500 Days
DPA	DPA	0	0	0	0	0
	NNODPA	0	0	0	0	0
	2-NDPA	-	0	0	0	0
	4-NDPA	-	0	0	0	0
	2,2'-diNDPA	+	-	-	-	0
	2,4-diNDPA	+	-	-	-	0
	2,4'-diNDPA	+	-	-	-	0

0 = not present

- = small peak detected

+ = significant peak present

The focus of this phase of the project was qualitative analysis, however, we did do a preliminary investigation as to the ability of SF CO₂ to quantitatively remove stabilizer derivatives. These results were less promising. A single base gun propellant manufactured in 1988 by Olin Corporation (St. Marks, FL) was extracted using SF CO₂ under similar conditions as the aforementioned single base propellants. The trapping conditions were first optimized for 100% recoveries, then the sample was subjected to three consecutive SF extractions. The total recovery of the three extractions for DPA, 2-NDPA, 2,4-DNT and DBP were much lower than the manufacturer's specifications. The extraction results indicated a severely diffusion limited extraction from the very dense polymeric NC matrix. As mentioned earlier, we did not grind samples prior to SFE due to our concerns for safety. Finer particles, and the subsequent large increase in surface area, would greatly enhance the rate of solute diffusion into the SF. However, propellant grinding is a routine process at all U.S. arsenals. It is also our opinion that if analytical protocols are developed based on derivative ratios, it may not be necessary to achieve quantitative extractions as long as the partial extractions are representative of the bulk. But clearly, more data are needed regarding quantitation and precision.

SFE also has the ability to reclaim components from unuseable propellant stocks currently in storage. A 500 gram capacity pilot-scale SFE facility to evaluate these options is currently under construction at the U.S. Naval Ordnance Station, Indian Head, MD under the direction of Robert Farncomb (49b). As part of the justification for this program, we performed analytical extractions on several samples of double base propellant (propellant containing nitroglycerin in addition to nitrocellulose) and four samples of pelletized nitrocellulose (PNC) and then analyzed by GC-MS. A HP Model 7680 SFE and pure CO₂ was used. It was desired to determine what compounds could be removed from the propellant matrix with pure CO₂.

The double base samples (PBXN-103, PBXN-106, PBXW-113, PBXW-114, PBXW-115 and Polaris A3 First Stage) were extracted at 350 atm and 50 °C for only 10 minutes. Samples ranging in size from 200-300 mg were placed in the extraction vessel. The SF CO₂ flowing at 4 mL/min was decompressed through the outlet restrictor onto an octadecylsilica trap cooled to 5 °C. After completion of the 10 minute extraction the trap temperature was raised to 40 °C and rinsed with 1.8 mL of acetonitrile. Rinses were collected in autosampler vials and chromatographed using GC-MS. Sample PBXW-115 was extracted three consecutive times to provide an indication of the degree of completeness of the extraction. Not surprisingly, these multiple extractions indicated that the initial 10 minute extraction was far from complete - as evidenced by the continued removal of extract in second and third extractions. However, in the proposed process operation, SF CO₂ will be continuously recirculated through the system. Thus, complete extraction in a short period of time is not so important as it would be for analytical surveillance purposes.

The PNC samples were also extracted under the described conditions and evaluated for lot-to-lot differences. GC-MS with the HP 5890 GC and the HP 5970 MSD was performed with 1 uL splitless injections onto a 50m x 0.2mm i.d., 5% phenyl methyl silicone column. Although standards were not provided, some peaks were tentatively identified from their mass spectra. Three of the four PNC extracts yielded identical TIC traces. Two, apparently isomeric peaks of the double base stabilizer, ethyl centralite, were identified in the chromatograms (Figure 20a). The fourth PNC extract (Figure 20b) contained only one ethyl centralite peak. This constituted the only lot-to-lot variation determined from the SF extracts.

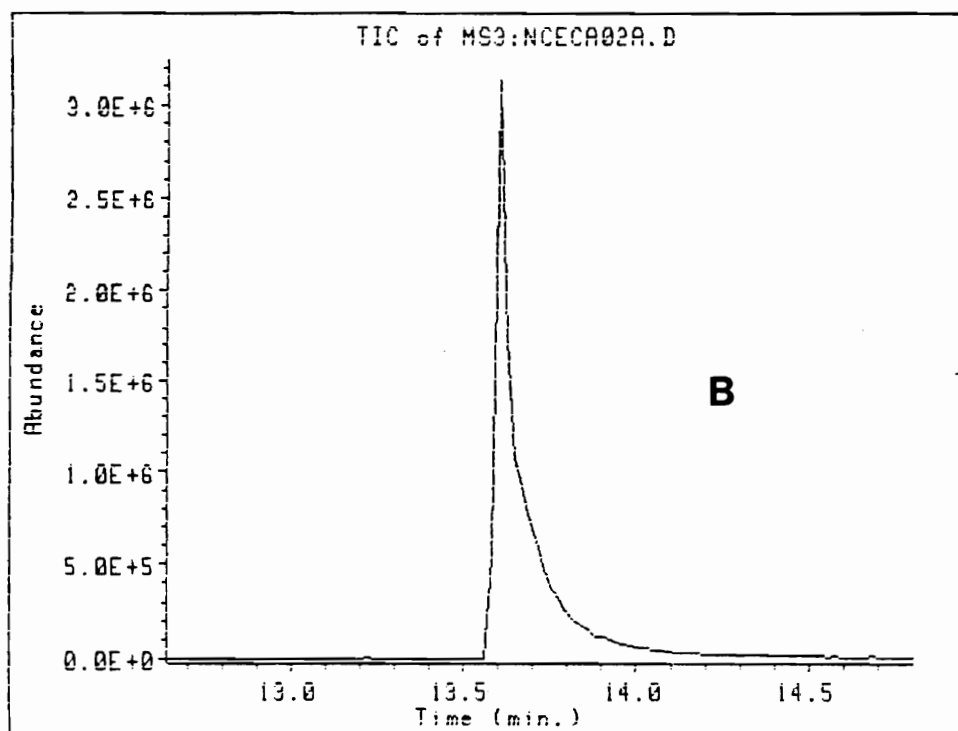
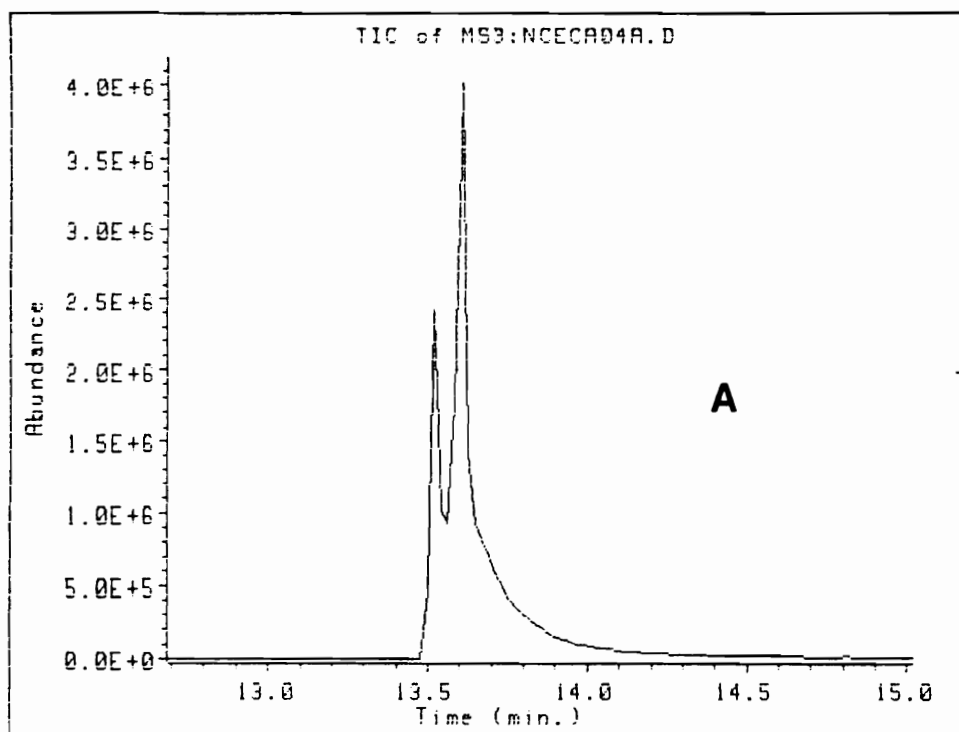


Figure 20 a-b. GC-TIC traces of two SF CO₂ extracts of pelletized nitrocellulose showing lot-to-lot differences. (A) two isomers² of ethyl centralite, (B) single isomer of ethyl centralite.

In the case of the double base propellants, bis (2,2-dinitropropyl) acetal and bis (2,2-dinitropropyl) formal are extracted from PBXN-106 (Figure 21). In addition, a trace quantity of *N*-phenyl- β -naphthylamine was identified at 15.50 minutes in the TIC. Figure 22 shows that three components are clearly extracted from PBXN-103, two of them identified as triethylene glycol dinitrate and the stabilizer ethyl centralite. The Polaris A3 First Stage extract (Figure 23) also exhibited three peaks in its TIC profile. These were identified as 2-nitrodiphenylamine, ethyl centralite and 1,3-benzenediol. Samples PBXW-114 and PBXW-115 (Figure 24) proved to have very similar extracts. The only identifiable peaks from the TIC profile were those of isodecylpelargonate and its isomers at 14 minutes into the chromatogram.

Concerning the analysis of extracted components from the single base propellants, GC provided what was believed at the time to be the best separation. However, to elute the more highly nitrated DPAs (tri and tetra), it was necessary to program the oven to 320 °C. Temperatures this high, can cause problems with excessive bleed and result in shortened column life - particularly if thicker stationary phases are to be used. Furthermore, it was suspected, and later confirmed in our work that GC does not allow one to directly separate *N*-nitroso compounds from their DPA analogs (50). Davidson (51) reported the thermal denitrosation of *NNODPA* and subsequent elution of this compound as DPA. He based his conclusion on the fact that DPA and *NNODPA* eluted from the GC both had identical mass spectra. Later work by Alley and Hayes (52) indicated that *NNODPA* and DPA remained structurally intact, but simply co-eluted under GC conditions. Their conclusion was based on a difference of response factors of about 50% between DPA and *NNODPA*. They believed that the FID flame was detecting two different compounds with different response characteristics. Their injector temperature was 105 °C. We have repeated this experiment and were able to reproduce

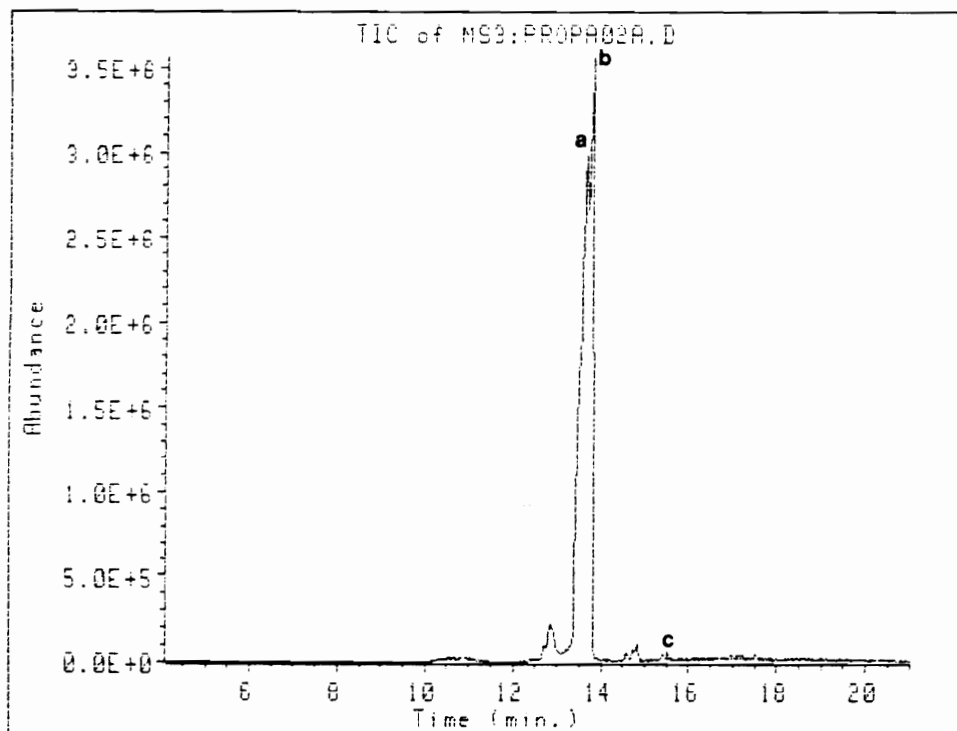


Figure 21. GC-TIC of SF CO₂ extract of double base propellant sample PBXN-106. (A) bis-2,2'- dinitropropyl acetal, (B) bis-2,2'- dinitropropyl formal, (C) N-phenyl-β-naphthalene.

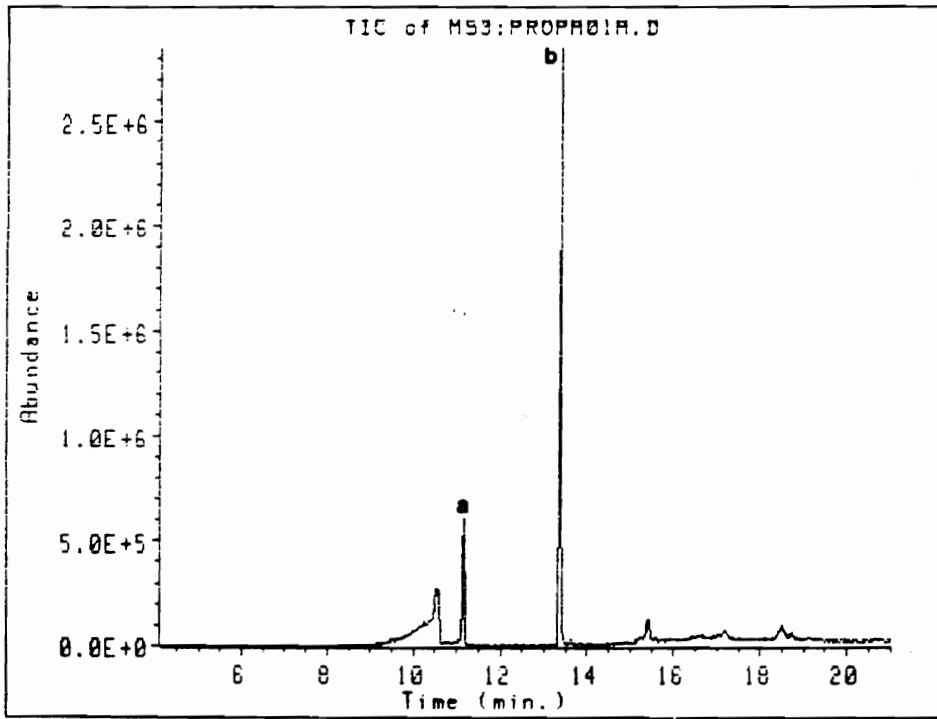


Figure 22. GC-TIC of SF CO₂ extract of double base propellant sample PBXN-103. (A) triethylene glycol dinitrate, (B) ethyl centralite.

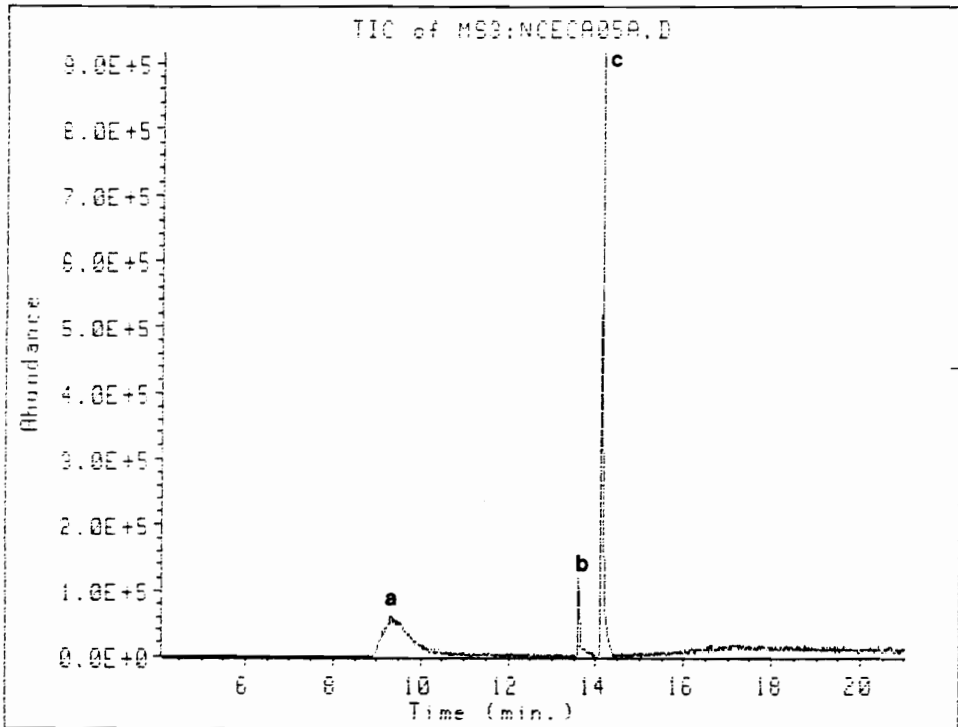


Figure 23. GC-TIC of SF CO₂ extract of double base propellant sample Polaris A3 First Stage. (A) 1,3 - benzenediol, (B) ethyl centralite, (C) 2 - nitrodiphenylamine.

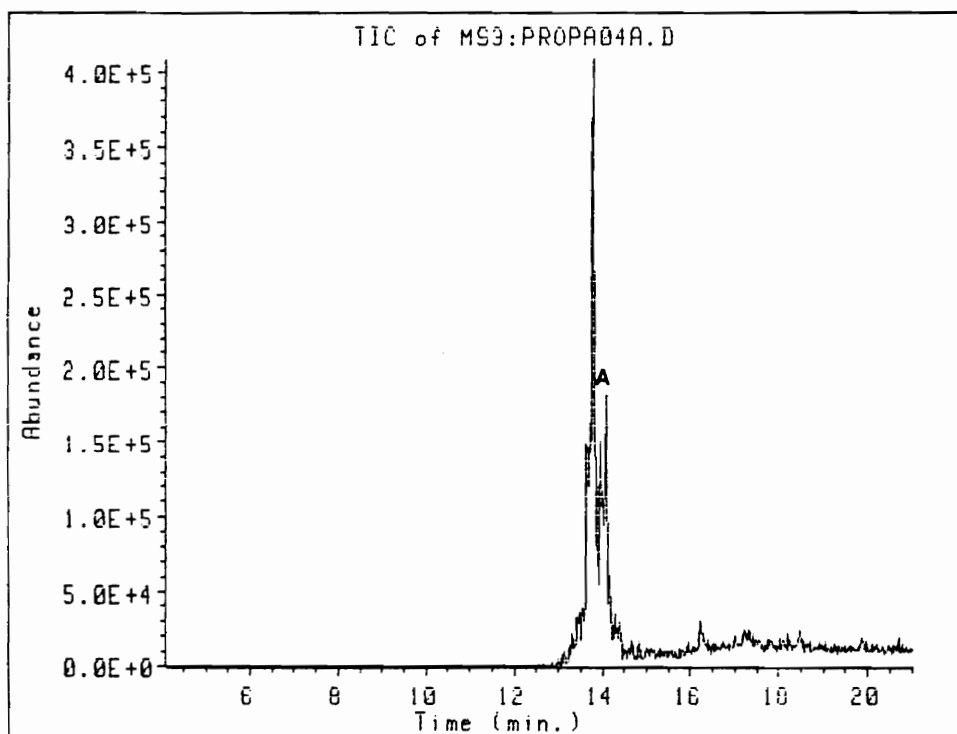


Figure 24. GC-TIC of SF CO₂ extract of double base propellant sample PBXW-115. (A) isodecyl pelargonate.

their results at the low injection temperature. However, we determined that by raising the the injection temperature of DPA and *NNODPA* to 300 °C, the difference in response factors is substantially reduced. Thus, in our opinion, the discrepancy in response factor is probably due to sample discrimination of the less volatile *NNODPA* in the heated injection port. This denitrosation of *NNODPA* occurred whether using cool-on-column or heated split-splitless injection techniques. The possibility that denitrosation does not lead specifically to DPA must also be considered. In addition to *NNODPA*, three other nitrated *N*-nitroso derivatives thought to be intermediates in DPA stabilized single base propellant were analyzed by GC in our laboratory, and each was found to undergo denitrosation (2-nitro-*NNODPA*, 2,4'-dinitro-*NNODPA* and 4,4'-dinitro-*NNODPA*). The failure of GC to elute *MNDPAs* intact may restrict it's usefulness in the analysis of single base propellant extracts - particularly relatively new specimens expected to have high concentrations of *NNODPA*. In the case of old propellant, this limitation may not arise because DPA and *NNODPA* can be completely absent from the extract. But, if the *N*-nitroso compounds are indeed important intermediates for every nitrated DPA as proposed by Becker and Hunold (53), then GC may be unable to effectively characterize even old propellant samples.

Reversed phase LC appears to be becoming the method of choice for propellant extract analysis (54). The Navy currently employs an isocratic method with an acetonitrile and water (65:35) mobile phase and a C-18 column. We used their method to separate a synthetic mixture of DPA derivatives (Figure 25) and an actual SF extract of a single base propellant. The resulting chromatograms lacked good resolution, particularly in the case of the propellant extract where large quantities of co-extracted 2,4 DNT blocked out several nitrated DPA peaks (Figure 26). Additionally, DPA and

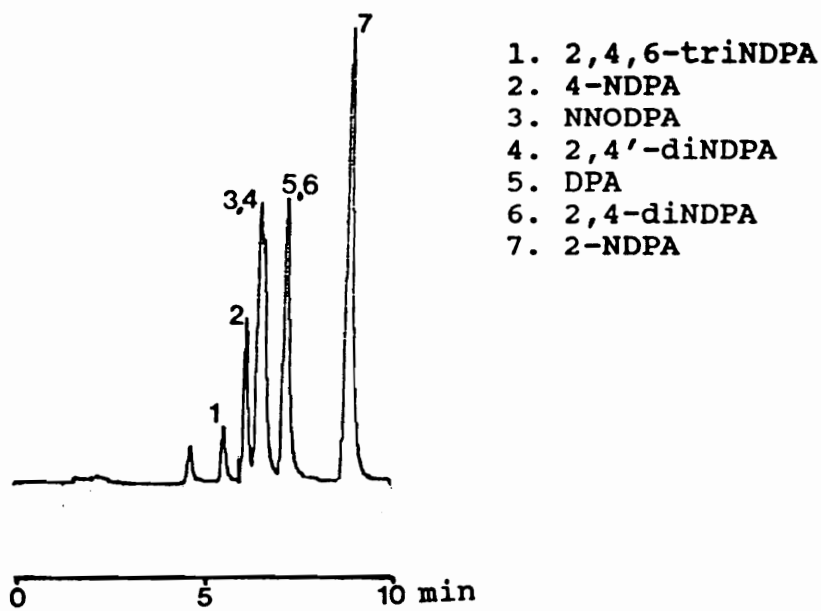


Figure 25. Reversed phase LC-UV trace of synthetic mixture of DPA stabilizer derivatives.

