Extraction of Additives from Polystyrene and Subsequent Analysis

Susan H. Smith

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Larry T. Taylor, Chair

Gary L. Long

James F. Wolfe

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(ABSTRACT)

The extraction of fifteen (15) polymer additives with supercritical carbon dioxide which are used as antioxidants, uv stabilizers, process lubes, flame retardants and antistats from eight formulations of polystyrene is demonstrated and compared to traditional dissolution/precipitation extractions. The purpose of the study was twofold: 1) the development of a high performance liquid chromatography (HPLC) method(s) for the additives and 2) the determination of the viability of supercritical fluid extraction (SFE) for the additives from polystyrene.

Separation of some of the additives was achieved using reversed phase liquid chromatography. Nine of the additives were assayed in this manner while, the remaining six additives could not be assayed using reversed phase liquid chromatography. In order to develop an extraction method for the additives, the effects of static extraction time, CO_2 density, and temperature were first investigated. These preliminary extractions revealed that a static extraction period which afforded an opportunity for the polymer to swell combined with a high CO_2 density and extraction temperature above the glass transition (T_g) yielded quantitative recoveries of the additives. Triplicate extractions of the various polystyrene formulations matched additive recoveries obtained by the traditional dissolution/precipitation method.

ACKNOWLEDGMENTS

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LIST OF ABBREVIATIONS

ACN: Acetonitrile
AO: Antioxidant
ASE: Accelerated Solvent Extraction
$CHCl_3$:   Chloroform
D: Dimers
ELSD: Evaporative Light Scattering Detector
FID: Flame Ionization Detector
FT-IR: Fourier transform infrared
GC: Gas Chromatography
GPC: Gel Permeation Chromatography
HALS: Hindered Amine Light Stabilizer
HPLC: High Performance Liquid Chromatography
IR: Infrared
LOD: Limit of Detection
LLC: Liquid Liquid Chromatography
LSC: Liquid Solid Chromatography
mg/mL: milligram per milliliter
MAE: Microwave Assisted Extraction
ODS: Octadecyl silane
PS: Polystyrene
RSD: Relative Standard Deviation
SF: Supercritical Fluid
SFC: Supercritical Fluid Chromatography
SFE: Supercritical Fluid Chromatography
SLPM: Standard Liter per Minute
T: Trimers
Tg: Glass Transition Temperature
THF: Tetrahydrofuran
µL: Microliter
µm: Micron
UV: Ultraviolet

CHAPTER 1

Introduction

Polystyrene was first recognized in 1831 by Bonastre who distilled storax obtained from the "Tree of Turkey," (liquidambar orientalis). He coined the material "styroloxyd." In 1839 Simon recorded findings corresponding to what he thought was the oxidation of styrene monomer by sunlight. The production of polystyrene from the monomer was discovered in 1869 by Berthelot. In 1900, Kronstein recommended that this "organic glass" be used as a water-white varnish. Patents were finally granted to F. E. Matthews to use styrene as an insulating material. The polymer was expensive and had its drawbacks such as crazing and coloring. Another thirty three years passed before French chemists pinpointed agents that could be used to retard the detrimental effects of polymerization (1).

Polystyrene was recognized in 1933 as a potentially viable molding material. Commercial introduction of styrene was hampered by the scientific community. The lack of understanding was due to confusion surrounding the relationship of alkyl derivatives of benzene to each other. Separations of the derivatives was difficult and the derivatives were actually being co-distilled together due to their similar boiling points. This added to the confusion and difficulty of separating the alkyl compounds. While benzene, methylbenzene and toluene can be readily separated by temperature, dimethylbenzenes have similar boiling points in the range of 137.5°C to 144°C.

Polystyrene was first introduced on a commercial scale in Germany in 1930 and then in the United States in 1937 (2). From 1930 to present time, polystyrene has grown to be a multi-billion dollar industry (3). Polystyrene is an atactic linear amorphous polymer. **(Figure 1.1)** Formation of monomer occurs by several different processes. In Method I, the starting material is ethyl alcohol which, when combined and reacted with hydrogen chloride, produces ethyl chloride and water. Ethyl chloride is reacted with benzene to form ethyl benzene that is then subjected to superheated steam in a nickel tube to produce styrene. In Method II, the starting material is ethylene gas that is passed through benzene while under pressure. Heat combined

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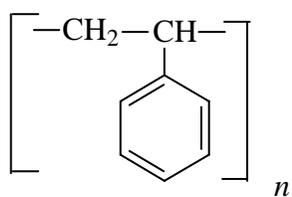
Figure 1.1: Repeat Unit of Polystyrene

with an aluminum chloride catalyst yields ethylbenzene. The ethylbenzene is then subjected to heat, pressure and steam to yield styrene. **(Figure 1.2)** If ethylbenzene is not cracked to obtain styrene directly, as in Method II, the ethyl benzene may be chlorinated to form chlorethyl benzene that is then passed through a nickel tube. This process improves the yield and imparts less brittleness to the final polymer.

Styrene synthesis may proceed in other ways, such as ethylene and acetylene with a catalyst in a nickel tube. However, these methods often lead to contaminating byproducts such as cyclohexane and cyclohexadiene. To initiate polymerization of styrene, it is placed in contact with sulfuric acid in an acetic acid solution that produces distyrene. Heating the distyrene liquid will cause further polymerization to produce a glossy solid that is referred to as metastyrene. Additional heating then breaks the methyl group and true polystyrene is produced. **(Figure 1.3)** The commercial production of polystyrene is dependent upon the purity of the monomer which must be determined with advanced analytical methods, such as gas chromatography (4). Contaminants can affect the polymerization characteristics and storage lifetimes of the styrene. An inhibitor p-t-butylcatechol (TBC), is added to prevent the styrene from polymerizing.

Desirable characteristics of polystyrene in order of importance are as follows: (a) dimensional stability at a variety of temperatures, (b) low-loss dielectric constant, (c) infinitesimal water absorption, (d) inertness toward acids, bases and salts, (e) insolublity in aliphatic alcohols-petroleum hydrocarbons- glycol ethers, (f) high refractive index thus allowing it to be a substitute for glass and gems in jewelry, and (g) low specific gravity of 1.05. Polystyrene is clear, transparent, easily fabricated, and has reasonable mechanical and thermal properties. It is slightly brittle and softens near 100°C and therefore may not be used in formulations requiring sterilization. It will degrade at elevated temperatures into a mixture of low molecular weight compounds and styrene. **(Figure 1.4)** The major application of polystyrene is in packaging. Specific additives are incorporated to achieve product characteristics that depend upon the end usage.

Method I:

C_2H_5OH + HCl $\longrightarrow$ C_2H_5Cl + H_2O
ethyl   *hydrogen*   *ethyl*   *water*
alcohol   *chloride*   *chloride*

+ C_2H_5Cl $\longrightarrow$ [benzene ring with CH_2CH_3] + HCl

benzene   *ethyl*   *ethyl*   *hydrogen*
            chloride   *benzene*   *chloride*

[benzene ring with CH_2CH_3] $\longrightarrow$ [benzene ring with $CH=CH_2$] + H_2

ethyl   *styrene*   *hydrogen*
benzene

Method II:

$2[C_2H_4]$ + [benzene ring] $\xrightarrow[\substack{aluminum \\ chloride}]{\substack{pressure \\ heat \&}}$ [benzene ring with $CH_2{-}CH_3$] $\xrightarrow[\substack{\& steam}]{heat,\ pressure}$ [benzene ring with $CH=CH_2$] + H_2

ethylene   *benzene*   *ethyl*   *styrene*   *hydrogen*
gas   *benzene*

or:

[benzene ring with $CH_2{-}CH_3$] + Cl_2 $\longrightarrow$ [benzene ring with $CHCl{-}CH_3$]

ethyl   *chlorine*   a *-chlorethyl*
benzene   *benzene*

Figure 1.2: Reactions leading to the formation of

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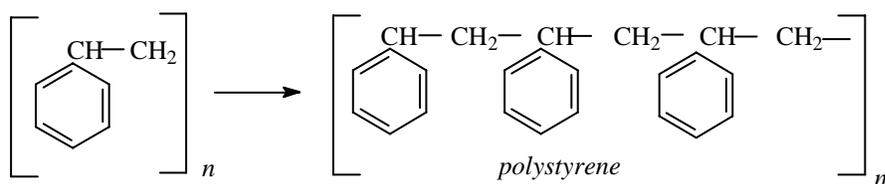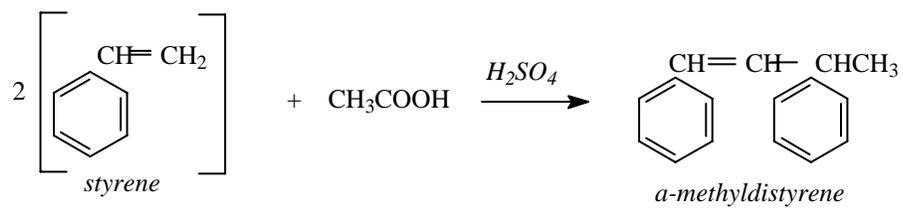
Figure 1.3: Reactions leading to the formation of polystyrene.
*Reference 1.

$$CH_2-CH-CH=CH_2$$

Dimers-Linear

$$CH=C-C\equiv CH$$

Ph   Ph

Dimers-Cyclic

$$CH_2-CH=C-CH_2-CH-CH_3$$

$$CH_2-CH_2-CH-CH_2-CH-CH_3$$
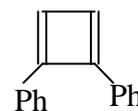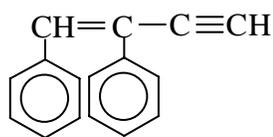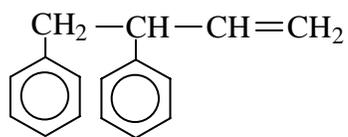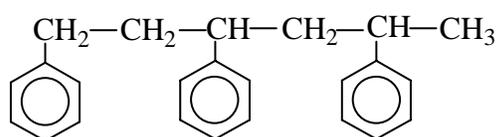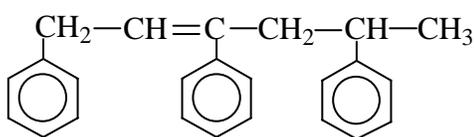
Trimers-Linear
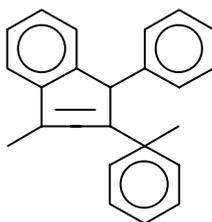
Trimers-Cyclic

Figure 1.4: Proposed structures provided by Huntsman Chemical Company of some polystyrene dimer and trimer isomers.

Polystyrene additives include antioxidants, uv stabilizers, processing lubes, antistats and flame retardants. With polystyrene they create a difficult matrix for extraction and subsequent identification using conventional solvent extraction and chromatographic methods. Three major factors must be considered when developing an analytical method for polymer additives: 1) the additives themselves are not pure compounds, 2) they are insoluble in the polymer matrix, and 3) they are in low concentration. The analytical technique, therefore, must first separate the additive from the polymer. The resulting extract must then be cleaned up to remove any low molecular weight oligomers that were extracted from the polymer and may interfere with analysis. The extract must also be handled carefully to avoid any additional additive decomposition. For instance, the antioxidants are labile, unstable compounds that often contain complex decomposition products (5).

Several other factors must be considered when developing a method for the full range of additives found in the polymer. These include volatility, molecular weight, purity and stability of the analyte as well as any matrix effects. Quality control and research protocols for compositional analysis of polystyrene have led to various analyte specific methodologies. However, the primary goal of our work was to identify the additives both qualitatively and quantitatively with minimal difficulty. The challenge was to develop methods that were not prone to interferences from other components in the polymer matrix.

Conventional methods of polymer extraction use large quantities of chlorinated solvents either in a Soxhlet extraction apparatus or a dissolution and precipitation extraction of the polymer resin. These methods are time-consuming and are scheduled to be environmentally restricted in the future. Furthermore, when analytes are present in small quantities, they may actually be lost in concentration steps following the actual liquid extraction. Supercritical fluid extraction (SFE) is particularly appealing because there is little solvent consumption, extractions are rapid with high recoveries and the extraction mode may be either off-line for method development or on-line where the analytes are directly sent to either a chromatograph or spectrometer.

Historically, additive analysis has been performed using a wide variety of analytical techniques such as titration, x-ray fluorescence, Fourier Transform Infrared (FT-IR), and chromatographic techniques. The chromatographic techniques include gas chromatography (GC), gel permeation chromatography (GPC), supercritical fluid chromatography (SFC), and high performance liquid chromatography (HPLC). Although the chromatographic methods are often cited in the literature, each one has its limitations when applied to polymer additives. GC is generally limited to thermally stable, low molecular weight analytes. GPC separates components based on their effective size in solution. According to Limpert and Jordi, adequate separations of typical antioxidants and uv stabilizers are possible with GPC using six 50 cm columns to achieve a high plate count (6). SFC has shown promise towards separation of polymer additives. However many industries do not have the instrumentation. One limitation associated with HPLC is detector constraint. By using an evaporative light scattering detector (ELSD) along with the ultraviolet (UV) detector this dilemma, however, may be solved. The ELSD enhances HPLC due to its unique ability to detect compounds that exhibit no chromophoric moiety, although the compound must be relatively non-volatile. Thus, the use of dual detectors such as UV combined with ELSD extends HPLC for the identification of additives in polymer extracts.

The scope of our research was to develop a HPLC method to separate common polystyrene polymer additives including antioxidants, uv stabilizers, processing lubes, flame retardants and antistat agents. The second phase of the research was to develop supercritical fluid extraction (SFE) techniques for eight polystyrene resins and compare the method to the dissolution/precipitation extraction method.

CHAPTER 2

Supercritical Fluid Extraction

(A) Introduction

The single most tedious, labor intensive and important task encountered in an analytical laboratory is sample preparation. Sample preparation is required to isolate the component(s) of interest from the matrix that may be either liquid, solid or semi-solid prior to separation, identification and quantification. Techniques to improve sample preparations have been lacking improvement and automation as compared to advancements seen in analytical instrumentation. The continued search and emphasis for non-toxic efficient methods of extraction have evolved in analytical chemistry due to increased concern for the health and well being of our environment. Along with the elimination of organic solvents, there is a need to improve the efficiency and turn around time for sample analysis. Therefore, the "perfect" extraction method would be simple, fast, nondestructive, quantitative and precise.

The scientific community has been aware of supercritical fluid extraction (SFE) since 1879 when the idea was first reported by Hanney and Hogarth (7). In the last decade SFE has received additional interest and has proved to be particularly appealing due to its numerous advantages. SFE is relatively fast with extraction times from hours to increments thereof. This allows the adjustment and selectivity of the extraction by changing the supercritical fluid density, modifying the fluid with a solvent or by adjusting the temperature. It is a clean extraction method whereby elimination of the supercritical fluid is accomplished by decompression of a relatively inert gas (8). Overall advantages include little solvent consumption and rapid extraction times with high recoveries. There are two options: on-line or off-line extraction. Off-line extractions are common for method development or where large samples dictate the method. On-line extraction for trace analysis is feasible when analytes transfer directly to the assay instrument (9).

