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Supercritical Fluid Extraction and determination of plastics additives

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City University of New York, 1991

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SUPERCRITICAL FLUID EXTRACTION AND DETERMINATION OF PLASTICS ADDITIVES

by

EVELYN A. WOLFE

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy, The City University of New York.

1991

This manuscript has been read and accepted for the Graduate Faculty in Chemistry in satisfaction of the dissertation requirement for the degree of Doctor of Philosophy.

17 July 91
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Abstract

SUPERCRITICAL FLUID EXTRACTION AND DETERMINATION OF PLASTICS ADDITIVES

by

Evelyn A. Wolfe

Adviser: Dr. David Locke

Supercritical Fluid Extraction (SFE) has been evaluated as an efficient technique for the quantitative extraction of plastics additives such as antioxidants and UV absorbers from polypropylene. The method is successful in providing a rapid, clean and quantitative extraction that takes no longer than 30 min. and suffers no problems of prolonged sample exposure to light, air, elevated temperature or reactive solvents. Gram samples of polypropylene containing Irganox 1010, Irgafos 168 and Irganox 3114 are extracted with supercritical carbon dioxide in a closed system for 15-30 min. at pressures between 8000-9000 psi and temperatures in the 60-90°C range. Depressurization of the extract-laden CO_2 across a trap packed with either silica or Chromosorb W causes deposition of the additive. It is then eluted from the trap with a small volume of methylene chloride and analyzed by HPLC with UV detection. No further cleanup was necessary. Recovery is studied as a function of pressure (density), temperature, time and plastic particle size. Recovery generally increases with density, time, temperature and decreased particle size, asymptotically approaching 100%. Irganox 245, Irganox 1076, Tinuvin P and Tinuvin 327 spiked onto pure polypropylene give recoveries between 70-96%. The solubility of these additives are measured at various pressures and temperatures. Irganox 1010 is the most soluble and Irgafos 168 and Irganox 245 are least soluble in supercritical CO_2. The solubility was successfully correlated with CO_2 density. Soxhlet extraction and conventional polymer dissolution procedures give similar results but require at least 24 hours in the case of the former and eight hours for the latter.

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INTRODUCTION

One of the most difficult problems in chemistry is the separation of complex materials into component parts, either to characterize a mixture or natural product or to remove a particular component from a matrix. While the separating capabilities, speed, selectivity, and information content of chromatographic techniques and associated detectors have increased substantially, little attention has been paid to preparing samples for introduction into chromatographic systems. This is a severe handicap to the advancement of separation science since sample preparation is often the slowest and most error-prone step of an analytical scheme. The most popular liquid solvent extraction technique which uses the Soxhlet apparatus, has undergone little modification in over seventy years. An improved version of this apparatus was described in 1912 *(1)*. However, over the past decade, exciting new developments have evolved to this challenge using supercritical fluids in extractions.

Supercritical fluid extraction (SFE) is a hybrid utilizing the advantages of both distillation and liquid extraction *(2)*. It is rapid, simple to perform, yields quantitative recovery, and usually there is no loss or degradation of the extracted analyte. It has the benefit that slight changes in temperature and pressure in the critical region cause large changes in the solvent density and, thus, its solubilizing power. In comparison with conventional processes, SFE offers considerable flexibility for extractive separations because of the numerous experimental parameters: pressure, temperature, choice of solvent, and additives called entrainers. High molecular weight, nonvolatile substances dissolve in supercritical fluids, typically 2-7 orders of magnitude in excess of the amount calculated from the ideal gas law. This is caused by the high density of the fluid, which can approach that of a liquid.

HISTORY

The earliest published work on carbon dioxide as a solvent was that of Gore in 1861 *(3)*; he reported solubility of naphthalene and camphor and insolubility for several carboxylic acids. He discovered the (then) strange phenomenon, that as solid camphor is dissolved in ethylene at increasing pressure it liquefies and then "vaporizes".

A number of other 19th century workers reported solubility or phase behavior of various inorganic and organic materials in carbon dioxide *(4-8)*. In 1906, Buchner reviewed most of the earlier work and made significant additions to the data *(9)*. He classified carbon dioxide-solute systems in terms of the type of two-component phase diagram obtained for the mixtures. A wide temperature range was used, and solubility determinations were qualitative.

Except for two papers by Quinn *(10-11)* in the 1920's, no new data on carbon dioxide solutions appeared until 1954, when Francis presented an extensive, quantitative study of the phase behavior of ternary systems containing carbon dioxide *(12)* and determined the solubilities of 261 compounds in near-critical, liquid carbon dioxide. He included many classes of organic compounds, e.g., aliphatics, aromatics, heterocyclics, and compounds with a large variety of functional groups.

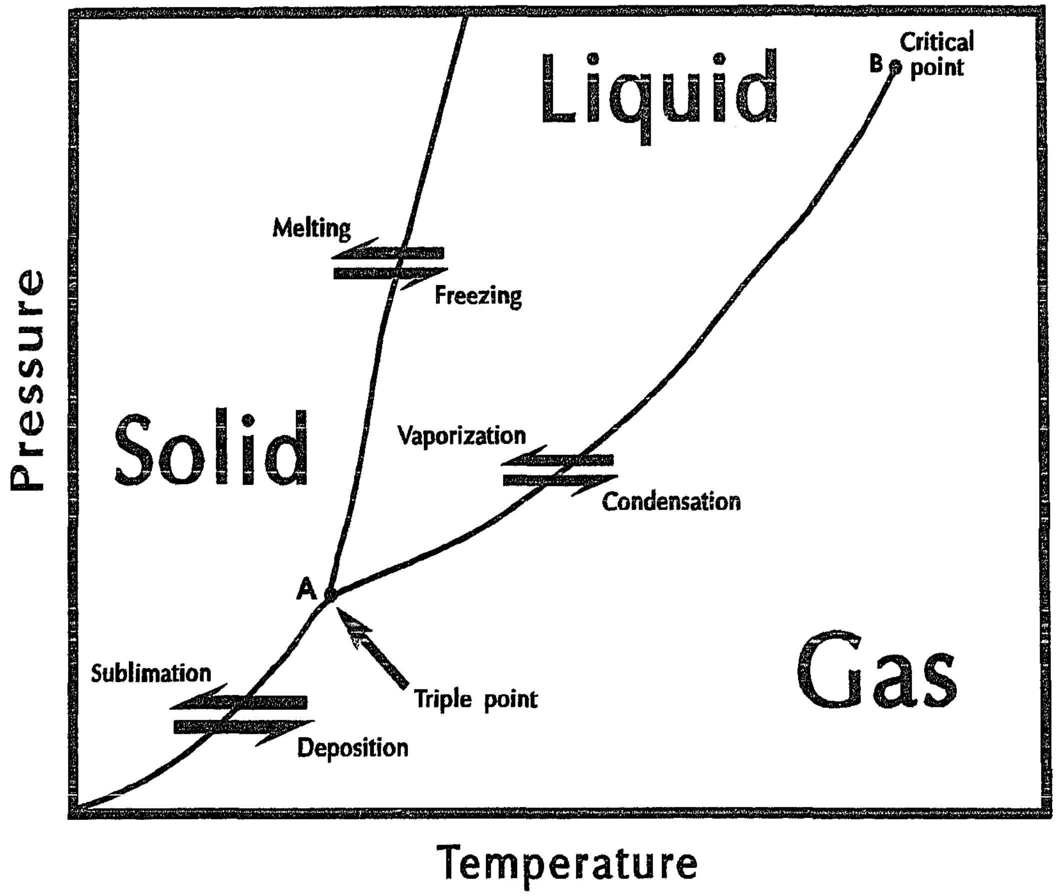
Around 1970, several other workers reported the phase equilibria of carbon dioxide-hydrocarbon systems over a wide temperature and pressure range *(13-16)*. These studies are of interest primarily for thermodynamics and phase theory. In the late 1970's, recognition of the potential utility of compressed carbon dioxide, both above and below the critical point, became more widespread *(17-18)*.

PHYSICAL CHEMISTRY OF SFE

A compound is in its supercritical state if it is above its critical temperature (Tc) and pressure (Pc). In Figure 1 *(19)*, the line from A to B is the vapor-pressure curve of a liquid. It represents the equilibrium between the liquid and gas phases at various temperatures. This curve ends at B, the critical point. The temperature at this point is the critical temperature, above which a material cannot exist as a liquid. The pressure at the critical temperature is the critical pressure, above which the material cannot exist as a gas. This paradox here is the reason supercritical fluids are sometimes referred to as "Science fiction extraction". However, supercritical fluids do have properties that can be measured and mechanisms that can be inferred from data.