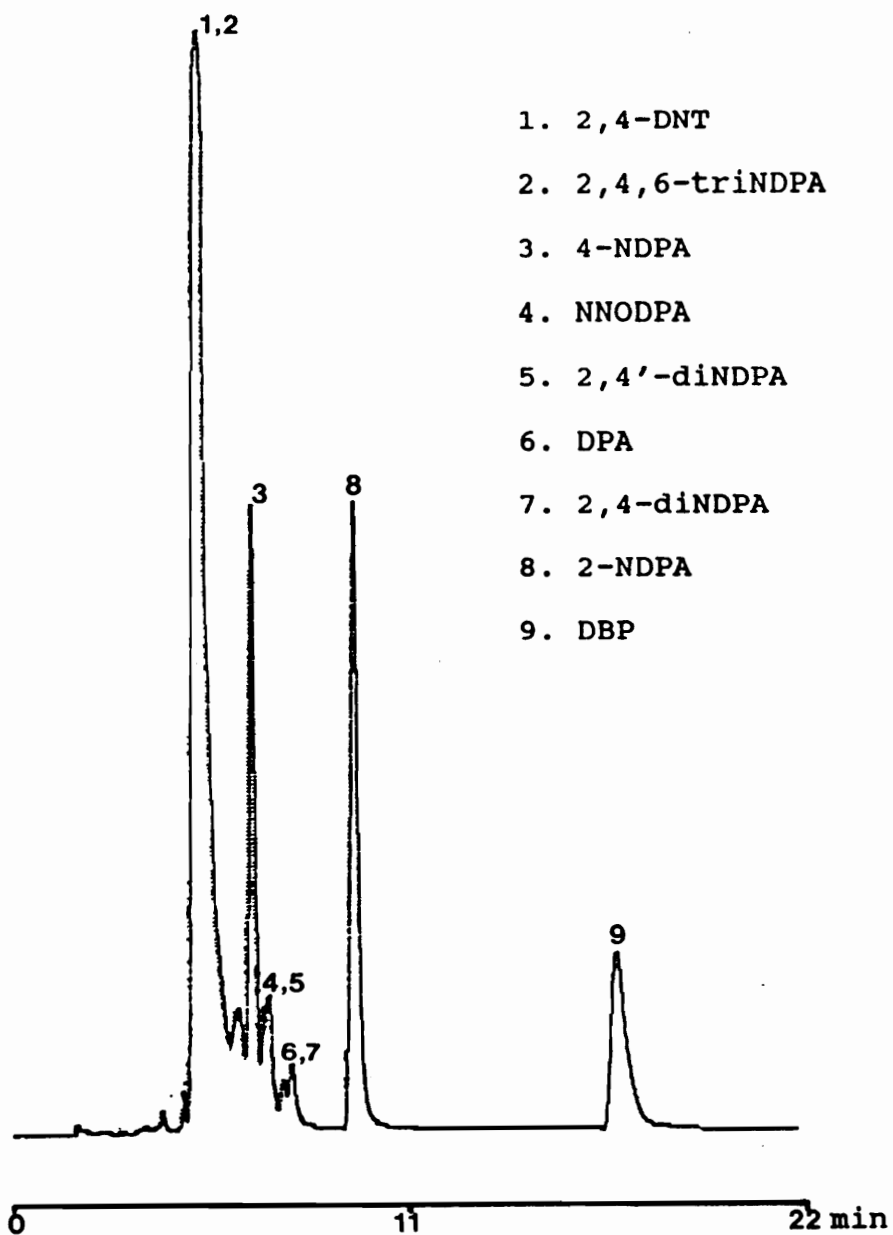


Figure 26. Reversed phase LC-UV trace of SF CO₂ extract of single base propellant manufactured in 1943.

NNODPA were found to coelute with 2,4' and 2,4-di*NDPA* respectively. Their LC method would be severely limited in such cases where *DPA*, *NNODPA*, *DPA* derivatives and large quantities of *DNT* isomers are all present in the extract.

Like GC, SFC is able to resolve nearly all nitrated *DPAs*, but without the need to operate at elevated temperatures. Figure 27 shows the SFC-FID trace for the separation of a model mixture of *DPA*, *NNODPA* and nitrated *DPAs*. Most of the peaks are relatively well resolved with the 25cm x 1mm i.d. packed column. Unfortunately, the column is unable to separate *DPA* and *NNODPA*. However, SFC clearly has no difficulty eluting the highly nitrated di- and tri- derivatives of *DPA*. In this regard it is a very nice compromise between GC and LC. An actual extract of single base propellant (control) is separated by packed column SFC in Figure 28. The quality of the separation is intermediate between LC and GC.

One very important advantage that SFC has over either GC or LC is the potential to do on-line SFE-SFC. Since the extraction fluid and the chromatographic mobile phase are both the same (SF CO_2), it is possible to perform SFE and SFC with the same instrument. During SFE, the SF is routed through the extraction vessel where it extracts analytes from the sample and deposits them following decompression onto a solid phase trap. When the extraction is complete a "switch" in the plumbing is initiated, and the SF then travels through the trap (under pressure) and onto the chromatographic column. As the SF density is increased during the pressure program, analytes are removed from the trap and dissolved in the SF. Further separation takes place on the column prior to detection. This procedure substantially reduces the total time and expense for sample preparation and analysis. Additionally, as a result of eliminating the injection solvent, there is no dilution factor to deal with. Subsequently, sensitivities can be increased far above those of conventional off-line liquid sample injections.

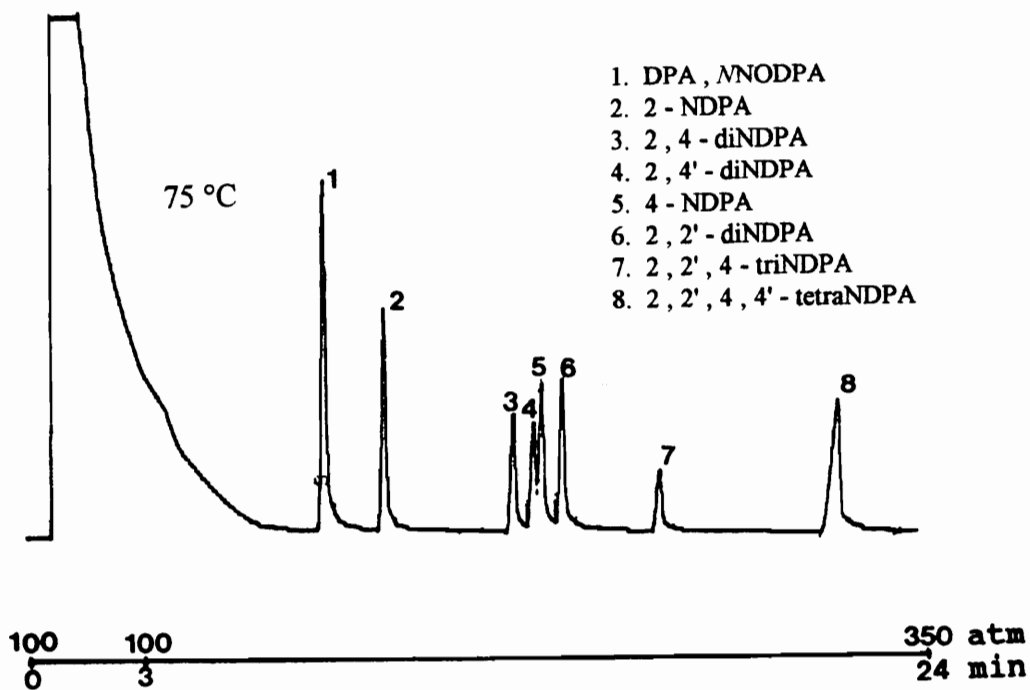


Figure 27. SFC-FID trace of synthetic mixture of DPA stabilizer derivatives.

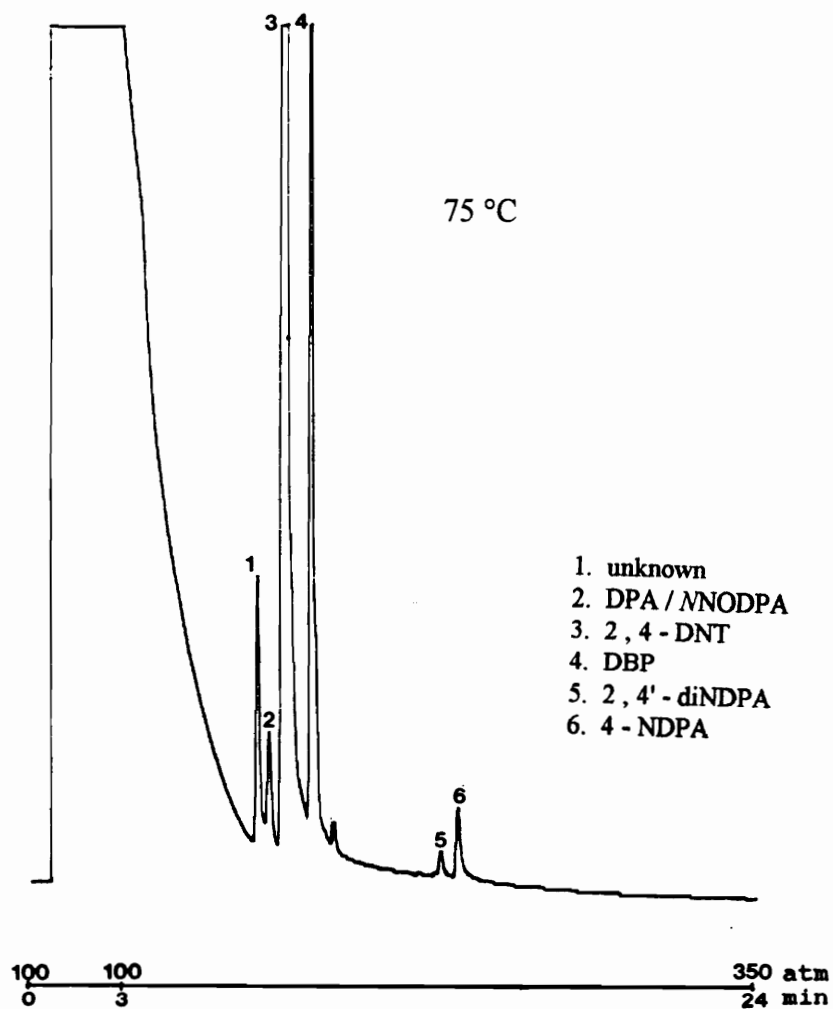


Figure 28. SFC-FID trace of SF CO₂ extract of single base propellant manufactured in 1943.

Figure 29 shows an SFE-SFC-FID trace for a five minute extraction of the single base sample that had been heated at 65.5 °C for 315 days. A 35 mg sample of the explosive was extracted on-line with a Suprex MPS 225 SFE/SFC system at a pressure of 350 atm and 100 °C onto a cryocooled trap maintained at -5 °C. Immediately following the extraction, SFC of the trap took place at 100 atm for 3 minutes and was then ramped to 400 atm in 25 minutes. Note the absence of a solvent peak as well as the improved "sensitivity" compared to conventional liquid injection (Figure 26). In the on-line analysis we were able to confirm the presence of three additional DPA derivatives present (2,4-diNDPA, 2,2'-diNDPA and 2,2',4,4'-tetraNDPA) that are not visible in the off-line SFC. In both cases 2-NDPA is obscured by the large 2,4-DNT peak. An early concern was the possibility that "aging" protocols at elevated temperatures might not accurately represent the behavior of DPA stabilized gun propellant under "normal" conditions. If the reaction mechanisms at surveillance temperatures are different from those experienced by stockpiled propellant, then the value of such testing could be suspect. Specifically, our experiences with *NNODPA* in the GC alerted us to the possibility that the *N*-nitroso group could rearrange and oxidize on the ring at elevated temperatures. If these nitrated DPAs, generated from *NNODPA* in the propellant, were actually present in the extract, they would be indistinguishable from those occurring through normal DPA stabilization of the nitrocellulose. Their presence could conceivably interfere with stability determinations. In order to see if there was any evidence to this effect, a study was performed on samples of *NNODPA* stored at ambient conditions, 40 °C and 65.5 °C. The samples were placed in sealed vials, removed periodically, dissolved in methylene chloride and then analyzed by SFC-FID. An open-tubular column (10m x 50um i.d. x 0.25 μm film thickness) coated with cyanopropyl stationary phase was employed with 100% CO₂ at 80 °C. After two years at ambient temperatures in

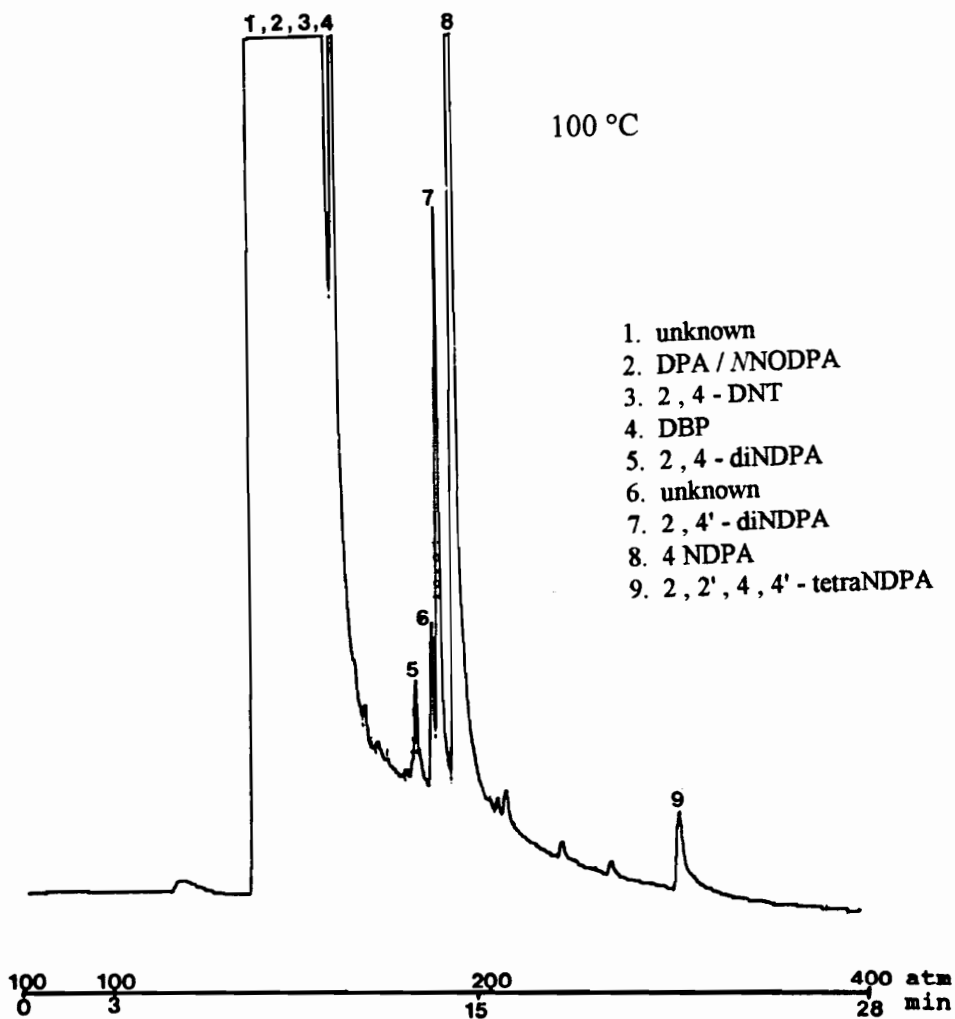


Figure 29. FID trace of an on-line SFE-SFC analysis of single base propellant manufactured in 1943. Five minutes extraction followed by SFC.

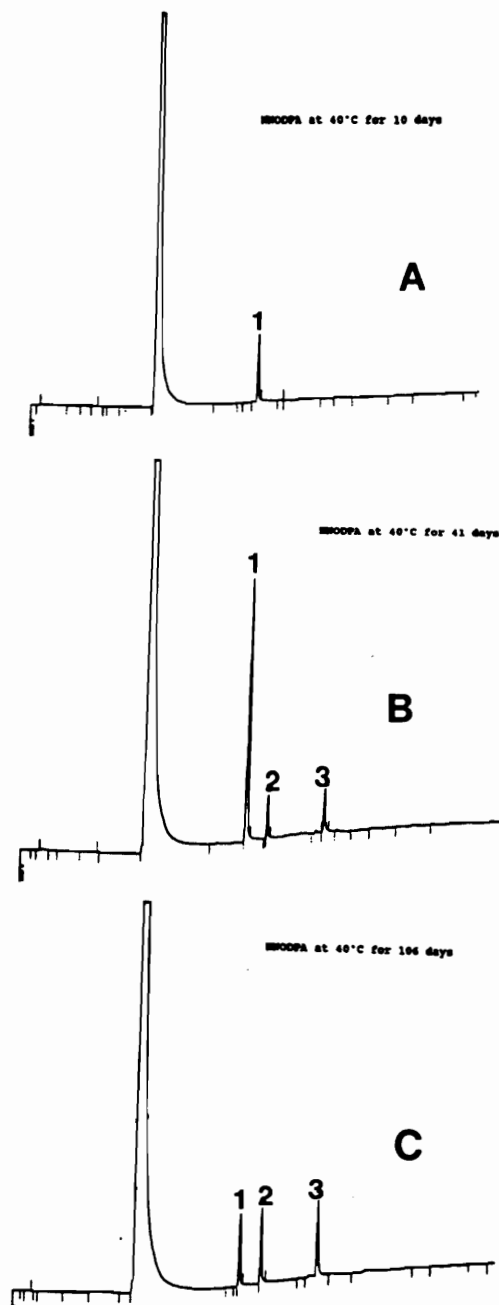


Figure 30 a-c. Capillary SFC-FID of thermally aged (40 °C) MNODPA. Individual samples were heated for variable times. Peaks are: (1) unknown, (2) 2 - NDPA, (3) 4 - NDPA.

the laboratory, *NNODPA* showed no apparent evidence of decomposition. After 10 days at 40 °C, a single peak was present in the chromatogram (Figure 30a). Retention time comparisons with standards revealed it to not be *NNODPA* and we were never able to identify this peak with standards and the FID. Figures 30b and c revealed the presence of two additional peaks. These were identified as 2-NDPA and 4-NDPA, both present in roughly equal concentrations. These results indicate that under these conditions, it is probably not a Fisher-Hepp rearrangement, since the para position would be heavily favored. Peak number 1 appears to be an intermediate from which the ortho and para positions are equally favored. This may be an intramolecular Bambruger mechanism (55) following oxidation of *NNODPA* to *NNO₂-DPA*. In this rearrangement the NO₂ group can migrate from the *N*-nitrogen to either the ortho or para positions on the ring. If this is the case, then peak number 1 might be the *NNO₂-DPA* intermediate - if such a species is indeed stable. However, we have no experimental evidence as to the actual identity of peak 1. The decomposition is more accelerated at 65.5 °C as evidenced by the presence of nitrated DPAs after only 10 days (Figure 31a-b). By the end of 106 days at this temperature peak 1 has completely given way to 2-NDPA and 4-NDPA. The results of this simple study imply that mononitrated DPAs can come directly from any *NNODPA* in the propellant independent of NC decomposition when subjected to elevated temperatures.

Conclusions

In summary, propellant stability is a key issue, as large quantities of World War II explosives exist today. The effectiveness and identification of intermediate DPA decomposition products for insuring propellant stability continues to be debated.

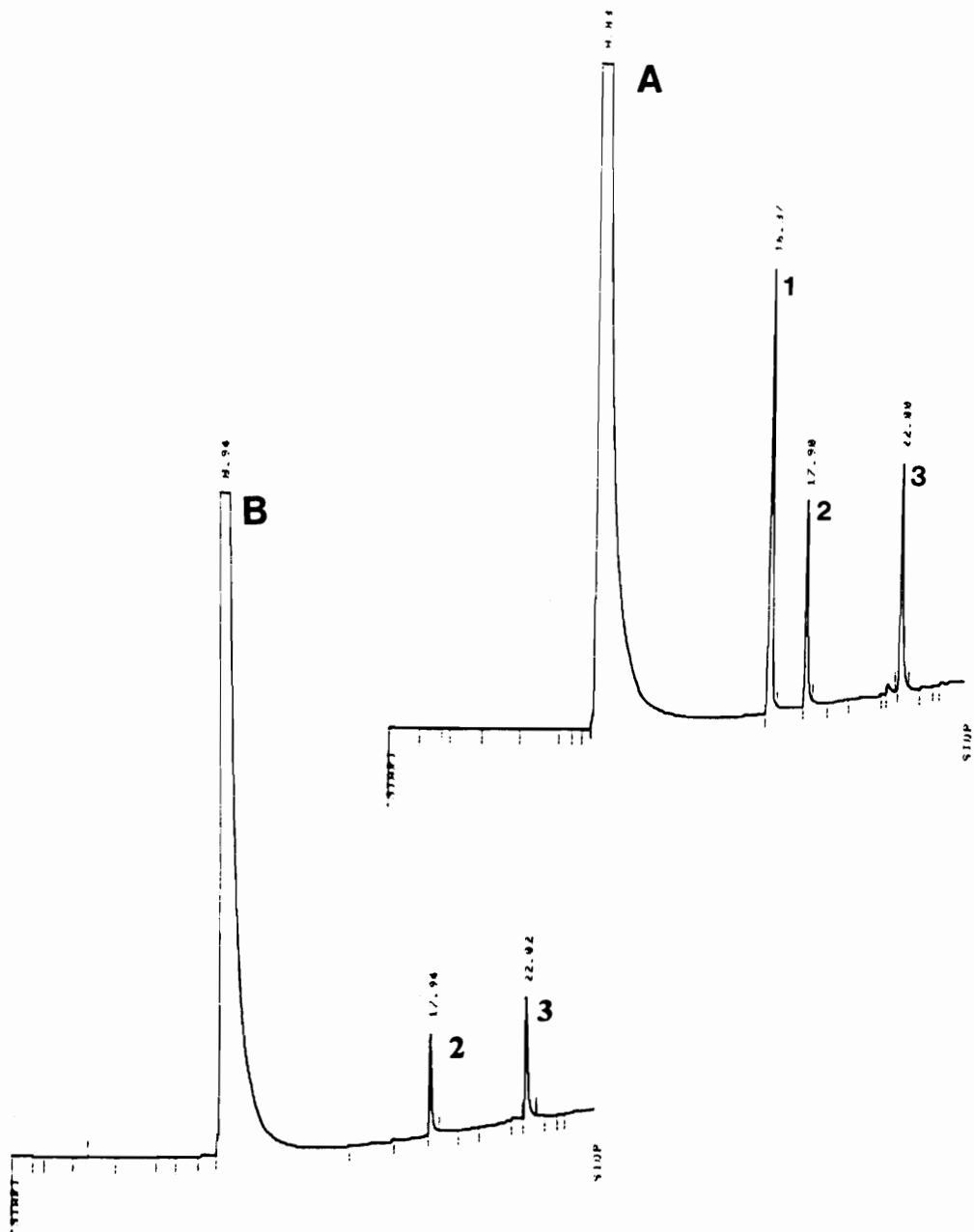


Figure 31 a-b. Capillary SFC-FID of thermally aged (65.5 °C) MNODPA. Individual samples were heated for variable times. Peaks are: (1) unknown, (2) 2 - NDPA, (3) 4 - NDPA.

Rapid, informative and reliable methods of analysis are required. The various features discussed during this feasibility study are compared in Table VIII regarding time of separation, organic solvent usage, integrity of eluted analytes, compatibility with mass spectrometric analysis, and adaptability to on-line SFE. It would appear from this study that propellant analysis of nonpolymeric components would best be accomplished employing (a) sample preparation by SFE, because of its efficiency and minimal organic solvent use, (b) isolation of individual extract components by SFC, because it affords faster and more efficient separations than HPLC while operating at temperatures considerably below those required for GC. SFC may also prove more amenable to interface with mass spectrometers providing a near universal and specific detector for the unambiguous identification of eluted components. We have also preliminarily demonstrated the desirability of performing on-line SFE-SFC. Such a system has the potential for providing greatly enhanced sensitivity with rapid overall analysis of the propellant and minimal sample manipulations. In conclusion, this study provides much hope that better, more scientific protocols for propellant surveillance are within our grasp.

Table VIII.

Comparison of chromatographic methods for propellant stabilizer analysis.

<u>Analytical Parameter</u> <u>Chromatographic Method</u>	Time Of Analysis	Organic Solvent Useage	Integrity Of Analytes Separated	Amenable To MS Detection	Compatible With on-line SFE
GC	Fast	None	Questionable	Excellent	Yes
SFC	Slower	Minimal	Excellent	Good	Yes
HPLC	Slowest	Considerable	Excellent	Good	No

CHAPTER 5

SFC-Chemical Ionization-Mass Spectrometry of Energetic Material Extracts

Introduction

In the previous chapter SFC was shown to provide separations of propellant extracts that were superior to LC at temperatures substantially lower than those needed in the GC analysis of the same compounds. It was also demonstrated that the ability of a SF to deposit its solute load upon decompression could readily be adapted to on-line extraction-chromatography techniques (i.e. SFE-SFC). Another important advantage SFs possess over liquids is superior detector compatibility. The use of SFC allows the separation chemist to transcend the boundaries between GC and LC detectors. SFC routinely incorporates traditional GC detectors such as the flame ionization detector (FID), electron capture detector (ECD), and sulfur chemiluminescence detector (SCD) as well as the multiwavelength ultraviolet detector (UV) common to LC. Additionally, SFC has been successfully interfaced with spectrometric detectors. Griffiths et al. (56) used a high pressure flow cell flow to perform on-line SFC-FTIR. The transparency of CO₂ in much of the IR region allowed fairly complete spectra to be collected. When SFC is interfaced with mass selective detection, a powerful analytical tool for the analysis of difficult mixtures can also be realized. Mass spectrometry (MS) provides universal and target compound detection, good sensitivity, and in some cases structural information for the identification of unknown components. Here we examine the use of a thermospray LC-MS system adapted to packed column SFC (PSFC) for the analysis of compounds routinely found in energetic material extracts.

During the evolution of SFC in the 1980s, capillary columns received the greatest amount of attention. They provided a large number of theoretical plates (> 100,000) and

their relatively low volumetric flow rates (< 0.5 mL/min) allowed for easy interfacing with most existing GC detectors. In addition, early efforts at interfacing capillary SFC (CSFC) with MS were moderately successful. Smith et al. (57) reported on the successful coupling of a $25\ \mu\text{m}$ i.d. column directly into the inlet of a mass spectrometer as early as 1982. Other applications soon followed and a great deal of enthusiasm was generated at the time for both SFC and the future of SFC-MS.