(B) *Principles and Properties of Supercritical Fluids*

Supercritical fluids have physiochemical properties that are a combination of liquid-like density and gas-like diffusivity and viscosity. Supercritical fluids form after a substance's exposure to heat above its critical temperature (Tc) and pressure above its critical pressure (Pc). The definition of critical temperature is the point at which a gas can no longer be converted to a liquid by an increase in pressure. The critical pressure is that point where a liquid can no longer be converted into a gas with an increase in temperature. Figure 2.1 depicts the supercritical fluid region for a pure substance. The region above the critical point is where the liquid or gaseous states are indistinguishable. Favorable characteristics of carbon dioxide contribute to its popularity. It is non-toxic, inexpensive, has a low critical temperature (31.3°C). Carbon dioxide exhibits low critical pressure (72.8 atm), is commercially availability in high purity grade, and does not support combustion. Carbon dioxide is the fluid of choice. However, there are instances where pure carbon dioxide in its density range (0.15 to 0.95 g/mL) is not capable of extraction. Inability to extract may be due to carbon dioxide's solvent power being too weak. This may be due to the inefficiency of CO_2 as a solvent, the analytes being strongly bound to the matrix, or the analytes being physically unattainable. A modifier added to carbon dioxide will enhance the extraction capabilities. Modifiers may include solvents such as methanol, acetonitrile and chloroform. Other supercritical fluids such as nitrous oxide or fluoroform achieve particular extractions due to their higher dipole moment (10). Refer to **Table 2.1** for a list of fluids and some of their properties. The most frequently used fluid is carbon dioxide for the aforementioned reasons. Limitations for the other fluids that restrict their use are high critical limits, toxicity, corrosiveness to pumping systems, combustion support and/or cost.

Supercritical fluids yield faster extractions due to their unique liquid and gas-like properties that enable them to diffuse into a matrix and to increase the mass transfer of analytes from the matrix. Matrix effects occur, based on the individual sample. Sample matrices vary from solid to liquid to semi-solid.
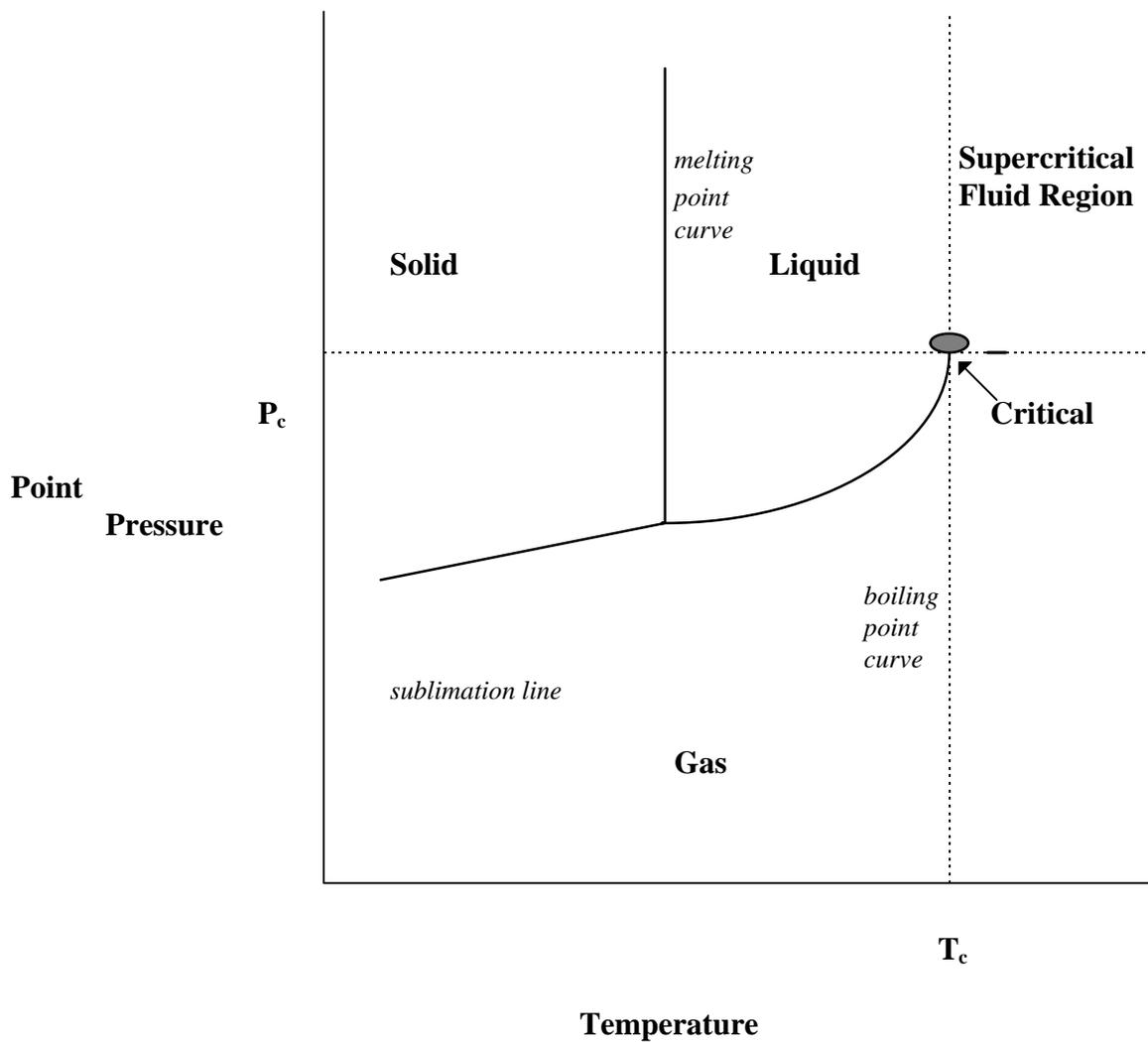
Figure 2.1: Supercritical Fluid Region for a Pure Substance

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Table 2.1: Properties of Common Supercritical Fluids*

Fluid	Critical Temperature T_c (°C)	Critical Pressure P_c (atm)	Dipole Moment (debye)
CO_2	31.3	72.8	0.00
N_2O	36.4	71.5	0.17
CHF_3	25.9	46.9	1.62
Xe	16.6	57.6	0.00
H_2O	374.1	217.6	1.51

*Reference 7

Characteristics of CO_2 such as lower viscosity and higher diffusivity make supercritical fluids more desirable than conventional solvents. Additionally, supercritical fluids possess zero surface tension that allows permeation and removal of analytes from within a matrix. Thus, supercritical fluids are desirable for polymer extractions where the fluid can swell the polymer to remove additives from within the matrix (11). By changing the pressure or temperature to regulate the density, manipulation of the solvent strength of supercritical fluid is possible. The largest adjustments occur near the critical point of the fluid. Varying the power of the supercritical fluid density, manipulation allows the extraction to be selective for specific analytes. St. Kuppers used polyethylene terephthalate to show that SFE is both solubility and diffusion controlled. The influence of temperature was explored in order to cite how diffusion controls the extraction where the solubility is high enough to dissolve the analyte molecules on the surface of the matrix. He also emphasized that for a polymeric matrix, the extraction conditions be carried out at a temperature above the glass transition temperature of the polymer. The polymer matrix at temperatures below the T_g of the polymer is impermeable or frozen (12).

(C) Operational Modes and Collection Strategies for Supercritical Fluid Extraction

Supercritical fluid extraction systems allow for static and/or dynamic modes. A fixed amount of fluid interacts continuously with the matrix in the static mode. The definition of a dynamic mode is a continuous supply of fresh supercritical fluid passing over the sample. Separate or combined modes include static and dynamic steps. Extraction times vary dependent upon the matrix analyte interactions (13).

The static mode removes surface analytes or swells the matrix before a dynamic step. In the dynamic mode a fresh continuous flow of supercritical fluid passes through the extraction chamber. The dynamic mode is generally a more exhaustive extraction than a static extraction. However, a disadvantage of the dynamic extraction may be that there are more co-extractives that complicate the analysis; especially with trace analytes. As a general guideline, three to ten vessel volumes of supercritical fluid are sufficient to obtain quantitative extraction. A static-dynamic mode is useful when the extraction is diffusion limited.

An important aspect of the extraction is the successful trapping or collection of the analytes. The trapping scenarios used are liquid-solvent traps and solid phase sorbent traps. The most common and easiest to use traps are liquid-solvent traps. A fixed restrictor from the extraction vessel leads to the vial containing the solvent. Supercritical fluids also undergo Joule-Thompson cooling upon decompression thereby helping to make it is possible to capture the components in a solvent after the extraction. Solvents most commonly used in a liquid trap are methanol, chloroform, acetone, hexane and methylene chloride. The choice of fluid is dependent upon the assay method selected. Solubility and compatibility with the analytes also dictate the solvent or mixture of solvents used in the method. Rapid expansion of CO_2 upon decompression is critical since it leads to aerosol formation. Aerosol formation is due to the decompressed fluid releasing as much as 500 to 1500 mL/min of gas when a liquid flow rate of 1 to 2mL was used for the extraction. Therefore, it is important to consider the decompression rate to limit the amount of bubbling which can create a loss of solvent. A solid phase sorbent trap collects extracts on a medium such as stainless steel beads, glass beads, Florisil, octadecylsilane bonded silica (ODS/C18) or other support material. The support material should match the polarity of the analytes. Cooling the trap assists in trapping. Rinsing the solid trap with a solvent to remove the collected analytes is critical after extraction.

Analyte loss from a solid trap may be due to the force generated by the decompressed gas, also referred to as blow-by. The term blow-by refers to the analyte going by the trap as an aerosol. Accidental rinsing of the analyte from the trap occurs due to condensed modifier(14). Eckard (15) studied the effects of trapping a polarity mix on three different solid phase traps (glass beads, octadecyl silica and porapak Q). There were notable differences with the different analytes on the different traps. Others have investigated trapping efficiencies in various solvents and found that mixed solvent systems typically yield better recoveries than single solvent systems (16). Overall, there are more variables that affect trapping onto a solid sorbent trap during method development.

SFE methods include off-line and on-line dependent upon the analyte concentrations and hyphenation methods available. Method development and large samples require off line methodology. On-line analysis can be beneficial for trace analyses

and when time is of the essence. Method development involves close scrutiny of numerous limits, including temperature that influences the density of the fluid.

D) SFE Instrumentation

Commercial instrumentation is available that consists of a hydraulic pump system (pressure control and fluid movement), a heated chamber, valves, nozzles, trap, trap rinse vial and a rinse solvent reservoir. Refer to **Figure 2.2** for a schematic of the Hewlett Packard 7680T SFE. Liquid CO_2 is withdrawn from the bottom of the gas cylinder, flows through the pump and is compressed to attain a desired pressure. A preheated zone brings the fluid to the proper temperature before it enters the extraction chamber. Valve switches maintain a static (fixed volume of CO_2) or dynamic mode (continual supply of CO_2). Extraction of eight individual sequential samples in the 7mL extraction vessels is feasible. Further explanation and discussion of the HP 7680T follow in Chapter 4.

E) SFE Applications

Successful SFE for numerous types of matrices include environmental, pharmaceutical, and polymeric matrices. The applications for supercritical fluid extraction are diverse and gaining increased acceptance in the chemical field. Hyphenated techniques including SFE extend its applications. Literature references describe assay of polymer homologue's additives including antioxidants and uv stabilizers using SFE/SFC-MS coupling (17). Determination of polymer additives on-line using SFE/SFC has shown that by using a cryofocusing trap it is possible to quantitate polyethyene and polystyrene additives (18). Other SFE applications include supercritical fluid fractionation of low molecular weight high density polyethylene wax with CO_2, propane, and propane modified CO_2 (19). It is possible to achieve the selectivity desirable for post polymerization fractionation to remove several molecular weight distributions from the parent polymer due to processing. Removal of residual solvent, unreacted monomer, fractionation of synthetic polymer, and purification of low molecular weight oils are feasible.

Extraction guidelines for polymers have been developed and encompass three major considerations (20). The variables which must be considered are: (1) the

Figure 2.2: Schematic of Hewlett Packard 7680T SFE Instrumentation

A: Pump
B: Heated Chamber
C: 7 mL Extraction Vessel
D: Valve
E: Nozzle
F: Trap (Solid Sorbent)
G: Trap Rinse Vial
H: Rinse Solvent Reservoir
I: Rinse Solvent Pump

CO_2
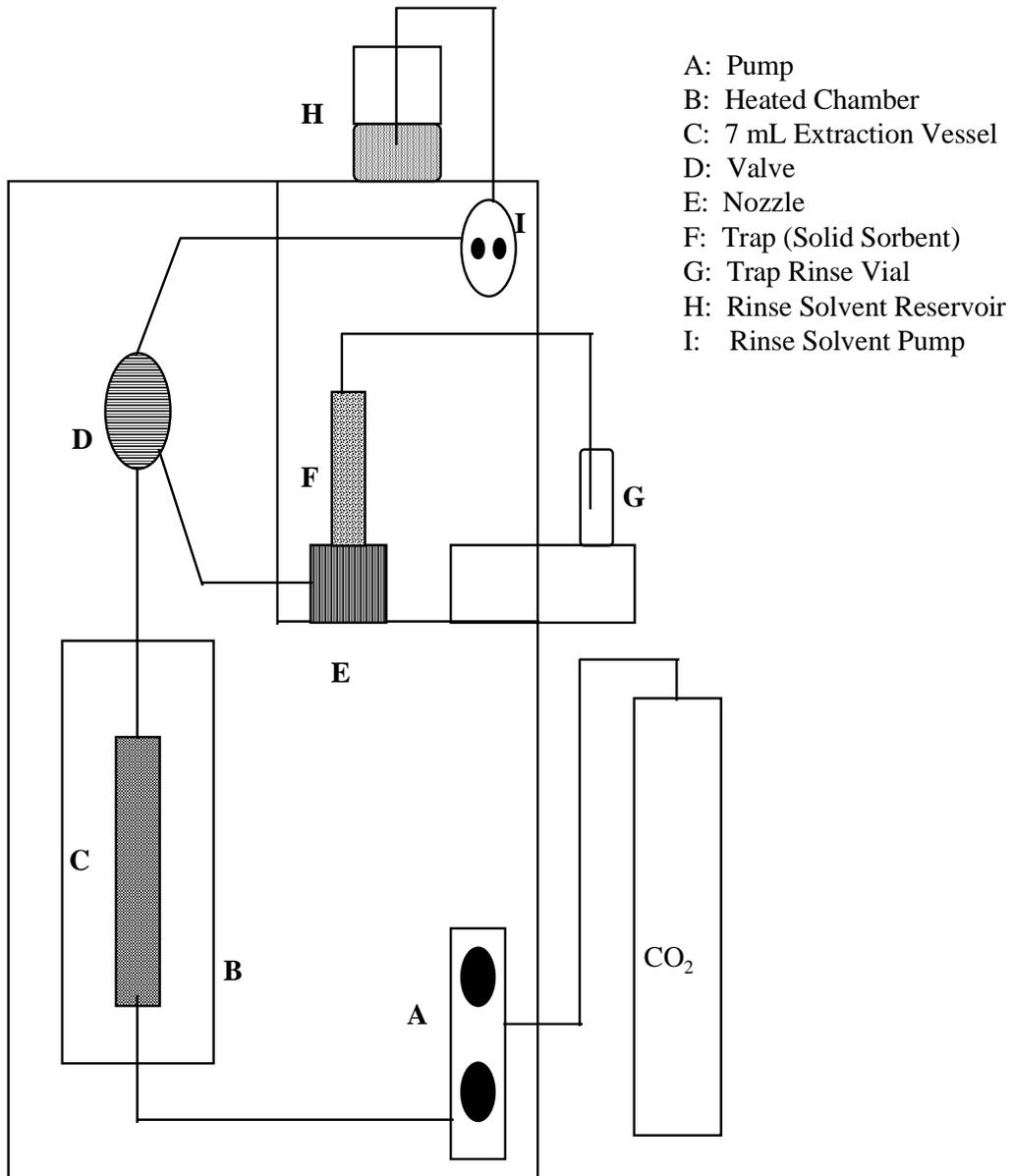
Reference 22

extraction temperature must be above the glass transition temperature (T_g) of the polymer, (2) if the extraction is diffusion limited, the temperature should be increased and/or modifier added in order to swell the polymer and (3) where the extraction is solubility limited, the extraction pressure must be increased, the temperature decreased and/or modifier added. Matrix analyte interactions may also be affected by temperature which may promote diffusion of analytes into the fluid. Finally, it may be more efficient to use a modified fluid to speed up the extraction. Elmore (21) and others have shown extraction times with pure CO_2 to be twice as long (40 minutes) as extraction times with modified CO_2 ($MeCl_2$ or hexane) for polyethylene (20 minutes).