The solubility of a solute in supercritical carbon dioxide is readily influenced by small variations in pressure or temperature. In both cases, the density of the supercritical fluid also changes. In addition to the density effect, vapor pressure and intermolecular

FIGURE 1



Phase diagram

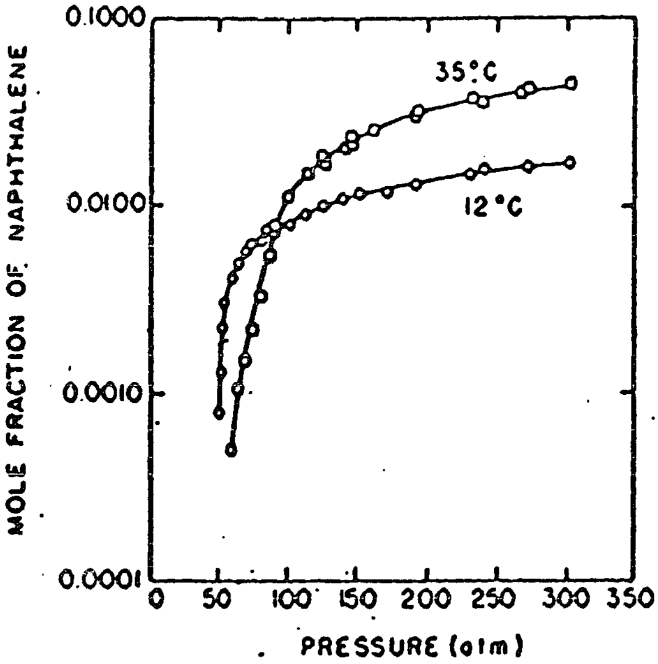
From reference 19

forces play an important role in determining solubility. To give an example of these statements, one can examine the phase behavior of naphthalene in a supercritical fluid.

In Figure 2 *(2)*, at a temperature of 12°C (T_R = 1.01, where T_R= T/T_c), an increase of the pressure from 50 atm to 100 atm, enhances the solubility of solid naphthalene in supercritical ethylene by a factor of ten. This increase in solubility exactly parallels the increase in density of ethylene as the pressure is increased along the reduced-density isotherm shown in Figure 3 *(2)*.

The effect of temperature is more apparent at higher pressures. For the 35°C (T_R = 1.09) isotherm in Figure 2, an increase of the pressure from 100 atm to 150 atm, which corresponds to a reduced pressure of 2 to 3, the solubility increases three fold. The change in density over the same change in reduced pressure is only about 0.1 in Figure 3. At this density, the temperature change has to do more with the increase in vapor or sublimation pressure of naphthalene than the decrease in density of ethylene. Around 120 atm, the density of ethylene is high enough that when the temperature increases, the vapor pressure of naphthalene increases faster than the decrease in the density of ethylene and the amount of

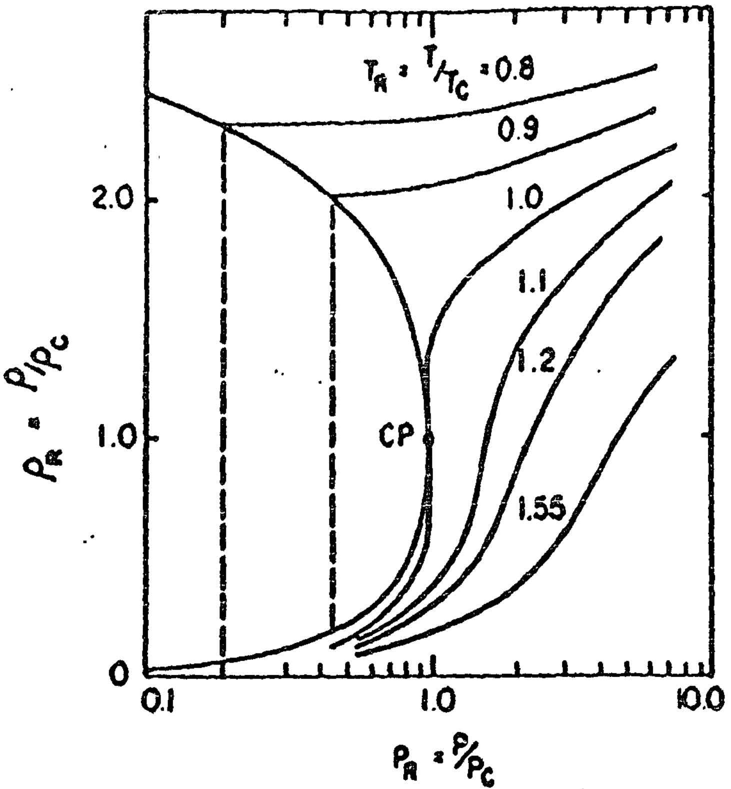
FIGURE 2



Solubility behavior of solid naphthalene in supercritical ethylene.

From reference 2.

FIGURE 3



Variation of the reduced density in the vicinity of critical point

From reference 2.

naphthalene in ethylene increases. Below this pressure, density is sufficiently low, that as the temperature is increased, the effect on the density of ethylene is greater than the effect on the vapor pressure of naphthalene and the solubility drops. This is referred to as retrograde solubility. One can also observe in the diagram that as the pressure decreases below the critical pressure, the density becomes gas-like and solutes drop out of solution. As shown in the above discussion, the solvent power of carbon dioxide is related to the density.

A simple mathematical model of intermolecular interaction shows how the bulk solution properties depend upon density *(20).* Consider a point dipole with a dipole moment, μ, immersed in a supercritical fluid. The inhomogeneous field of the dipole will polarize the fluid and give rise to a reaction field, R at the dipole.

$$R = f\mu \qquad (1)$$

where f can be written in the form

$$f = (1/a^3)[2(\varepsilon-1)/(2\varepsilon+1)] \qquad (2)$$

where a = radius of the point dipole, ε = dielectric constant of the fluid.

The interaction energy of a spherical nonpolarizable point dipole in its own reactive field is then

$$\tau = -1/2\ \mu\ R = -1/2\ f\ \mu^2$$

$$= -\ (1/a^3)\ [\mu^2\ (\varepsilon-1)/(2\varepsilon+1)] \qquad (3)$$

Based on dielectric constant measurements for carbon dioxide, which has no dipole moment, the Clausius-Mossotto function has a density dependence which is written

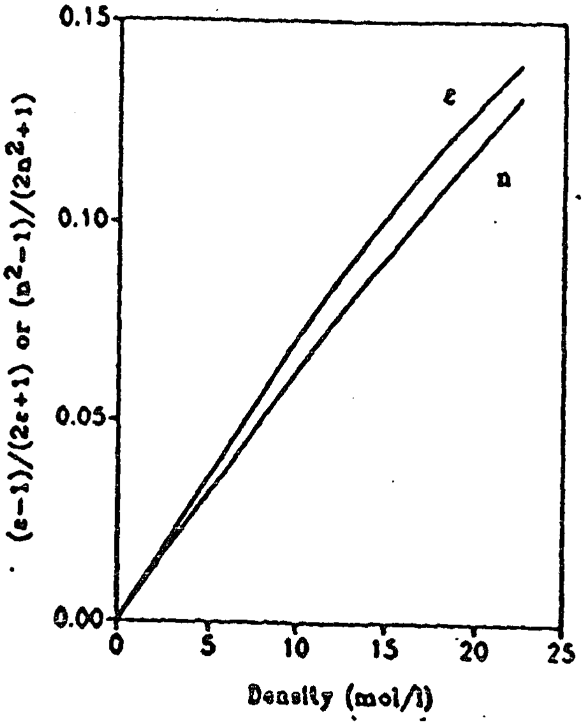
$$(1/d)\ [(\varepsilon-1)/(\varepsilon+2)] = A_\varepsilon + B_\varepsilon d + C_\varepsilon d^2 \qquad (4)$$

where d is the molar density and A_ε, B_ε , and C_ε are respectively, the first, second, and third dielectric virial coefficients representing the contribution from the individual molecules, pairs, and trios of molecules. The dielectric virial coefficients for carbon dioxide at 323K are A_ε = 7.350 cm^3/mol, B_ε= 50.7 cm^6/mol^2, C_ε = -2515 cm^9/mol^3 *(21)*.

These data can be used in the Clausius-Mossotti equation to solve for the dielectric constant in equation 3. Figure 4 shows the density-dependence of the interaction energy, which according to equation 3, varies almost linearly with carbon dioxide density *(22)*.

If instead of considering a point dipole, one looks at a nonpolar, polarizable spherical molecule of radius a, surrounded by

FIGURE 4



Density dependent portions of interaction energies as modeled by the dielectric (ε) and refractive index (n) for CO_2.

nonpolar solvent molecules, the interaction energy is *(23)*

$$\tau = - (3/4) \{[h\alpha_2 (\upsilon_1\upsilon_2) (n^2-1)]/ [a^3 (\upsilon_1+\upsilon_2) (2n^2+1)]\} \qquad (5)$$

where h = Planck's constant

υ = absorption frequency of light

n = refractive index of fluid

α = fluid polarizability

The density dependence of the refractive index is given by the Lorentz-Lorenz function

$$(1/d)\ [(n^2-1)/(n^2 + 1)] = A_R + B_R d \qquad (6)$$

where A_R = 6.658 cm^3/mol, B_R = 3.3 cm^6/mol^2 for carbon dioxide at 323K *(20)*. This relationship shows that the interaction energy of equation 5 is nearly linear with carbon dioxide density as shown in Figure 4.