However, limitations with CSFC were soon realized (58). Capillary columns in SFC-MS were typically $50\ \mu\text{m}$ i.d. with a film thickness of $0.25\ \mu\text{m}$. These narrow i.d. columns normally handle no more than 10 ng per component before losses in chromatographic resolution arise as a result of column overloading. Additionally, separations with narrow bore capillary columns often resulted in analysis times greater than 60 minutes. The reduced capacity of the columns also required that injection volumes be split prior to deposition on the column and that analyte solution concentration normally be greater than 50 ppm.

The limitations associated with CSFC helped spur development in PSFC. Packed columns in SFC are typically 1.0 - 4.6 mm i.d. and range from 3 - 25 cm in length. They incorporate many of the stationary phases found in conventional LC. The larger capacity of these columns allows less troublesome and more reproducible direct injections. Analysis times are much shorter than CSFC and the 1.0 mm i.d. columns can be used with many GC detectors without difficulty. On the other hand, the volumetric flows resulting from 2.0 - 4.6 mm i.d. columns made them more amenable to LC detectors. Criticized in the past for their poor efficiencies, recent applications with packed columns have demonstrated as many as 28,000 theoretical plates in the analysis of primary and secondary amines (59). Recent instrument designs (60,61) have emphasized the use of packed columns and their value in SFC is now firmly established.

The higher flow rates of packed columns are a source of difficulty when interfacing them with the high vacuum environment of the MS. For that reason, the majority of SFC-MS studies to date have involved capillary columns. Their relatively low liquid flow rates (1 - 5 $\mu\text{L}/\text{min}$) can be introduced directly into many MS sources without modification to their vacuum systems. Their primary requirement is that the restrictor tip be heated to prevent analyte spiking and to overcome Joule-Thompson cooling at the restrictor exit (62). The vast majority of SFC applications use CO_2 as the primary fluid. Since CO_2 has an ionization potential (13.6 eV) just above that of most organic compounds (7-11 eV), and the resulting ion source pressure following introduction of the mobile phase is still fairly low, analyte ions could be produced by charge exchange (CE) processes. Thus it was possible to use the mobile phase CO_2 from CSFC to generate "electron-impact (EI) like" spectra via charge exchange in the MS source (63-65). However, CE with CO_2 is an inefficient process and results in very low MS sensitivities. For this reason, most CSFC-MS applications have involved chemical ionization (CI). At least three reviews discuss CSFC-MS (58,66,67) in some detail and there exists at least one commercially available system dedicated to CSFC-MS (68).

Interfacing packed column SFC systems to the mass analyzer requires greater modification than for CSFC-MS. Arpino et al. (69) have discussed some of the difficulties involved in coupling PSFC to MS and the subsequent failure of the technique to meet early expectations. The problem lies primarily in that conventional EI/CI sources (that accommodate GC and CSFC flows) are unable to handle the high mobile phase loads emanating from packed columns. Researchers have employed a number of approaches aimed at dealing with the high flows from PSFC for the purpose of interfacing with the mass analyzer. These include flow splitting (70), mobile phase removal (71), atmospheric pressure ionization (72) and moving belt interfaces (73). However, we feel

that probably the simplest method for coupling PSFC to the mass spectrometer, is to use an existing LC-MS interface. These systems offer ready made vacuum systems capable of handling high volumes of SFC mobile phase with little or no modification.

Henion et al. (74) used a particle beam interface to perform on-line packed column SFC-MS. Two skimmers were employed to remove volatile solvent clusters, while allowing the less volatile analyte particles to traverse the interface into the MS source. Helium nebulizing gas (delivered coaxially) and post-column alcohol solvents were used to provide an enriched particle beam to the source. Thus, in the source, the vacuum was unaffected by the mobile phase, and ionization could take place by conventional means. They used 4.6 mm i.d. columns and were able to generate EI spectra of synthetic mixtures of polymer additives, corticosteroids and xanthines following removal of the mobile phase. However, sensitivities were in the ug range due to analyte loss in the momentum separators and solute-solute clustering in the source.

The thermospray (TS) interface is another LC-MS interface whose vacuum system was designed to handle high liquid chromatographic flowrates - up to 1.5 mL/min of aqueous based mobile phase. Games et al. (75,76) used the device for spray deposition onto a moving belt and for the direct introduction of SFC eluent into the TS source. They used a Finnigan MAT Thermospray and methanol as a mobile phase (CO_2) modifier (20-25%) to perform proton transfer positive ion chemical (PCI) ionization. Approximately half the mobile phase from a 4.6 mm i.d. column was delivered to the TS source from a stainless steel tee positioned after the column. They achieved PCI spectra of phytoecdysteroids and sulphonamides consisting primarily of protonated molecular ions and $(\text{M}-\text{H}_2\text{O})\text{H}^+$ fragments (in the case of phytoecdysteroids). The spectra described above were acquired with 25 μg injections. However, they reported sensitivities to be generally in the low ng range (77). All of their separations were performed isobarically.

In this chapter we report on the use of a Vestec TS LC-MS interface to perform pressure programmed SFC-CI-MS of energetic material extracts. Unlike most previous packed column PCI-MS applications, we did not use liquid organic modifier in the mobile phase to provide solvent moderated PCI, rather, we used a separate gas line into the source in order to deliver conventional CI reagent gases (primarily CH₄). We also report on the use of CO₂ moderated negative chemical ionization (NCI) in this interface. The system is the most affordable LC-MS interface on the market and offers true "benchtop" operation which was another goal of our work.

The non-polymeric components of energetic materials offer interesting applications for the combination of SFC and MS. The compounds and mixtures studied here represent those found in extracts of single base propellants (52,78). Their analysis from a variety of matrices is important in determining (a) the stability of explosives, (b) the potential source of explosives in forensic investigations, and (c) the environmental contamination resulting from their manufacture. Some of the important decomposition products that result from propellant aging are thermally labile and thus are not amenable to GC. SFC offers good resolution of both primary and secondary stabilizers, plasticizers and gelatinizers; while CI mass spectrometry affords the analyst the benefits of target compound analysis.

Experimental

SFC. Supercritical fluid chromatography was performed using a Suprex (Pittsburgh, PA) 200A supercritical fluid chromatograph. The system consisted of (a) a 250 mL syringe pump capable of achieving pressures to 500 atm and delivering both pressure and density gradients, (b) a column oven with a temperature range to 160 °C and (c) a single control module for the entering operating parameters for both the pump and the oven.

Separations took place on a 25 cm x 2mm i.d., 5 μ m column (Keystone Scientific, Inc., Bellefonte, PA) with the sample being delivered via a Valco Model C6W (Houston, Texas) 2 μ L external loop injector. Back pressure was controlled by incorporating a 20 cm piece of 25 μ m i.d. fused silica (Polymicro Technologies, Phoenix, AZ) as a restrictor. All separations were performed using 100% SFC Grade CO₂ or 4.0% w/w methanol modified CO₂ (Scott Specialty Gases, Plumsteadville, PA). Unless otherwise specified, all propellant test mixtures were analyzed at 75 °C and an initial pressure of 100 atmospheres (atm) for 2 minutes, and then ramped to 350 atm in 15 minutes.

SFE. Supercritical fluid extractions of the propellants were performed using an Hewlett Packard 7680 SFE, previously discussed in greater detail (79). Propellant samples (300 mg) were placed in a 1.5 mL vessel and extracted at a flow rate of 2.0 mL/min for 45 minutes using 100% CO₂. A density of 0.90 g/mL at 50 C was maintained in the extraction vessel. The extracts were collected on an octadecyl silica trap at a temperature of 10 C and then rinsed with 1 mL of hexane at 40 C.

Chemicals. *N*-nitrosodiphenylamine (NNODPA), 2,6-dinitrotoluene (2,6-DNT) and diphenylamine (DPA) were purchased from Aldrich Chemical Co.(Milwaukee, WI). Nitrated derivatives of DPA and NNODPA were provided by Steroids Ltd. (Chicago, IL). The phthalate mixture was purchased from Supelco, Inc. (Bellefonte, PA). Nitroglycerin samples and single base propellants were provided by the Naval Ordnance Station (Indian Head, MD) and Olin Winchester Corp. (St. Marks, FL). All samples were prepared in HPLC grade methylene chloride (Aldrich Chemical Co.).

Thermospray MS. A Vestec Model 201 LC-MS Thermospray Interface was used to

integrate the the SFC with the mass spectrometer. The system was designed to provide thermospray ionization and mass selective detection for LC flow rates up to 1.5 mL per minute. It consists of two oil diffusion pumps operating at 300 L/s and 150 L/s respectively, both backed by a single mechanical pump. The two diffusion pumps differentially pump the vacuum manifold, the source, and the analyzer regions of the 800 amu quadrupole mass spectrometer. In addition to the two diffusion pumps, a single mechanical pump is also connected to the source directly opposite the sample inlet. Vaporized mobile phase (~99+ %) is removed primarily in the source by the aforementioned mechanical pump, while the heavier solute molecules travel through the ion aperture sampling cone to the mass analyzer. During LC-MS operation, sample ions are produced in the source from a mobile phase aerosol containing a volatile buffer (80). The sampled ions typically yield MW information in the form of positive or negative adducts of the buffer species (i.e. ammonium acetate) being used in the chromatographic mobile phase.

For use with a supercritical fluid mobile phase, the system underwent only minor modifications. The 60cm x 100um i.d. stainless steel capillary provided with the LC vaporizer probe was too long and narrow to accomodate fused silica restrictors. It was subsequently replaced with shorter and wider piece of tubing. This tubing was brazed flush with the tip of the original probe (Figure 32) and liberal amounts of high temperature adhesive were used to increase the thermal mass near the end of the probe housing. At the rear end of stainless steel capillary the necessary fittings were added so that a fused silica restrictor could be placed in the tubing, maneuvered into place flush with the end of the probe tip, and tightened into position with a vacuum tight ferrule arrangement. Very localized heating could be delivered to the restrictor end via the thermospray tip heater (Figure 33). The interface could be switched back to LC-MS

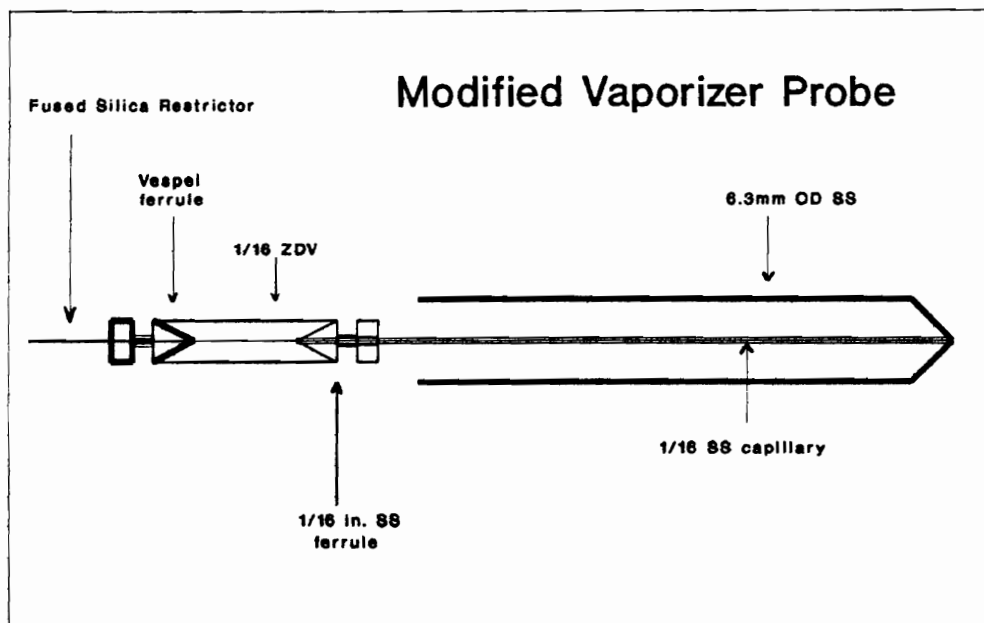


Figure 32. LC Thermospray vaporizer probe modified for SFC restrictors.

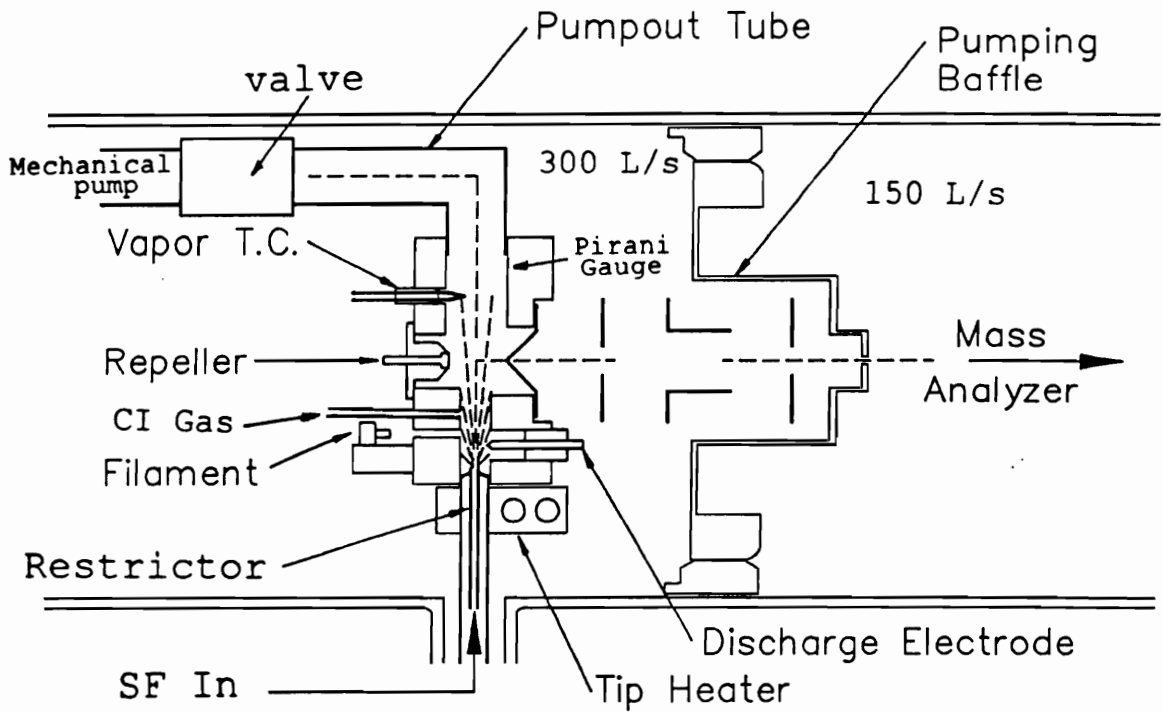


Figure 33. Schematic showing the thermospray interface, including modifications for SFC (CI gas line, pirani gauge in source, needle valve on vapor pump line and modified vaporizer probe).

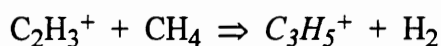
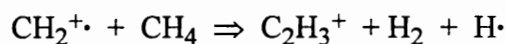
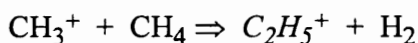
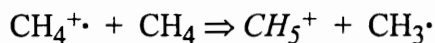
operation by merely replacing the modified probe with the conventional TS probe. Additionally, the source was ordered from the manufacturer with a 1/16" o.d. piece of tubing entering the source block near the restrictor exit - to be used as an inlet for chemical ionization reagent gases. A pirana gauge (Edwards, Wilmington, MA) and Whitey Model 45F8-A valve (Highland Heights, OH) placed between the source and the vaporizer pump allowed source pressures to be monitored and vaporizer pumping speeds to be reduced. High purity methane (Scott Specialty Gases, Plumsteadville, PA) was delivered into the source through a Nupro SS1 needle valve (SGE, Inc., Austin, TX). Perfluorotributylamine (Scientific Instrument Services, Inc., Ringoes, NJ) was used for manually tuning the mass spectrometer in the methane PCI mode. Data were acquired and processed with a Teknivent (St. Louis, MO) Vector/One Workstation.

Results and Discussion

Conventional EI ionization requires ion source pressures in the order of 10^{-5} torr to eliminate ion-molecule interactions. These high vacuums are unattainable after direct introduction of the decompressed packed column mobile phase into the source. Thus, an alternative means of ionization must be used. In our work with the thermospray interface for the study of energetic material extracts we used both positive (PCI) and negative (NCI) chemical ionization, thereby enabling analyte ions to be formed at high (> 1 torr) ion source pressures.

For work in the positive ion mode, methane was used as the CI reagent gas. The methane was introduced through the CI reagent gas line and was maintained at a pressure of 1 torr in the source. When methane is bombarded by electrons in such a high pressure environment, short-lived positively charged radicals are produced (81). These primary ions (shown in bold type) react with other methane molecules through ion-molecule

interactions to generate the secondary reagent gas ions as shown below. The ions of CH_5^+ (m/z 17) and C_2H_5^+ (m/z 29) constitute approximately 90% of the ion current. When these reagent ions come



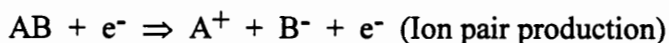
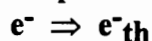
into contact with an analyte molecule with a lower proton affinity (PA) than themselves, proton transfer or electrophilic addition can take place. Total energy transfer during this process does not exceed 5 eV (82) which is less than half the energy involved during conventional electron impact ionization. Consequently, PCI with methane is a relatively "soft" ionization technique that normally produces stable, even-electron molecular ions of high intensity with only minor fragmentation.

Since CH_5^+ is a very strong Bronsted acid, it reacts with most organic molecules by proton transfer, generating an MH^+ ion. The reaction with CH_5^+ can also be sufficiently exothermic to induce some fragmentation. Additionally, C_2H_5^+ can react with analyte molecules by electrophilic addition to produce $(\text{M}+\text{C}_2\text{H}_5)^+$ ions with a m/e of $\text{M}+29$. Since it is a weaker Bronsted acid than CH_5^+ it creates fewer fragments. Another ion produced by electron bombardment of methane and constituting approximately 5 % of the total ion current, is C_3H_5^+ . It generally forms adducts of low intensity at $\text{M}+41$.

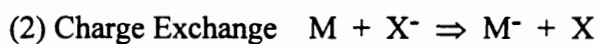
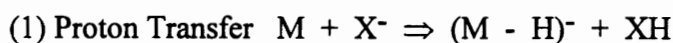
The thermospray interface was also used in this study to monitor negative ions generated in the ion source following SFC. This technique requires that a reagent gas be

used to provide both thermal electrons and collisional deactivation of the inherently unstable molecular anions (83). Since CO₂ is known to be a good moderating gas for NCI, the opportunity for it to be used as both the mobile phase during chromatography and the CI reagent gas once it exits the restrictor in the MS source is attractive. Once in the source, negative ions can be generated by electron attachment between the sample molecules and thermalized (e⁻_{th}) electrons, or by ion-molecule reactions whereby the negatively charged reagent gas ions react with neutral analyte molecules. The general classes of reactions that can take place during NCI by either direct electron capture or ion-molecule reactions (82) are shown below. In our work with energetic materials, most of the spectra

Electron Capture Processes



Ion Molecule Reactions



observed when using mobile phase CO₂ as the CI gas involve electron capture or possibly charge exchange processes with some fragmentation.

The flow rates emanating from packed columns are very high compared to those of capillary SFC. Thus, we wanted to determine the effect of large CO₂ partial pressures

on the methane reagent gas (RG) spectrum since even small amounts of additive are known to have a large effect on the methane RG spectrum (81). Preliminary studies indicated that the RG spectra varied considerably as a result of changing the partial pressure of CO₂, as would occur during normal SFC pressure programming. The spectrum of only methane in the source at a pressure of 1 torr and a temperature of 140 °C generated the expected CH₄-RG spectrum with ions at m/z 17, m/z 29 and m/z 41 (Figure 34). Figure 35a illustrates the effect of introducing mobile phase CO₂ into the source with the methane already present at a pressure of 1 torr. At a typical initial pump pressure of 100 atm, the SFC flow rate was approximately 100 uL/min (e.g. fixed restrictor) and the resulting CO₂ partial pressure in the source was 0.2 torr. All three important methane reagent gas ions (CH₅⁺ at m/z 17, C₂H₅⁺ at m/z 29 and C₃H₅⁺ at m/z 41) are present in the ion source, as well as the protonated monomer and dimer of CO₂ at m/e 45 and m/e 89 respectively. After the pump was ramped to 400 atm, as is routinely done during SFC, the CO₂ partial pressure was increased to 0.6 torr and the resulting methane reagent gas spectrum (Figure 35b) showed only C₂H₅⁺ of the original three methane RG ions. The protonated dimer of CO₂ at m/e 89 dominated the RG spectrum. Thus, it would appear that high concentrations of CO₂ in the source as a result of the high packed column SFC flow rates, significantly reduced the number of methane reagent ions available for PCI. Figure 35c shows the methane RG spectrum, again at an SFC pump pressure of 400 atm, but with the thermospray source temperature now raised to 315 °C. Again, the protonated dimer of CO₂ formed the base peak, but the three methane reagent gas ions have reappeared and account for a much greater percentage of the total ion current than they did at 400 atm and the lower source temperature (140 °C). Figures 36a-b and 37a-b illustrate the effect of temperature on the RG spectrum at four different pressures spanning the normal range of an SFC pressure program. The general trend was

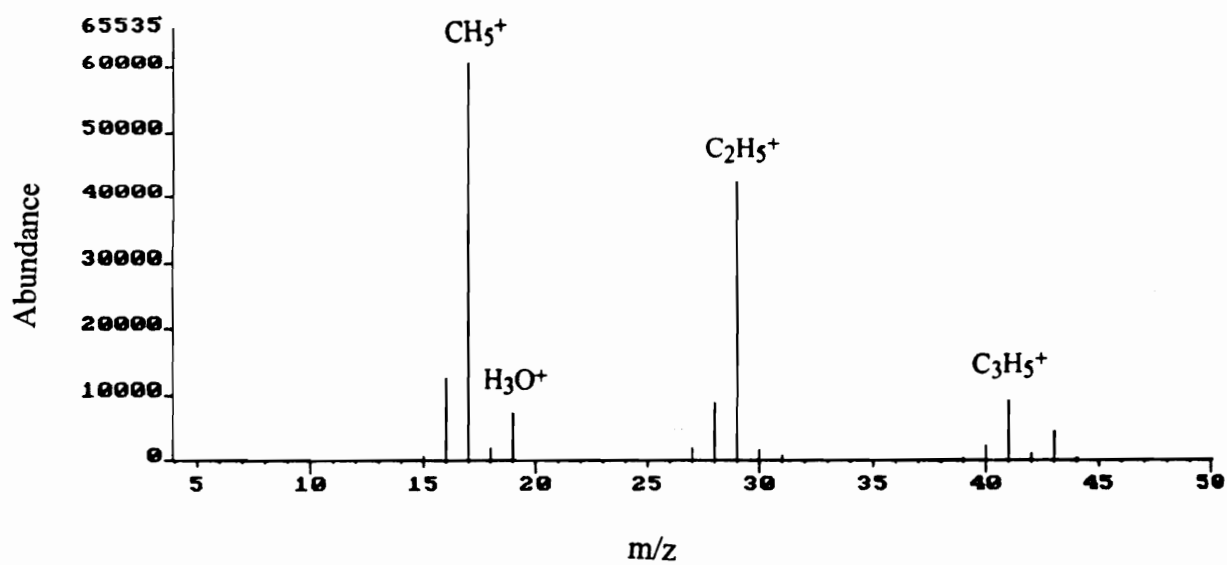


Figure 34. Pure CH₄ reagent gas spectrum from the modified thermospray source with the discharge electrode on.