CHAPTER 3

Polystyrene Additives

A. *Properties, Classification and Background*

Polymer additives are substances compounded into a resin to enhance or improve specific resin characteristics. Additives function by contributing to the quality, life and usefulness of the resin. Based on chemical profiles and overall functions, additives are commonly divided into categories. Common additives used in various formulations include some combination of the following: antioxidants, uv stabilizers, fillers, pigments, rubbers, processing lubricants, antistats and flame retardants.

Additives are typically present in small quantities, somewhat dependent upon their desired function. Their concentrations are typically less than a percent, but may range from 0.1% upwards to 10% for some flame retardants. Surface additives are attached to the exterior and are incompatible with the polymer. Surface additives include mineral oils, waxes, esters and fatty acids.

Antioxidants function by blocking chain reactive oxidative degradation mechanisms. Polymers not protected by antioxidants are subject to oxidative attack that may shorten the polymer's life due to discoloration, cracking, brittleness and loss of mechanical properties. The scavenging free radical mechanism is widely accepted as the means whereby polymeric materials are protected by antioxidants. The proposed free radical mechanism involving the antioxidant Irganox 1076 is depicted in **Figure 3.1** (23). "R•" represents the polymer chain that is subjected to oxidation by O_2. The primary acting antioxidant serves as a scavenger of the initiating free radical and terminates or inhibits the process by forming a non-propagating species. For example, hindered phenols function by providing a trap for the radicals and the active unpaired electrons.

$$R\bullet \; + \; O_2 \longrightarrow RO_2\bullet$$

$RO_2\bullet \; + \;$ C(CH3)3 — [ring: OH, C(CH3)3, CH2CH2COC18H37] Irganox 1076 $\longrightarrow$

$RO_2H \; + \;$ C(CH3)3 — [ring: O•, C(CH3)3, CH2CH2COC18H37]

$\longrightarrow$ C(CH3)3 — [ring: O, C(CH3)3, CH2CH2COC18H37]
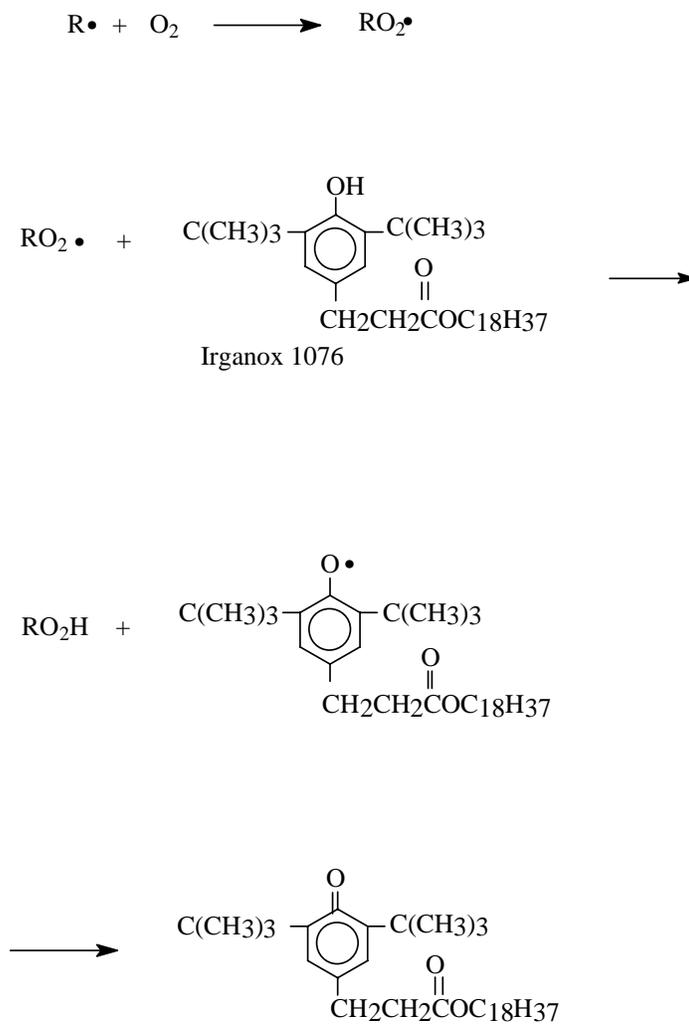
Where: R $\bullet$ = *polymer chain*

Figure 3.1: Proposed Free Radical Mechanism for the Antioxidant Irganox 1076

Primary acting antioxidants are structurally hindered phenols and secondary aromatic amines. **(Figure 3.2)** Hindered phenols and aromatic amines are structures that have a labile hydrogen atom, will not bond with molecular oxygen, and whose free radical will decompose to form a stable product. The radicals are essentially trapped by phenols that form a stable complex. The use of phenols must be monitored to avoid undesirable color effects due to their tendency to form highly conjugated units in the molecule (24).

Decomposition initiated by heat and light also contribute to the oxidative process. Excess peroxides in the resin may lead to further free radical attack of the polymer. UV absorbers **(Figure 3.3)** commonly classified as hindered amine light stabilizers (HALS) can soak up energy and impede bond cleavage.

Processing lubricants are added to enhance extrusion, injection molding, and casting. The lubricant's main function is to prevent the polymer from adhering to metal surfaces during manufacturing. Lubricants are typically fatty acids such as stearic acid (C_{17}) or salts of fatty acids such as zinc stearate. The higher the fatty acid carbon number the less compatible it tends to be with the polymer and will tend to adhere to the surface of the machinery. Other lubricants, sometimes referred to as slip agents include waxes and silicones **(Figure 3.4).**

Antistats **(Figure 3.5)** function to help bleed off static electricity that is inherent in the polymer. The low amount of water on the surface of the resin results in static electricity. The antistat's function involves increasing the hydrophilic and hydroscopic nature of the surface of the polymer's surface. This facilitates a leak off path. Safety issues such as electrical discharge may be dangerous to workers especially if flammable organics are present. Internal and external antistat agents may be used. An internal electrostatic dissipation is often remedied by using a conductive filler such as carbon black. External antistat agents are commonly quaternary amines and ammonium salts.

Flame retardants function by forming a layer on the surface of the polymer that serves as a barrier to oxygen penetration and serves to protect the polymer from heat. Flame retardants cool the combustion by diluting the combustion gases and then react with free radicals formed during the decomposition. Transfer of heat is prevented due to

OH

C(CH3)3——⬡——C(CH3)3

$$O$$
$$\parallel$$
CH2CH2COC18H37
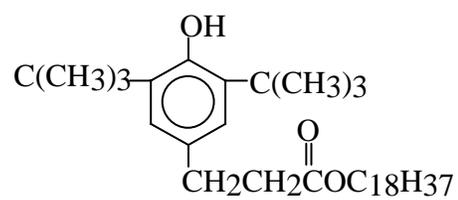
Irganox 1076
Octadecyl 3,5-di-tert-butyl-4-hydroxycinnamate

[H19C9——⬡——O——]3 P
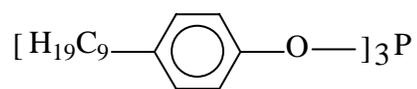
Wytox
Tris Nonyl Phenyl Phosphite

Figure 3.2: Molecular Structures of Primary Antioxidants

OH

N

N

N

CH$_3$
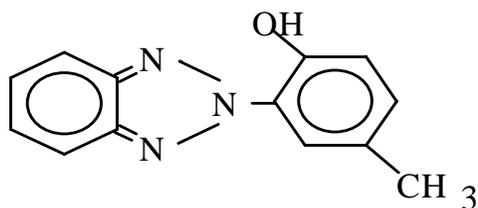
Tinuvin P
2-(2'-hydroxy-5'-methylphenyl)benzotriazole

O   O

HN — O — C —(CH$_2$)$_8$ C — O —   NH
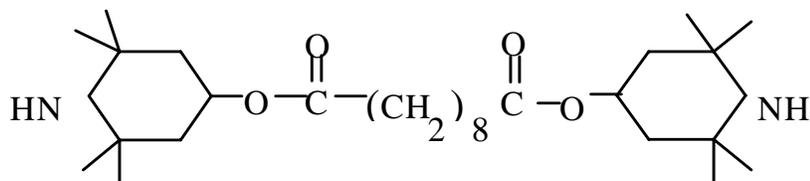
Tinuvin 770
bis (2, 2, 6, 6-tetramethyl-4-piperidyl)sebacate

Figure 3.3:   Molecular Structures of UV Stabilizers

$$\overset{\displaystyle O}{\underset{\displaystyle \|}{}}$$

$$CH_2{=}CHCN[(CH_3)_{18}]_2 \qquad\qquad Zn(C_{18}H_{35}O_2)_2$$

Acrawax   Zinc Stearate

$$CH_3(CH_2)_7CH{=}CH(CH_2)_{11}\overset{O}{\overset{\|}{C}}NH_2 \qquad CH_3(CH_2)_{16}\overset{O}{\overset{\|}{C}}OH$$

Mold Pro 830   Mold Pro 678

$$(R_2{-}Si{-}O{-})_n$$

Mineral Oil   R= monovalent organic radical

Silicone Fluid
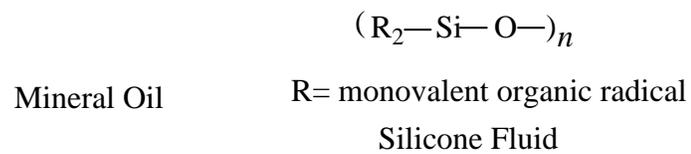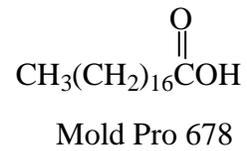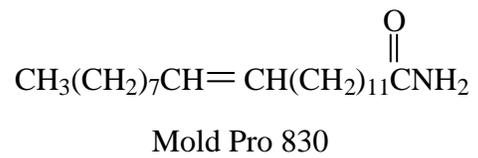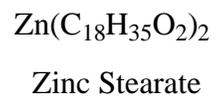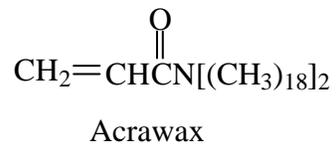
Figure 3.4: Molecular Structures of Process Lubes

$$Na-O-\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}-O-alkane$$
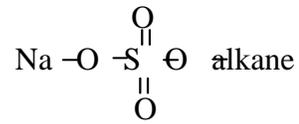
Hostastat
Sodium Alkyl Sulfonate

$$HO-\overset{\displaystyle O}{\underset{\displaystyle O}{\overset{\|}{\underset{\|}{S}}}}-O-CH_2-CH_2-\overset{\displaystyle C_2H_5}{\underset{\displaystyle C_2H_5}{N}}-CH_3$$
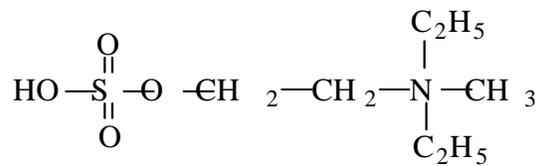
Larostat

Quaternary Ammonium Compound
Modified Fatty Diethyl Methyl
Ammonium Sulfate

Figure 3.5:   Molecular Structure of Antistats

char formation that also suppresses the fuel supply to the fire. Commercial flame retardants usually contain chlorine, bromine, phosphorous and antimony. UV stabilizers must be used in conjunction with halogenated compounds due to their sensitivity to light. Desirable characteristics of a flame retardant include compatibility with the polymer, thermal and light stability, low toxicity and low cost. Flame retardants do not migrate to the surface, nor do they increase smoke or toxic gas formation and they do not impact the polymer's physical properties. Brominated bisphenol is frequently used in polystyrene **(Figure 3.6).**

Other additives include substances such as rubber (butadiene) which functions to reduce the brittle properties of polystyrene. Impact grade polystyrene, for example, has polybutadiene dispersed throughout the polymer (25). Refer to **Table 3.1** for additive package compositions (26). These concentrations are for guidance and may vary in the actual resins themselves.

B. Analytical Chemistry of Polystyrene Additives

The extraction of polystyrene additives in resins is similar to numerous other matrices where extraction is required using Soxhlet or dissolution/precipitation methods followed by subsequent analysis. Subsequent analysis for organic additives is usually done by gas chromatography and for inorganic additives is carried out by infrared spectroscopy. Resins modified with rubber are often identified using physical rather than chemical analysis.

Surface additives may be removed by washing with a hot solvent such as methanol. Surface additives are essentially attached to the outer surfaces of the resin and may include mineral oil, mineral waxes, esters, fatty acids and amides. The hot solvent (methanol) will also dissolve some oligomers. The solution can then be evaporated and assayed using infrared spectroscopy. The inorganic additives are separated by taking several grams of the surface washed polymer and placing the material in a centrifuge tube. Solvent is added, warmed and stirred then cooled and centrifuged. The supernatant is saved and the resin is treated again. The remaining contents in the tube can be analyzed by x-ray diffraction or emission spectroscopy.
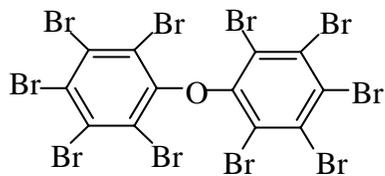
Great Lakes 83
Brominated diphenyl ether
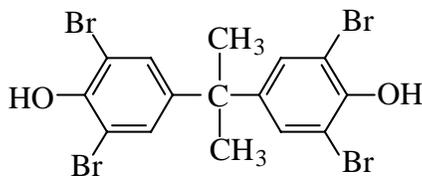
Great Lakes 59
Halogenated bisphenol A
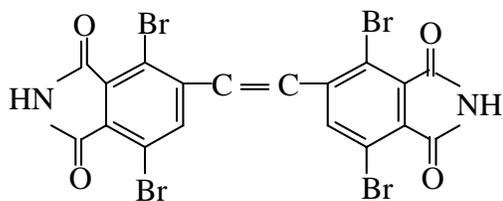
BT-93
1,2-bis(dibromophthalimido)ethane

Figure 3.6: Molecular Structures of Flame Retardants

Table 3.1: Polystyrene Formulations*

Resin	R %	M. O. %	ZnSt ppm	StAc ppm	Irg1076 %	TinP%	Tin770 %	TNNP %	AC ppm	BT93 %	DE83 %	S. O. %	HS %	E %
201			1000											
208		3.0	1000											
334	8.5	2.5	1000		0.1				200					
765	8.8	1.5		1000	0.1	0.2	0.2							
779	10.0	1.5		2500	0.2	0.3	0.5			13				
1119	10.0	2.0			0.1			0.2						
F7000	10.0	2.0			0.2						11.7			0.4
P8001	7.0	1.5	1800									1.2	2.9	

Legend:

R :   Butadiene Rubber   TNNP or Wytox: Tris nonyl phenylphosphite
M. O.:   Mineral Oil   AC: Acrawax
ZnSt: Zinc Stearate   BT93:   1,2-bis tetrabromophtalimido ethane
StAc: Stearic Acid   DE83:   decabromodiphenyl oxide
Irg1076: Irganox 1076   S. O.:   Silicone Oil
TinP: Tinuvin P   HS: Hostastat
Tin770: Tinuvin 770   E: Erucamide

*Reference 26

C. Dissolution/Precipitation Extraction

(1) Introduction/Principles and Properties of Solvent Extraction

The general modes of extracting polystyrene in industry are Soxhlet and Dissolution/ Precipitation. These techniques have been used for many years. Solubility differences between the analyte(s) of interest and the other components in the matrix are the primary considerations in the extractions. Variables to consider include the rate of precipitate formation, co-precipitation of additional components and even post-precipitation (27).