Because the solubility depends on solvent strength, which is related to the dielectric constant and refractive index of the solvent, equations 3 and 5 predict that a given compound will be more soluble in a supercritical fluid with a larger dielectric constant or refractive index at the same temperature and density. It is interesting to note that Figure 4 mimics the behavior of the density isotherms in Figure 3 beyond the critical point. The only difference is that density is changing non-linearly with pressure but linearly with the interaction energies, which, therefore, are more dependent on density.

In general, the dielectric constant of a solvent does not give a good measure of solvent polarity: dielectric constant is a bulk or macroscopic property, whereas solvent-solute interactions occur at the molecular level. Refractive index and dielectric constant are not primary properties but surrogate properties for measures of polarity. So, the models of equations 3 and 5 are inadequate for polar solvents due to the difficulty of describing the local field acting on each solvent molecule and the configuration of solvent molecules around the solute *(24-25)*. Thus, empirical correlations are often used to characterize solvent-solute interactions. Hyatt *(26)* investigated the π^* parameter by observing the bathochromic shift of the visible charge-transfer band with increasing solvent polarity of an azo dye in carbon dioxide. π^* is the solvent dipolarity/polarizability parameter which is related to the refractive index and dielectric constant of a solvent. It was observed that supercritical carbon dioxide has a π^*-polarity close to those of hydrocarbons and fluorocarbons.

There are numerous solvents which can be used in supercritical fluid extraction, with a wide range of critical properties, as listed in Table 1 *(27)*. Supercritical carbon dioxide has been the choice for most SFE studies, primarily because of its attractive characteristics. As shown in Table 1, carbon dioxide becomes supercritical at a temperature of 31°C, just a few degrees above ambient, and a pressure of 1070 psi, within the working conditions of modern HPLC instruments. It has low toxicity and reactivity, and high purity at low cost. In general, supercritical carbon dioxide is an excellent solvent medium for nonpolar and slightly polar species such as polycyclic aromatic hydrocarbons (PAHs), polychlorinated biphenyls (PCBs), aldehydes, esters, alcohols, organochlorine pesticides, and fats, but less useful for more polar compounds *(27)*.

The extraction of more polar species in supercritical carbon dioxide is more challenging. More polar solvents, such as supercritical ammonia, can be used, but there are several severe limitations of these solvents. They are difficult to pump because they tend to dissolve pump seals, are chemically reactive and are

TABLE 1

Characteristics of Representative Supercritical Fluids

Fluid	Critical temperature (°C)	Critical pressure (atm)
CO_2	31	73
N_2O	36	72
NH_3	132	112
MeOH	240	78
$CClF_3$	29	38
Ethane	32	48
Ethylene	10	51

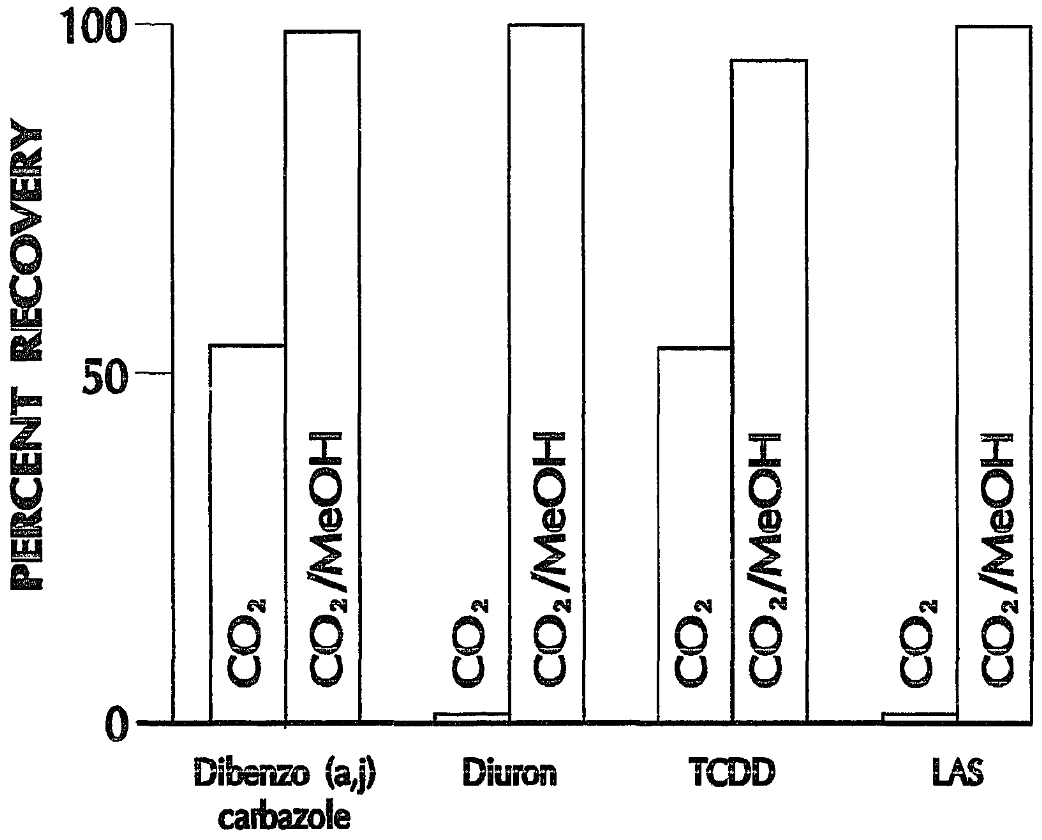
From reference 27

likely to be too dangerous for routine use. Supercritical methanol is seldom used because of its high critical temperature, and because it is a liquid at ambient conditions, which causes difficulty in sample concentration after extraction.

Because of the practical difficulties in using polar fluids such as ammonia and methanol for supercritical fluid extraction, extractions of highly polar analytes can be done using carbon dioxide containing a few percent of these polar solvents as modifier. Carbon dioxide has a small polarizability and no dipole moment, so additives affect the polarity of the solvent (i.e. the refractive index of equation 5) and the dielectric constant (equation 3). Polar cosolvent molecules also interact with functional groups on the solutes. Methanol and acetone are common modifiers. Figure 5 *(27)* shows the increase in extraction efficiencies obtained in by adding a methanol modifier for extractions where the recovery using pure carbon dioxide was not quantitative.

Methanol acts as either a Lewis acid or base; acetone is a weaker Lewis base and slightly acidic *(28)*. The dipole moment of acetone is 2.88 Debye compared to 1.7 Debye for methanol. Based on these properties, IR measurements were done on the systems

FIGURE 5



Comparison of extraction efficiencies obtained using carbon dioxide and carbon dioxide modified with methanol.

TCDD - 2,3,7,8-tetrachlorodibenzo-p-dioxin

LAS - linear alkylbenzenesulfonate

From reference 27

methanol/acridine and acetone/benzoic acid. The results showed Lewis acid-base interactions *(29)*. It was concluded that acid-base interactions are a secondary cosolvent effect superimposed on a primary effect determined by cosolvent concentration.

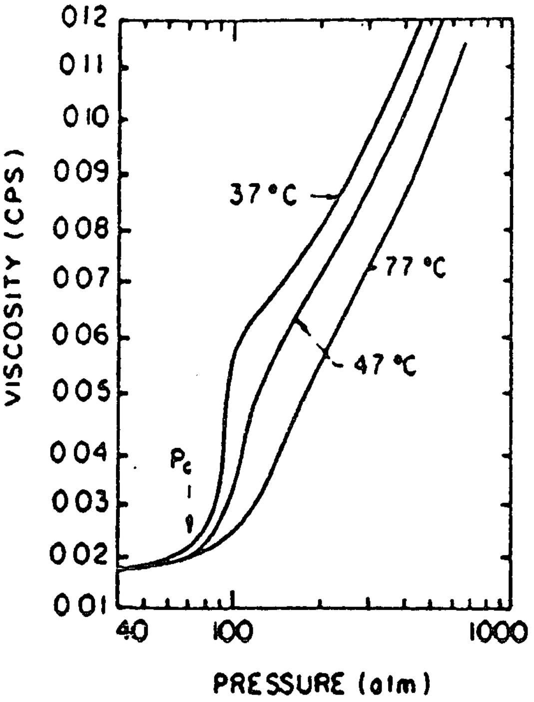
TRANSPORT PROPERTIES

In addition to its unique liquid-like density characteristics, an SCF solvent has certain other physicochemical properties that add to its attractiveness as a solvent. It exhibits transport properties of diffusivity and viscosity that are intermediate between those of a gas and a liquid. In addition, the zero surface tension of a supercritical fluid allows easy penetration into microporous materials. Because supercritical fluids have solute diffusivities an order of magnitude higher (10^{-4} vs. 10^{-5} cm^2/s) and viscosities an order of magnitude lower (10^{-4} vs. 10^{-3} $N.s/m^2$) than liquid solvents, they have better mass transfer characteristics. Quantitative SFEs are generally complete in 10-60 min., whereas liquid solvent extraction times can range from several hours to days.