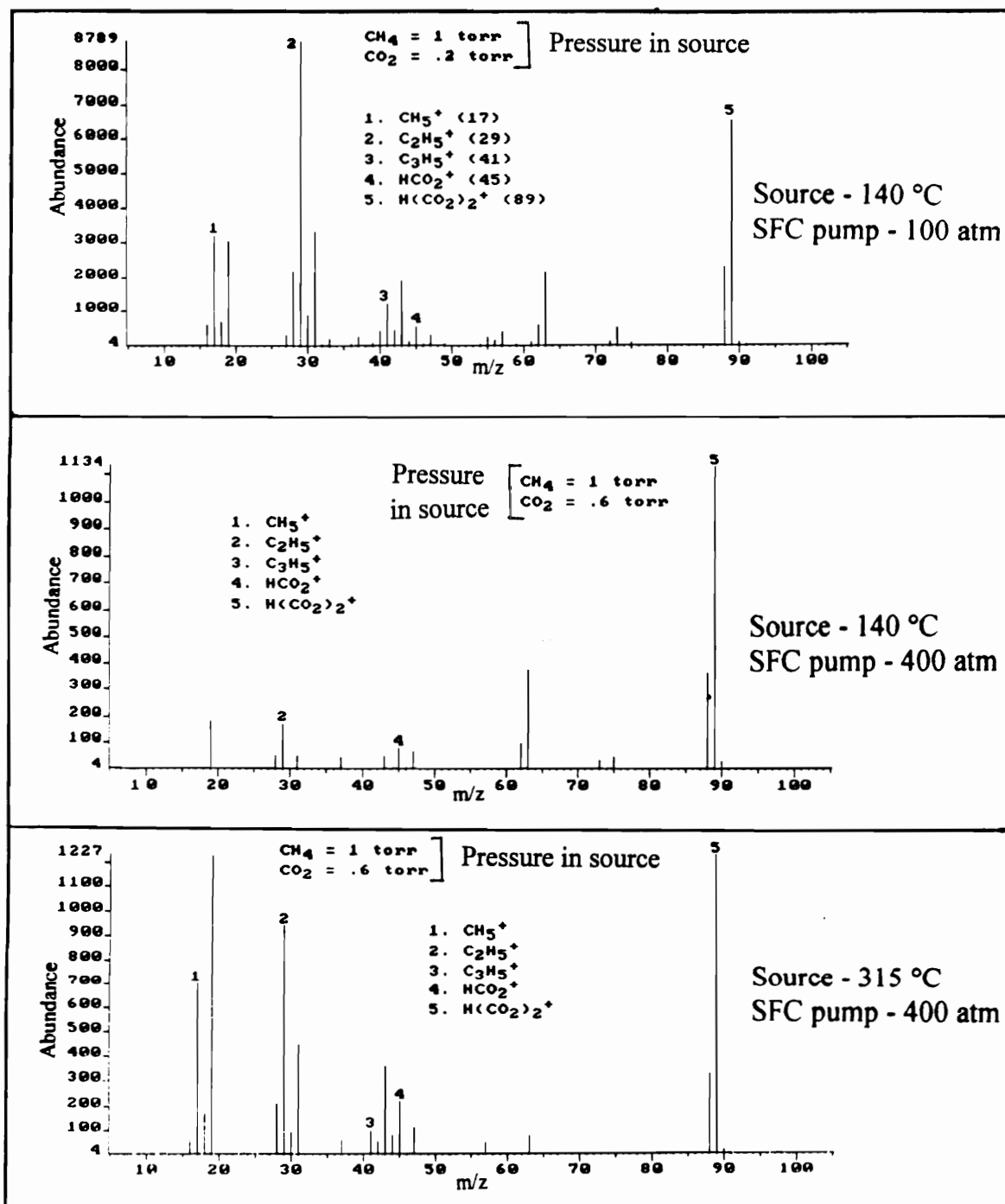


Figure 35 a-c. The methane PCI background spectra seen under conditions typical of the beginning and the end of an SFC pressure program at a relatively low source temperature of 140 °C - and at high pressure (400 atm) and a source temperature of 315 °C.

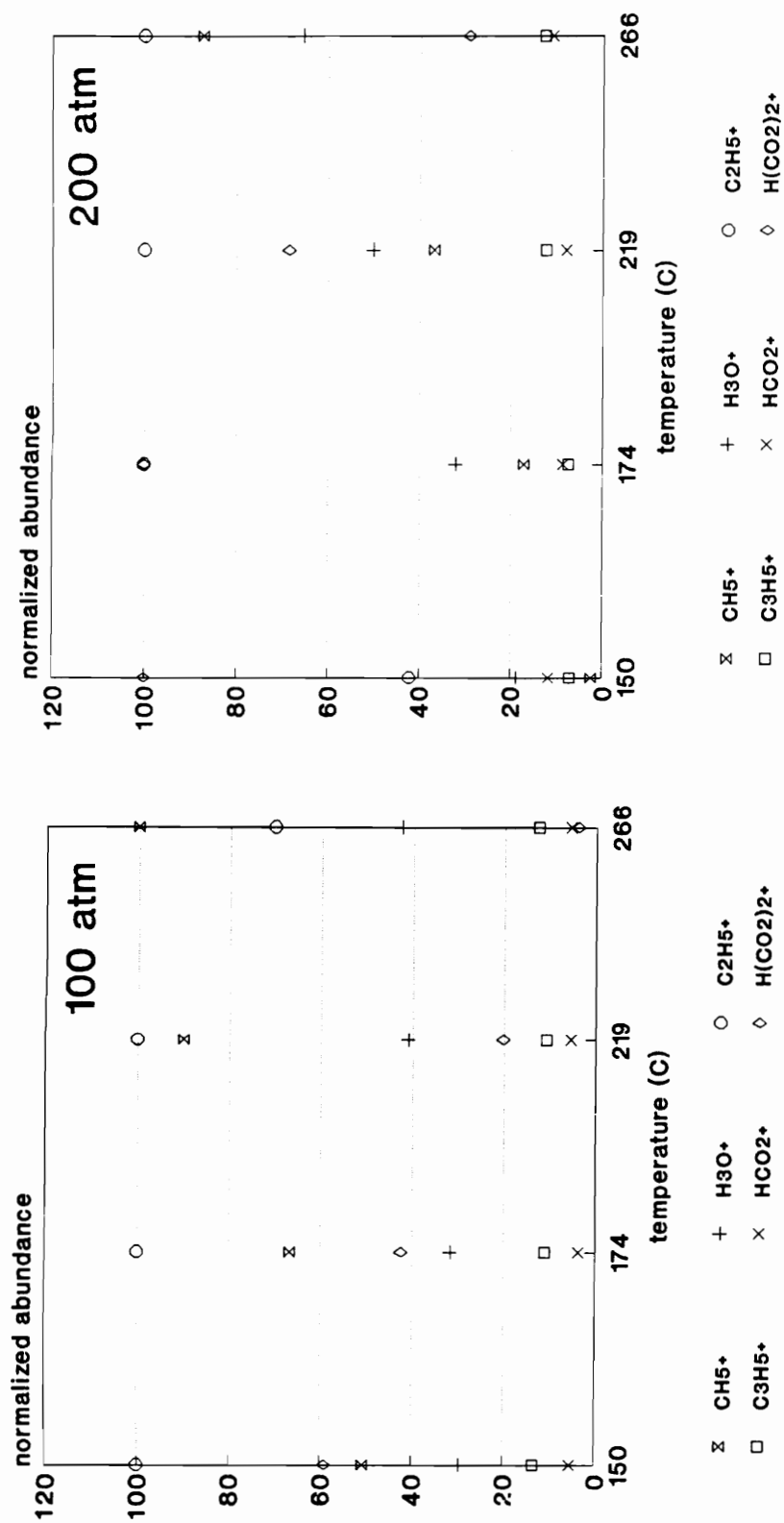


Figure 36 a-b. Normalized abundance of reagent gas ions plotted as a function of source temperature with SFC pump at 100 atm and 200 atm.

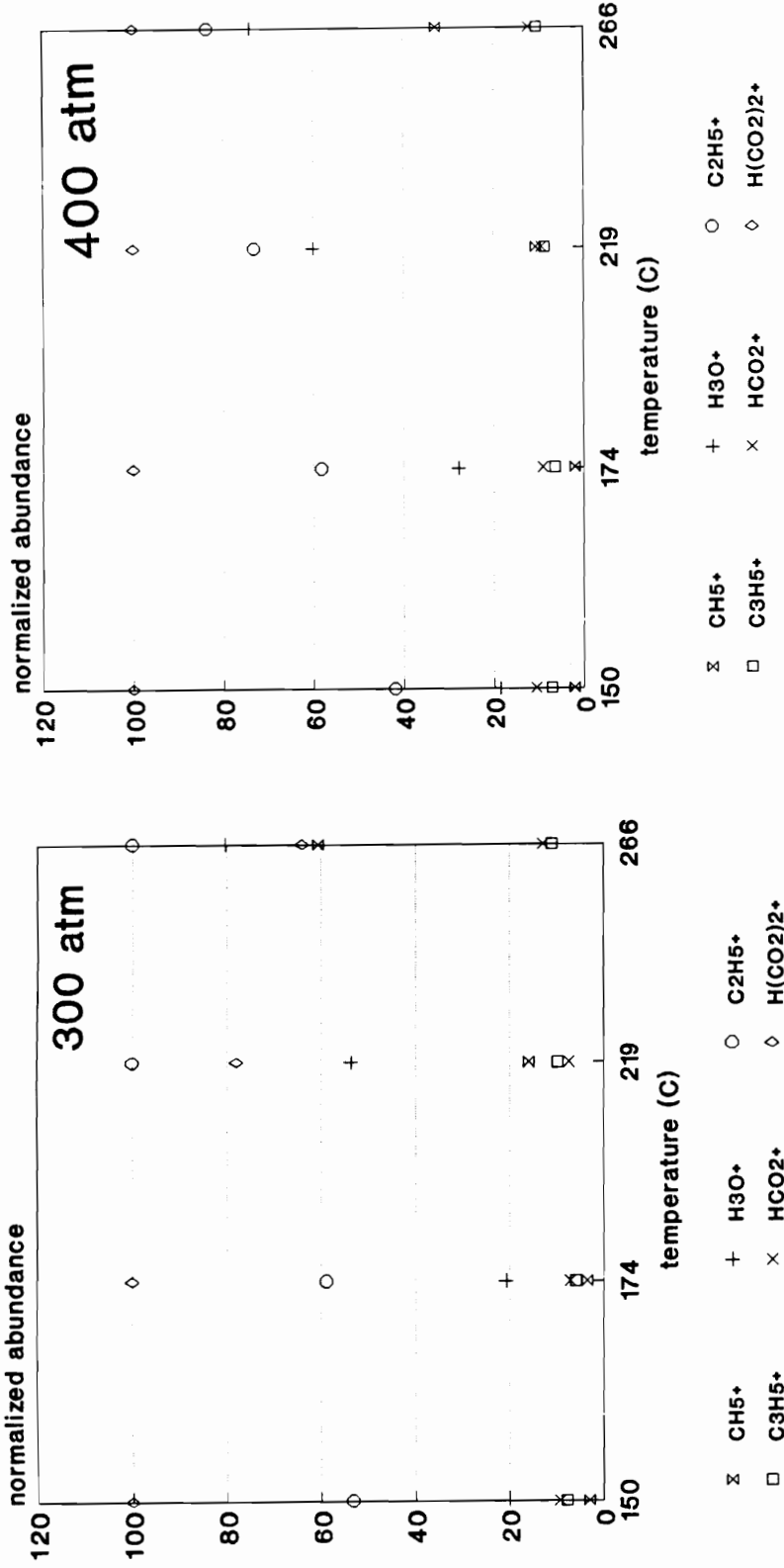


Figure 37 a-b. Normalized abundance of reagent gas ions plotted as a function of source temperature with SFC pump at 300 atm and 400 atm.

for CH_5^+ and C_2H_5^+ to increase in relative abundance as the temperature increased while the C_3H_5^+ ion was unaffected by increasing temperature at any of the pressures studied. The data clearly indicated that in the mixed reagent gas system of $\text{CO}_2 + \text{CH}_4$, higher source temperatures resulted in higher relative concentrations of methane RG ions. Thus, operating the source temperature at the highest possible value allowable for the sample in question, might provide better methane PCI performance when the SFC is delivering high partial pressures of mobile phase CO_2 into the ion source. Indeed, it was found, that at least in the case of DPA, an elevated source temperature at constant pressure (200 atm) resulted in enhanced signal (Figure 38). However, there could be other factors contributing to improved PCI signal at higher temperatures in addition to a greater abundance of methane reagent ions.

Since it had been determined that source temperature influenced the nature of the methane/ CO_2 ion profile in the source, a propellant test mix consisting of DPA, 2,6-DNT, 2-NDPA and 4NDPA was analyzed at source block temperatures of 140 °C and 320 °C. Figure 39 shows the TIC and individual methane PCI spectra for the four compounds present in the test mixture at a temperature of 140 °C. The only peaks present in the spectra of 2,6-DNT and 4-NDPA were the protonated molecular ions at m/z 183 and 215 respectively. At this temperature the base peak in the 2-NDPA spectrum was the M-16 peak at m/z 199. When the source temperature was increased to 320 °C (Figure 40), this fragment was replaced by the molecular ion. This was opposite to what would be expected to occur in the case of thermally induced fragmentation. In Figure 39 (140 °C), the methane PCI spectrum for DPA exhibited a small peak at m/z 214 as a result of adduct formation with HCO_2^+ in addition to the molecular ion at m/z 170. The low intensity HCO_2 adduct at 214 in the PCI spectrum of DPA was found to disappear at 320 °C (Figure 40). The $[\text{M-O}]\text{H}^+$ peak at m/z 199 for 2-NDPA at 140 °C might reflect an

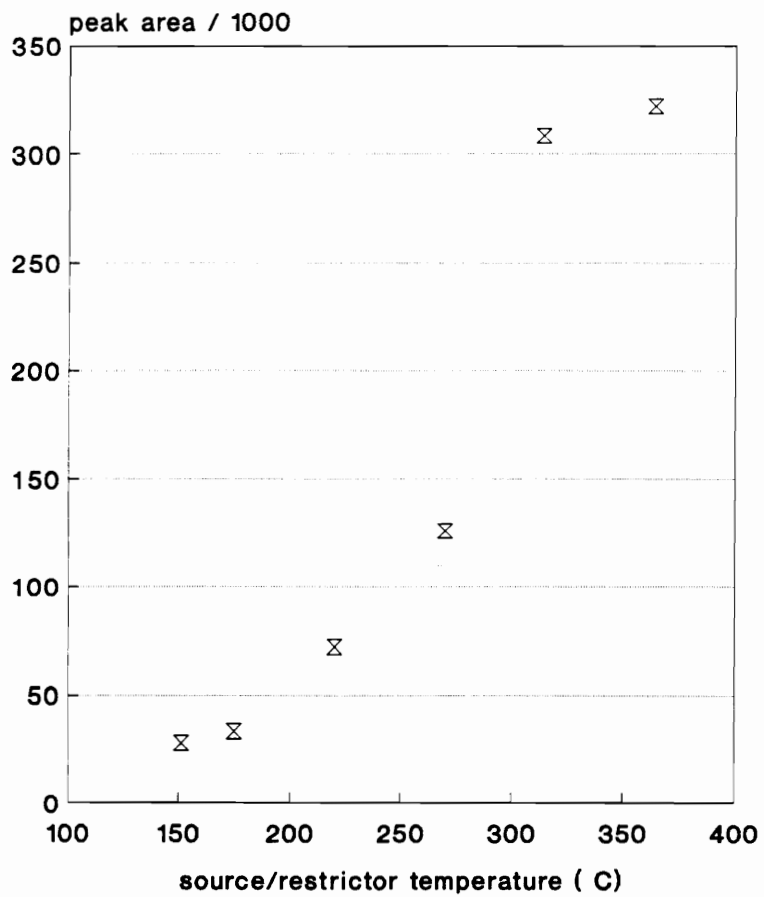


Figure 38. DPA peak area under the TIC trace plotted as function of source/restrictor temperature.

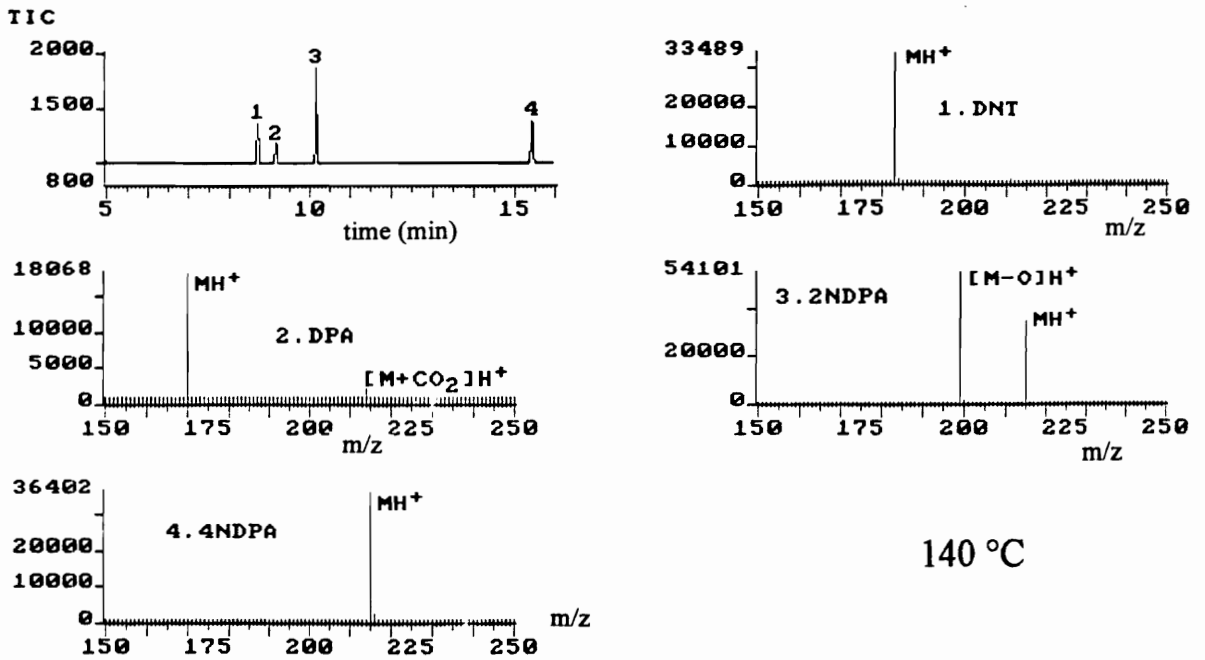


Figure 39. The TIC and SFC-methane PCI mass spectra of the propellant test mixture analyzed at 140 °C.

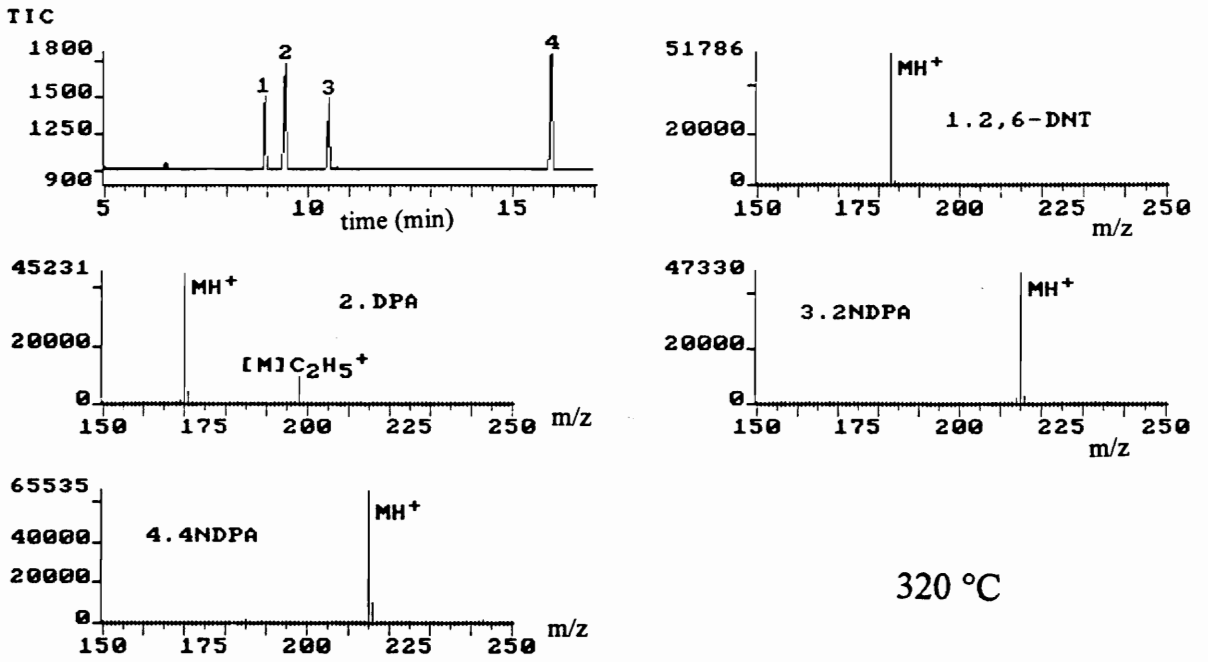


Figure 40. The TIC and SFC-methane PCI mass spectra of the propellant test mixture analyzed at 320 °C.

analyte interaction with negatively charged CO₂ clusters which are known from NCI studies (*vide infra*) to be present in high concentrations at this low source temperature. At a source temperature of 320 °C (Figure 40), the base peak for every compound in the propellant test mix was the protonated molecular ion. DPA was seen to have a small peak at m/z 198 from adduct formation with C₂H₅⁺. Thus, overall there appeared to be only minor changes in the spectra of the test mix compounds over the range of ion source temperatures studied, even though the abundance of reagent gas ions varied substantially. This result was not unexpected considering the very low proton affinity of CO₂ relative to the analytes. The total ion current traces also showed no appreciable band broadening at the lower source temperatures as was reported for capillary SFC-MS (84). Apparently, even at low restrictor tip temperatures, the mobile phase exit velocity using the 2mm i.d. packed column provided adequate analyte delivery to the ion exit aperture.

Detailed detection limit studies are not reported here, but in general, sensitivities in the methane PCI mode required nanogram level injections which could be a result of high source pressure and "quenching" from CO₂. However, Wilkes et al. (85) reported compound dependent detection limits much lower (pg range) with an instrument configuration very similar to the one used here. For example, they reported a full scan mass limit of detection of 60 pg for 2NDPA. In our studies, PCI spectra of the four component test mix were free of background noise and consisted primarily of protonated molecular ions with only minor fragmentation and/or adduct formation. However, others have reported on the use of collision induced fragmentation or the discharge electrode to create fragments for greater structure elucidation in SFC-CI-MS (86,87).

The same test mix with CO₂, both neat and in combination with methane was used for electron capture NCI. The discharge electrode at a potential of 1000 eV provided ionizing electrons. The source pressure and temperature were varied and the

resulting NCI reagent gas spectra were evaluated. In the NCI mode with only CO₂, background ions were observed at m/z 45 (HCO₂⁻), m/z 60 (CO₃⁻) and m/z 75 (?). Also, clusters were found to occur at higher MWs (m/z 160, m/z 172 and m/z 176) whose intensity at any temperature always increased with increased partial pressure of CO₂ in the ion source. This pressure dependent background noise was excessive at thermospray source temperatures below 200 °C, but at higher temperatures the clusters were significantly reduced, presumably due to their thermally induced dissociation. The pressure dependence of the NCI background accounts for the baseline rise seen in the TIC profile (SFC-NCI-MS) of the propellant test mix in Figure 41. As was the case with methane PCI, there was no significant chromatographic band broadening with the source at lower temperatures as previously reported for capillary SFC-MS (84). The volumetric flow escaping the restrictor even at low temperatures was apparently adequate to carry solute particles within range of the sampling cone. The 2,6-DNT standard used in the test mixture had a small peak that eluted approximately one minute later. This small impurity had the same spectrum and retention time as 2,4-DNT. It (apparently 2,4-DNT) also coeluted with DPA interfering with its relatively weak response in the negative ion mode. The failure of DPA to generate a strong signal was not unexpected since it contains no strong electron attracting group.

Figures 42-44 show the CO₂ buffered NCI spectra for 2,6-DNT, 2NDPA and 4NDPA collected at a source temperature of 366 °C. In all three cases the base peak is the molecular anion. There is also a substantial peak at M-30 for 2,6-DNT which could result from the loss of an NO group (Figure 42) or reduction to the corresponding amine (82,88). Both 2-NDPA (Figure 43) and 4-NDPA (Figure 44) have peaks at M+14 (m/z 228) probably resulting from NO loss and subsequent nucleophilic addition of CO₂⁻ (32).

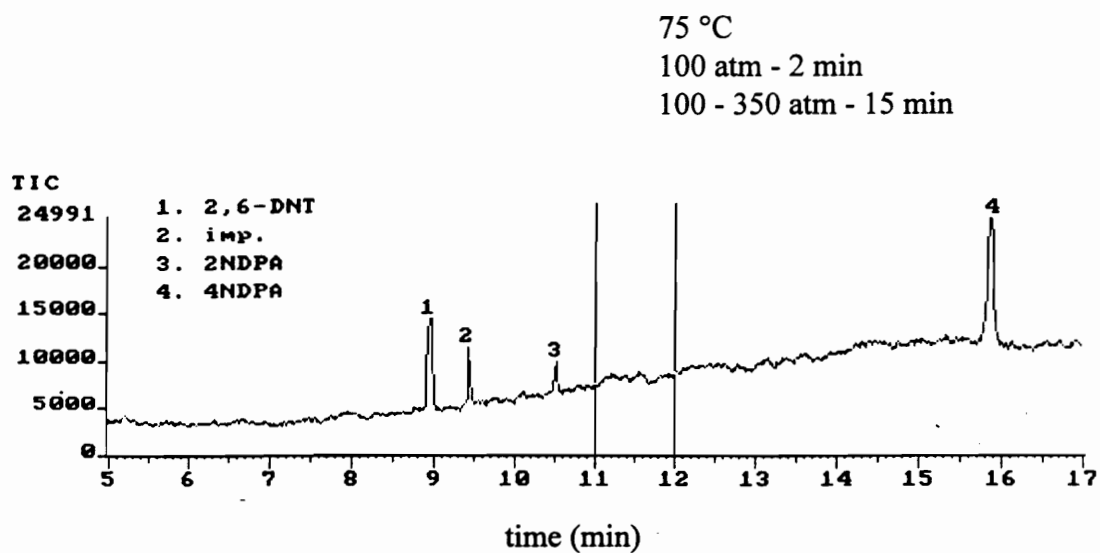


Figure 41. TIC of the SFC-CO₂-NCI separation of the propellant test mixture.