In one variation of the Dissolution/Precipitation technique, additives may be extracted from polystyrene granules (~3 grams) and dissolving them in cold sulfur-free toluene (50 to 100 mL). This dissolution is followed by re-precipitation of the polymer with ethanol or methyl alcohol in ~300mL of solvent, then the extract must be re-concentrated to claim the additive. Slonaker and Sievers described a method to obtain polymer free additive extracts using n-hexane at zero degrees Celsius (28). The two most commonly used methods in industry are outlined below for typical extraction of beaded or pelletized polystyrene.

For Soxhlet extraction the beaded samples are used without further treatment, however, the pellet samples are roughly ground to pass through a 12 mesh (1.7mm diameter) screen. A 25 gram sample is placed in a 33 mmi.d. x 94 mm cellulose thimble and secured with glass wool. The appropriate solvent, typically methanol, hexane, isopropyl alcohol or a 1:1 v/v mixture of isopropyl alcohol and hexane are added to the flask. Typical solvent volume is approximately 150mL with extraction time varying from 16 to 24 hours dependent upon the temperature of extraction and the additives being extracted.

The dissolution/precipitation extraction method uses the resin as received. First, 10 grams of the resin is weighed and place into a 500mL Erlenmeyer flask that contains 100 mL of either methyl ethylketone (MEK) or chloroform. The flask is shaken on a wrist action shaker until the resin is completely dissolved. A magnetic stirring bar is then added and the flask is placed on a magnetic stirrer. The "non-solvent," usually 100mL of methanol, is added dropwise to precipitate the polymer. The resulting supernatant is then

filtered through Whatman No. 4 filter paper under normal gravity. The filtrate is then centrifuged (10,000 rpm), if the solution is cloudy, to settle the low molecular weight waxes.

D. Experimental

(1) Dissolution/Precipitation Extraction

To establish a baseline for the actual additive content of the resin packages the conventional dissolution/precipitation extraction method was used. First five grams of the resin (unground) was placed in a 250 mL Erlenmeyer flask. Then, 50mL of chloroform was added to the flask. The flask was stoppered and a magnetic stirrer was added. The contents were stirred until all the resin had dissolved. Once the polymer was in solution, 50 mL of methanol was added dropwise to precipitate the polymer. The supernatent was then gravity filtered through a Whatman Number 1 filter. The process was repeated an additional time on the precipitated polymer to see if additional additives could be removed from the polymer matrix. Each resin was extracted in triplicate.

(2) Extract Analysis

After the extraction was completed, the samples were stored in the dark in the refrigerator until analysis. This was due to the light sensitivity of the various additives. The samples were then analyzed using the HPLC methods developed in Chapter 4. The extracts were analyzed using a Hewlett Packard Series 1050 HPLC. An ODS Spherisorb column (250 mm x 4.6 mm, 5 µm particle size) was used with a 1 mL/min flow rate and UV detection at 280 nm. Quantitation involved the use of 5 point calibration curves for each additive, and standards ranged from 50 ppm to 280 ppm with correlation coefficients ranging from 0.997 to 0.999 for all analytes monitored. Refer to **Figure 3.7** for an example of the calibration plot for Irganox 1076. Each extracted analyte peak was identified by retention time comparison. The values obtained were assumed to be the actual concentration of additive in the resin. **Table 3.1** gives the approximate additive values in the polystyrene.

External Standard Calibration Curve

y = 25787x + 104207
R2 = 0.9994
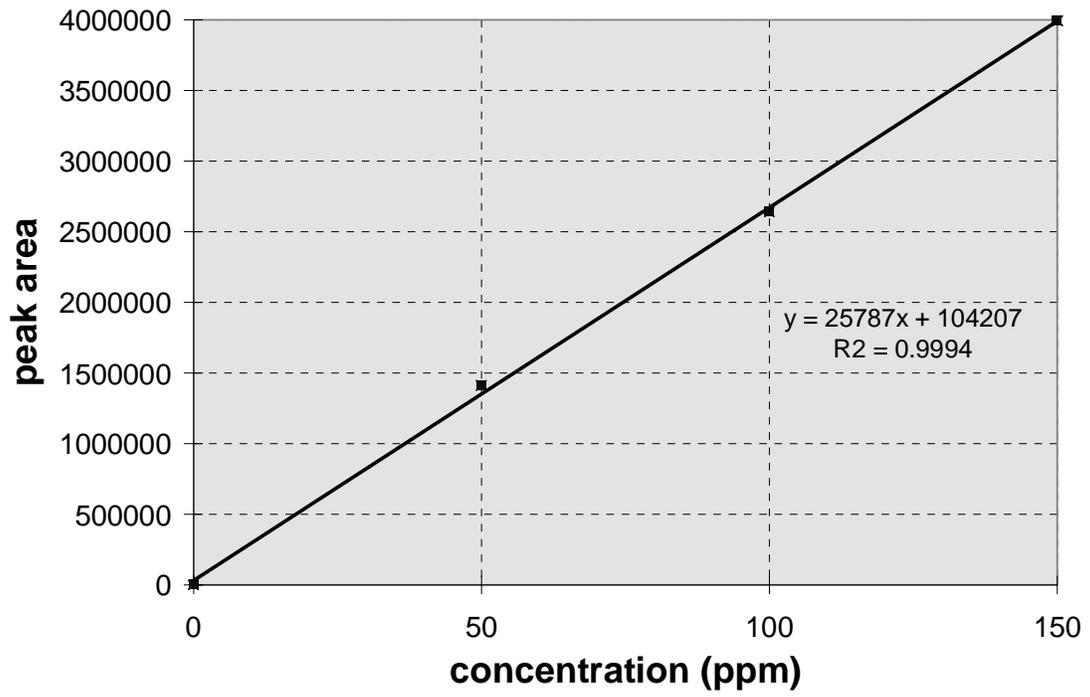
Figure 3.7: Calibration Plot for Irganox 1076.

E. Results and Discussion

The dissolution/precipitation procedure extracts the majority of the analytes; however, the extracts require clean up to remove some of the oligomers and lower molecular weight waxes which are in the extract. While methanol is capable of dissolving most additives, it is not selective and other unwanted oligomers also dissolve. Polymer extraction procedures using organic solvents are not capable of dissolving many inorganic compounds or metallorganic (i.e. zinc stearate) compounds. Along with these drawbacks, most surface additives, including antistats may be removed from the polymer by washing the polymer with a low boiling solvent that does not attack the polymer. Ultimately, an ideal procedure would extract all the additives with high yield and minimal contamination.

The dissolution/precipitation procedure was easy, although time consuming. The resins required a minimum of an hour to completely dissolve in chloroform. The filtering step also required approximately an hour to complete. Cleanup was tedious and the resins containing rubber made it extremely difficult to clean the glassware. It is noteworthy to mention that the resins containing rubber required longer dissolution times of an additional thirty to forty minutes. According to R. Miller, the dissolution/precipitation extractions with a two pass yield about ninety-two percent recoveries. However in this study, recoveries ranged from eighty to ninety percent for a first pass yield. The exception was Irganox 1076 from resin package 7000 where the first pass yield was only twenty-two percent. It is noteworthy that additional extraction of additives occurred in all the resin packages during the second extraction as shown in **Table 3.3.** The one exception is the one step dissolution/precipitation extraction of Tinuvin 770 from two of the resin packages. This would indicate that normally the procedure is not quantitative in nature. Therefore, exhaustive extraction would require numerous dissolution/precipitation steps, extended extraction times, or changes in solvent or temperature to obtain quantitative results. Refer to **Table 3.2** for the percent of additive extractables determined for the dissolution/precipitation extraction. Other researchers such as Spell and Eddy (29) have determined that the extraction solvent, the temperature, the polymer's density and particle size all impact the time required to

Table 3.2: Dissolution/Precipitation Extraction Total and Absolute Mass Extracted

Polymer	% RSD *n=3*	μg Additive/g Polymer Extracted (Average)
Irganox 1076		
334	4.5	75
765	3.1	117
779	0.8	131
1119	6.7	51
7000	3.5	131
Tinuvin P		
765	1.2	83
779	1.4	112
Tinuvin 770		
765	1.4	12
779	3.3	55
Wytox		
1119	11.9	13

Table 3.3: Percent Extractables using the Dissolution/Precipitation Extraction Process

Polymer	1st Extraction, %	2nd Extraction, %
Irganox 1076		
334	85.79	14.21
765	88.04	11.96
779	89.12	10.88
1119	81.67	18.33
7000	21.59	78.41
Tinuvin P		
765	84.04	15.96
779	86.10	13.90
Tinuvin 770		
765	100	0
779	100	0
Wytox		
1119	78.12	21.88

exhaustively extract additives. For example, polyethylene in a powdered 50 mesh requires 3 hours of shaking with chloroform in order to extract the additives. While, talc-filled polypropylene requires a minimum of 72 hours to extract the additives.

Disadvantages associated with the dissolution/precipitation technique include the following: a) lengthy amount of time to perform theextractions, b) large volumes of organic solvents required, c) disposal costs associated with the generation of large quantities of organic waste and d) extract clean up steps prior to analysis. With all of these problems, it is questionable that the method is quantitative due to a loss ofanalytes in the polymer precipitation step or rinsing of the glassware. The data shown in**Table 3.3** indicate that Wytox, a phosphite exhibited a slightly higher relative standard deviation (% RSD). The higher RSD values for Wytox might be linked to the fact that a buffer must be added to the mobile phase in order to prevent hydrolysis.

Although the Soxhlet and dissolution/precipitation methods have been around for years, they have numerous drawbacks. Extraction times are lengthy, requiring a minimum of one hour to three days for the extraction alone (30). These methods are dependent upon the temperature of the extraction, solvent used, the matrix, and the additive being extracted. Analysis of the extracts is subject to numerous handling steps that contribute to error. Co-extractives such as dimers, trimers, and low molecular weight waxes are a problem. Besides the handling problems, the additives themselves are seldom pure components. The polymerization process introduces degradation products or contaminants. Other constraints include the need for a great deal working space inside and outside a fume hood, large quantities of glassware, re-concentration steps, and lengthy clean-up. These methods are time-consuming, use organic solvents which are scheduled to be restricted in the future, and exhibit other limitations. For instance, loss ofanalytes can occur where analytes are present in small quantities due to concentration steps. Careful consideration is given during solvent selection because it strongly influences analyte's solubility. Furthermore, high purity grade solvents reduce possible contaminants. Overall, the traditional methods are very labor intensive and expensive. With these problems at hand, another method that could eliminate any of the drawbacks would be beneficial.

The use of supercritical fluid extraction (SFE) is a promising alternative technique that overcomes many of the traditional sample preparation pitfalls.

CHAPTER 4

HPLC Method Development & Supercritical Fluid Extraction
of Polystyrene Additives

A. Introduction

The quantitative analysis of polymer additives in polystyrene relies on traditional extraction methods that are laborious, time consuming, and use large quantities of organic solvents. These conventional methods (i.e., Soxhlet and Dissolution/Precipitation) are sufficient for extracting additives from the polymer matrix. However, the search for more efficient methods of extraction that use little or no organic solvent is ongoing. Introduction of new sample preparation methods such as microwave assisted extraction (MAE), sonication extraction, and accelerated solvent extraction (ASE) are designed to replace traditional techniques. Along with these methods, supercritical fluid extraction (SFE) is a forerunner replacement method for Soxhlet extraction and dissolution/precipitation extraction (31, 32). The use of SFE can eliminate some of the problems encountered with the traditional techniques while yielding similar extraction efficiencies. Another aspect of additive analysis is the number of different assay methods required to identify the additive components incorporated into the polymer. The ideal scenario would be to identify all the additive components qualitatively and quantitatively with one method.

Numerous publications and research papers (33-35) outline polymer additive extraction with subsequent analysis using high performance liquid chromatography (HPLC). The major deficiency noted in these reports is that they typically address few additive types such as antioxidants anduv stabilizers. Published research seldom addresses the entire additive package in a given polymer. This is partially due to HPLC separation difficulties where additives possessing similar structures and similar retention times result in overlapping peaks. Other publications discuss SFE coupled with SFC (36-40). SFE combined with chromatography has also been used to determine oligomer

content (41, 42). Jordan (43) used HPLC in combination with a mobile phase elimination interface to assay standard mixtures of polymer additives byFourier Transform Infrared Spectroscopy (FT-IR). By eliminating the mobile phase and depositing the additives on a germanium disc it was then possible to positively identify the additives by their characteristic spectra. Thus, there are numerous hyphenated techniques that have proven useful for the analysis of polymer additives. However, many laboratories do not have the instrumentation available or funding to obtain specialized equipment. Therefore, many manufacturing plants want to establish simple methods for laboratory technicians using existing laboratory equipment.

The purpose of this study was to first develop a HPLC method for fifteen additives in order to identify the various additive components in the resins. The HPLC method development included attempts to find a "universal" method for the polystyrene additive package. The second phase of the study was to determine whether supercritical fluid extraction was capable of extracting the additives quantitatively from eight different polystyrene resins. The SFE method development concerned the effects of supercritical fluid density, extraction temperature, static extraction time, and dynamic extraction time. Finally, a detailed comparison of supercritical fluid extraction efficiencies with dissolution/precipitation extraction is shown.

B. HPLC Experimental

(1) HPLC Method Development

HPLC method development began by determining the solubility of the fifteen additives in various solvents and combination of solvents at ambient temperature and with heat. Refer to **Table 4.1**. Four additives: acrawax, zinc stearate, silicone fluid, and BT-93 were not soluble in any of the organic solvents studied. The aforementioned four additives, and mineral oil were therefore not assayed using reversed phase chromatography. Mineral oil is soluble in chloroform, and is typically assayed using normal phase chromatography with a refractive index detector or by high temperature gas chromatography (GC). Acrawax analysis usesFourier Transform Infrared Reflectance (FT-IR) spectroscopy. A combination of titration and x-ray

Table 4.1: Solubilities of Additives

Polymer Additive	MeOH	CH$_2$Cl$_2$	1:1 MeOH & CH$_2$Cl$_2$	ACN	THF	MeOH & Heat (50°C)	H$_2$O	Other
Antioxidant								
Irganox 1076	S	N	N	N	S	N	I	
Wytox 312	I	S	I	I	N	S	I	
UV Stabilizers								
Tinuvin P	S	N	N	N	N	S	I	
Tinuvin770	S	N	N	N	N	N	I	
Process Lubes								
Acrawax	I	I	I	I	I	I	I	*
Zinc Stearate	I	I	I	I	N	I	I	*
Mold Pro 830	M	S	M	I	N	I	I	
Mold Pro 678	S	N	N	N	N	N	I	
Mineral Oil	I	S	I	I	N	I	I	*
Silicone Fluid	I	I	I	I	N	I	I	*
Flame Retardants								
Great Lakes DE-83R	I	S	I	I	I	I	I	
Great Lakes BA-59	I	S	I	I	I	I	I	
BT-93	I	I	I	I	N	I	I	
Antistats								
Larostat	S	N	N	N	N	N	S	
Hostastat	I	I	I	I	N	I	S	

Conditions: 1 mg/mL additive to solvent and ambient conditions unless otherwise stated.
Where ACN: Acetonitrile
        THF: Tetrahydrofuran
        MeOH: Methanol
        S : Soluble
        M: Moderately Soluble
        I: Insoluble
        N: Not Determined
        *: Soluble in Benzene, Chloroform, Ether, and Carbon Disulfide

fluorescence identifies both zinc stearate, and silicone fluid. Finally, qualitative determination of flame retardant BT-93 is possible by GC. Reversed phase liquid chromatography was used to assay the remaining ten additives.