Viscosity is a measure of the resistance to flow of a substance. In Figure 6 *(2)* is shown the variation of viscosity of carbon dioxide with pressure and temperature. Although the viscosity is seen to change rapidly in the critical region, even at pressure levels of 300-400 atm the viscosity is only 0.09 centipoise (cps), an order of magnitude below viscosities of typical liquid organic solvents.

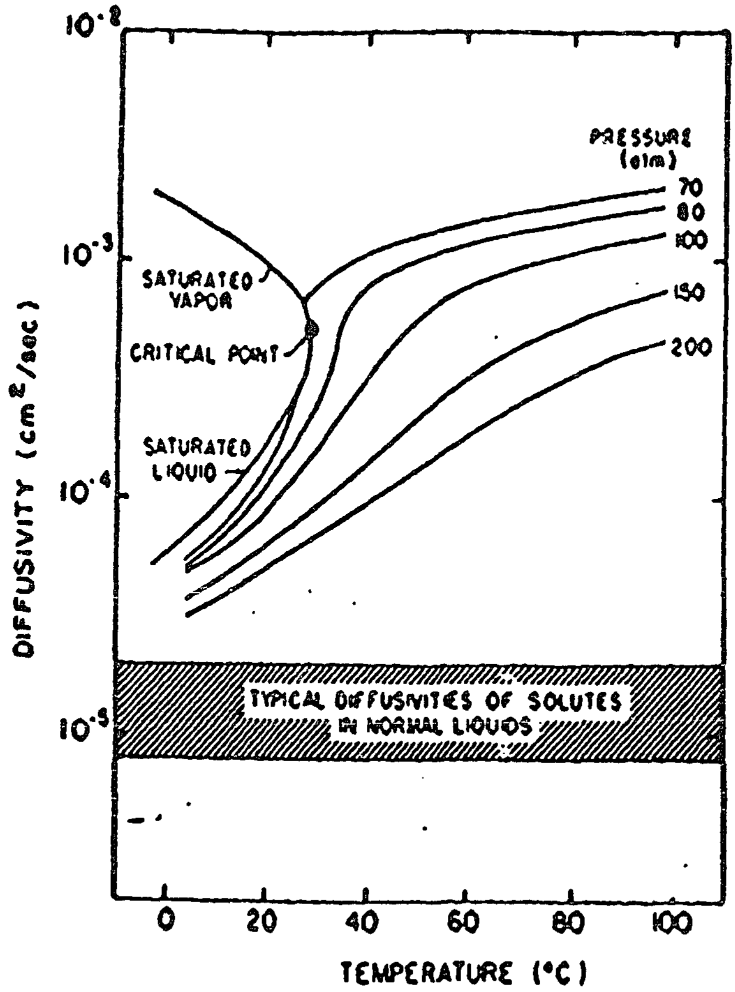
Figure 7 *(2)* shows the self-diffusivity of carbon dioxide over a wide pressure-temperature range. The diffusivity of a supercritical fluid is three orders of magnitude less than a gas and two orders of magnitude greater than a liquid. The higher diffusivity of SCFs relative to liquids results in faster mass transfer and will, therefore, result in shorter interphase equilibration times than required for liquid extraction. In addition, significant buoyancy effects in supercritical fluids enhance mass transfer rates with convective mixing *(30)*.

FIGURE 6



Viscosity behavior of carbon dioxide.
From reference 2.

FIGURE 7



Diffusivity behavior of carbon dioxide
From reference 2

ULTRASONIC SUPERCRITICAL FLUID EXTRACTION

Ultrasound can be used in supercritical fluid extraction for the extraction of porous material. It produces intense sinusoidal variations in density and pressure which have the potential of improving solute penetration and enhancing overall extraction rates *(31)*. For a given power input, the amplitude of the resulting density waves will be approximately twice as great as in a gas or liquid. These density waves induce convection of solvents into the inner pores of a material.

The experiments are done in high-pressure stainless steel cells equipped with two sets of 0.75-in. diameter windows (for observation during extraction) and a commercial 20 kHz high power ultrasonic horn. The cell geometry is designed to maximize the sonic energy per unit volume and to create resonance effects to transfer energy from the sonic horn to the fluid. The phenomena of micro-streaming which has been observed in sonicated liquids *(32)*, also occurs in supercritical fluids. This involves the development of miniature swirling cells which are produced from the sound waves and are on the scale of a few millimeters. These have relatively high velocities and, therefore, produce large enhancements in mass transport.

Commercially available ultrasound equipments can generate 100 or 200 watts of energy with an ultrasound tip that is about one half inch in diameter. This high energy density expresses energy as heat in the small region around the tip. So, with only small exposure to sound, a large increase in temperature is obtained in a localized region of the system. This affects local density by increasing the solute-solvent interactions and, therefore, leads to enhanced solubility within the region.

This technology is in its infant stage, but with promising commercial potentials. Its main advantage is in improved mass transport into porous material. It is a reliable and efficient way of inducing mixing, which is always a problem in high pressure extraction.

ADVANTAGES OF SUPERCRITICAL FLUID EXTRACTION

The properties of gas-like diffusivity and viscosity, zero surface tension, and liquid-like density combined with the pressure-dependent solvent power of a supercritical fluid have provided the driving force for applying SCF technology to a whole range of separations problems. Increased governmental scrutiny and regulation of common industrial solvents, such as chlorinated hydrocarbons, have made carbon dioxide a safe and nontoxic alternative industrial solvent. For example, in 1989 the Environmental Protection Agency (EPA) began a four-year program to develop supercritical fluid extraction methods with the ultimate goal of reducing the amount of methylene chloride used for extractions in EPA methods by 95% *(27)*. This extraction technology affords certain advantages over normal extraction solvents. Because of the relatively low temperatures used, heat-sensitive components may be extracted without thermal decomposition. Furthermore, SCF's can be used to vaporize thermally labile, nonvolatile substances at moderate temperatures. Under these conditions, the selectivity may be too low for liquid extraction. Because supercritical fluid can solubilize nonvolatile compounds at moderate temperatures, the energy required is less than needed for distillation.

In addition, the extracted material may be easily recovered from the supercritical fluid because relatively small changes in temperature or pressure result in considerable changes in solubility. Essentially complete separation of supercritical fluid and solute with high solvent recovery can be accomplished by isothermal decompression or isobaric heating. This is a distinct advantage over most types of liquid extraction, where considerable energy may be expended to evaporate the solvent.

Unlike supercritical fluid extraction, the extraction of many samples using liquid solvents requires long periods of time. This may produce a sample diluted in a large volume of solvent which requires additional concentration if trace analysis is desired. This can result in incomplete recoveries, loss or degradation of analytes, and large volumes of waste solvents. Liquid extractions are particularly unsuited to the analysis of trace organics when sample sizes are limited. For example, it is difficult to concentrate a liquid solvent extract to a known volume less than 100 µL *(33).* Even with a 1-µL on-column injection in capillary GC, only 1% of the sample can be analyzed.

Soxhlet extraction is another technique that is used extensively in industrial laboratories. However, it requires a long extraction time, large sample size and large volumes of solvents. The technique is technician-dependent. It is nondiscriminating because the solvent remains at one strength throughout the extraction, although this could be advantageous in instances where there are several components of interest in the sample matrix. Certain precautions must be followed in deciding which mixed solvent system should be used for Soxhlet extraction. Knowledge of possible azeotropes is necessary. It is possible that a low boiling azeotrope will form and collect in the top of the Soxhlet apparatus. If the volume of the azeotrope is enough to fill the reservoir at the top of the Soxhlet apparatus, and, thus, allows the solvent to be returned to the boiling flask, there is no problem. However, if the volume of the azeotrope is not enough to fill the top reservoir, the temperature of the solvent in the boiling flask will increase until it boils. It will remain at this temperature until the top reservoir is filled. As the lower boiling azeotrope is returned to the boiling flask, the solvent reservoir will vigorously boil. The superheated vapor will rise rapidly, and even the best condenser will not prevent the vapor from escaping. However, although this can be a problem, it does not happen often, and, in these cases, the azeotropic compositions should be made up initially, as in the case of benzene-methanol for which the azeotropic mixture is approximately 50-50.