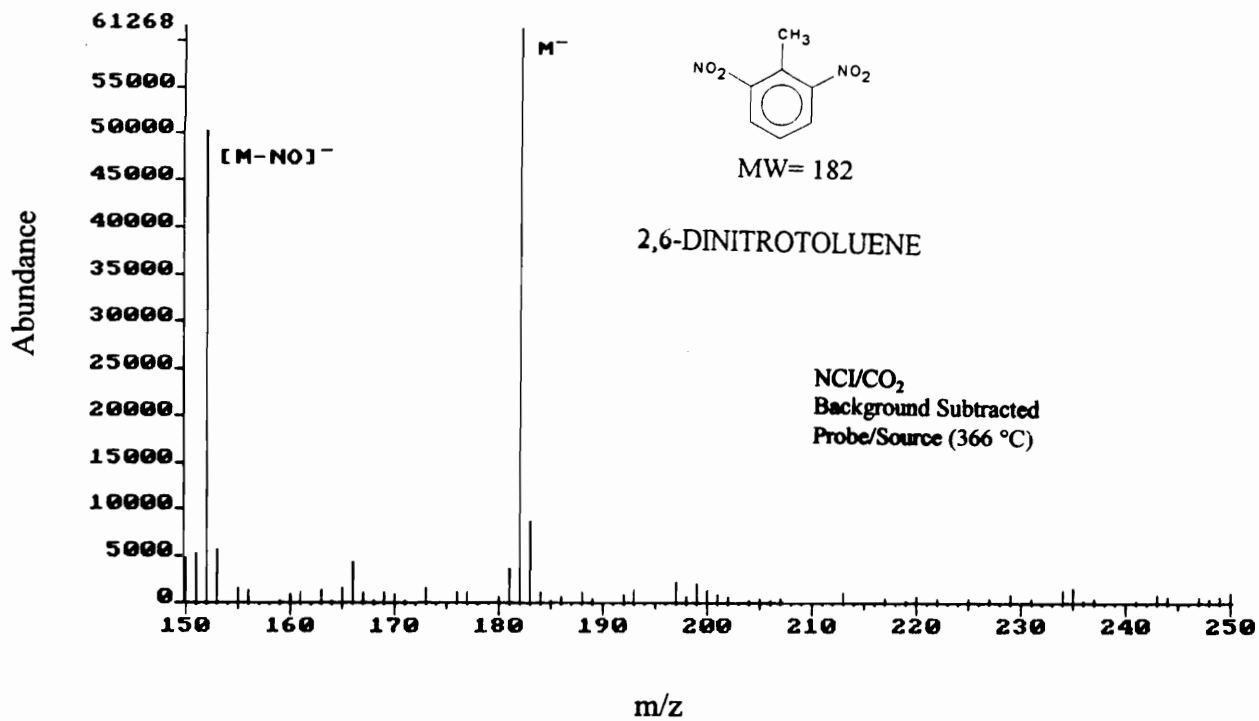


Figure 42. SFC-CO₂-NCI mass spectrum of 2,6-DNT.

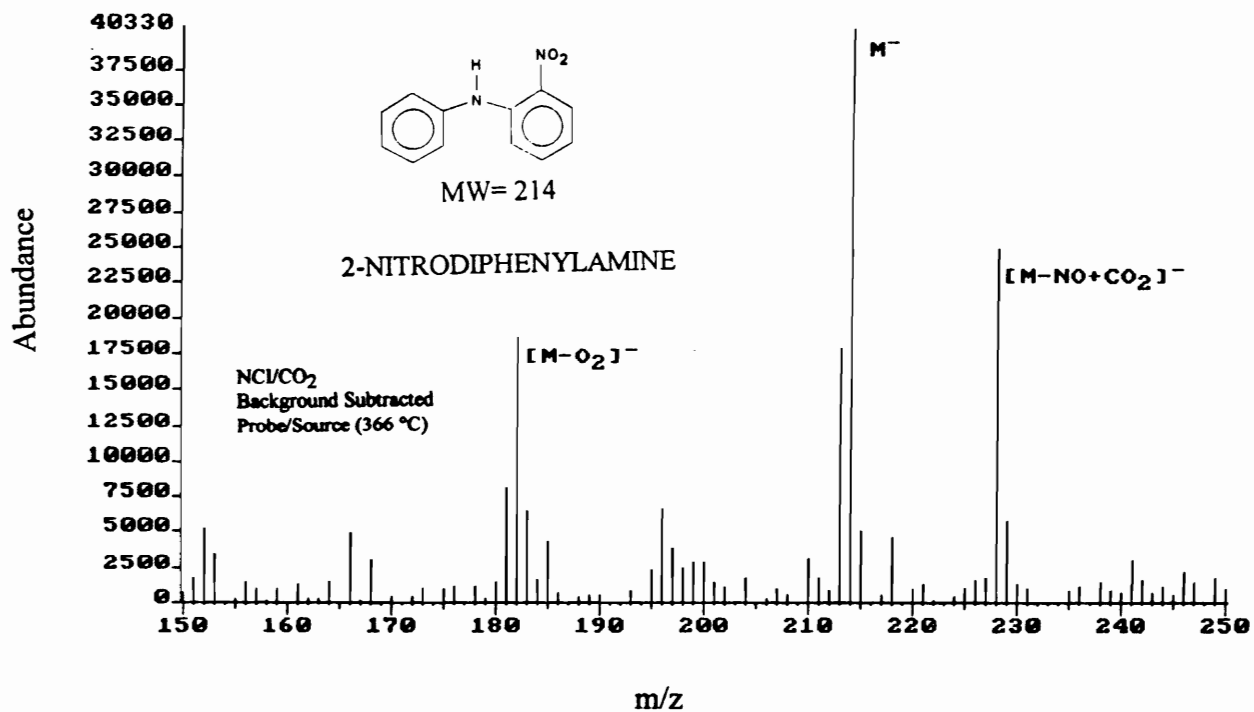


Figure 43. SFC-CO₂-NCI mass spectrum of 2-NDPA.

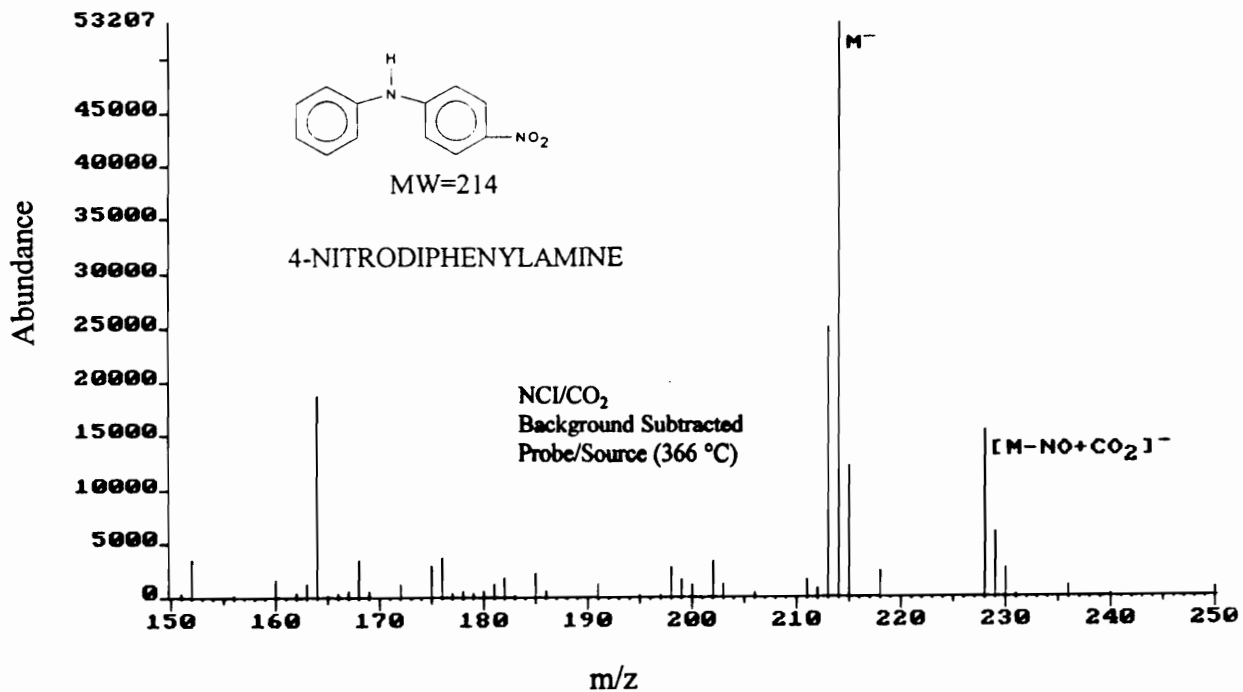


Figure 44. SFC-CO₂-NCI mass spectrum of 4-NDPA.

Sensitivity for the three nitrated compounds was considerably greater while operating under NCI conditions than during methane PCI. Figure 45 compares the test mix component peak areas evaluated under conditions of methane PCI, NCI with neat CO₂, and NCI with CO₂ and methane present at two different partial pressures (0.5 and 1.0 torr). Previous studies had indicated that sensitivity during capillary SFC-NCI-MS improved after the addition of small quantities of NH₃ or CH₄ reagent gas (84). However, we found that the greatest sensitivity for our test mix compounds during packed column SFC-NCI-MS occurred with neat CO₂. A 1 - 2 order of magnitude increase in peak area when the ionization method was changed from methane-PCI to neat CO₂ buffered NCI was realized. Unlike capillary SFC-MS there was no improvement in sensitivity when additional methane moderating gas was added to the source. This effect would seem to indicate that the quantity of CO₂ alone, delivered to the ion source from the 2mm i.d. packed column, is adequate to provide satisfactory NCI conditions in the thermospray source. However, during NCI, the presence of methane at 1 torr in the source resulted in less background interference. The additional gas apparently increased the dissociation of solvent clusters even at lower source temperatures. The response of DPA to changing NCI-RG gas conditions is difficult to ascertain due the coeluting 2,4-DNT. In the bar graph (Figure 45) the response is plotted as a combination of the impurity plus DPA.

The ion source/probe tip temperature was also evaluated as to its effect on signal response in the NCI mode. The propellant test mix was analyzed at five different source block temperatures ranging from 120 - 365 °C. Only mobile phase CO₂ entered the source - no additional methane moderating gas was added. Figure 46 shows a plot of the peak area for each of the test mix compounds plotted as a function of the source temperature they were acquired. For 2-NDPA and 4-NDPA, an optimum temperature

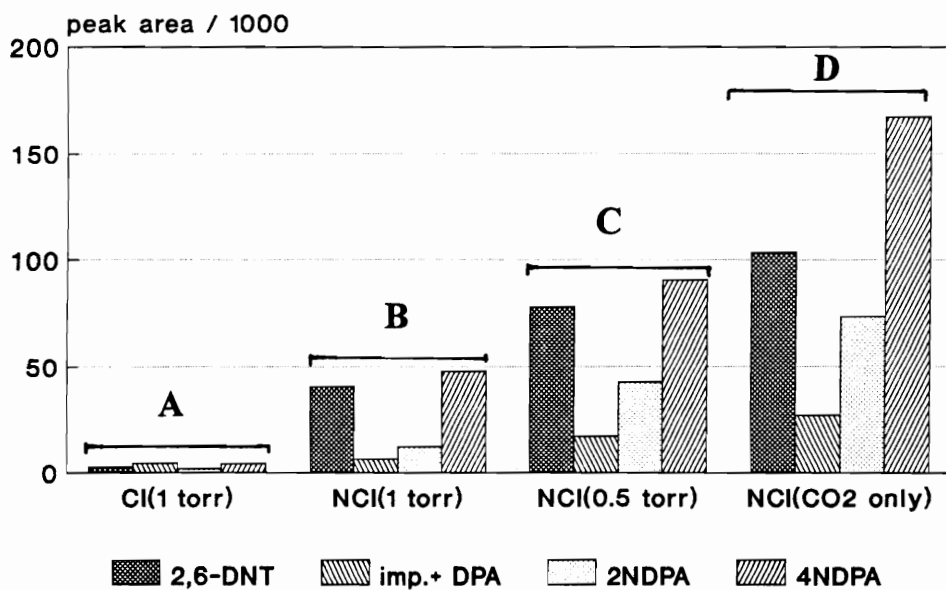


Figure 45. Peak area of each component in the test mixture plotted as a function of ionization conditions. (A) PCI with 1 torr of CH₄, (B) NCI with 1 torr of CH₄ also present in source, (C) NCI with 0.5 torr of CH₄, (D) NCI with only CO₂ in the source.

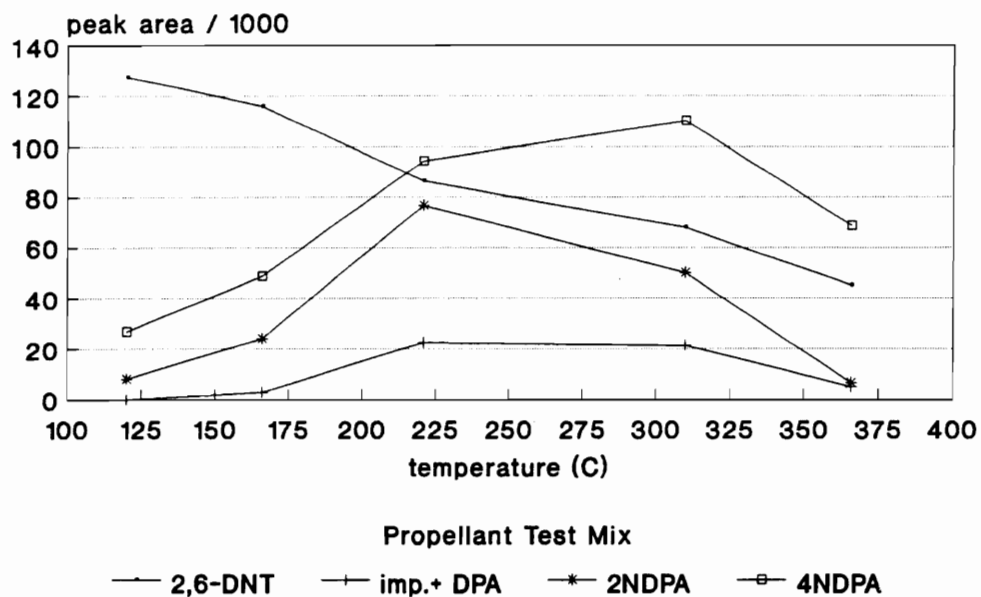


Figure 46. Peak area of each component in the test mixture plotted as a function of ion source / restrictor temperature under NCI conditions with neat CO₂.

was discovered for maximum peak area the peak area increased with temperature up to a maximum, at which point the peak area. For 2,6-DNT maximum sensitivity occurs at the lowest temperature studied. In the case of DPA, again the impurity interferes with its interpretation, but the combination of peak areas appear to follow the general trend. This phenomenon can be explained by volatility. Increasing restrictor/source temperature would generally allow for more efficient, cluster-free delivery of the analyte into the sampling region, however, increasing temperature also enhances ion volatility. For the least volatile of the analytes, 4-NDPA, this temperature of maximum sensitivity was shifted toward a higher temperature value than the less volatile components of the mixture. When CO₂ buffered NCI is used to analyze a compound with high electron affinity in combination with the optimum ion source temperature and selected ion monitoring, very good sensitivity can be achieved. Figure 47 shows a TIC trace for the SFC-NCI-MS analysis of 2,6-DNT. The TIC profile shows that by using only CO₂ buffered NCI at a low source temperature and selected ion monitoring for the base peak (m/z 182), a 400 femtogram injection for 2,6-DNT is observed with a S/N of 20:1. This increased sensitivity in NCI probably results from the high mobility of electrons in electron capture processes (88).

A common analytical problem encountered in propellant analysis is to identify stabilizer derivatives in extracts of propellants that might indicate greater age and/or instability for a particular lot of explosive (89). As was discussed in Chapter 4, many nitrocellulose (NC) based propellants are initially stabilized with DPA. As the propellant ages, the NC denitrates and the escaping NO₂ can further autocatalyze NC decomposition. The DPA stabilizer is thought to react with escaping NO_x to produce nitrated derivatives of DPA thus preventing any further interaction with the NC and subsequent autocatalysis. The primary decomposition product in the DPA stabilization

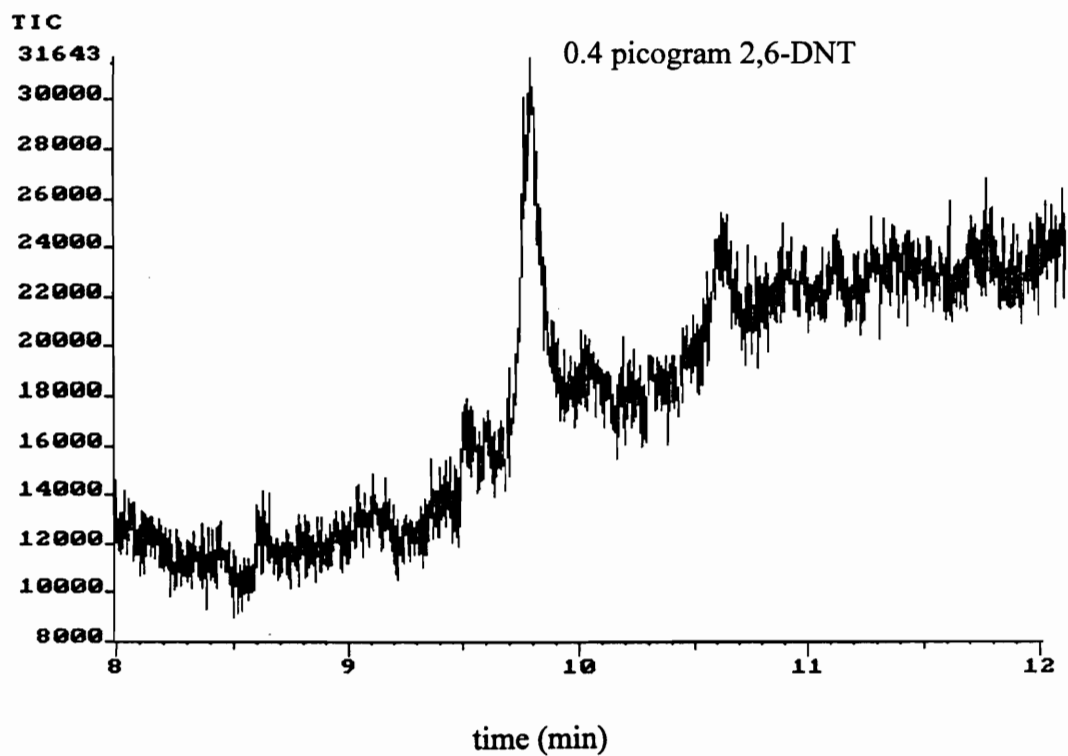


Figure 47. TIC of the neat CO₂ moderated SFC-NCI-MS of a 0.4 pg injection of 2,6-DNT. For maximum sensitivity the source temperature was lowered to 124 °C and single ion monitoring for the base peak at 182 was used resulting in a signal-to-noise of 20.

process is *N*-nitrosodiphenylamine (*NNODPA*). Further aging of the propellant leads to the formation of 2NDPA, 4NDPA and more highly nitrated derivatives of DPA. Figures 48 and 49 show the TIC and extracted ion current profiles (EICP) for a mixture of DPA and seven of its derivatives. The TIC (Figure 48) was extracted at the expected protonated molecular ion for each one of the stabilizer compounds. These extracted ion currents (Figure 49) indicate that target compound analysis of DPA derivatives could be easily achieved by monitoring the sample for the protonated molecular ion at the desired level of nitration (i.e. mono, di, tri, tetra, etc.)

A proposed scheme for the decomposition of DPA stabilized NC propellants involves several *N*-nitroso intermediates (53). Davidson (51) determined that *NNODPA* denitrosated back to the original DPA during gas chromatography, and previous work by this laboratory found that to also be the case for other nitrated *N*-nitrosodiphenylamines (90). It might be expected that SFC of these same compounds at comparatively low temperatures would allow their elution intact without any thermal denitrosation. Using the mass spectrometer under methane PCI conditions confirmed this expectation .

Budde et al. (91) found that during LC thermospray MS of *NNODPA*, the compound denitrosated in the hot region near the tip of the thermospray interface. They also determined that the resulting free radicals could abstract a hydrogen to form DPA, or could join with each other to produce tetraphenylhydrazine (TPH) with a MW of 336 (Figure 50). The protonated molecular ion of (TPH) at m/z 337 was considered diagnostic of the highly carcinogenic *NNODPA*. Since the restrictor tip during SFC is often operated at temperatures comparable to the vaporizer tip during LC-MS, we anticipated this protonated TPH ion during SFC-PCI-MS. Figures 51 and 52 shows the TIC and extracted ion current profiles for a mixture of *NNODPA* and three nitrated *N*-nitroso (*NNO*) compounds (*NNO*-2-NDPA, *NNO*-2,4'-diNDPA and *NNO*-4,4'-diNDPA).

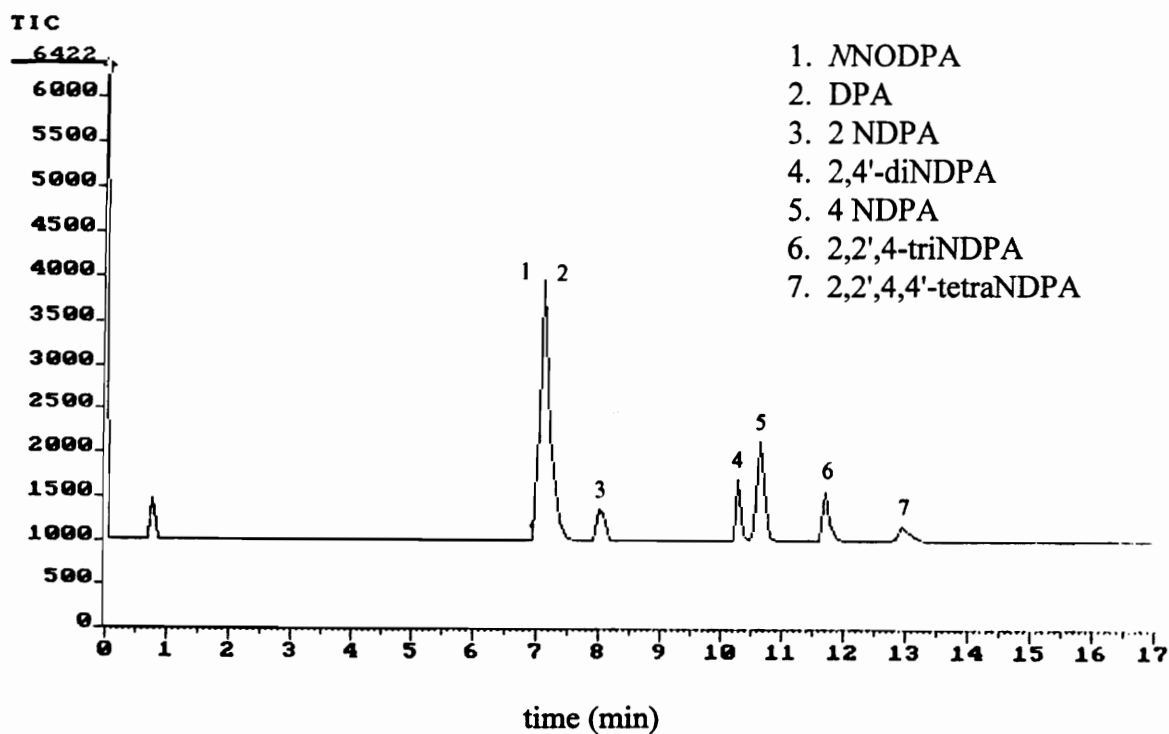


Figure 48. TIC of the SFC-CH₄-PCI-MS analysis of a synthetic mixture of DPA and its derivatives.