(2) Sample Preparation

Huntsman Chemical Company (Chesapeake, VA) supplied the additives, dimer/trimer fractions, and the polymer resins. The polystyrene resin formulations used in this study are outlined in Chapter 3, Table 3.1. The HPLC instrument used was a Hewlett Packard Model 1050 (Wilmington, DE) equipped with an automatic injector and UV detector. An evaporative light scattering detector (ELSD), (Alltech Varex, MK III) was used in tandem after the UV detector. Solvents were reagent grade and consisted of 1, 2-dichloroethane (CH_2Cl_2), acetonitrile (ACN), tetrahydrofuran (THF) and methanol (MeOH). The water (H_2O) was ultrapure HPLC grade.

(3) Analysis

Isocratic and gradient elution profiles were employed. Refer to **Table 4.2 and Table 4.3** for a listing of the different columns, gradients, and conditions used successfully or semi-successfully to establish HPLC reversed phase methods for the additives. The dimer/trimer fraction and the similarity of the other additives contributed to overlapping peaks and interferences in a majority of the separations.

Preliminary HPLC separations used an ODS-2 Keystone Spherisorb, 5 μm, 250 mm x 4.6 mm column. The mobile phase began with 78% MeOH and increased at a rate of 1.2% MeOH per minute under ambient conditions. Addition of 2% (n-butyl-amine) was added to the mobile phase and the eluent flow rate was 1 mL/min. Three additives, Irganox 1076, Tinuvin 770, and Wytox exhibited good separations. The remaining additives were problematic.

To separate the remaining seven additives the mobile phase began with 20% MeOH and increased at 24% per minute to 70% MeOH, then a 13 % increase per minute, and finally a 2.4% increase per minute to 100% MeOH in 18 minutes. The eluent flow rate was 1 mL/min at ambient temperature. This mobile phase scheme resulted in the separation of five of the seven additives: Larostat, Hostastat, Great Lakes 59, Mold Pro 830, and Mold Pro 678. However, the

Table 4.2 HPLC Chromatographic Conditions used for the Separation of Additives

HPLC Method Number	Mobile Phase*	Column Temp. °C	HPLC Gradient Program
Preliminary	MeOH: Water*	ambient	78-100% MeOH @ 1.2% per min.
1	MeOH: Water*	ambient	20-80% MeOH @ 24% per min. 70-30% MeOH @ 13% per min. 100% MeOH @ 8% per min.
2	ACN:Water*	ambient	20-80% ACN @ 24% per min. 70-30% ACN @ 13% per min. 100% ACN @ 8% per min.
3	ACN:Water*	50	50:50 linear
4	MeOH	ambient	isocratic
5	MeOH: Water*	ambient	95:5

Note: The column was an ODS-2 Keystone Spherisorb, 5 µm, 250 mm x 4.6 mm.

Detection with UV @280 nm and ELSD Conditions are given in Table 4.3.

*The mobile phase was modified with 2% triethylamine or n-butylamine.

Table 4.3 ELSD Conditions used During the HPLC Separation of Additives

ELSD Conditions			
HPLC Method No.	**Drift Tube, Temp, °C**	**Nitrogen Flow, Standard Liters Per Minute**	**Time, minutes**
Preliminary	89°C	2.3	all
1 & 2	112°C	3.2	2.5
	92°C	2.45	3.0
	80°C	2.0	12.5
3	116°C	3.2	all
4	80°C	2.0	all
5	82°C	2.1	all

dimer/trimer fractions masked one of the Mold Pro 830 peaks. Tinuvin P and Great Lakes 83R did not separate in this chromatographic run. **Figure 4.1** depicts the separation using HPLC Method 1.

Believing that acetonitrile is a "better" solvent than methanol, we decided to use the same gradient and substitute acetonitrile for methanol. Therefore, HPLC Method 2 began with 20% ACN with an increase of 24% per minute to 70% ACN, then a 13% increase per minute, and finally a 2.4% increase per minute to 100% ACN in 18 minutes. The eluent flow rate was 1 mL/min at ambient temperature. This gradient resulted in the separation of only three of the additives: Hostastat, Larostat, Great Lakes 59 plus the dimer/trimer fraction. Four additives were not chromatographed. **Figure 4.2** depicts the separation using HPLC Method 2.

Considering the separation problems encountered with both HPLC Method 1, HPLC Method 2, and the limited solubility of the additives in organic solvents, we decided to apply heat to the column. Nielson (44, 45) had shown improved peak shape in his study of polymer additives by using 40°C to 55°C column temperatures for polyethylene additives. HPLC Method 3 used a 50:50 ACN:Water linear gradient, and a column temperature of 50°C. The additives in solution were heated to 50°C before analysis. The higher column temperature was expected to enhance the solubility of the additives and to prevent them from precipitating out of solution onto the head of the column. Refer to **Figure 4.3** for the separation using HPLC Method 3 with column heat. Unfortunately, this linear gradient resulted in a poor separation. The dimer/trimer fractions masked the majority of the additives. Hostastat and Larostat peaks overlapped one another, and Great Lakes 59 exhibited two peaks.

HPLC Method 4 used 100% MeOH. This method is adequate for several of the resin packages. It is not valid however, for the two antistats either Hostastat or Larostat, or where the uv stabilizer, Tinuvin 770 or the antioxidant, Wytox are present. These additives require a mobile phase with water or with n-butylamine modified water. Where both of the antistats are present, HPLC Method 1 must be used for an adequate separation. For Tinuvin 770 or Wytox, HPLC Method 5 was efficient and answered the need for a modified mobile phase.

1 Larostat
2 Hostastat
3 Hostastat
4 Hostastat
5 Great Lakes 59
6 Mold Pro 830
7 Dimers/Trimers
8 Mold Pro 678
9 Great Lakes 59
10 Dimer/Trimers

time, minutes

0   25
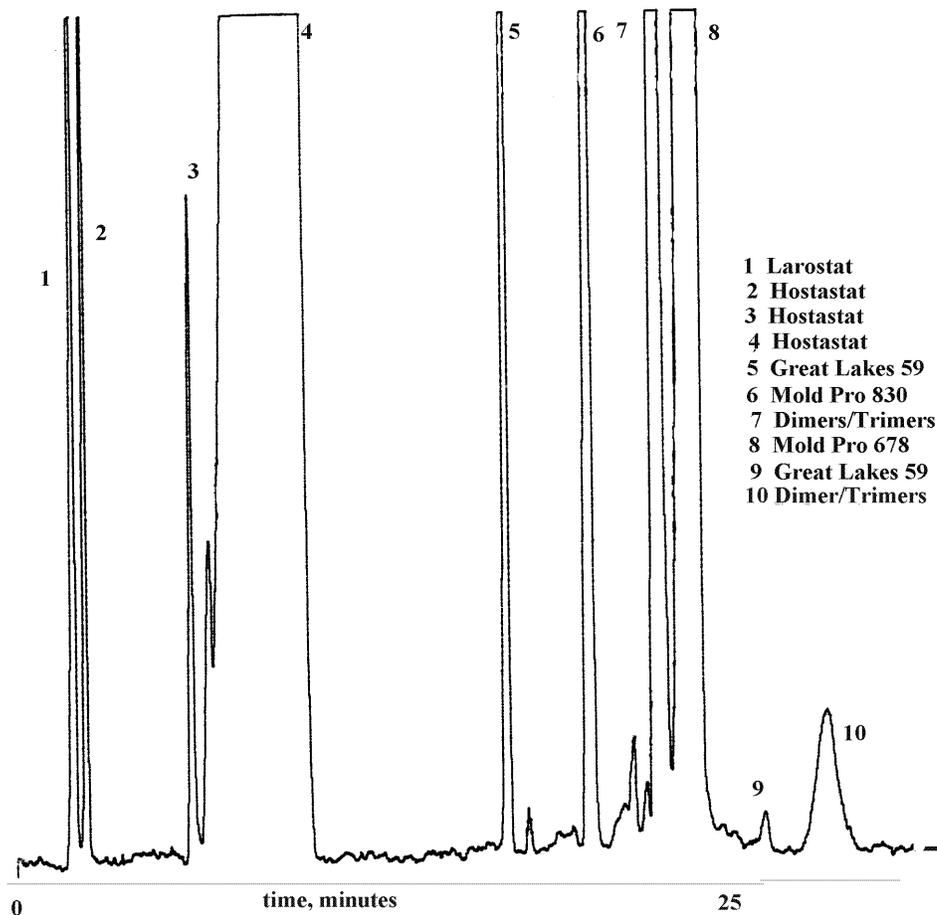
Figure 4.1: HPLC Chromatogram of Additives using HPLC Method No. 1. Conditions: Methanol:Water 20:80 (24%/minute), 70:30 (13%/minute), 100:0 (8%/minute), ambient temperature, and UV detection at 280nm
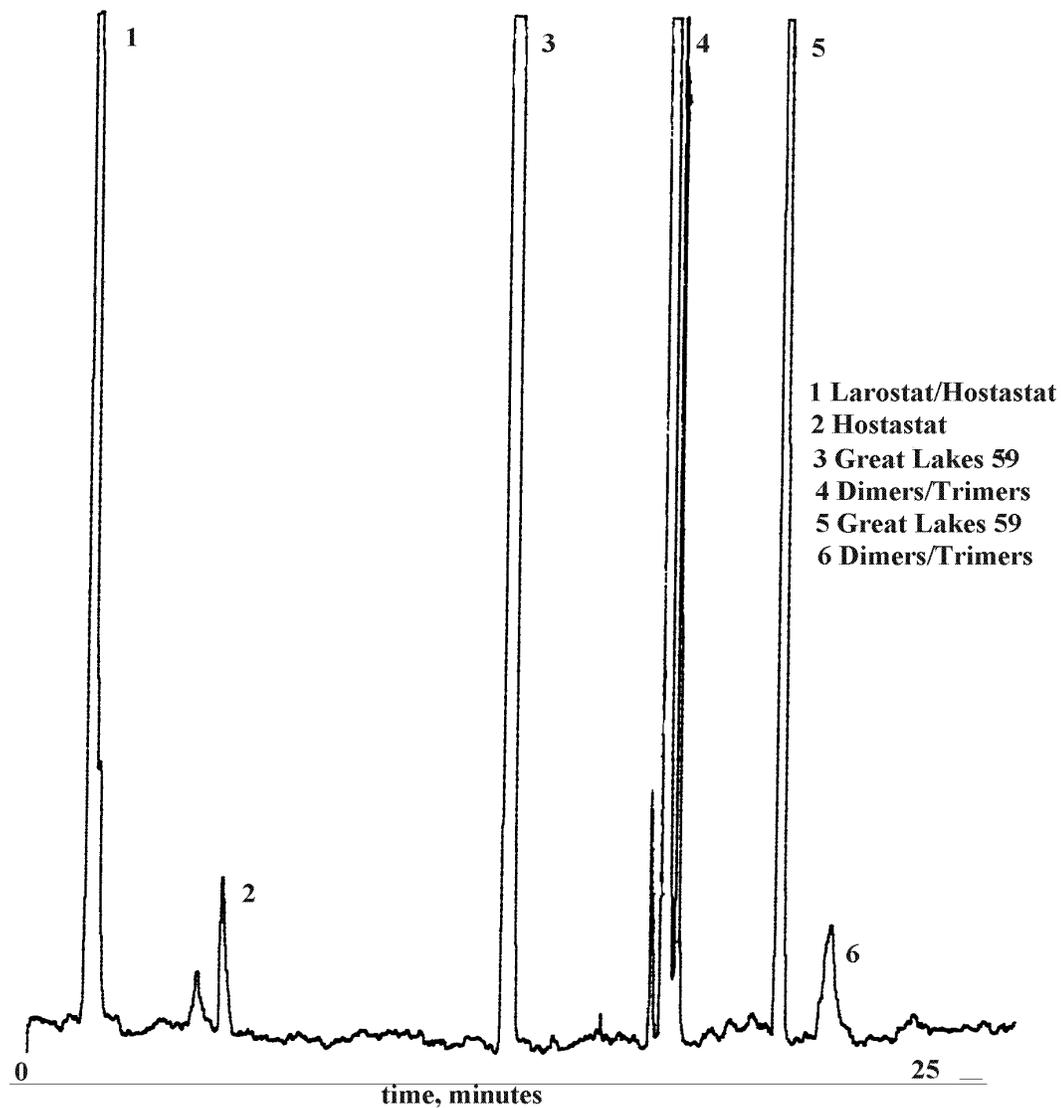
Figure 4.2: HPLC Chromatogram of Additives using HPLC Method No. 2. Conditions: Acetonitrile:Water 20:80 (24%/minute), 70:30 (13%/minute), 100:0 (8%/minute), ambient temperature, and UV detection at 280nm.