TECHNIQUES & APPLICATIONS OF SUPERCRITICAL FLUID EXTRACTION

Various techniques can be used to identify and quantitate the material extracted by supercritical fluids. Methods that have been used to collect extracted analytes upon depressurization of the supercritical fluid fall into two categories: off-line SFE in which the analytes are collected for subsequent analysis, and on-line SFE where the analytes are transferred directly to a chromatographic system.

Off-line supercritical fluid extraction is adaptable to sample sizes ranging from a few milligrams to several grams. It is simpler to perform and the extract is collected on sorbents such as silica or bonded-phase packings, eluted with solvents, and then analyzed by any appropriate method. Direct depressurization of the extract into empty receiving vessels can be done when large quantities of materials are used. However, the disadvantage in this method is the losses of trace samples during depressurization from the volatile components.

Off-line SFE has been used extensively in processing application, such as in the food industry for the extraction of tea and coffee *(34-36)*, and nicotine from tobacco *(37)*.

Off-line SFE has also been used as a quantitative analytical procedure for a variety of analytes. For example, it is used in the pharmaceutical industry for the extraction of camomile leaves *(38-39)*. The products selectively extracted were bisabolol, its oxides, proazulenes, coumarins, and fragrant components; polysaccharides, acids, and flavonoids were not extracted. Other pharmaceutical applications include the supercritical fluid extraction of vitamins K1 *(40)*, A and E *(41)*, and menadione in animal feed *(42)*. Several other applications of SFE to the pharmaceutical industry have been reported including the detection of residues of a small group of veterinary drugs in freeze-dried pig kidney *(43-44)*.

Supercritical fluid extraction is also applied in agriculture for the extraction of lignin from wood *(45-47)*, the determination of anthraquinone in paper and wood*(48)*, oil hydrocarbons from sedimentary rocks *(49)* ,and in the extraction of coal tar-contaminated soil samples *(50)*. PAHs *(51-52)*, PCBs *(53-58)* and pesticides *(59-63)* have been extracted from soil, fly ash, sediment, air and diesel particulates.

On-line SFE is particularly attractive for small sample sizes and/or trace analysis where low levels of analytes are present. It eliminates the traditional extraction and fractionation procedures that are often far more time-consuming than the actual chromatographic analysis. This technique is readily automated using interface valves. It is faster, and there are no intermediate reconcentration steps in which solutes are lost or contaminants introduced. This results in maximum sensitivity, but it also requires some special experimental considerations. There is a need for highly pure supercritical fluids, because contaminants are concentrated inside the chromatography column during extraction. For example, samples with high fat contents will result in poor chromatograms because the fat is also extracted and deposited inside the column *(33)*.

On-line SFE is often coupled with capillary GC (SFE/GC) and both packed and capillary supercritical fluid chromatography (SFE/SFC). Selection of the system for on-line SFE should be based on the chromatographic technique that is best suited to the analytes.

If the target analytes are amenable to capillary GC analysis, SFE/GC would be a better choice than SFE/SFC simply because capillary GC yields faster separations and is simpler to perform for such compounds.

On-line SFE/GC is more commonly used in industry. By depressurizing the system, the extract is directly deposited inside a column. The extracted analytes are cryogenically focused in the GC column stationary phase during the SFE step, and then the analysis is performed in a normal manner. Several modes of operation are possible utilizing the on-line SFE/GC approach including quantitative extraction and analysis, selective extraction or fractionation, and periodic sampling and analysis of the extraction effluent at various pressures for qualitative characterization of a sample matrix. In most cases, extraction, concentration, and separation are completed in less than one hour per sample. The extraction of several materials using this technique have been reported *(64-69)*.

On-line SFE/SFC coupling has been achieved by flowing the extract through an injector loop, by collecting the analytes on an accumulator trap containing a sorbent material, and by thermally trapping the analytes at the head of the SFC column. Once the extraction is completed, the extracts are swept from the accumulating device into the SFC column by the SFC mobile phase, and the analysis is carried out under appropriate chromatographic conditions. SFE/SFC has been used as an injection method for samples that are difficult to dissolve in liquid solvents, as demonstrated by the analysis of a heavy hydrocarbon wax that was placed in the extraction cell as a slurry in chloroform *(27)*. The use of SFC allows the application to a wider range of compounds than is possible with GC including thermally labile and less volatile species *(70-75)*.

PLASTICS ADDITIVES

Plastics additives are a complex and important group of compounds that are incorporated into a diversity of products. Plastics are widely used in consumer products, such as rubber, paints, textiles, furniture, toys, cars, and electronics, and, in industrial applications, such as plastic resins. Plastics additives are frequently used to improve optical properties, resist aging, modify bulk mechanical properties, assist in processing, and, on the whole, improve the performance of plastics *(76)*.

Plastics additives can be divided into two principal groups, each group containing subgroups of compounds. These groups are process additives and functional additives.

Process additives are further subdivided into processing stabilizers and processing aids. These additives facilitate the processing of a plastic. For example, rigid PVC which is a thermoplastic, cannot be processed in the absence of stabilizers and lubricants. Virtually all thermoplastics are processed in the molten state under shear, because the molten polymer must pass through narrow slots and pipes in the shortest possible time. Therefore, lubricants are added to improve the flow properties and reduce the adherence of the melt to machine parts. They act as melt promoters; antiblock, antitack and antistatic agents, as well as color and impact improvers *(77)*. Esters, fatty acids, fatty amides, metallic stearates, waxes, fluorinated polymers and silicones are some examples of process additives.

Functional additives are subdivided into stabilizing additives and modifiers. These impart properties to the plastic and enhance properties already present. For example, polypropylene has low light and weather resistance, and after a few months of outdoor exposure, it becomes brittle. This is a result of photodegradation which involves two distinct processes *(77)*. The first is photolysis, which involves absorption of UV radiation and the formation of free radicals. The second is autoxidation, which involves the interaction of the free radical formed during photolysis with oxygen to form a peroxy radical. This then attacks the polymer backbone by hydrogen abstraction, generating another free radical. This free radical can then react, with oxygen, leading to the formation of a hydroperoxide which then rapidly undergoes photolysis. As these processes proceed, more and more free radicals are generated and an ever increasing number of polymer chains are broken or altered. However, certain light stabilizers render polypropylene highly light-stable and oxidation-resistant. The most important light stabilizer classes are 2-hydroxybenzophenones, 2-hydroxyphenylbenzotriazoles, hindered amines and organic nickel compounds *(78)*. Another important class of functional additives is antioxidants. Organic materials react with molecular oxygen in an autoxidation process which is initiated by heat, light, mechanical stress, catalyst residues, and reaction with impurities to form alkyl radicals. The free radical can, then, in turn react, and degradation of the polymer results. Manifestations of oxidation are aging, discoloration, changes in surface appearance (loss of gloss, cracking, hardening), loss of transparency and mechanical properties. Antioxidants interrupt the degradation process by chain terminating primary antioxidants and by hydroperoxide-decomposing secondary antioxidants *(79)*. Antioxidants include hindered phenols, phosphites and thioesters.

ANALYTICAL DETERMINATION OF PLASTICS ADDITIVES

The diversity and applications of plastics are increasing, and as they do, the number of additives available to modify plastic properties increases. These additives are not chemically bonded onto the polymer but, instead, are physically dispersed throughout the matrix. Plastic failures can often be attributed to the leaching of additives from the polymer, the chemical transformation of certain additives, and the omission of essential additives during formulation processes. Thus, there is a need for reliable methods to identify and quantitate additives in plastics, particularly in connection with medical plastics and food packaging where the identities and levels of potentially toxic substances must be accurately known and controlled.

From an analytical point of view, three main problems are associated with the analysis of polymer additives: the additives are situated in a more or less insoluble polymer matrix; the high reactivity and low stability of many types of additives, especially antioxidants, and the low concentrations (0.1% to 1.0%) of additives present in many matrices. Given the nature of the polymer matrix, the choice of analytical techniques that can be applied without prior separation of the additive from the polymer is limited. In addition, any extract of the polymer is susceptible to contamination by low molecular weight polymer "wax", which is difficult to remove and may interfere with subsequent analysis.

The factors mentioned above combine to make the handling of extracts a difficult job if quantitative information is required. Antioxidants, in particular, are unstable compounds, and form a complex mixture of decomposition products. This can interfere with the interpretation of results, and loss of material by decomposition is likely to be significant because the quantities present are initially low.

To summarize, the determination of additives in polymers presents the analyst with some difficult problems. Low concentrations are present, complex mixtures may be involved, and the extraction of the additives is time consuming. Because of these problems, it is necessary to develop an efficient extraction technique for the quantitative and qualitative determination of plastics additives.

This study evaluates supercritical fluid extraction as a method of extraction of additives from plastics. Supercritical fluid extraction is a faster and cheaper alternative to conventional extraction methods, and could well come to replace the existing methods.