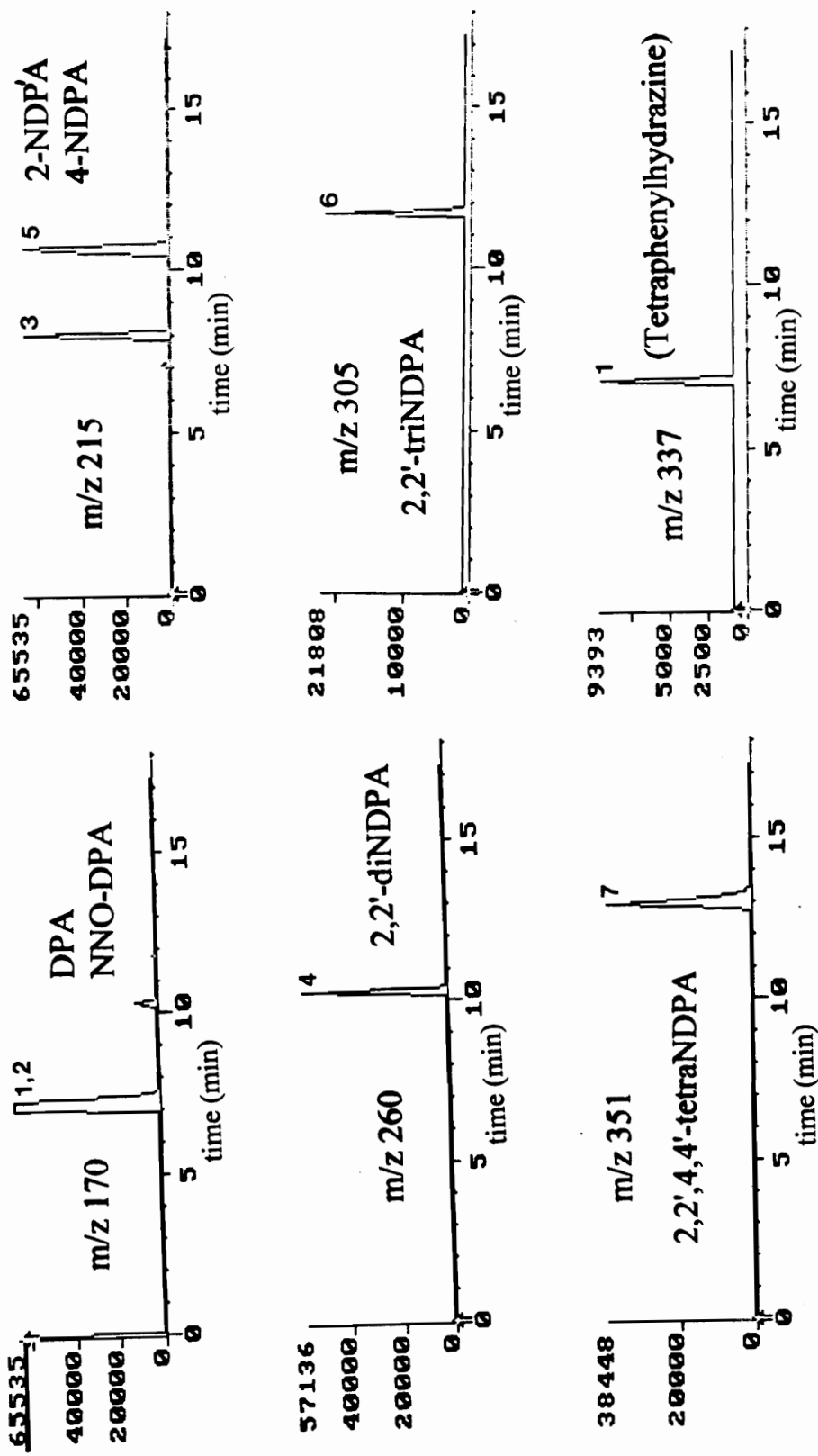


Figure 49. The TIC from Figure 48 extracted at m/z values of the expected protonated molecular ions. The total ion current at the selected m/z is plotted as a function of time.

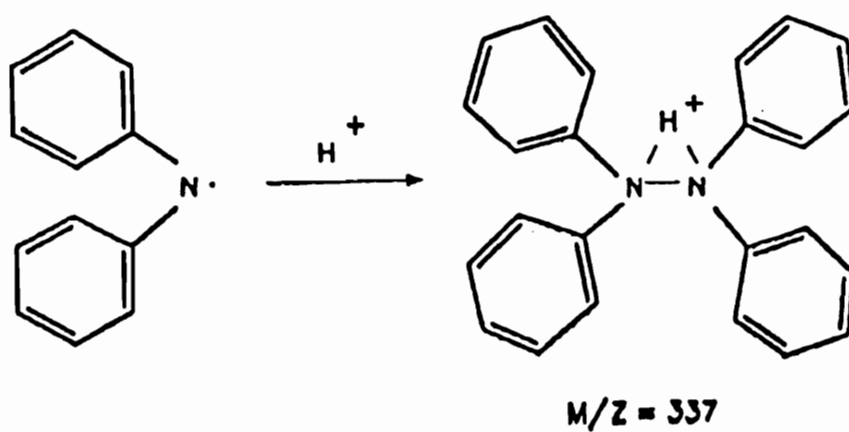
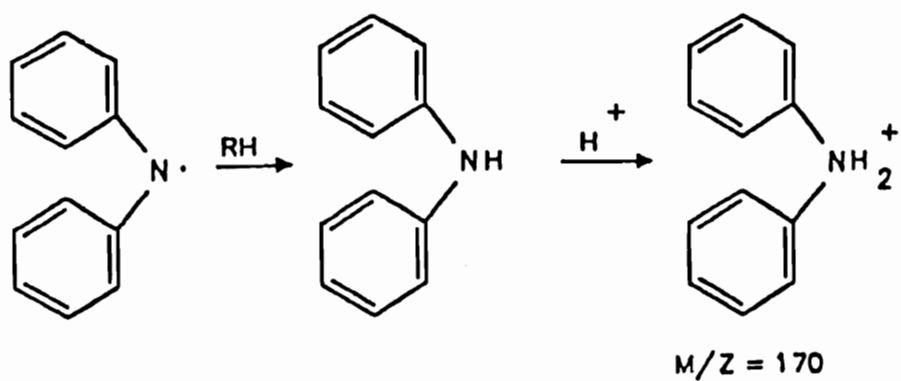
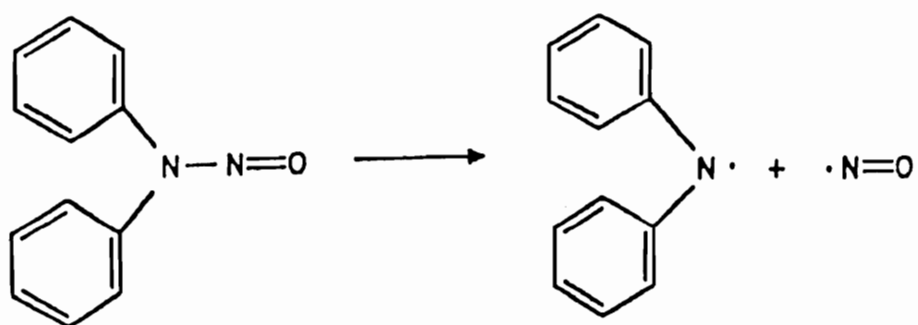


Figure 50. Rearrangement of NNODPA to DPA and tetraphenylhydrazine (91).

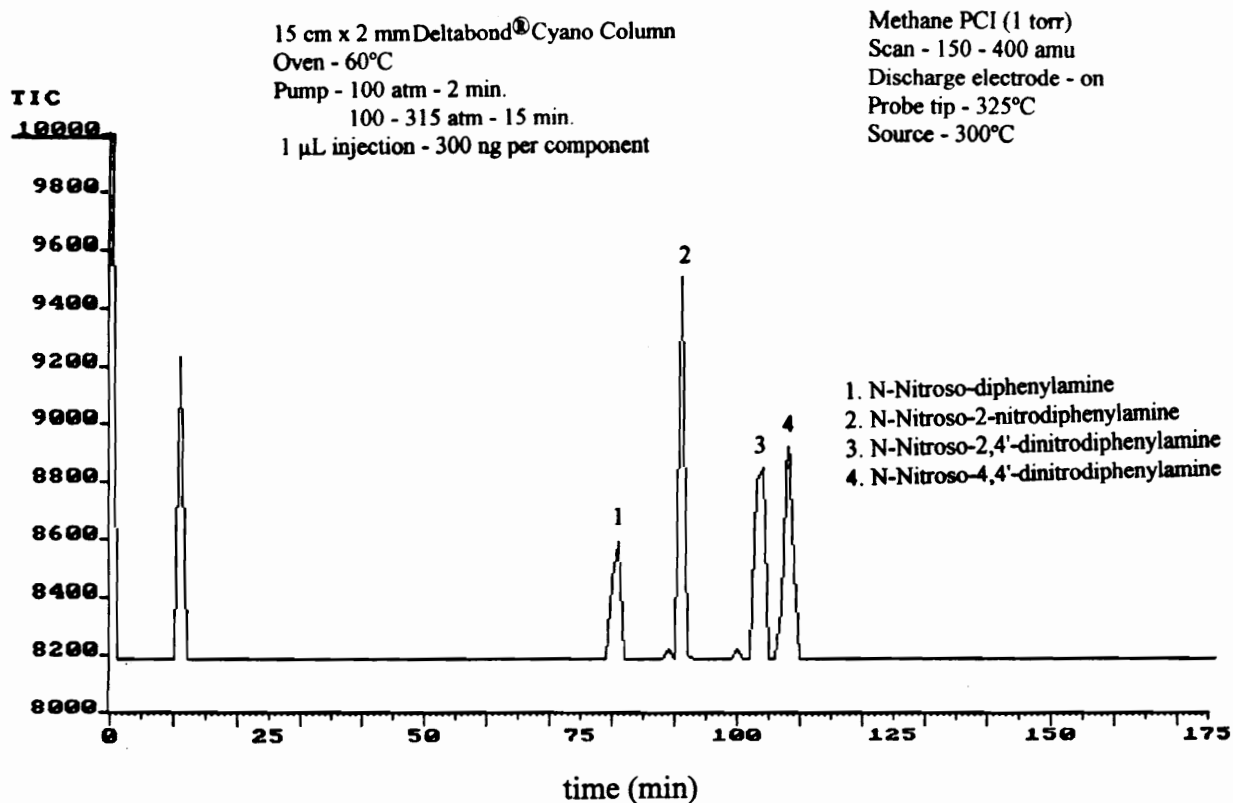


Figure 51. TIC of the SFC-CH₄-PCI-MS analysis of a mixture of *N*-nitroso compounds.

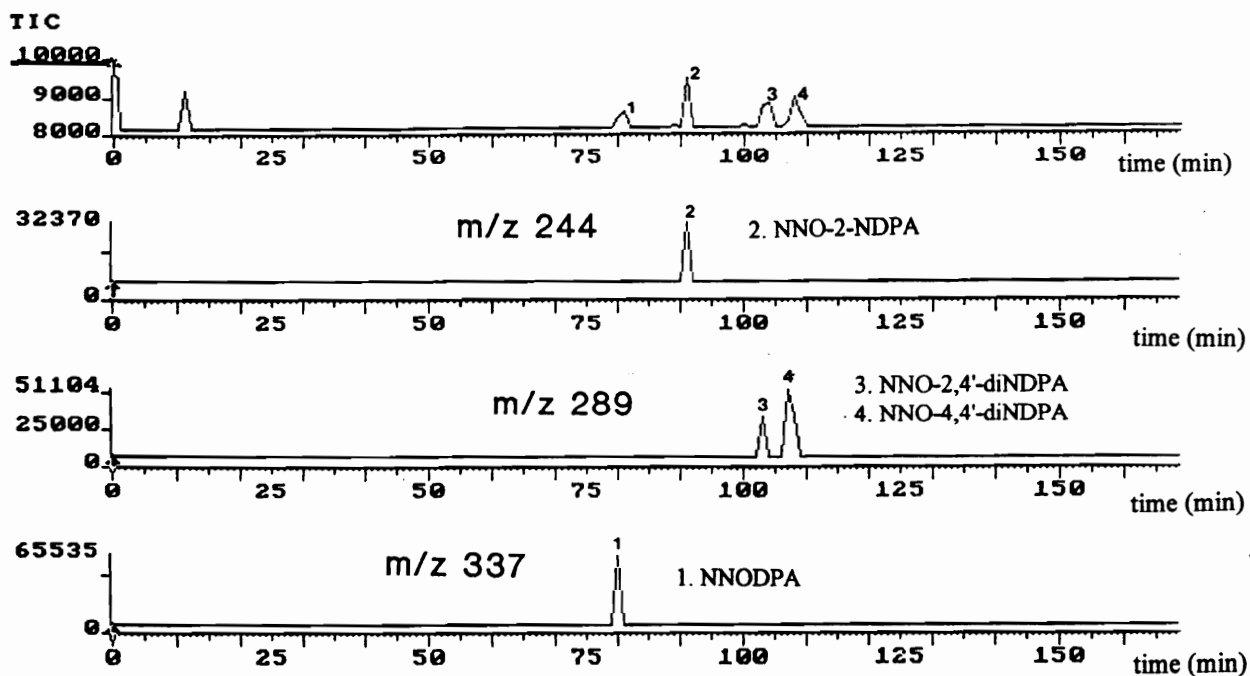


Figure 52. EICs for the protonated molecular ions of the mixture of nitrated *N*-nitrosodiphenylamines under methane PCI conditions.

The TIC was extracted for the expected protonated molecular ions of the three nitrated *NNO* compounds. For *MNODPA*, the TIC was extracted at m/z 337, representing protonated TPH. All four compounds were found to elute intact from the SFC using the 2mm packed column.

It was also possible, by operating the source and restrictor at comparatively lower temperatures (i.e. 200 °C), to generate the true protonated molecular ion for *MNODPA* at m/z 199. Figure 53 shows the TIC and resulting spectra for the SFC-methane PCI analysis of a mixture of DPA and *MNODPA*. The TIC shows that the two peaks of DPA and *MNODPA* are baseline resolved and exhibit spectra expected from their protonated molecular ions.

Two separate single base, DPA stabilized gun propellants were extracted by supercritical CO₂ in order to demonstrate the effect of long-term aging on stabilizer composition. One sample, considered relatively recent was manufactured in 1988; while the older sample was manufactured in 1943. Figure 54 shows the TIC trace originating from the SFC-PCI-MS analysis of a DPA stabilized NC gun propellant manufactured in 1988. Analysis of the extract using methane PCI and selected ion monitoring for the protonated molecular ions of the original stabilizer (e.g. DPA at m/z 170, and its primary decomposition product *MNODPA* at m/z 199) revealed the presence of both peaks in the extract. Both peaks were also present in the extract of the 1943 sample. Methane PCI was used to monitor for these two ions since they do not exhibit the high electron affinities needed for good sensitivity in NCI. However, when using CO₂ moderated NCI to scan for mono and di-nitrated decomposition products of DPA in the "recent" and "older" propellant extracts, an important difference could be seen. The presence of two peaks at m/z 214, (the molecular anions of 2-NDPA and 4-NDPA) as well as a peak at m/z 259 representing the molecular anion of a di-nitrated diphenylamine, were detected

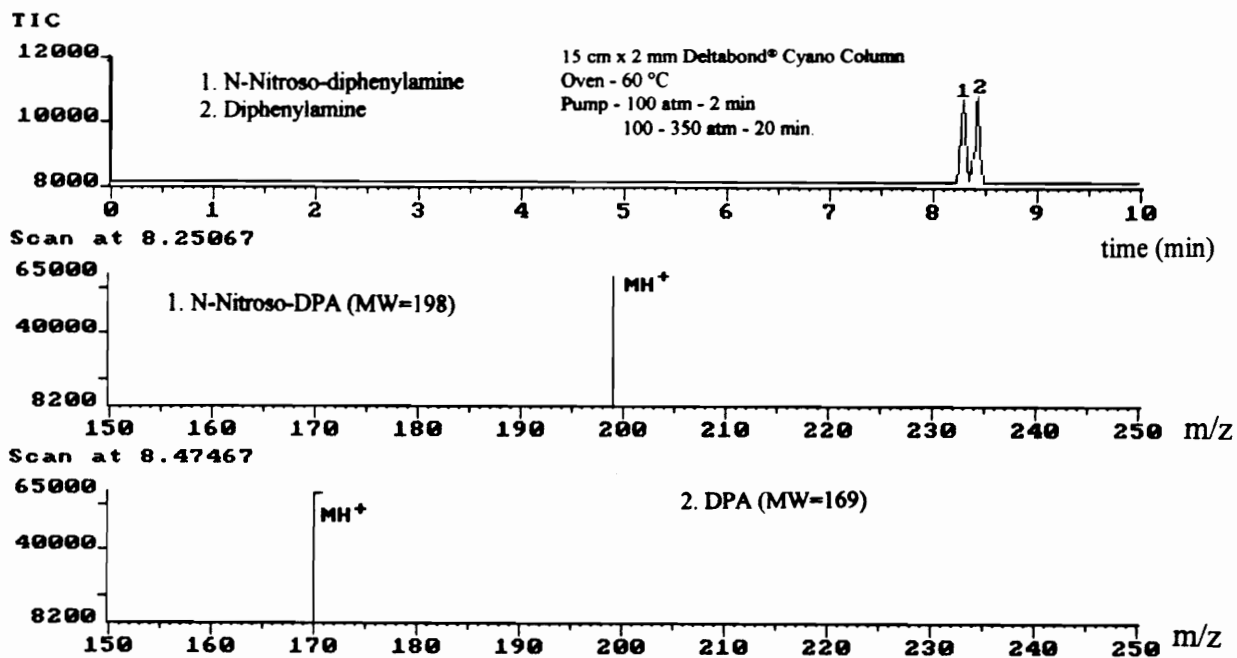


Figure 53. TIC and SFC methane PCI mass spectra of a mixture of DPA and NNODPA. The lower source/restrictor temperature (200 °C) allowed the protonated molecular ion of NNODPA to be identified.

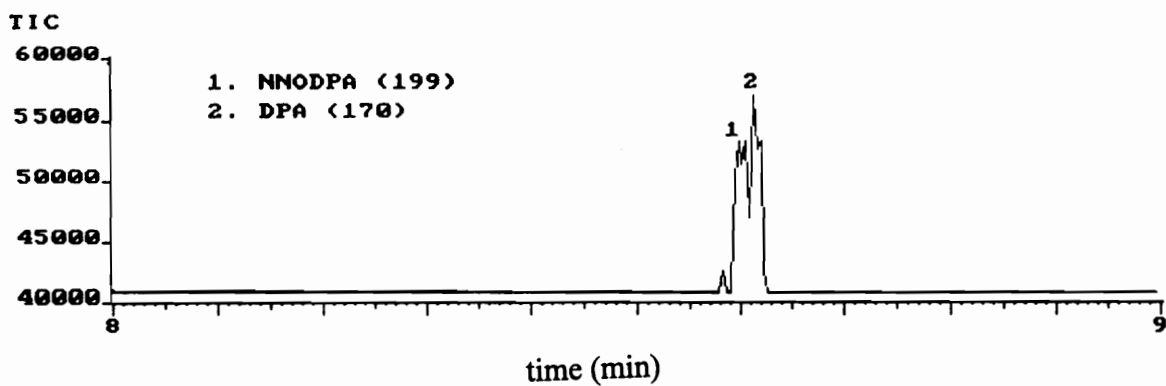


Figure 54. SFC methane PCI-MS of a supercritical fluid extract of a recently manufactured (1988) DPA-stabilized gun propellant. The extract was monitored for the protonated molecular ions of DPA and NNODPA.

in the 1943 sample (Figure 55) but not in the more recent (1988) extract. Thus, the selected ion current profiles (SICP)s of the two supercritical fluid extracts indicated a much higher degree of aging and potential instability for the 1943 manufactured propellant than the relatively new propellant manufactured in 1988. The determination of 2-NDPA in the 1943 extract is a very good example of target compound analysis. Recall that in the SFC-FID of this sample, a large amount of 2,4-DNT eluted near 2-NDPA, completely obscuring its signal and preventing its identification in the extract. By taking advantage of the potential selectivity afforded by mass spectrometry, specific analytes can be determined in difficult environments.

SFC-PCI-MS can also be used to separate and identify phthalate esters that are often used as plasticizers in propellants. Methane PCI is particularly effective at analyzing these compounds due to their propensity for cleavage at the ester linkages and rearrangement to generate a dominant single peak at m/e 149 with very few additional criteria for distinguishing between the various phthalate esters. Figure 56 shows the NBS EI Library spectrum for dibutyl phthalate (92). Methane PCI is a "soft" enough ionization technique to give protonated molecular ions for these compounds. Figure 57 shows the TIC for the PSFC separation of a mixture of four phthalate esters. The more diagnostic MH^+ peak was present for every compound in the mixture, especially dibutyl phthalate, which now has the quasi-molecular ion at m/z 279 as its base peak.

Another potential application for SFC-CI-MS is in the analysis of propellant compounds in industrial waste streams and as contaminants in natural waters. The large quantities of stored propellant have resulted in the contamination of nearby ground and surface waters. The TIC for the CH_4 -PCI-SFC-MS analysis of a water sample derived

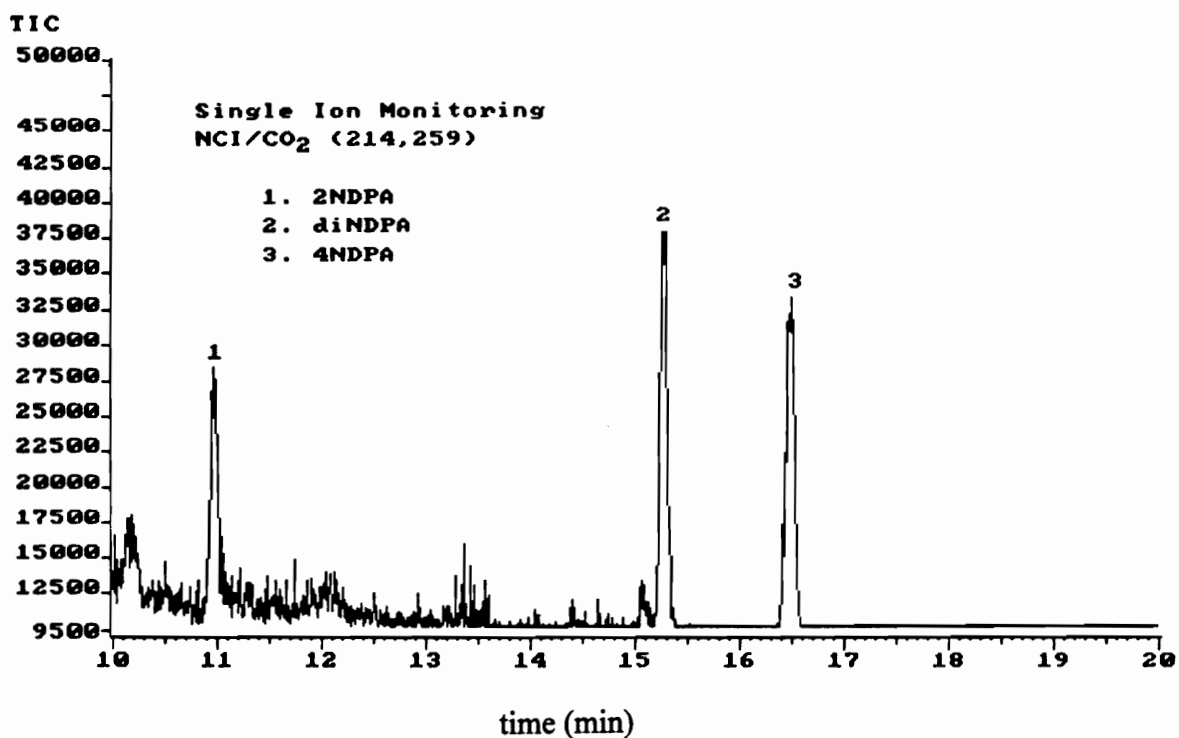


Figure 55. SFC CO₂ moderated NCI-MS of a supercritical fluid extract of a DPA-stabilized gun propellant manufactured in 1943. The extract was monitored for the protonated molecular ions of mono-nitrated and di-nitrated DPA derivatives.

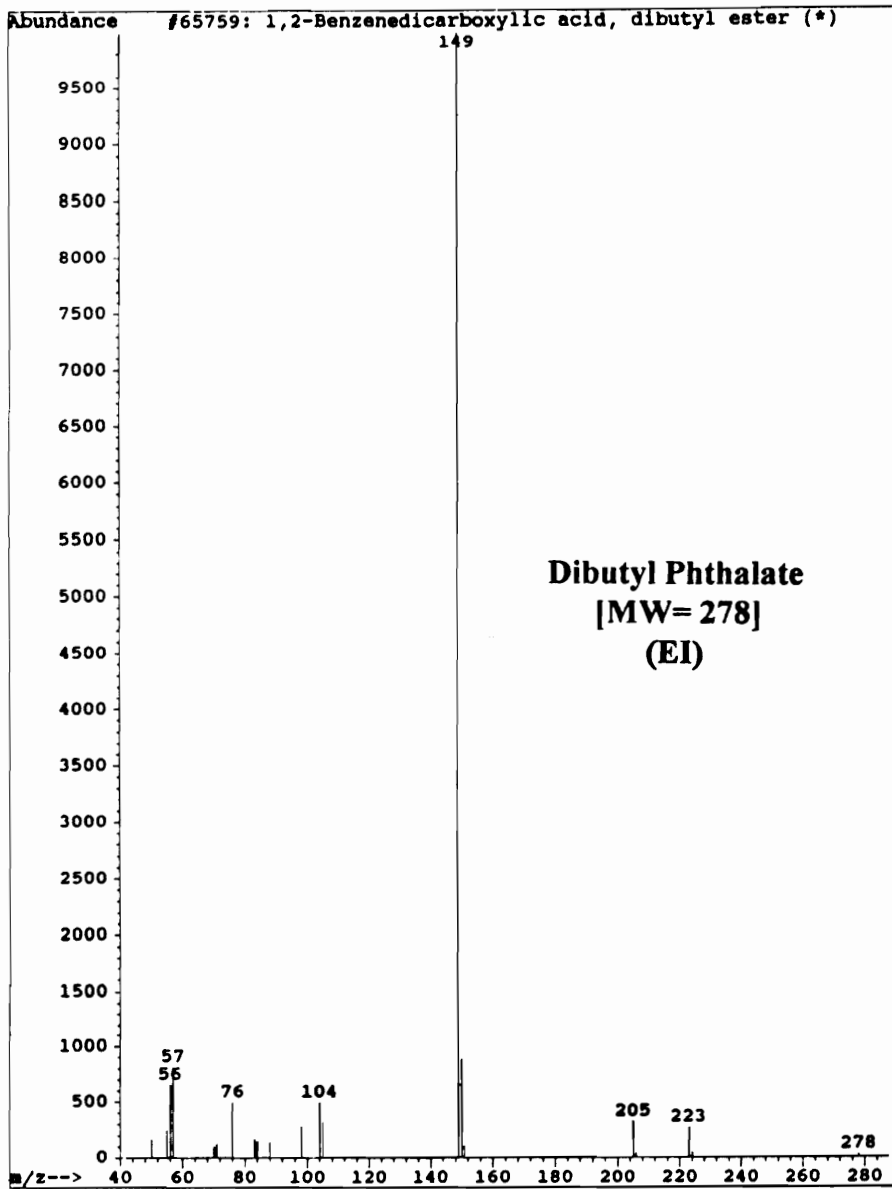


Figure 56. Electron impact spectrum of dibutyl phthalate.