1 Larostat/Hostast
2 Unknown
3 Great Lakes 59
4 Dimers/Trimers
5 Dimers/Trimers
6 Dimers/Trimers
7 Great Lakes 59
8 Dimers/Trimers
9 Dimers/Trimers
10 Great Lakes 59
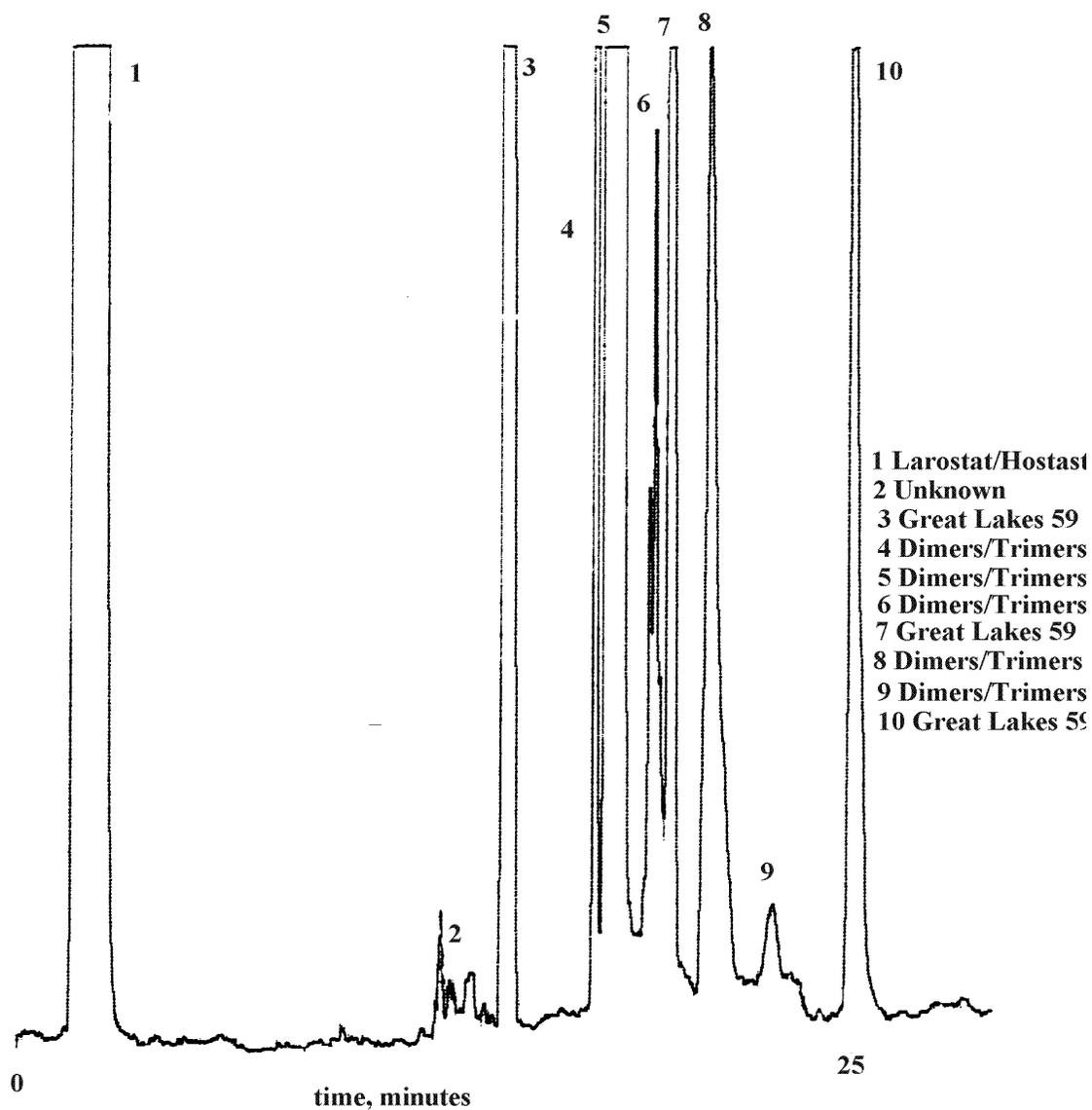
Figure 4.3: HPLC Chromatogram of Additives using HPLC Method 3. Conditions: Acetonitrile:Water (50:50) Linear Gradient , 50°C Column Heat, and UV Detection at 280nm.

C. Results and Discussion of HPLC

HPLC reversed phase is employed in approximately 80% of liquid chromatography analyses. UV detection is highly sensitive, has a wide linear range, and is relatively unaffected by temperature fluctuations while being suitable for gradient elution (46). It is capable of recognizing compounds that absorb ultraviolet or visible light at wavelengths above 200nm. Many common polymer additives do not contain achromophoric moiety. UV detection is therefore incapable of detecting those compounds without a chromophore. Other detectors such as refractive index, lack sensitivity and can only be used with isocratic gradients. Of the additives we examined, mineral oil is assayed using normal phase chromatography with a refractive index detector or by using high temperature GC. Unfortunately, limitations of normal phase HPLC include simple mixtures and routine target compounds. Therefore, we chose reversed phase chromatography with UV detection complemented with ELSD for assaying the remaining polymer additives.

During preliminary HPLC method development, analyses centered on synthetic mixtures of additives. Refer to the appendices for sample chromatograms of single additives injected which exhibited several peaks due to residual byproducts and contaminates in the synthetic mixtures. Initial chromatograms did not exhibit peaks for either Tinuvin 770 or Wytox (phosphite ester). Reversed phase chromatography with water in the mobile phase encountered problems analyzing phosphite esters. This is because the phosphite esters are prone to hydrolysis. An additive, such as 2% triethylamine (TEA) or n-butylamine added to the mobile phase allows detection of these additives.

In HPLC Method 1, the mobile phase scheme resulted in the separation of five of the seven additives: Larostat, Hostastat, Great Lakes 59, Mold Pro 830, and Mold Pro 678. However, the dimer/trimer fractions masked one of the Mold Pro 830 peaks. The remaining two additives, Tinuvin P and Great Lakes 83R did not exhibit any peaks in the chromatographic run. It is questionable why Tinuvin P did not exhibit a peak. Speculative analysis would indicate that other additives or the dimer trimer peaks masked

the Tinuvin P peak. The Great Lakes 83R missing chromatographic peak is either due to it's limited solubility or it could have been masked by other additives.

In HPLC Method 2, the dimer/trimer peaks overlapped with Mold Pro, and Tinuvin P. Overall, HPLC Method 1 with the methanol gradient exhibited better separation of the components than HPLC Method 2 using acetonitrile. Considering the unsatisfactory results in HPLC Method 1 and HPLC Method 2 we decided to raise the temperature. Raising the temperature should enhance the solubility of the additives, thereby improving the separation.

Because antistats are insoluble in methanol and soluble in water, resin packages containing these additives required HPLC Method 1 or HPLC Method 2. These methods eluted and separated Larostat and Hostastat at the beginning of the chromatographic run. The use of these gradients was only necessary if both additives were present in the extract. Referring to Table 3.1, this would not be likely. The use of one of these two HPLC Methods will be necessary if trying to assay these two antistats at the same time. Another method would be preferable when identifying other analytes because these mobile phases with significant quantities of water extend the analysis time considerably.

HPLC Method 3 that used acetonitrile and column heat exhibited a better separation than HPLC Method 2 with methanol and no column heat. However, the improved separation only included additional peaks from the dimer/trimer fraction and one additional peak from the Great Lakes 59. There was no appreciable resolution of the Mold Pro's or of Tinuvin P. It was apparent that heating the column and the samples improved the solubility, and enhanced the separation. Disadvantages of heating the column include promoting degradation of the silica based stationary phase and difficulties trying to assay thermally labile solutes.

Analysis of the additives used isocratic and gradient reversed phase chromatography with UV detection at 280 nm. An ELSD in conjunction with the UV detector enhanced detection. Refer to the Appendix C for a sample chromatogram showing both UV and ELSD detection using HPLC Method No. 4 for resin 779. The ELSD functions by recognizing molecules that do not contain chromophores. Calculations of the ELSD limits depend on the solvent mixtures used (i.e., the drift tube

temperature and the flow of nitrogen settings adequately nebulize the eluant). The ELSD overcomes numerous obstacles since it is capable of detecting any sample less volatile than the mobile phase (47). It is sensitive and is able to detect low nanogram quantities without regard to functional groups or optical characteristics. The ELSD nebulizes the mobile phase and the sample analyte detection occurs by a photodiode measuring the amount of laser light that shines through a flow cell. The ELSD limits had to change to reflect the changing mobile phase. Manual adjustment had to be made to change the ELSD settings to assure that the mobile phase was evaporated. Evaporation of the mobile phase created a noisy baseline, as was evident when large percentages of water in the mobile phase had to be eliminated. The ELSD chromatograms agreed with those obtained by UV detection.

HPLC Method 4 that used a methanol isocratic scheme proved to be efficient for the majority of the resin packages. Refer to **Table 3.3** and note that most of the resin packages only contain a few additives. The overall preferred method would be the methanol: water gradient at ambient temperature. Selections of either isocratic or gradient mobile phases based on the analysis required by the resin package allow flexibility.

Recent studies have shown that the effect of acetonitrile:water mobile phase composition on the adsorption characteristics of reversed phase liquid chromatography to be comparable to the adsorption characteristics of a methanol/water mobile phase. In both mixtures the surface diffusion dominance for the intraparticle diffusion in ODS silica gel particles had similar tendencies and therefore the two may be analogous (48). There was no appreciable improvement using acetonitrile over methanol as evident in the chromatographic runs. With all the variables to consider, it was possible to design a chromatographic method to identify the majority of the additives. We also realized that trying to develop a single method to identify all the additives is not practical, and would probably not be needed for the real world samples and applications. Typically, the resin packages contain three to four additives. Consider that the resin typically contains an antioxidant, uv stabilizer, and the one or two other additives. With that in mind, the remaining chromatography will use the gradient for the analyte(s) of choice.

D. SFE of Polystyrene Additives

(1) Extraction

All extractions were performed using a Hewlett Packard (Wilmington, DE) Model 7680T supercritical fluid extractor employing carbon dioxide (CO_2) as the supercritical fluid. Carbon dioxide without helium headspace was donated by Air Products and Chemicals, Inc. (Allentown, PA). Refer to Figure 2.2 for the SFE instrumentation schematic. The SFE system uses a cryogenically cooled (4°C) dual head reciprocating pump that delivers the extraction fluid that becomes supercritical when it enters the heated chamber. The first pathway for the supercritical fluid is through the extraction vessel. The extraction vessels used were 7 mL and loaded according to **(Figure 4.4)**. The first layer consisted of Ottawa sand (20-30 mesh, Fisher Scientific) followed by the ground polymer, and finally the celite. The path for the extraction fluid is through the extraction vessel, to the variable restrictor and on through the solid phase trap (6 cm x 0.45 cm). For this work, the solid phase trap used contained stainless steel beads. Rinsing of the trapped analytes from the stainless steel bead trap involved using a mixture of HPLC grade methanol and chloroform (EM Science) as the rinse solvent. Collections of the trap rinsings were in 2 mL capped amber vials.

A preliminary study to determine the SFE limits began by setting up an extraction scheme for resin 334. First, grinding the polymer pellets in a miracle mill to a very small particle size increased the surface area of the sample. Grinding the resins is only possible under liquid nitrogen. The liquid nitrogen cools the resins so that they can fracture. Increasing the surface area of the sample aids in the extraction of the additives from the resin. The increased surface area allows the supercritical fluid to permeate more of the sample. Next, a static step programmed at the beginning of the extraction swells the resin **(Figure 4.5)** before the dynamic step. Third, the extraction involved taking the polymer to its glass transition point (T_g). Literature references polystyrene as having a T_g of 80°C to 100°C with a crystalline melting point of 240°C. Optimization of polymer extractions occur near the T_g point (49), whereas extraction inhibition can occur near the polymers melting point (T_m). **Figure 4.6** shows a
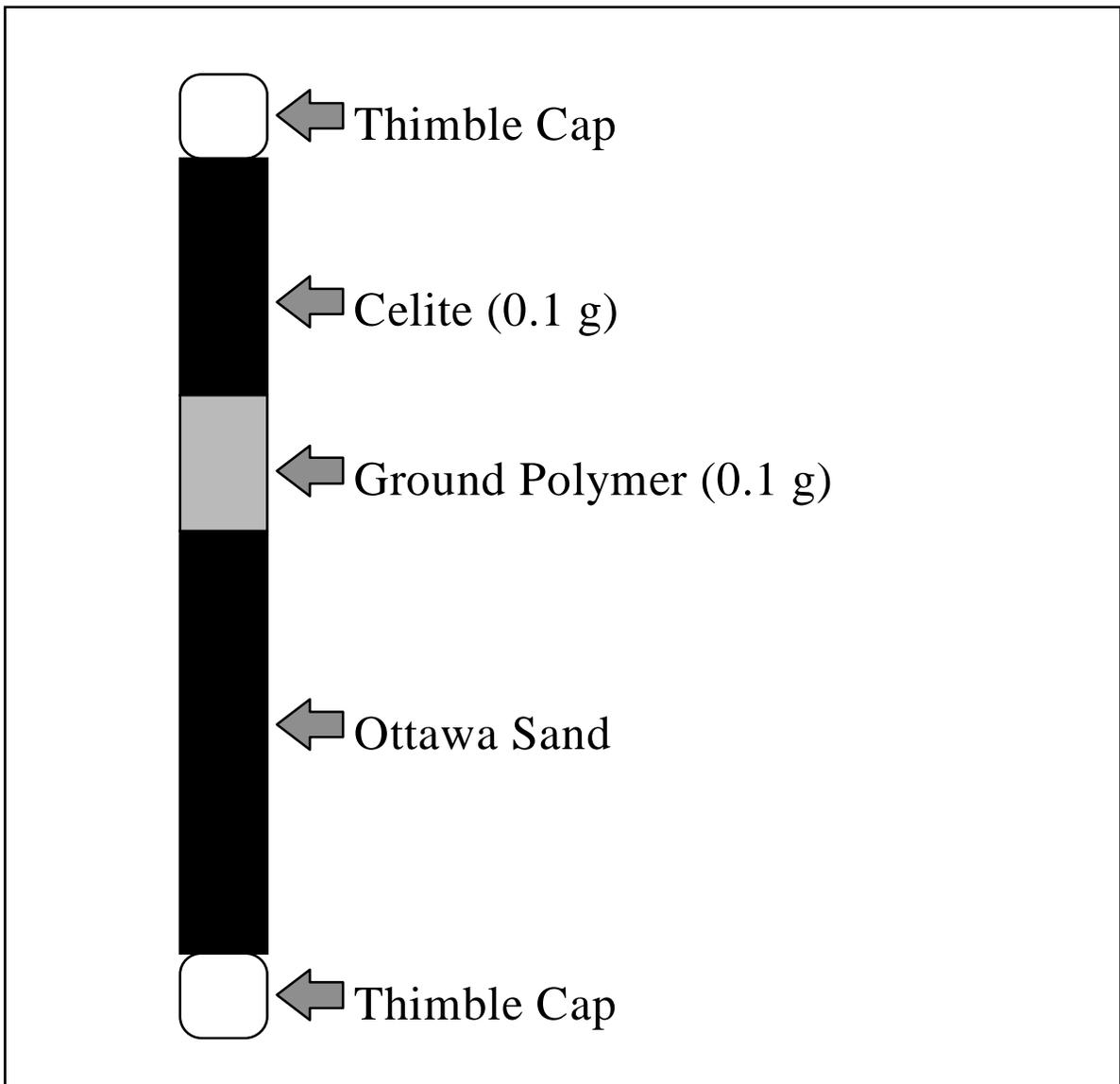
**Figure 4.4:** Diagram of a 7 mL SFE Extraction Vessel Loaded with Ground Polymer
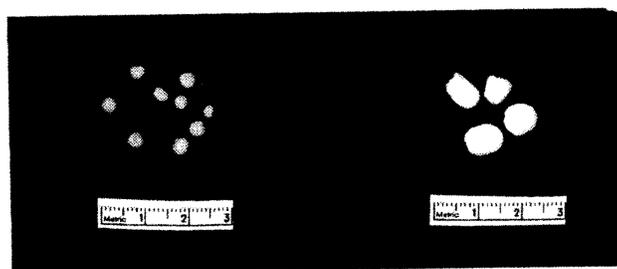
Before   After

Polymer 334

Figure 4.5: Polymer Before and After Exposure to CO_2
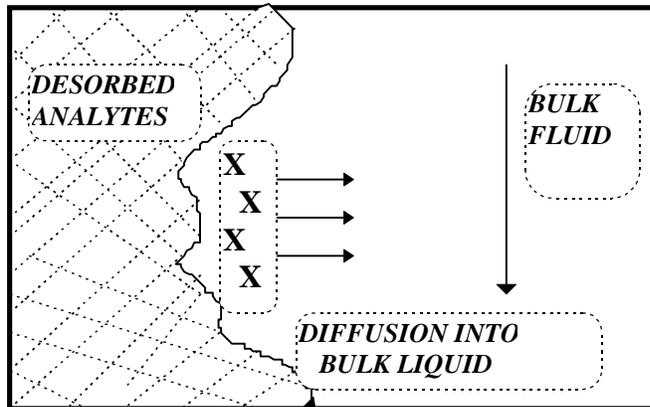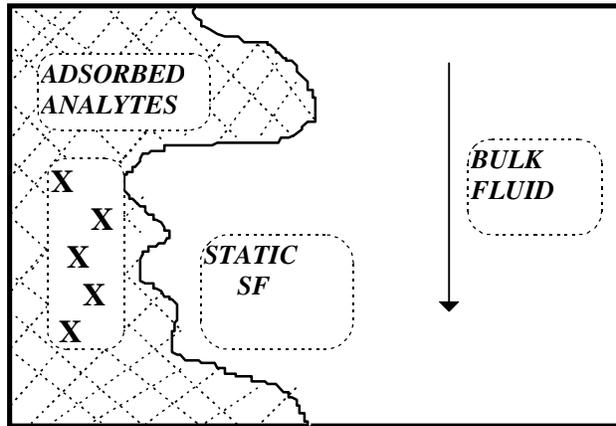
Figure 4.6: SFE of an Analyte from a Polymeric Matrix
*Reference 50

graphical depiction of the extraction and removal of analytes from a polymeric matrix. Refer to **Table 4.4** for a listing of the SFE conditions used for resin 334.