A) EXTRACTION OF PLASTICS ADDITIVES

In some cases, rapid additive determination can be carried out without extensive pretreatment steps such as extraction. Direct spectroscopic methods such as ultraviolet absorption, infrared, fluorescence or phosphorescence *(80)*, and X-ray fluorescence *(81)* have been reported with little success owing to the interference of highly absorptive impurities in the sample. In situ spectroscopic techniques are not likely to be of value in the analysis of samples of unknown composition.

Direct determination of additives at both ambient and high temperature has been studied using gel permeation chromatography

(GPC) by analyzing polymers with high performance UltraStyragel GPC columns *(82)*. Polymers such as polystyrene, polyols, poly (vinyl chloride), urethanes, oils, waxes and silicones are soluble in organic solvents such as tetrahydrofuran at room temperature. The additives content in these types of polymers was determined by dissolving the entire sample and injecting an aliquot of the solution directly into the chromatograph. Antioxidants such as BHT, Irganox 1010, Irganox 1076, Irganox 565, and Ethyl 330, and UV absorbers such as Tinuvin P and Tinuvin 144 were analyzed in some of the above-mentioned polymers. Polymers soluble at high temperature were analyzed by using a non-UV absorbing mobile phase to accommodate a UV detector and a refractive index detector added to the chromatograph. Polymers such as polyolefins, polyesters and nylon soluble at temperatures above 100°C, were analyzed by this method.

GPC (steric exclusion chromatography) was used for the isolation of additives from polymers *(83)*. A simple and inexpensive gravity-flow system was evaluated employing Sephadex LH-60 with tetrahydrofuran as eluent, and recoveries were shown to be quantitative for a range of additives. Problems were encountered in the recovery of antioxidants and stabilizers. One factor limiting the wider use of steric exclusion chromatography in plastics analysis has been the detection limit obtainable with small sample loadings. Larger columns would allow greater loadings but they are expensive and are difficult to produce satisfactorily in the laboratory.

In some cases the above methods are useful, but generally suffer disadvantages from interferences associated with nonspecificity. A more desirable approach for most plastics additives is the extraction and determination of each additive in the polymer. This requires extraction of the additives followed by chromatographic separation. Wheeler *(80)* reviewed several polyolefin extraction procedures. Most involved lengthy treatment of ground polyolefin with a volatile organic solvent under heat. Crompton *(84)* extracted polyolefins in various volatile organic solvents from 6-24 hours prior to chromatographic analyses of the extracts. Another extraction method commonly used involves the dissolution of the polymer in boiling toluene under reflux, followed by precipitation of the high molecular weight fraction with ethanol *(85)*. The filtrate then contains the additives plus low molecular weight polymer "wax".

Other extraction apparati described include Soxhlet and related extractors *(86-87)*, tightly capped bottles in which sample and solvent are heated under pressure *(88)*, Wiley extractors *(89)*, and flasks in which the sample is merely steeped in solvent *(90)*. In order to increase the efficiency of extraction, surfactants and ultrasonic devices have been used *(91)*. Attempts to increase the polymer surface-area to volume ratio before extraction have included the use of ball mills and Wiley cutting mills *(92-94)*, microtomes *(95)* and grinding with solid carbon dioxide *(96)*.

B) DETERMINATION OF PLASTICS ADDITIVES

After extraction, it is necessary to determine the identities and concentrations of the plastics additives with precision.

1) PAPER CHROMATOGRAPHY

Wheeler *(80)* reviewed the literature on the applications of paper chromatography in the examination of polymers for antioxidants. He pointed out that, because most antioxidants are highly polar, they cannot be efficiently separated on normal paper except by the use of highly polar mobile phases.

A major contribution to paper chromatographic methods is the work of Zijp, who devised a comprehensive scheme for the systematic identification of antioxidants and accelerators *(97)*. In the part of his scheme which relates to antioxidants, Zijp used acetylated paper and two solvent systems, one for basic and one for phenolic constituents. Identification was based on the R_f value of each constituent and the colors produced by various spray reagents.

Unfortunately, the number of antioxidants now in use is so great that no single R_f value, even in conjunction with a variety of spray reagents, is likely to be specific enough to identify any component unambiguously. The analyst is therefore, forced to consider the use of multiple solvent systems to achieve the specificity required. Paper chromatography then becomes too lengthy a procedure for routine use.

2) THIN-LAYER CHROMATOGRAPHY

Thin-layer chromatography (TLC) gives good separation efficiency, and allows a greater variety of corrosive spray reagents to be used than paper chromatography *(98)*.

Simpson and Currel *(99)* used TLC in the determination of additives such as antioxidants and accelerators. Comparatively small samples of polymer materials are required, and, by means of the techniques described, it was possible to identify additives in extracts containing several different components. The method can be used to detect additives at low concentrations (1-10 μg per sample), and quantitative determinations of greater accuracy are possible.

3) GAS CHROMATOGRAPHY

The attraction of gas chromatography lies in its ability to simultaneously separate and estimate sub-microgram amounts of complex mixtures. However, many polymer additives are not volatile, and low stationary phase loadings have to be used to reduce retention times to reasonable values and to prevent decomposition and distortion of peaks. Non-volatile sample components can be converted into more volatile derivatives such as trimethylsilyl ethers *(100)* The formation of derivatives before chromatography does, however, lead to sample loss and can often lead to the appearance of spurious peaks on the chromatogram. Nevertheless, despite these limitations, gas chromatography has found numerous applications in the determination of additives in polymers.

Gas chromatography is particularly useful for the characterization of more volatile substances such as mixtures of fatty acids or of alcohols, esters or hydrocarbons which are used in polymer formulations.

Pyrolysis GC has also been used to analyze plastics additives *(101)*. The fragments or derivatives can be examined by gas, liquid or gel permeation chromatography. Perlstein *(102)*, used this technique with two different stationary phases, and was able to differentiate accurately between five commercial stabilizers.

4) HPLC ANALYSIS

Most of the plastics additives are low-volatile, high molecular weight compounds, and it is, therefore expected that High Performance Liquid Chromatography (HPLC) would be the most suitable general method for analysis. Analysis time in HPLC can be shortened considerably without loss of peak resolution by optimising the parameters of column length and diameter, flow rate, sample size and support particle size.

Both isocratic *(98,103-104)* and gradient elution *(103,105)* normal phase separations of polyolefin additives are reported in the literature. Separations are usually performed on silica supports using hexane, heptane, methylene chloride or chloroform as mobile phases *(103.-107)*. Normal phase HPLC has good resolution but the retention times of the additives may be affected by the accumulation of polar material on the silica gel, decreasing its adsorption ability *(108)*.

Reversed phase HPLC (RPLC) provides reproducible retention times. Most of the RPLC separations of additives were performed on C-18 type columns using MeCN:H_2O, CH_3OH:H_2O and MeCN:THF mixtures as the mobile phase *(107-113)*. Many analyses have been performed in the isocratic mode of separation *(108,112)*.

Additives separated by HPLC, have been characterized and identified with a tandem detection system which consisted of an ultraviolet absorbance detector and a LC-mass spectrometer with a moving belt interface*(114)*. The two detectors were operated in series with minimal loss of chromatographic resolution. The LC-MS system was found to operate satisfactorily as a LC detector. A linear response was observed between the integrated ion current of eluted peaks and the amount present. Quantitative data were obtained with a precision of less than 10% relative standard deviation, and sensitive detection limits were achieved (less than 10 ng for some solutes).

Size exclusion chromatography (SEC) is also used for the analysis of additives in polyolefins *(115-116)*. Although it is a simple analytical method and the retention times are reproducible, SEC suffers poor resolution in the number of components that can be resolved because many additives may be of similar molecular size.

5) SUPERCRITICAL FLUID CHROMATOGRAPHY (SFC)

Raynor et al.,*(117)* used capillary SFC as a general method for the separation and identification of a wide range of polymer additives and coupled this technique to FTIR microspectrometry for the application. A wide variety of ultraviolet absorbers, light stabilizers, antioxidants, metal deactivators, and slip agents varying in polarity and molecular mass from 225 to 1178 were separated on a nonpolar capillary column by using carbon dioxide as the mobile phase. There was no significant interference from the mobile phase and good quality spectra were obtained from samples determined at levels of the order of 100 ng.

Doehl et.al., *(118)* used capillary SFC with a flame ionization detector to determine polymer additives of low to medium polarity that cannot be detected by UV absorption. All the compounds were eluted with carbon dioxide or nitrous oxide from open-tubular capillary columns with non-polar DB-1 or SE-54 stationary phases in less than twenty minutes. When C_{18} or cyano bonded phase was used, the more polar additives were strongly absorbed.