15 cm x 2 mm Delatbond® Cyano Column

Oven - 75 °C

Pump - 100 atm - 2 min

100 - 350 atm - 15 min

500 ng injected

Restrictor/Source - 250 °C

Scan 145 - 400 amu

CH₄ at 1 torr (1.2 - 2.0 torr)

Discharge Electrode - on

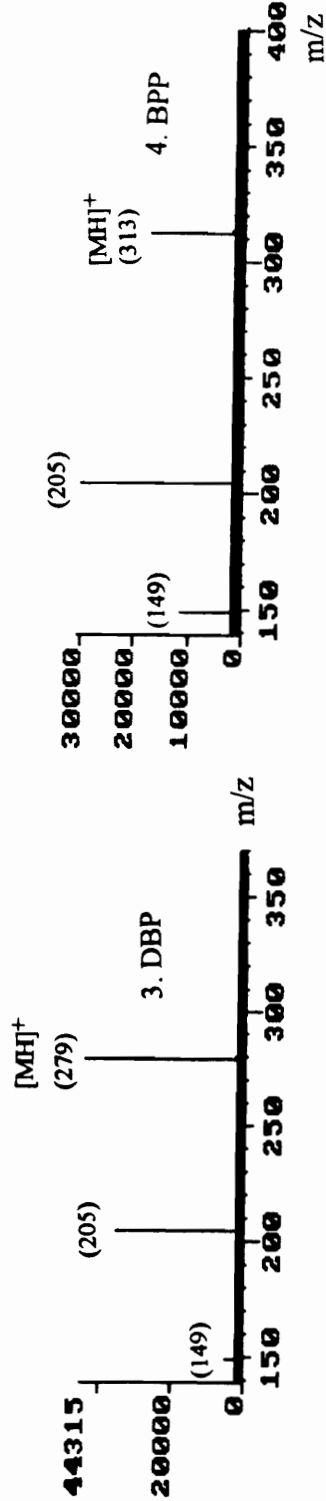
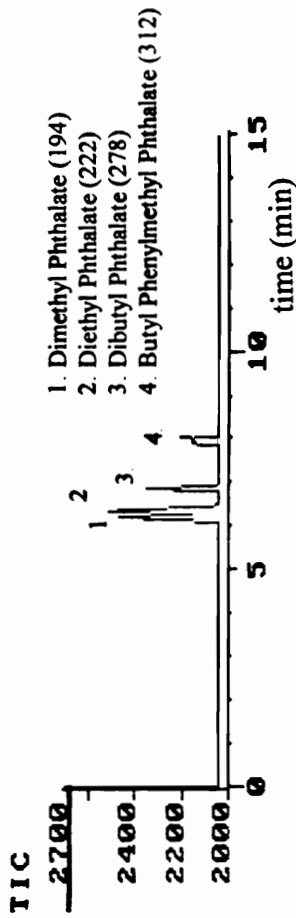


Figure 57. TIC and SFC methane PCI mass spectra of a mixture of four phthalate esters.

from a propellant waste stream (Indian Head, MD) is shown in Figure 58. The large and late eluting solvent peak is due to the direct injection of water onto the polar cyano column. Peak number 1 was determined to be the stabilizer DPA. The second peak was found to be nitroglycerin (NG). When the spectrum for NG was collected at a source/restrictor temperature of 321 °C, there was a single peak m/z 165 representing the $[M-HNO_3]H^+$. However, when the restrictor/source temperature was reduced to ~218 °C, the protonated molecular ion of the NG at m/z 228 could also be seen, as well an additional fragment at m/z 182. CO_2 buffered SFC-NCI also proved useful for the determination of propellant compounds in an aqueous matrix. A one ppm solution of 2,4-DNT, 2,6-DNT and TNT was injected into the SFC using CO_2 moderated NCI-MS detection. Slack and McNair (93) had previously quantitatively extracted the sample from 1 liter of spiked water using a combination of solid phase extraction and SFE. The sample was then selectively monitored for molecular anions at m/z 182 (2,4-DNT and 2,6-DNT) and m/z 226 (TNT). Figure 59 shows the resulting TIC trace for SFC- CO_2 moderated-NCI analysis of the extract. The high sensitivity and selectivity of NCI-MS for these compounds in combination with the low analysis temperatures and good resolution of SFC demonstrate good potential for the technique's application to propellant analysis out of a variety of matrices. In addition, the ease at which packed columns are incorporated into on-line SFE opens up the possibility that extraction and analysis of specific analytes from highly contaminated matrices can be achieved using on line SFE-SFC-CI-MS.

We also wanted to do a preliminary investigation into the use of methanol modified CO_2 for SFC-CI-MS in the thermospray interface. As mentioned earlier, Games et al. (75,76) used methanol modifier in CO_2 to perform proton transfer PCI in a Finnigan MAT Thermospray. In their studies they used methanol modifier at

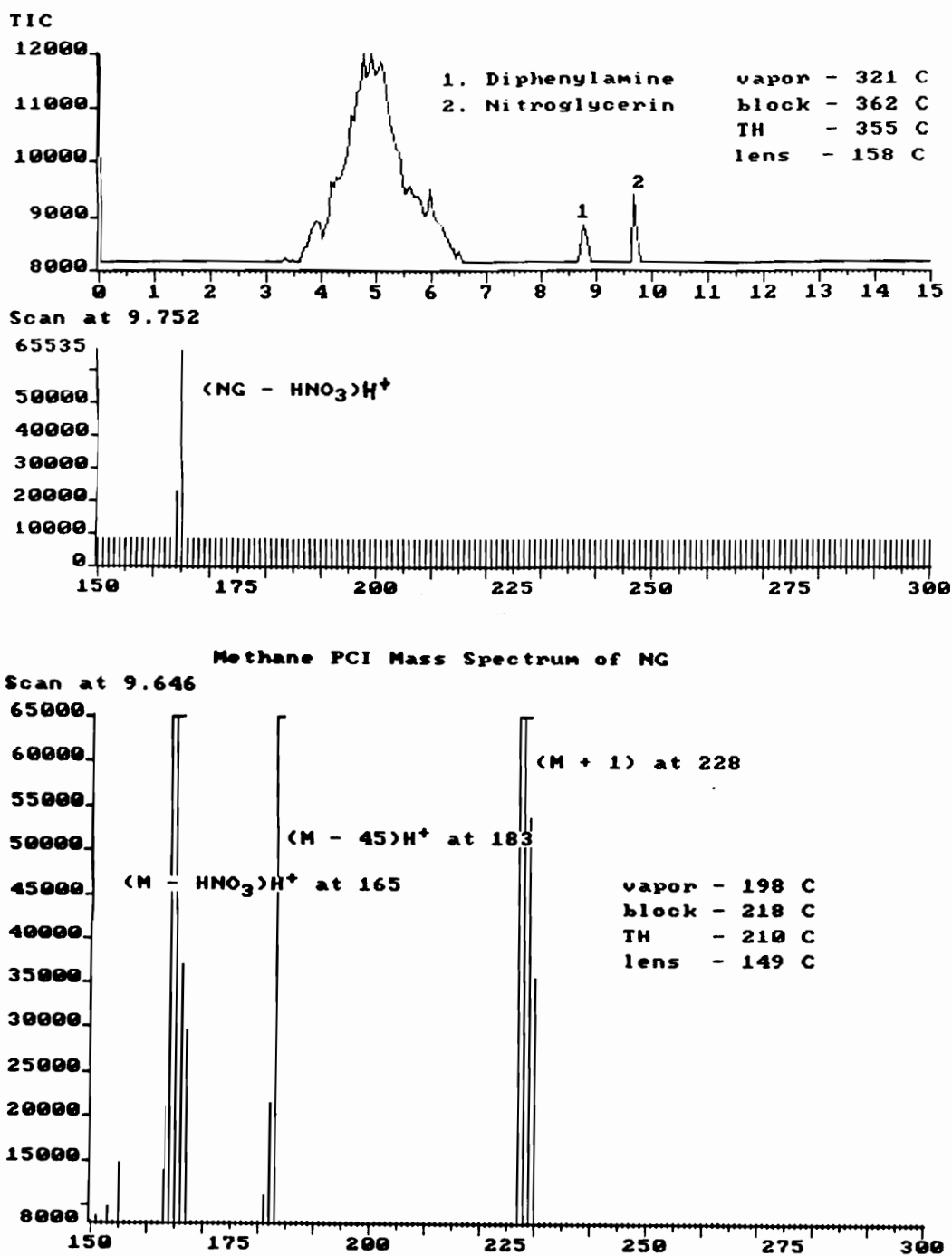


Figure 58. TIC and CH₄-PCI mass spectrum of nitroglycerin from a sample of industrial waste water. Lowering the source/restrictor temperature allowed the protonated molecular ion to be identified.

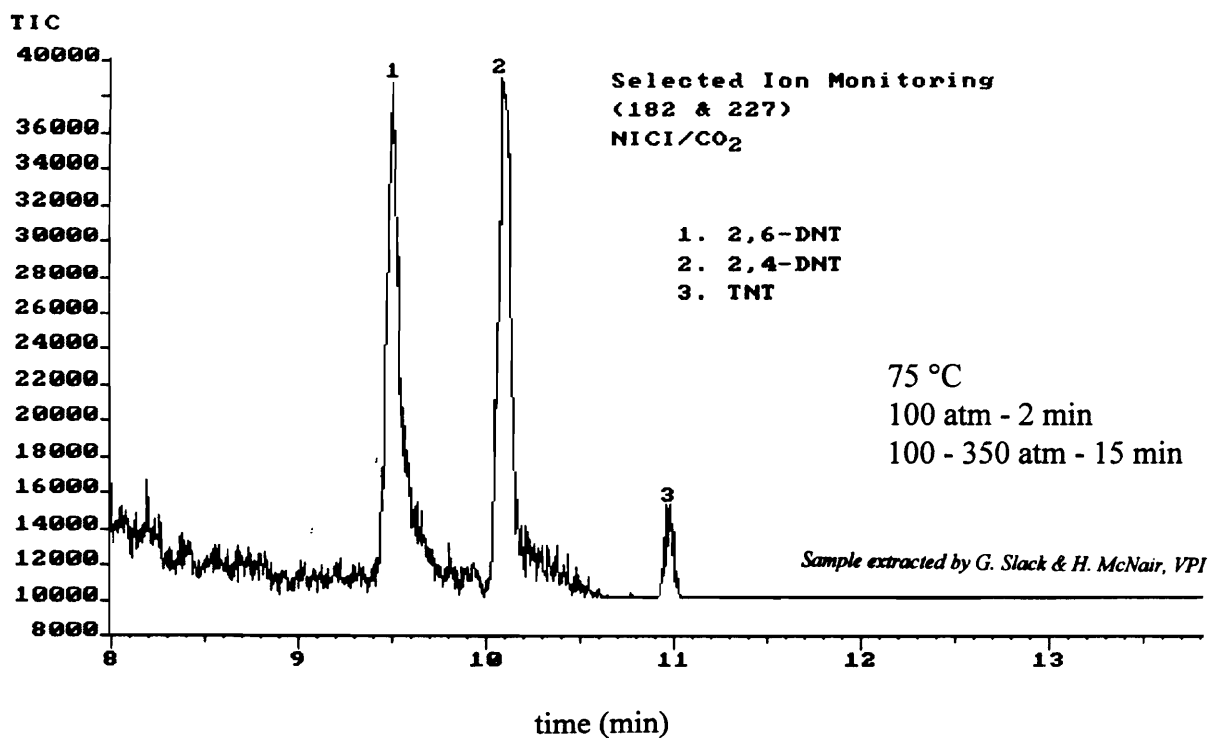


Figure 59. TIC of SFC-CO₂-NICI analysis of propellant wastewater SPE-SFE extract monitored for the molecular ions of di- and tri-nitrotoluenes.

concentrations of 20-25 % (v/v). This is an unusually large amount of modifier for SFC, and in actual practice would rarely be used. We chose to use 4.0% (w/w) methanol in CO₂; a concentration more likely to be encountered during the SFC of polar compounds. The modifier was delivered via a premixed cylinder pressurized with 1200 psi helium. In this type of commonly used modified fluid delivery, the gas supplier places the desired amount of modifier in the cylinder, then fills the remainder of the tank with liquid CO₂ (Appendix 1). Very energetic shaking of the cylinder is then required to provide adequate mixing of the two fluids. We were unable to generate proton addition of DPA with the discharge electrode and only 4.0% (w/w) methanol in the mobile phase, even though the RG spectrum indicated the presence of protonated molecular ions of CH₃OH at m/z 33 and its dimer at m/z 65; with the dimer being predominate at higher source pressures. Methanol has a much higher proton affinity (PA) (184.9 kcal mol⁻¹) compared to methane (130.5 kcal mol⁻¹) (88), and must apparently be present in higher concentrations (than 4.0 %) if it is to be the only supply of protons in the source. However, by adding methane to the source (0.8-1.0 torr), PCI spectra could again be acquired. The spectra of DPA following separation with methanol modified CO₂ was simple, consisting of a single protonated molecular ion at m/z 170. The presence of methanol in the mobile phase does not appear to interfere with the character of SFC-CH₄-PCI spectra. This condition would not be expected to produce more fragmentation than CH₄ following collision with an analyte molecule. Figure 60 shows the TIC and CH₄-PCI mass spectrum of cholesterol (MW=387) eluted with 4.0% methanol in CO₂. The mass spectrum consists of a single fragment at m/z 370 representing the loss of a water from the parent (M-H₂O)H⁺. Another example of CH₄-PCI from the methanol modified mobile phase is the mass spectrum of 5,6-benzoquinone shown in Figure 61. It too, is a

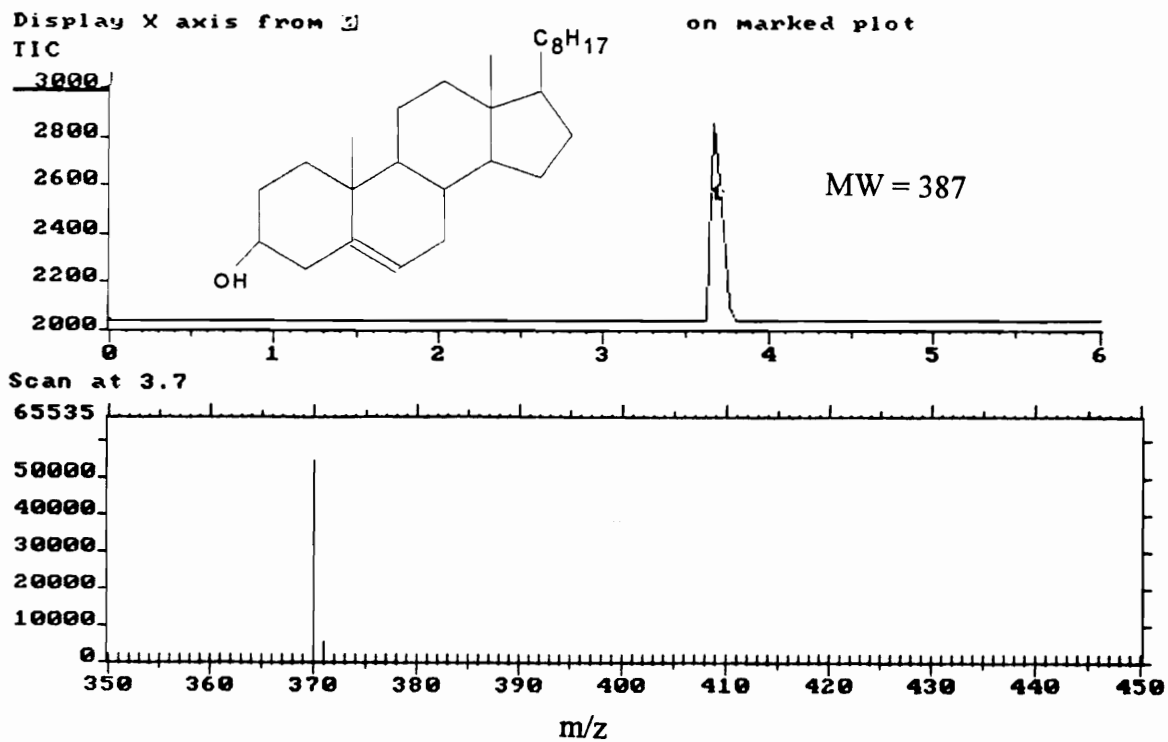


Figure 60. TIC and CH₄-PCI mass spectrum of cholesterol eluted with 4 % of methanol in CO₂.

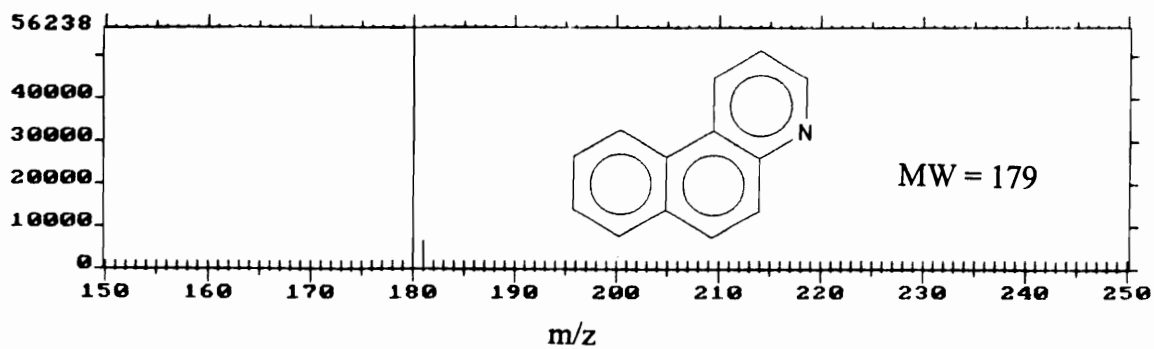


Figure 61. SFC-CH₄-PCI mass spectrum of 5,6-benzoquinone eluted with 4 % methanol in CO₂.

single peak consisting of the protonated molecular ion at m/z 180. Mulcahey et al. had previously been unable to elute this compound using pure CO_2 (94).

These results indicated that methanol modified mobile phases could be accommodated in the SFC-PCI mode. This is a very important attribute, since many SFC detectors are rendered useless by the presence of organics in the SF. We did not attempt to use higher modifier concentrations than 4.0%. However, it is likely that less CH_4 reagent gas would be required as the mobile phase becomes richer in methanol and it begins to play an increasingly important role as a CI reagent gas.

Conclusions

The LC-thermospray interface can be readily adapted to perform PSFC-CI mass spectrometry. Both PCI with CH_4 and NCI with mobile phase CO_2 were shown to be useful in the analysis of propellant extracts. Packed columns allowed the use of lower restrictor temperatures than capillary columns without deterioration of peak shapes. The presence of CO_2 in the RG resulted in significant fluctuations in the ion profiles at different temperatures and pressures during CH_4 -PCI. However, due to the relatively low PA of CO_2 it did not interfere with the resulting spectra. PCI spectra proved to be very simple, usually consisting of single protonated molecular ions; while NCI provided a little more fragmentation (although still considerably less than EI). The NCI with mobile phase buffered CO_2 proved to be particularly useful for the identification of nitrated stabilizer derivatives. Because of the simplicity of the spectra, the identification of complete unknowns is unlikely - but the combination of retention time comparisons and molecular weight analysis is a powerful tool for target compound analysis in difficult mixtures. The future combination of SFE-SFC-CI-MS could be a powerful analytical tool for propellant analysis as well as many other applications. Packed columns could easily

accommodate a UV detector in-line with the MS, providing a means of sample preparation, accurate quantitation and target compound analysis in a single step. Additionally, the ability of PCI systems to accommodate methanol modifiers (and potentially many others) could allow the detection of more polar analytes (i.e. pharmaceuticals).

CHAPTER 6

Conclusions and Future Work

Conclusions

Many applications of SFs to separations related to polymeric materials were evaluated. SF CO₂ was shown to be superior to liquid solvents for separating extremely narrow MWDs (of relatively low MW) from high density polyethylene. It was found that the temperature and density increment between successive extractions exerted a strong influence on the resulting MWD. The high level of crystallinity at the temperatures studied (≤ 100 °C) restricted MWs to low values. Using propane as a modifier in CO₂ was demonstrated to alleviate some of the effects of extracting at temperatures below the T_m.

SF CO₂ was found to provide more efficient separations of NC propellant extracts while maintaining the integrity of *N*-Nitroso compounds than the accepted LC and GC methods. The LC-thermospray interface was also found to be a viable means of performing on-line mass spectral analysis of NC extracts with packed column SFC and pressure programming under chemical ionization conditions. The abundance of CH₅⁺ and C₂H₅⁺ were found to decrease rapidly with increasing CO₂ pressure in the source. Increasing the temperature of the source was shown to alleviate this effect and allow higher sensitivities at high pressures in the PCI mode. It was determined that operating the source/restrictor at the proper temperature was critical in controlling fragmentation and sensitivity in both PCI and NCI.

The many unique physicochemical properties of SFs were discussed in Chapter 1. These properties were shown to give SFs several advantages over conventional liquid

solvents in applications related to the separation and subsequent characterization of oligomers and additives from polymeric materials.

In Chapters 2 and 3 the compressibility of SFs allowed for minute changes in solvent strength so that the fractionation of several different MWDs from a parent polymer of "broader" distribution could be achieved. In the case of SF CO₂, the high density polyethylene wax showed only partial solubility in the SF. This made it possible to fractionate very narrow MWDs from the feedstock. However, the low solubility of the oligomers in CO₂ restricted the MW range to less than 2000 and resulted in recoveries of ~30%. SF propane, a stronger solvent for polyethylene than CO₂, removed MWDs throughout the MW range of the parent but with much larger polydispersities. The use of a propane-CO₂ SF mixture provided solvent strengths intermediate between the two pure fluids. This resulted in higher gravimetric recoveries than pure CO₂ and lower polydispersities than pure propane. Not surprisingly, increasing the extraction temperature generated higher MWDs and recoveries at constant density. This was probably due to improved diffusion of oligomers into the SF and the reduction of crystalline interactions as oligomer T_m values are traversed.

In the case of polymeric NC, the polymer was completely insoluble in SF CO₂. However, all the additives and stabilizer derivatives were soluble. This afforded a unique opportunity to remove the additives free from interferences with co-extracted oligomers. In Chapter 4, single base propellant samples were extracted with SF CO₂ and the extracts were qualitatively characterized with a variety of chromatographic techniques. These results indicated that SF CO₂ removed the same analytes as the existing liquid solvent based methods. The ability of SF CO₂ to extract a variety of propellant additives and decomposition products, and then deposit them upon decompression, make it a likely

candidate for both analytical sample preparation and process scale regeneration of military explosives.

Synthetic mixtures of stabilizer derivatives and actual propellant extracts were analyzed by a variety of chromatographic techniques. SFC was shown to provide a good overall separation at substantially lower temperatures than GC. On-line SFE-SFC of the extracts was also demonstrated. The extracts of single base propellants that had undergone accelerated aging via storage at elevated temperatures were also characterized. All chromatographic techniques (LC, GC, SFC) complimented each other in providing an overall picture of DPA and its nitrated derivatives in the "aged" and "unaged" extracts. As the storage time at surveillance temperatures is increased, more highly nitrated derivatives of DPA (i.e. di, tri, tetra) begin to appear; as the primary stabilizer, NNODPA and mononitrated derivatives are depleted. Also, doubts were raised as to the actual validity of current surveillance programs incorporating accelerated aging. The primary decomposition product, NNODPA, was found to rearrange to nitro-substituted DPAs at elevated temperatures. The mechanism was shown to change as the temperature was increased. This implied that stabilizer profiles may not be representative of overall propellant stability.

While SFC was used to perform efficient separations of propellant compounds, it was still desired to have even greater confidence in extract characterization. In Chapter 5 the packed column SFC was interfaced with a modified LC-TS-MS system. The high pumping capacity accommodated pressure programming from packed columns up to 2.0mm i.d. The presence of large amounts of CO₂ in the source did not appreciably affect the quality of the spectra. This system allowed for target compound detection of all the stabilizer derivatives and propellant additives using various methods of chemical ionization. *N*-Nitroso compounds were shown to elute intact from the SFC. The SFC-

CI-MS system was demonstrated to have excellent potential in the analysis of a wide range of propellant based mixtures. It was also found to be compatible with methanol modified CO₂.