The first attempt to extract Irganox 1076 from resin 334 used the following conditions: the fluid was CO_2 at a pressure of 378 bar (0.75 g/mL) and an extraction temperature of 90°C using a stainless steel bead trap maintained at -10°C. The rinse solvent was methanol. The resin was ground in a miracle mill (MC 17B) with liquid nitrogen.

A standard U. S. 1 mm mesh sieve screened out the larger particles of ground resin. **Figure 4.5** shows the general sample loading scheme used for the extraction cell. The method used a liquid flow rate of 1 mL/min CO_2 with a static extraction time of 10 minutes followed by a 5 minute dynamic extraction. With extraction recovery of only 50%, it was evident that several limits were inadequate.

The second attempt to extract Irganox 1076 from resin 334 used an increased extraction temperature of 110°C with a reduced density of 0.71 g/mL and a slight increase in pressure of 383 bar. Reduction of nozzle temperature was from 90°C to 50°C, and a mixture of methanol and chloroform replaced the methanol rinse solvent. An increased recovery of 72% resulted.

Establishment of a third design to extract Irganox 1076 from resin 334 concentrated on lowering the parameters of the extraction. The parameters included a slight decrease in the pressure of 374 bar, a decrease in extraction temperature to 110°C, and a slight decrease in the nozzle temperature to 45°C. The recovery obtained increased to 86%. With this increased recovery, it was time to expose resin 334 to extended extraction timelines to generate data for an extraction profile. The extraction CO_2 fluid pressure was 374 bar (0.77 g/mL), 90°C extraction temperature with a stainless steel bead trap maintained at -10°C. Extraction began with a ten minute static extraction, followed by an increased dynamic extraction time ranging from 10 minutes to increasing incrementally to a total of 2 hours. The variable restrictor setting remained set at 45°C during the extraction and rinse steps. A mixture of methanol and chloroform rinsed the trap after extraction. No additional sample clean up was necessary. Refer to **Figure 4.7**

Table 4.4: SFE Conditions for Resin #334

Parameter	1st Attempt	2nd Attempt	3rd Attempt
Extraction Fluid	CO_2	CO_2	CO_2
Density, g/mL	0.75	0.71	0.77
Pressure, bar (psi)	378 (5495)	383 (5553)	374 (5406)
Chamber Temperature, °C	90	110	110
Nozzle Temperature, °C	90	50	45
Trap Temperature, °C	-10	-10	-10
Static Time, minutes	10	10	10
Dynamic Time, minutes	5	5	5
Rinse Solvent	MeOH	75:25 (MeOH:CHCl$_3$)	75:25 (MeOH:CHCl$_3$)
Recovery of Irganox 1076, %	50	72	86

**Extraction Profile of Irganox 1076
from Polymer #334**
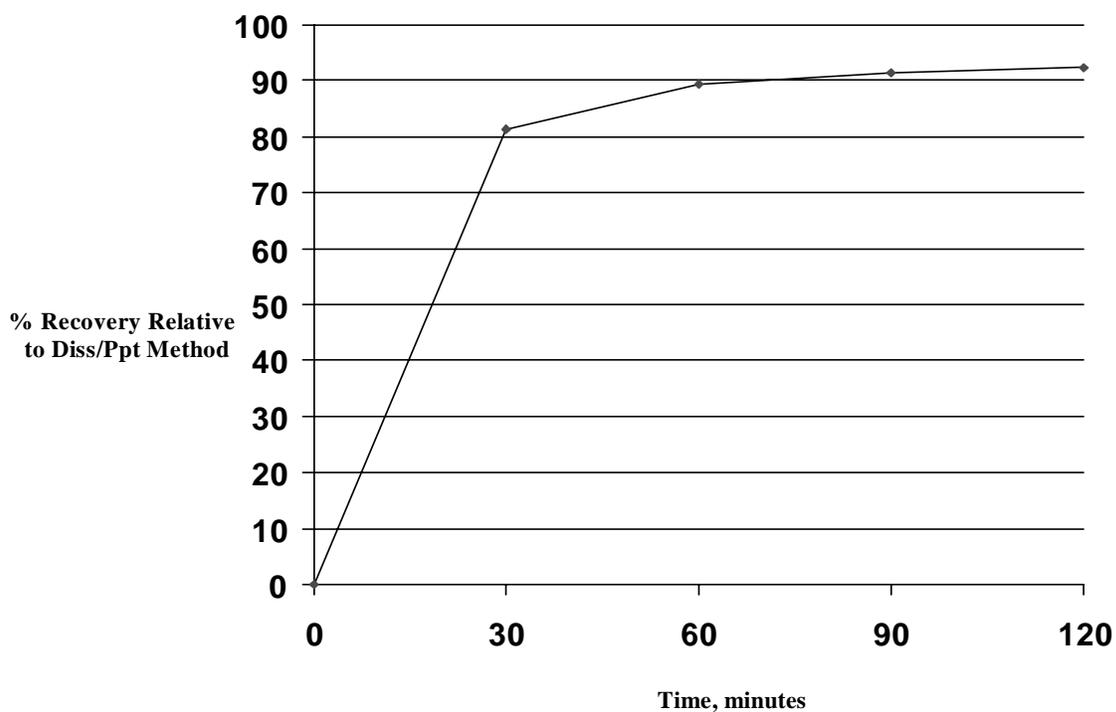
Figure 4.7: Extraction profile of Irganox 1076 from resin 334. Extraction conditions: CO_2 at 110°C and 374 bar (5391 psi) with a static time of 10 minutes and dynamic time increasing 30 minutes for each successive extraction.

for the extraction profile generated of Irganox 1076 from resin 334 using the 3rd attempt extraction parameters.

(2) Sample Preparation

With the basic extraction conditions determined for resin 334 the method changed slightly for extraction of the other resins. The extraction profile generated from the establishment of the extended extraction times helped design the final method. As shown in **Figure 4.7**, the minimum extraction time should be 60 minutes. That is the point where the extraction showed an approximate 90% recovery and additional extraction time did not extract additional significant quantities. Refer to **Table 4.5** for a listing of the extraction limits for the resins. Grinding of the resins to a smaller particle size to increase the surface area of the samples was accomplished using a miracle mill under liquid nitrogen before analysis. The ground resin fractions were screened through a 1 mm standard sieve. Extractions of the polymers performed in triplicate should be sufficient to ascertain the method. The 7 mL extraction vessels loading began with Ottawa sand, ground polymer, followed by celite. It is worthy to note, that celite mixed with the polymer aids in allowing the extraction fluid to surround the polymer particles. After extraction, the small particles of polymer appeared swollen and cemented together. Therefore, it is important to leave headspace in the extraction cell to allow for the polymer's expansion.

(3) Extract Analysis

Analysis involved the use of external standards due to the nature of the extracts and the occurrence of coextractives and low molecular weight waxes and oligomers. Analysis of the extracts obtained from triplicate extractions using supercritical CO_2 used a Hewlett-Packard (Wilmington, DE) 1050 Series HPLC with an autosampler and a UV Detector. The column was an ODS-2 spherisorb (4.6 mm x 25 mm) with 5 μm particle size. Refer to the HPLC method development section and Table 4.2

Quantitation involved using five point calibration curves ranging from 10 to 2800 ppm with correlation coefficients ranging from 0.997 to 0.999 for the analytes measured. Determination of the calibration curves involved plotting the areas of the standards. Comparison of analytes to the standards was then feasible. Specific retention times

Table 4.5: SFE Extraction Parameters for the Resins

Parameter	Condition
Extraction Fluid	CO_2
Density, g/mL	0.70
Pressure, bar (psi)	374 (5406)
Chamber Temperature, °C	110
Nozzle Temperature, °C	55
Trap Temperature, °C	-10
Static Time, minutes	10
Dynamic Time, minutes	60
Thimble Vessel Volumes	11
Rinse Solvent	75:25 (MeOH: Chloroform)

determined with the standards were used for the sample chromatographic runs. Determination of the percent recovery of the SFE extracted analyte was accomplished by comparing the ratio to the analyte concentration obtained by dissolution/precipitation.

E. Results and Discussion of SFE

The experimental section outlines the extraction and extract analysis procedure. The striking similarities of the chromatograms of the extractables using either method is interesting. Refer to **Figure 4.8** for a side by side comparison of extract chromatograms showing both types of extraction, the dissolution/precipitation and SFE methods.

Sample preparation involved grinding the sample resins. The purpose of the grinding is two-fold, it increases the surface area of the matrix, which in turn improves the extraction efficiency. There are previous studies in which the extraction values obtained from pellets were much lower (50% to 90%) as compared to the dissolution/precipitation methods (51). The variations of recoveries of this magnitude are matrix dependent.

Limitations of SFE for polymeric materials is hampered due to diffusion of the analytes across the matrix and by the analytes solubility in the supercritical fluid. Extractions are also known to be temperature dependent. While increasing the temperature increases the extraction, so does increasing the pressure. With an increased pressure it is also likely to increase the solubility of the additives. However, while increasing the pressure of the extraction fluid, there will be a drop in the diffusivity capacity of the fluid. Since diffusivity is pressure dependent, an optimal combination of temperature and pressure should control the solubility. The sequential steps of melting and cooling the polymer during recycle processes increases the polymer's crystallinity. This is an important aspect, since increasing crystallinity will decrease the effectiveness of the supercritical fluid on the permeability of the polymer matrix. Additional considerations due to equilibrium and rate studies of analyte matrix interactions in SFE have shown that solubility enhancement occurs by staying near the critical point of the fluid. By increasing the temperature it may be possible to overcome the activation energy barriers (52).
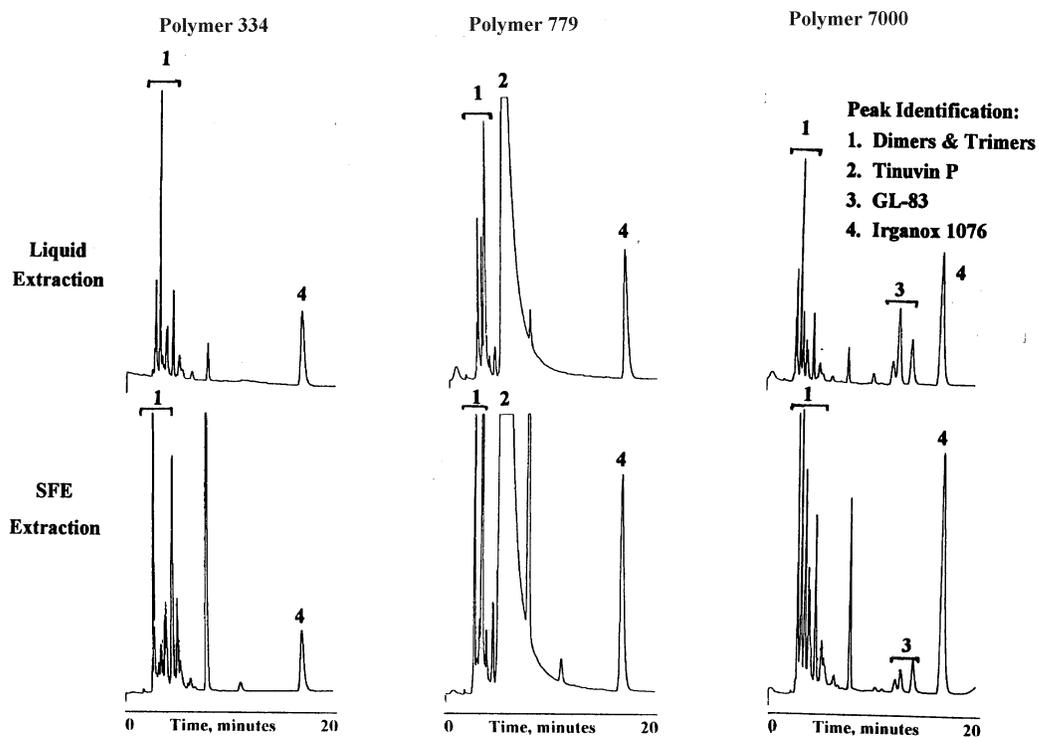
Figure 4.8: Comparison of HPLC Chromatograms of the Dissolution/Precipitation Extracts and the SFE Extracts of three Resins. Conditions: Methanol, 1 mL/min eluent flow, spherisorb ODS-2 column, ambient temperature, 280 nm UV detection.

Subsequent HPLC analysis methodology of the extracted resins relied on the particular additives contained in that resin. For resins 334 and 7000, HPLC Method 4 was used to assay Irganox 1076. With the presence of Irganox 1076, Tinuvin P, Tinuvin 770 and Wytox, HPLC Method #5 was used to analyze resins 765, 779 and 1119.

HPLC demands removal of insoluble materials from sample solution. It is crucial to prevent accumulation of analytes at the head of the column (53). Flushing the column was necessary after several injections with tetrahydrofuran to prevent build up of low molecular weight waxes and other coextractives. Filtering or centrifuging the extract solutions removes butadiene rubber and other coextractive solids in solution. Further sample treatment was avoided, since it often introduces additional contaminants from the filters themselves or from trace impurities that may be in the centrifuge tubes.

The data shown in **Table 4.6** indicate that SFE is feasible for the additives. The SFE RSD's ranged from 1.7 to 13.8%. Comparisons of the SFE recoveries are against the dissolution/precipitation extractions, since there was no data available for comparison to Soxhlet methods. SFE is usually within extraction recoveries of the dissolution/precipitation method. In three instances, SFE results exhibited greater than 100% recoveries as compared to the dissolution/precipitation extractions. Resin 1119 SFE's assay of Wytox resulted in 156%. The unusually high recovery is due to an unstable varying baseline along with a high RSD of 10.6%. Overall, the higher recoveries may indicate that there are problems with coprecipitation of additives in the dissolution/precipitation extraction. Another explanation may be that there is some decomposition of the additives themselves and/or the polymer processing that could contribute to variability in the analytical results. Quantitation performed by external standard calibration showed that SFE generally had higher recoveries as compared to the dissolution/precipitation method. This demonstrates that the dissolution/precipitation technique may give low recoveries for some additives that may exhibit a solubility dependence.