EXPERIMENTAL

CHEMICAL AND SUPPLIES

The plastics additives studied were Irganox 1010, Irganox 3114, Irganox 245, Irganox 1076, Irgafos 168, Tinuvin P and Tinuvin 327 (Table 2 and Figure 8) (*77*). These chemicals, and pure commercial polypropylene samples were obtained from CIBA-Geigy Corporation, Ardsley, New York . The commercial polypropylene was stated to contain 0.05% each of Irganox 1010, Irgafos 168 and Irganox 3114. The carbon dioxide was supplied by the Linde Division of Union Carbide and was bone-dry grade. Acetonitrile, ethyl acetate, methylene chloride, methanol and toluene were all obtained from Fisher Scientific Corporation and were of HPLC grade.

APPARATUS

The basic components of the SFE apparatus used during this study are shown in Figure 9. The carbon dioxide, supplied through a single stage tank regulator, is pressurized by a Newport Scientific

TABLE 2

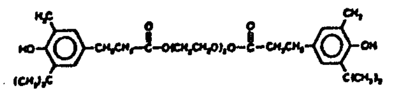
PLASTICS ADDITIVES STUDIED

Trade Name	Chemical Name	MW
1. Tinuvin P	2-(2-hydroxy-5-methylphenyl) -2H-benzotriazole	225
2. Tinuvin 327	2-(3,5-di-tert-butyl-2 -hydroxyphenyl)-5-chlorobenzotriazole	358
3. Irgafos 168	tris(2,4-di-tert-butylphenyl) phosphite	647
4. Irganox1076	octadecyl-3-(3,5-di-tert-butyl -4-hydroxyphenyl) propionate	537
5. Irganox 245	triethylene glycol bis-3-(3-tert-butyl -4-hydroxy-5-methylphenyl) propionate	587
6. Irganox 3114	tris(3,5-di-tert-butyl-4-hydroxybenzyl) isocyanurate	784
7. Irganox1010	Pentaerythritol tetrakis[3-(3,5-di-tert-butyl-4-hydroxyphenyl) propionate]	1178

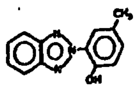
1 & 2 are UV light stabilizers
3, 4, 5, 6 & 7 are Antioxidants

FIGURE 8

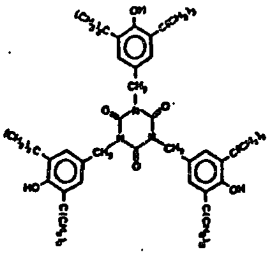
PLASTICS ADDITIVES



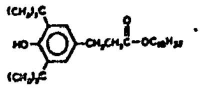
IRGANOX 245



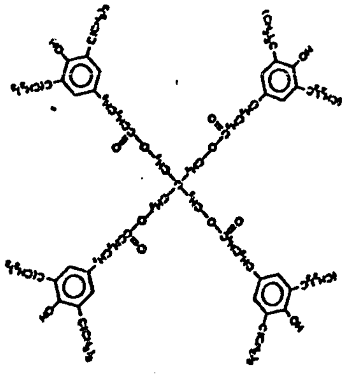
TINUVIN P



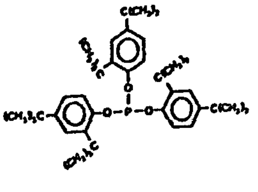
IRGANOX 3114



IRGANOX 1076

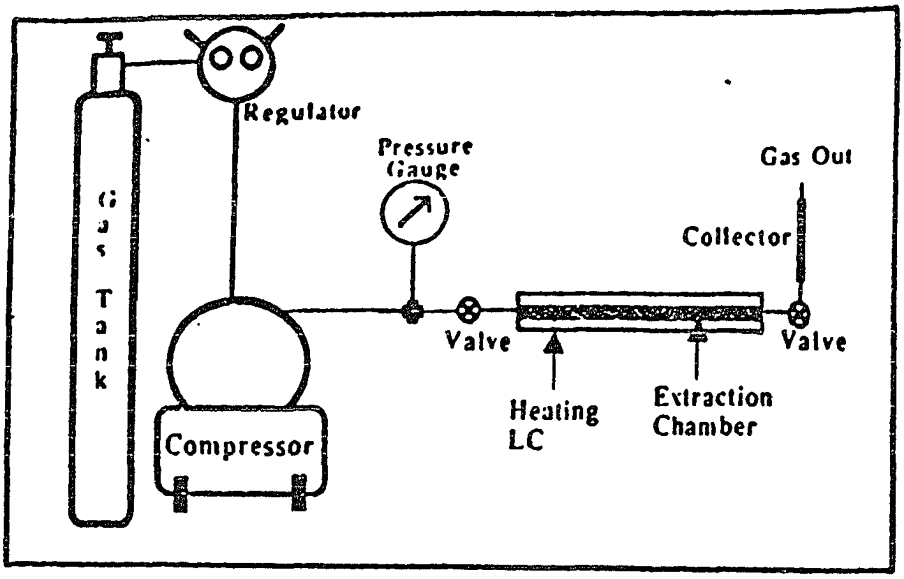


IRGANOX 1010



IRGAFOS 168

FIGURE 9



Schematic of the Supercritical Fluid Extraction motor-driven single-ended diaphragm compressor with a maximum output of 10000 psi. The output pressure of the compressor was controlled by varying the carbon dioxide supply pressure at the tank regulator. Experimental pressure was read on a pressure gauge connected to the extraction assembly via a "T" junction. The extraction chamber was thermostated in a Scientific Systems Inc. liquid chromatographic column oven, which controlled temperature in the 0°C to 99°C range (± 1°C).

The extraction train consisted of a 12" X 3/8" o.d. stainless steel extraction tube, 1/4" stainless steel connecting tubes, Swagelock fittings and an Autoclave Engineers model-valve. This was connected to the collector by Swagelok elbow union.

PROCEDURE

Prior to each extraction, the extraction chamber was disassembled, cleaned with methylene chloride, and dried. The sample was loaded into the extraction chamber between two glass wool plugs pre-washed with methylene chloride and inserted into each end of the extraction chamber to prevent displacement of the sample. All parts were then reassembled and care was taken to prevent possible leaks at high pressures during extraction. With the valve open, carbon dioxide was allowed to flow through the extraction train under low pressure (~100 psi) to remove any air present in the extraction chamber. The valve was then closed, the compressor turned on and the system pressurized with carbon dioxide until the required pressure was obtained. At the completion of an extraction, both the pump and the gas supply were shut off and the valve was opened slowly to bleed out the extract-laden carbon dioxide. Once all the carbon dioxide had passed through, the apparatus was disassembled and all the parts after the extraction chamber including the trap were washed with about 40-50 ml of methylene chloride. This solvent was evaporated in a Büchi rotary evaporator to 1 ml at 40°C. This solution was then analyzed using a Perkin-Elmer Series 400 HPLC with an LC-235 diode array detector capable of spectral plot and overlay of spectra with the capability of monitoring all wavelengths at the same time. The instrument was first calibrated with solutions of the pure additives to determine response characteristics and retention times. A Perkin Elmer LCI-100 computing integrator was used. HPLC-grade acetonitrile (ACN) and ethyl acetate (EtAc) mixtures used as the mobile phases were first degassed with Helium for 15 minutes. For Irganox 1010, 80/20 (v/v) ACN/EtAc was used at a flow rate of 1 ml/min., whereas for the other additives, 60/40 (v/v) ACN/EtAc was used at a flow rate of 1.2 ml/min. The HPLC column was Partisil 5 ODS, 25 X 0.46 cm. The amount of compound extracted was calculated by comparing the peak areas of the compound in the concentrated extract solution with that in a standard solution of similar concentration. Each run was replicated two or three times and the detector response was a linear function of the amount injected.

EVALUATION OF TRAPS

The efficiency of trapping systems was determined by spiking additives onto filter paper and using SFE at pressures between 6000-9000 psi and temperatures between 80°C and 99°C. Adsorbent traps evaluated contained silica, Chromosorb W or Florisil. The relative merits of the three traps were determined in terms of recovery by the trap. Each trap was filled with the adsorbent supported with two glass wool plugs before each extraction. The inlet end of the trap was connected to the extraction train through the Swagelock elbow union while the other end was connected to a frit to prevent blowing out of the adsorbent material during the depressurization process.

a) EFFICIENCY OF TRAPPING

One ml of a standard solution containing 50 µg each of the pure additives in methylene chloride was spiked onto a Whatman no.1 filter paper prewashed with methylene chloride. The methylene chloride was evaporated, and the filter paper cut into pieces and packed into the extractor. Before the extraction, a Tygon tube (2' X 1/4" od.) was connected to the frit and a glass tube was fitted to the other end which was inserted into an Erlenmeyer flask containing 100 ml of methylene chloride. The extraction was carried out at pressures between 6000-9000 psi and temperatures between 80°C and 99°C for 30 min. The depressurized carbon dioxide was passed through the Tygon tube into the solvent; this solvent was then used to flush the tube. The resulting solution was concentrated on the rotary evaporator for quantitative determination.