Future Work

The use of SFs to fractionate other polymers should be explored. Additionally an experimental design that allows efficient SF extractions polymers at or above their melting points with analytical instrumentation should be developed. On-line SFE-SFC with the thermospray interface configured for SFC should be explored for the target analysis of compounds in complex matrices.

APPENDIX

Experimental Determination of Changes in Methanol Modifier Concentration in Premixed Carbon Dioxide Cylinders

Introduction

Many applications involving SFs have failed because the SF lacked adequate polarity and/or solvent strength for the particular sample matrix. In the previous chapter, methanol from a premixed cylinder was introduced as a mobile phase modifier to increase the polarity of CO₂ and allow it to solvate more polar compounds. It was shown that the use of 4% v/v methanol in CO₂ allowed the elution of 5,6-benzoquinone in 5 minutes using the SFC-CI-MS system. This compound previously could not be eluted with pure CO₂. Modifiers (co-solvents) are becoming increasingly important in both SFE and SFC and can have surprisingly large effects even at relatively low concentrations. Indeed, the underlying tone being communicated by users at various national and international meetings, is that the future of SFE and SFC hinges on demonstrating their ability to separate ever more polar and higher molecular weight species. Traditional SFs, (carbon dioxide by far being the most widely used) were chosen largely for their moderate critical parameters and availability, but have been unable to deliver the solvent strengths required for increasingly more difficult separations.

In order to enhance a SF's solvating ability, it is normally necessary to add measured quantities of a co-solvent that has a demonstrated affinity for the analytes in question. This "modifier" can change SF solvent behavior in a variety of ways (13,95-97). By "competing" with analytes for active sites on chromatographic stationary phases and increasing the overall polarity and density of the SF, a small amount of modifier can have a surprisingly large effect. The mechanisms of interaction between analytes and modified fluids are not well understood, but there appears to be an unusually high

concentration (e.g. clustering) of the co-solvent in the vicinity of some solutes. This accounts for a localized density and polarity that is greater than the bulk fluid. Solvatochromic dye studies indicate that polar analytes tend to concentrate within such clusters (98-100).

SFE/SFC instrument manufacturers appear to be addressing the importance of modifiers by providing two pumps in their systems; one to deliver the primary fluid while the second provides the co-solvent at a rate or volume designed to generate a fixed concentration. In the last few years advances in mixing strategies have greatly improved the utility of the two pump system. In some SFCs it is even possible to deliver modifier gradients - a technique demonstrated to be more effective than conventional pressure gradients (101).

A popular alternative to using two pumps has been the use of premixed fluid mixtures, traditionally prepared by suppliers of high purity specialty gases. It was in this way that the 4% methanol mobile phase was introduced into SFC-CI-MS system described in Chapter 5. This method eliminates the complexity and expense of operating a second high pressure pump in the SFE or SFC system. However, there appear to be serious limitations to the use of premixed cylinders as a result of shifts in the vapor-liquid equilibria (VLE) as the liquid phase contents are depleted. The purpose of this study is to provide experimental evidence as to the direction and magnitude of modifier concentration changes that take place during the normal usage life of a premixed gas cylinder.

Experimental

A Hewlett-Packard (HP) G1205A SFC (Wilmington, DE) was used for the delivery of both premixed and dynamically mixed methanol modified mobile phases. For

dynamic mixing, the instrument uses two reciprocating pumps (60) to deliver a predetermined combination of the primary fluid and secondary additive (or additive mixture). Mixing took place at SFC pump pressures and ambient temperatures in the connecting tubing dead volume prior to the column and injector. The instrument was equipped with an HP 7673 GC/SFC Autosampler, a 5 μ L pneumatically operated injection loop, and an HP Series 1050 Multiple Wavelength UV Detector (MWD) set to 254 nm. All separations were done on a 250 x 4.6mm i.d. (5 μ m particles) Deltabond[®] cyano column (Keystone Scientific, Inc., Bellefonte, PA). The SFC was always operated in the "downstream" mode, so pressures were recorded at the column exit. Pressure drop across the 25cm cyano column was 38 atmospheres (atm), deviating only slightly from this value with mobile phase composition. Total liquid flow (methanol + CO₂) rate was maintained at 2 mL/min for all separations.

The phenylthiohydantoin (PTH) derivatized amino acids, α -aminobutyric acid and norleucine, were purchased from Aldrich Chemical Co. (Milwaukee, WI). Reagent grade methanol (Fisher Scientific, Raleigh, NC) was used to dissolve the amino acids and was also used as the source of methanol in the dynamically mixed mobile phases. Pure SFC grade CO₂ was provided by Air Products and Chemicals, Inc. (Allentown, PA) and methanol-modified SFC grade CO₂ (2.0% w/w nominal) with helium headspace (1200 psi) was purchased from Scott Specialty Gases, Inc. (Plumsteadville, PA). A Model I10 Industrial Weight Indicator (Ohaus Corporation, Florham Park, NJ) was placed under the modified cylinder to monitor the change in mass during cylinder drawdown.

Results and Discussion

Poor mixing and fluctuating modifier content in premixed gas cylinders have long been suspected as a source of erratic chromatographic behavior in SFC. Many SFC

systems manufactured in the 1980s consisted of a single syringe pump used for mobile phase delivery. When a modified mobile phase was desired to elute more polar compounds from the column, premixed cylinders prepared at the desired concentration were usually ordered from the supplier. A recent model by Schweigardt and Mathias (102), incorporating a modified Peng-Robinson equation of state (EOS) with three binary interaction coefficients, was used to model vapor-liquid equilibrium (VLE) changes as the liquid volume in a premixed cylinder is depleted. They specifically modeled the dimensions of the 1.04 ft³ aluminum tank from which most SFC mobile phases are provided. The model predicted that percent methanol concentrations in the mobile phase could increase two-fold during the usage-life of the cylinder. As the liquid volume in the cylinder is depleted, the total void volume above the liquid increases. Since the primary fluid (carbon dioxide) has a much higher vapor pressure than the modifier (methanol) it preferentially moves into the vapor phase, occupying the newly created void volume. The amount of methanol leaving the liquid phase is considered negligible compared to CO₂. Thus, the resulting shift in mass balance leaves the methanol at higher percent compositions in the liquid as the cylinder continues to be depleted. Figure 62 provides an empirical view of the concentration shifts that occur as the liquid phase is removed from the cylinder, while, the actual the magnitude of the theoretical predictions is plotted in Figure 63.

Experiments were conducted to determine if the proposed model correctly predicts VLE shifts in premixed cylinders. The HP-SFC was used to generate dynamically mixed methanol-CO₂ mobile phases. Berger and Wilson (103) had previously used such an apparatus to separate phenylthiohydantoin derivatized amino acids (PTH-AA)s with methanol-modified CO₂. They found that retention times for the

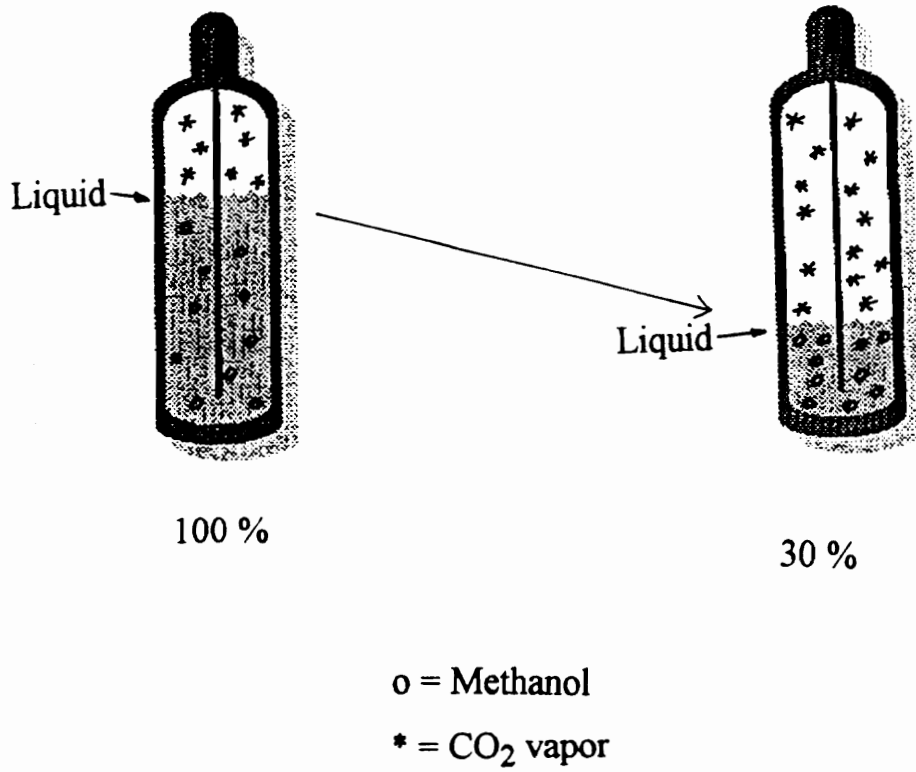


Figure 62. Empirical view of modifier concentration changes that occur during liquid depletion.

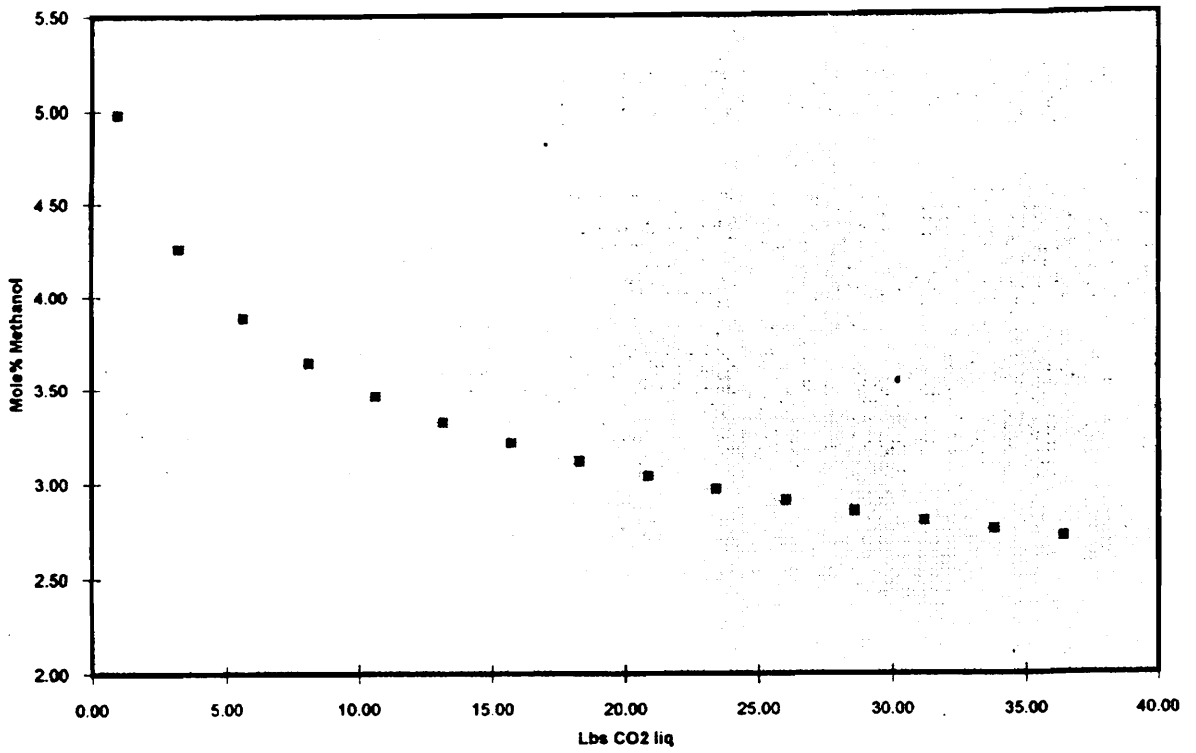


Figure 63. Theoretical plot for 2.5 % w/w methanol in CO₂ as the premixed cylinder's contents are depleted.

more polar PTH-AAs were especially sensitive to the concentration of methanol in the mobile phase. This was particularly the case at low concentrations of the modifier. Based on their results, we chose to use two PTH-AAs, PTH- α -aminobutyric acid and PTH-norleucine, probe analytes to determine methanol concentration shifts during premixed cylinder usage.

A "calibration curve" of retention time (RT) versus percent methanol using dynamic mixing was prepared for the two PTH-AAs. Figure 64 shows SFC-UV traces for PTH α -aminobutyric acid collected at methanol percentages ranging from 1-5%; while, Figure 65 shows the RTs of the two PTH-AAs plotted as a function of percent (v/v) modifier composition. Each point on the graph represents the average of four injections, with RSDs for the RTs averaging 0.6%. These "calibration curves", generated via dynamic mixing of pure CO₂ and liquid methanol, were to be used as references for determining methanol composition in the premixed cylinder.

After the calibration plots were generated, the pure CO₂ cylinder was replaced with one that contained a mixture of methanol in CO₂. The tank was reported to have been mixed at a nominal concentration of 2.0% w/w (2.2% v/v) for 40 lbs of liquid/gas carbon dioxide and pressurized with 1200 psi of He headspace. The probe analytes were injected (n=4), their RTs determined, and the percent methanol found through graphical interpolation from the calibration curves of RT versus percent methanol modified CO₂. A quantity of the mixed mobile phase was then rapidly released into the atmosphere. The cylinder was then given at least 4 hours to reestablish VLE before the next series of injections. Proceeding in this manner, the shift in modifier composition during tank depletion was experimentally determined. Additionally, the system was periodically checked against the original calibration curve by reverting back to dynamic mixing and

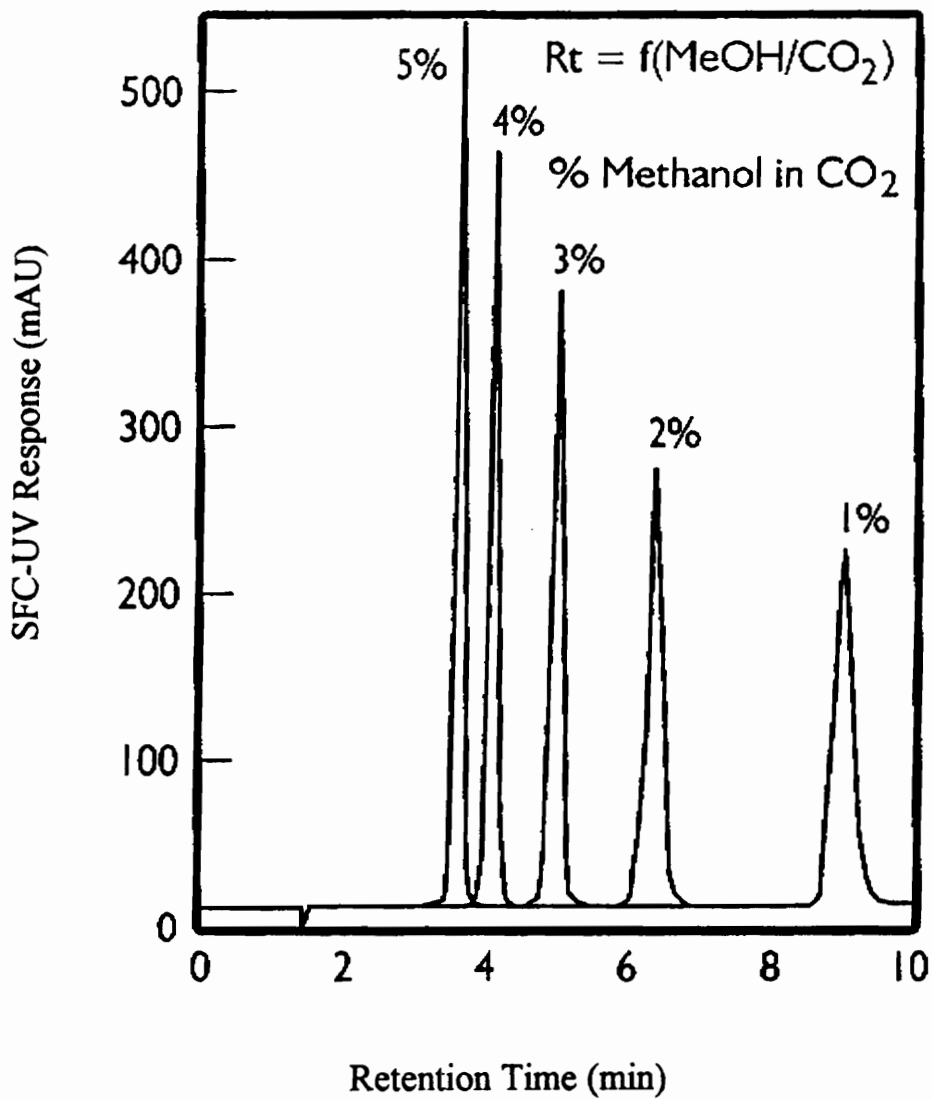


Figure 64. SFC-UV traces of PTH α -aminobutyric acid via dynamic mixing.

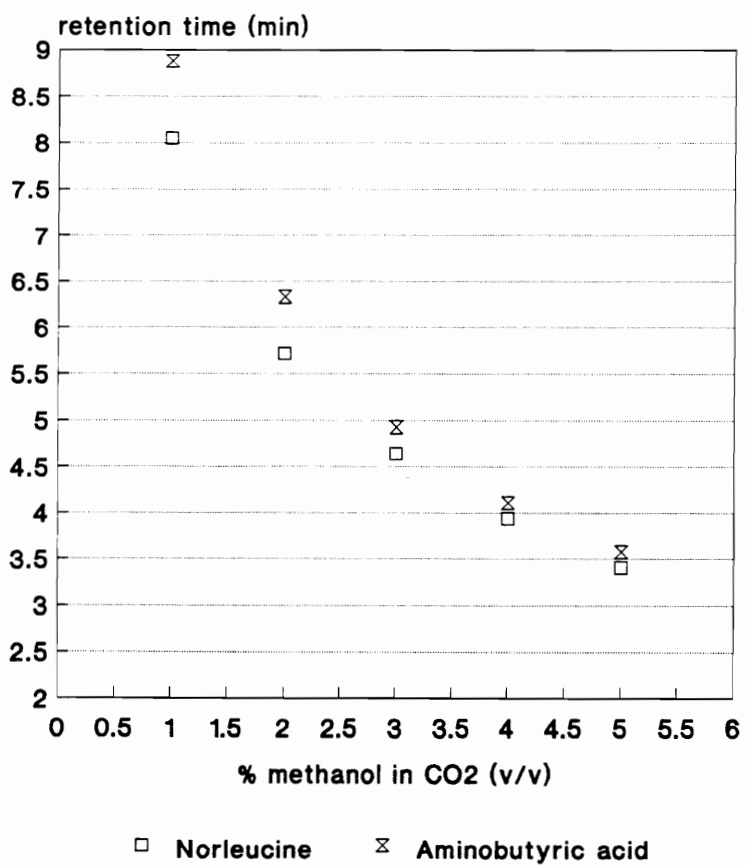


Figure 65. Percent methanol calibration curves via dynamic mixing.

injecting PTH- α -aminobutyric acid. The calibration curve was found to be valid throughout the entirety of the experiment.

Figure 66 shows the shifts in RTs that α -aminobutyric acid experiences as liquid phase CO₂ is removed from the cylinder. Table IX shows the RTs of the two analytes and the corresponding modifier compositions (determined from the calibration curves) at different stages of cylinder drawdown. Percent RSDs for the premixed cylinder were quite good, indicating complete mixing of the methanol and CO₂ in the tank. However, as predicted from the model of Schweighardt and Mathias, the concentration of methanol in the mobile phase increased as the cylinder contents were depleted. Both calibration curves revealed a concentration of 3.0% v/v methanol after 26.3 pounds of liquid CO₂ had been removed from the cylinder - an increase of over 100% from the initial measured value (~1.3% v/v). Although the initial readings were low compared to the manufacturer's specifications, this observation does not negate the fact that the methanol composition in the mobile phase was experimentally found to more than double during what would be considered normal cylinder usage.

Conclusions

The concentration of methanol in a premixed cylinder was found to increase as the cylinder contents were depleted. The results confirm the general VLE predictions of Schweighardt and Mathias. Users of such cylinders for SFC may see negative shifts in analyte RTs, loss of selectivity and occasional reversals in elution order during the normal life of the cylinder. These phenomena would probably not be observed over the course of a single day (particularly for capillary applications), but might become an issue if the same analyses are being performed over the course of several days or weeks. The authors feel that for SFE, the use of such cylinders at concentrations less than 5% would

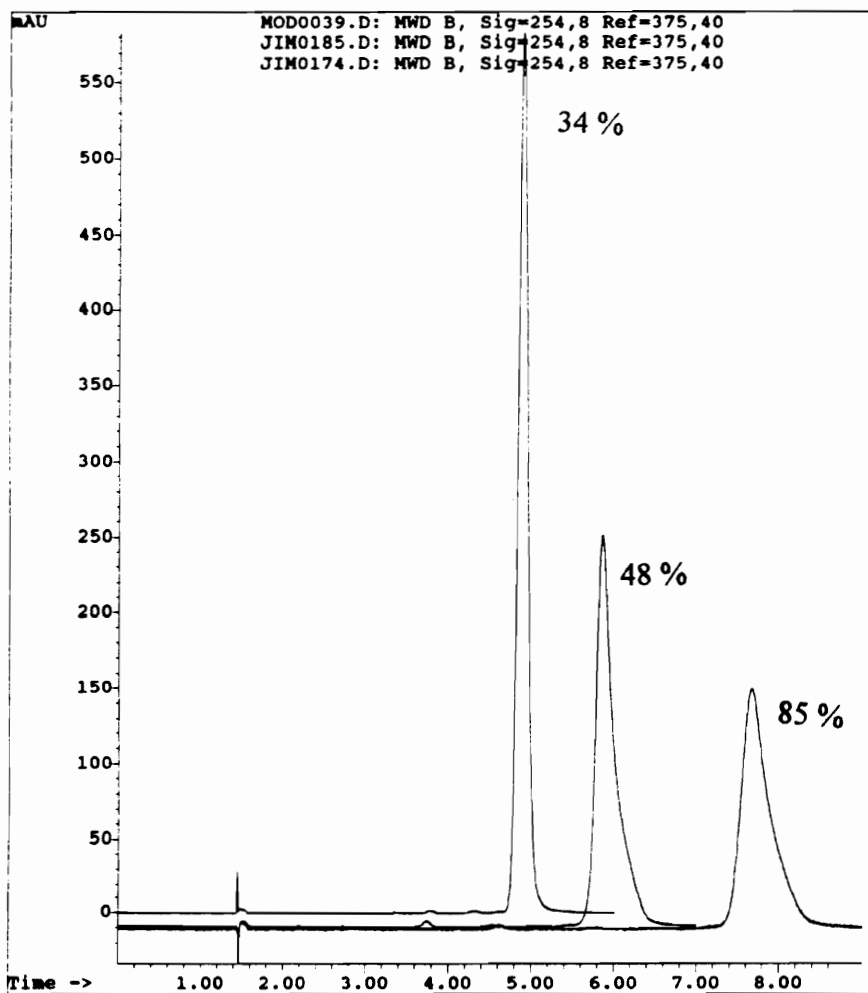


Figure 66. SFC-UV traces for PTH α -aminobutyric acid collected at various stages of premixed cylinder depletion. Percent values refer to amount left in cylinder.

Table IX

Table of retention times and corresponding % of methanol value at three stages of premixed cylinder depletion.

Cumulative pounds of liquid removed from 90 lb cylinder	α -Aminobutyric acid RT _{min} (RSD) % MeOH	Norleucine RT _{min} (RSD) % MeOH
(40 lb of liquid)		
5.8	7.68 (0.15) 1.4 % MeOH	7.31 (0.93) 1.2 % MeOH
20.8	5.87 (0.61) 2.3 % MeOH	5.53 (0.31) 2.2 % MeOH
26.3	4.89 (0.20) 3.0 % MeOH	4.61 (0.38) 3.0 % MeOH

rarely pose a problem (particularly with liquid trapping) since most extraction conditions are established well above threshold values. However, at higher initial concentrations of methanol (>5%), the continued increase in concentration during cylinder drawdown could result in the existence of two phases in the cylinder. For supercritical fractionation studies that rely on a continuous and predictable variation in solvating strength of the SF, the variability in the mobile phase composition as a function of tank volume could make the results very difficult to interpret.

We also suspect that the same VLE shifts that result in increases in modifier concentration in premixed cylinders result in higher concentrations of impurities in pure CO₂ cylinders as their liquid volumes are reduced during use. Additionally, helium is known to be quite soluble (0.04 mole fraction at 2000 psi) in liquid CO₂ under the pressure-temperature conditions typically found in He headspace pressurized cylinders. It is quite possible that as pure CO₂ tanks with He headspace are depleted, there can be retention time shifts as a result of He preferentially moving into the void volume above the liquid level. Studies are currently underway to verify these presumptions.

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Vita

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