A paired t-test was used to evaluate whether there were significant differences in recoveries between the dissolution/precipitation and SFE methods. To determine if the values were significantly different the critical value, P=0.05 is 3.18 for a two-tailed

Table 4.6: SFE Recoveries Relative to Dissolution/Precipitation Extraction

Polymer	RSD n = 3	% Recovery Relative to Dissolution/Precipitation Extraction
Irganox 1076		
334	4.0	83
765	1.7	87
779	9.1	82
1119	8.0	113
7000	8.5	90
Tinuvin P		
765	9.4	101
779	6.4	89
Tinuvin 770		
765	13.8	99
779	1.9	93
Wytox		
1119	10.6	156

significance level with 95% confidence. The values determined for Irganox, Tinuvin P, Tinuvin 770 and Wytox were well below the critical t-value of 3.18. Based on t-values below the critical value, it is likely that observed differences in the data is due to sampling error. The data from the SFE and dissolution/precipitation extractions came from the same population and an observed difference is the result of chance (54). In conclusion, there was no significant difference in the two methods.

The polymers changing physical properties during its transitions through the different phases may actually influence the rate and way that additives are extracted. This could explain the difference in the recoveries and could be the limiting factor determining whether the oligomers or additives are extractable during the different physical changes. First, the polymer matrix swells and then passes through the transition stage where it transforms from a rigid material to a semi-rigid material and finally to a molten state. Bartle and others examined a model for dynamic extraction using a supercritical fluid and applied a theoretical model to a real life model using a polymer matrix (55). The polymer was ground before extraction and thus the particles in the range of 0.6 mm to 1.2 mm fit the model. Our work involved using polymer samples that were ground and sieved to result in the using fractions meeting the 1.0 mm size.

Polystyrene's physical limits of interest are the glass transition point, T_g of 80°C to 100°C and melting point, Tm of 110°C to 125°C. The extractions were carried out close to the T_g and just below the melting temperature of 110°C. Careful consideration was given at this point, since it is believed that the extraction should be carried out above T_g but below T_m. Heating the polymer to its melting stage could result in it clogging the entire SFE system, should it migrate through the extraction cell and into or past the trap.

F. Conclusions

HPLC methodology can assay the majority of polystyrene additives. However, it is not possible to use HPLC to assay the additives that are not soluble in any organic solvent. Considering the diverse additive packages, it is necessary to use a HPLC method specific to the analytes of interest. Unfortunately, in real world samples there is not a single universal method due to the complexity of the compounds used as antioxidants, uv stabilizers, process lubes, antistats, and flame retardants. Besides the additives

themselves, the polymer processing results in byproducts, decomposition products, and low molecular weight waxes and oligomers that further complicate the matrix.

It has been demonstrated that SFE may be used as an alternate extraction method to dissolution/precipitation extraction for a majority of polystyrene additives. SFE optimum parameters for polystyrene extraction require that the extraction temperature be maintained above the T_g of the polymer but slightly below the melting point. This technique combined with the high dissolution power of the supercritical carbon dioxide fluid results in rapid, easy and quantitative results.

Refer to **Table 4.7** for a comparison of conventional versus SFE solvent usage and time for a typical extraction. The solvent consumption savings of 100mL per sample and 1 hour time savings in sample preparation exemplify the attractiveness of SFE versus the conventional method of extraction. Based on this data it is more economically feasible to use SFE (excluding instrumentation, and return on investment).

In summary, of the fifteen additives in the eight resin packages, four were insoluble (acrawax, zinc stearate, silicone fluid, and BT-93) in organic solvents. The flame retardant, Great Lakes BA-59 and the antistat, Larostat were not contained in any of the resin packages examined. Mineral oil is typically analyzed using normal phase liquid chromatography or high temperature GC. Of the remaining eight additives, four additives show near quantitative extraction results for six different resin packages. Refer to**Table 4.5**. The remaining additives include Hostastat, Mold Pro 830, Mold Pro 678, and Great Lakes DE-83R that can be assayed., however, they were not analyzed in detail. Refer to **Table 4.8** for a summary of the HPLC and SFE Method development and reference of other available assay methods for the additives.

There are additional interests in using SFE methodology for various applications to polymer systems. For instance, volatile compounds could be analyzed using on-line SFE/GC for the analysis of non-polar to medium polar analytes trapped from within a polymeric matrix (56). The current method used to extract the mineral oil involves a series of approximately seven steps. The steps involve dissolving the polymer, precipitating, filtering, evaporating and redissolving prior to analysis by normal phase liquid chromatography. SFE would significantly reduce the amount of time involved in

extracting mineral oil before assaying. Other methods, such as multidimensional chromatography using combined micro size exclusion (SEC) are options that can separate additives from the polymer. Transfer of the analytes on-line to a capillary GC for further separation and identification by mass spectrometry (57) is also promising. Future work to fully use the extended capabilities of SFE will probably concentrate on forms of fractionation (58) to selectively extract additives or oligomers.

Table 4.7: Comparison of Conventional versus SFE Extraction for a Sample

Dissolution/Precipitation	SFE
Sample Preparation	**Sample Preparation**
Dissolution: 1 hour	Grinding: 5 minutes
Precipitation: 15 minutes	Extraction: 70 minutes
Analysis: 30 minutes	Analysis: 30 minutes
Organic Solvent Use	**Organic Solvent Use**
Extraction: 100 mL	Extraction: 2 mL
Analysis: 30 mL	Analysis: 30 mL
TOTAL TIME: 2 hour & 45 minutes	**TOTAL TIME: 1 hour & 45 minutes**
TOTAL SOLVENT: 130 mL	**TOTAL SOLVENT: 32 mL**

Table 4.8: Additive Method Summary

Polymer Additive	Contained in Polystyene Formulation(s)	HPLC Method Developed?	SFE Method Developed?	Other Assay Methods Available**
Antioxidant				
Irganox 1076	334, 765, 779, 1119, F7000	Yes	Yes	GC
Wytox 312	1119	Yes	Yes	No method
UV Stabilizers				
Tinuvin P	765, 779	Yes	Yes	GC
Tinuvin770	765, 779	Yes	Yes	GC
Process Lubes				
Acrawax	334	No	No	FTIR
Zinc Stearate	201, 208, 334	No	No	Titration & X-Ray Fluorescence
Mold Pro 830	F7000	Yes	Qualitative	No method
Mold Pro 678	765, 779	Yes	Qualitative	GC (for surface applied additive).
Mineral Oil	208, 334, 765, 779, 1119, F7000, P8001	No	Not analyzed	NP HPLC
Silicone Fluid	P8001	No	Not analyzed	FTIR
Flame Retardants				
Great Lakes DE-83R	F7000	Yes	Qualitative	GC-Qualitative
Great Lakes BA-59*	none	Yes	Not in resins	GC-Qualitative
BT-93	779	No	No	GC-Qualitative
Antistats				
Larostat*	none	Yes	Yes	No Method
Hostastat	P8001	Yes	Yes	FTIR

Where *: Not contained in any of the resins examined.
   **: According to Huntsman Chemical Company

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Appendix A
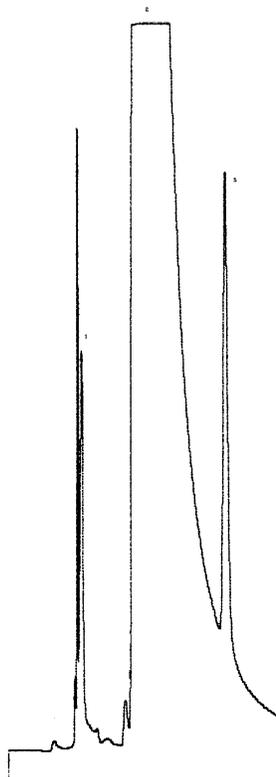
HPLC Chromatogram with UV detection of Tinuvin P (major peak) which shows additional peaks from impurities in the synthetic additive. HPLC Method No. 5 with the following Conditions: ODS-2 Spherisorb, 5 μm particle size, 1 mL/min flow and 50 μL injection volume.
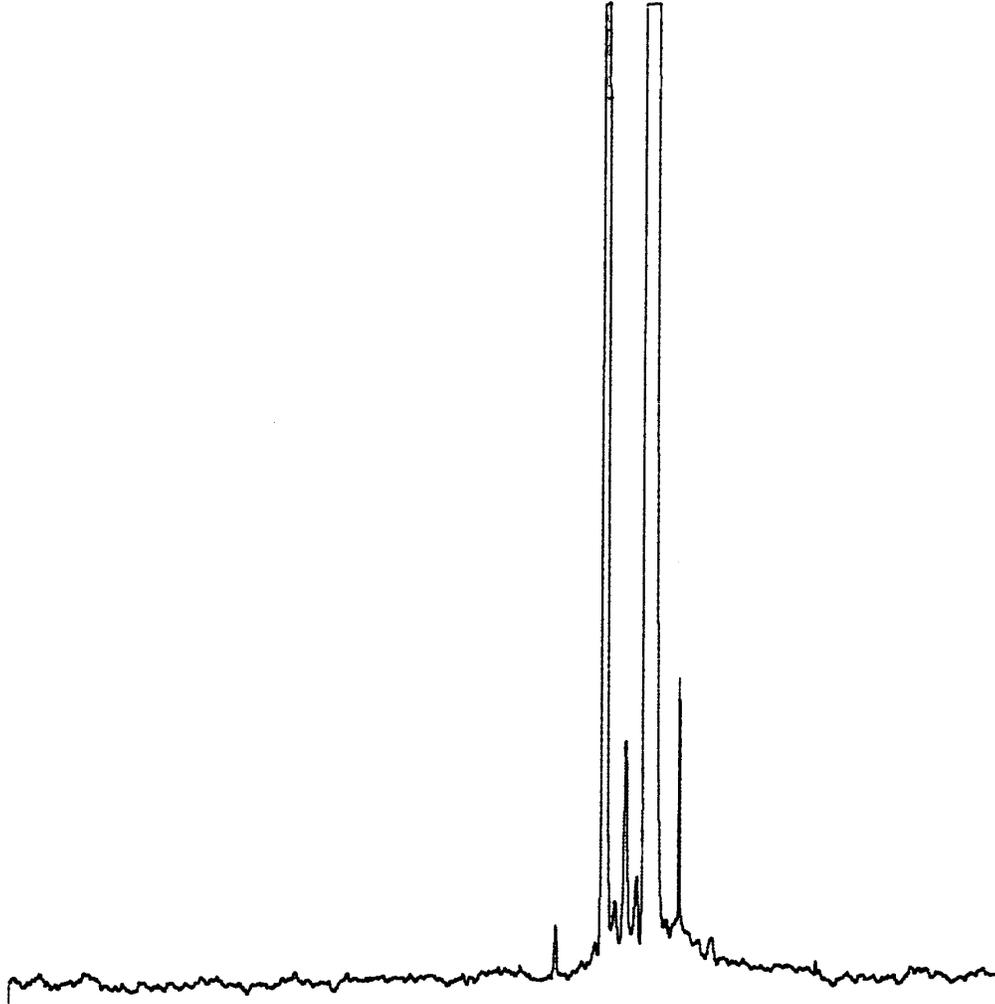
HPLC Chromatogram with UV detection of Mold Pro 830 which shows additional peaks from impurities in the synthetic additive. HPLC Method No. 1 was used.

Peak Identification:
1. Dimer/Trimer
2. Tinuvin P
3. Irganox 1076
4. Unknown
5. Tinuvin 770
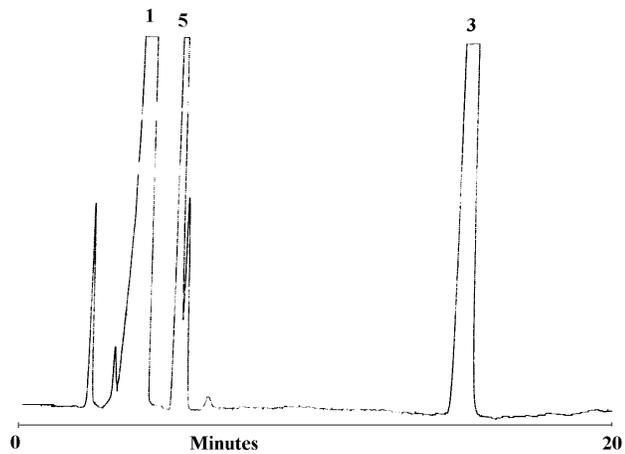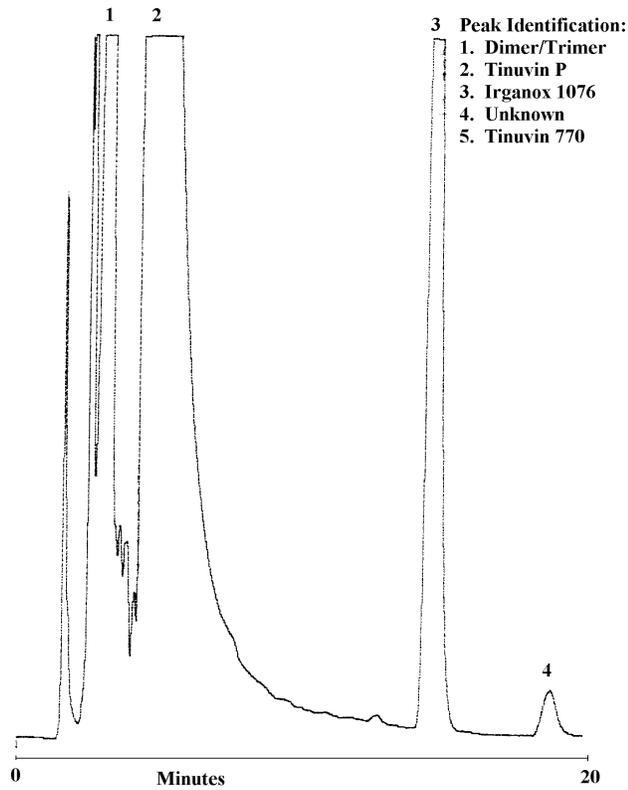
HPLC Chromatogram with UV and ELSD detection shown respectively. HPLC Method No. 4 with the following Conditions: ODS-2 Spherisorb, 5 μm particle size, 1 mL/min flow and 50 μL injection volume.

Vita

Susan H. Smith

The author, Susan Hoover Smith, was born on October 27, 1962 to Mr. and Mrs. Alan Charles Hoover of Cleveland, Ohio. Her father's career with Corning Glass brought the family to VA in 1972 after living and moving every 18 months from Cleveland, OH to Raleigh, NC to Corning, NY to Louisville, KY to Oneonta, NY and finally to Christiansburg, VA. With his death in 1975, the family moved to Wooster, OH and then two years later back to Christiansburg, VA. She remained in the area and received her Bachelor of Science degree in Chemistry from Radford University in May of 1986. She went to work at the Radford Arsenal for Hercules in May of 1986 as a Chemist in the Water, Wastewater and Air Analysis laboratory. She worked for Hercules for eight years in the various production laboratories and was reduced in force due to the decline of propellant manufacturing due to cold war in 1994. It was then, that she decided to pursue a Master of Science degree in Chemistry and chose Dr. Larry Taylor as an advisor. During her final semester at Virginia Tech she was offered an opportunity to take a job with Alliant Techsystems, formerly Hercules as a Quality Control Process Engineer. She took the position and six months later applied for a new position as the Quality Assurance Specialist for the commercial division of Alliant Techsystems known as New River Energetics which manufactures small arms propellant.