The washed adsorbents and filter paper that remained in the extraction chamber were carefully removed and sonicated with methylene chloride. They were then Soxhlet-extracted to quantitatively determine if there was any remainder of additives on both the filter paper and adsorbents. Results which are averages of three separate runs are shown in Tables 3-8.

TABLE 3

EVALUATION OF SILICA TRAP

SFE Conditions: 9000 psi, 99°C, 30 min.

	% Recovery (±RSD)* of Additives Spiked Onto Filter Paper		
Sample	Irganox 1010	Irgafos 168	Irganox 3114
Collector	98±3	76±5	90±5
Filter Paper	0.1±1	21±6	5±3
Sonicated silica (after washed)	0	0.8±2	0
Methylene Chloride (in flask)	0	0	0

*RSD = % relative standard deviation
n = 3

TABLE 4

EVALUATION OF FLORISIL TRAP

SFE Conditions: 9000 psi, 99°C, 30 min.

Sample	% Recovery (±RSD)* of Additives Spiked Onto Filter Paper Irganox 1010	Irgafos 168	Irganox 3114
Collector	99±2	75±4	90±2
Filter Paper	0.1±1	21±3	6±2
Sonicated silica (after washed)	0	0.5±1	0
Methylene Chloride (in flask)	0	0	0

*RSD = % relative standard deviation
n = 3

TABLE 5

EVALUATION OF CHROMOSORB W TRAP

SFE Conditions: 9000 psi, 99°C, 30 min.

	% Recovery (±RSD)* of Additives Spiked Onto Filter Paper		
Sample	Irganox 1010	Irgafos 168	Irganox 3114
Collector	98±3	76±3	90±2
Filter Paper	0.1±1	21±4	5±2
Sonicated silica (after washed)	0	0.3±1	0
Methylene Chloride (in flask)	0	0	0

*RSD = % relative standard deviation
n = 3

TABLE 6

EVALUATION OF SILICA TRAP

SFE Conditions: 6000 psi, 80°C, 30 min.

Sample	% Recovery (±RSD)* of Additives Spiked Onto Filter Paper			
	Irganox 245	Tinuvin P	Tinuvin 327	Irganox 1076
Collector	10±4	96±4	97±2	82±3
Filter Paper	25±5	0.02±1	0.05±1	0.05±1
Sonicated silica (after washed)	0.08±2	0	0.03±1	0
Methylene Chloride (in flask)	0	0	0	0

*RSD = % relative standard deviation
n = 3

TABLE 7

EVALUATION OF FLORISIL TRAP
SFE Conditions: 6000 psi, 80°C, 30 min.

	% Recovery (±RSD)* of Additives Spiked Onto Filter Paper			
Sample	Irganox 245	Tinuvin P	Tinuvin 327	Irganox 1076
Collector	11±4	95±3	97±2	80±4
Filter Paper	23±4	0.03±2	0.05±1	0.05±1
Sonicated Florisil (after washed)	0.1	0	0	0.09±2
Methylene Chloride (in flask)	0	0	0	0

*RSD = % relative standard deviation
n = 3

TABLE 8

EVALUATION OF CHROMOSORB W TRAP

SFE Conditions: 6000 psi, 80°C, 30 min.

	% Recovery (±RSD)* of Additives Spiked Onto Filter Paper			
Sample	Irganox 245	Tinuvin P	Tinuvin 327	Irganox 1076
Collector	71±6	95±3	96±4	85±3
Filter Paper	25±4	0.03±1	0.05±1	0.05±1
Sonicated CHW (after washed)	0.06±2	0	0	0
Methylene Chloride (in flask)	0	0	0	0

*RSD = % relative standard deviation
n = 3

OPTIMUM EXPERIMENTAL CONDITIONS

For a given fluid, SFE recovery is controlled by four experimental parameters, pressure, temperature, equilibrium time, and sample particle size. Knowledge of the effect of these conditions is essential to establish optimum SFE conditions.

a) EFFECT OF EQUILIBRATION TIME

Four different equilibration times were studied; 10, 15, 30 and 60 minutes. All extractions were done at a pressure and temperature of 9500 psi and 99°C, respectively. The commercial polypropylene containing Irganox 1010, Irganox 3114 and Irgafos 168 had the additives incorporated into the plastic. The other additives were spiked onto filter paper. Results which are averages of three runs are shown in Table 9.

TABLE 9

EFFECT OF EQUILIBRATION TIME

SFE Conditions: 9500 psi, 99°C

	% Recovery (±RSD)* of Additives in Commercial Plastics		
TIME (min.)	Irganox 1010	Irgafos 168	Irganox 3114
10	71±4	68±6	82±4
15	85±4	70±4	86±7
30	98±5	75±7	89±5
60	98±6	75±4	91±4

*RSD = % relative standard deviation

n = 3

b) EFFECT OF PRESSURE AND TEMPERATURE

Once the optimum equilibrium time was determined, pressures were varied from 6000-9000 psi at three temperatures ranging from 60-80°C. The effect of pressure and temperature on the extraction of the additives not in the commercial polypropylene sample available was also studied. One ml of a solution containing 50 µg each of the pure additives in methylene chloride was spiked onto 2 grams of pure polypropylene which was allowed to dry, and then extracted. Results are shown in Figures 10-20 and an outline of the percentage recovery at the optimum conditions for each additive is indicated in Tables 10 and 11. Each extraction was replicated three times and the standard deviation of each is indicated.

EFFECT OF PLASTIC PARTICLE SIZE ON IRGANOX 1010, IRGANOX 3114 & IRGAFOS 168

The effect of polypropylene particle size on the percentage recovery of Irganox 1010, Irganox 3114 and Irgafos 168 was studied to determine if the extra step of grinding before the extraction could be eliminated.

FIGURE 10
EXTRACTION STUDY OF IRGANOX 1010 (8000 psi)

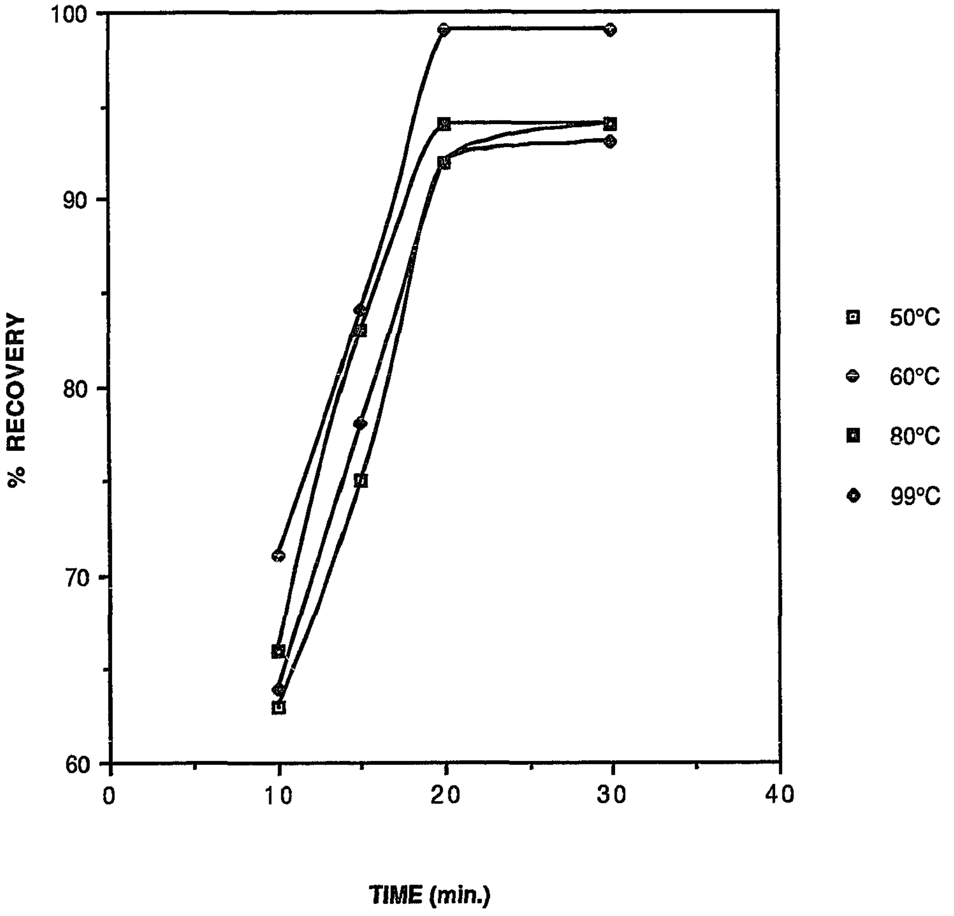


FIGURE 11
EXTRACTION STUDY OF IRGANOX 1010 (7000 psi)

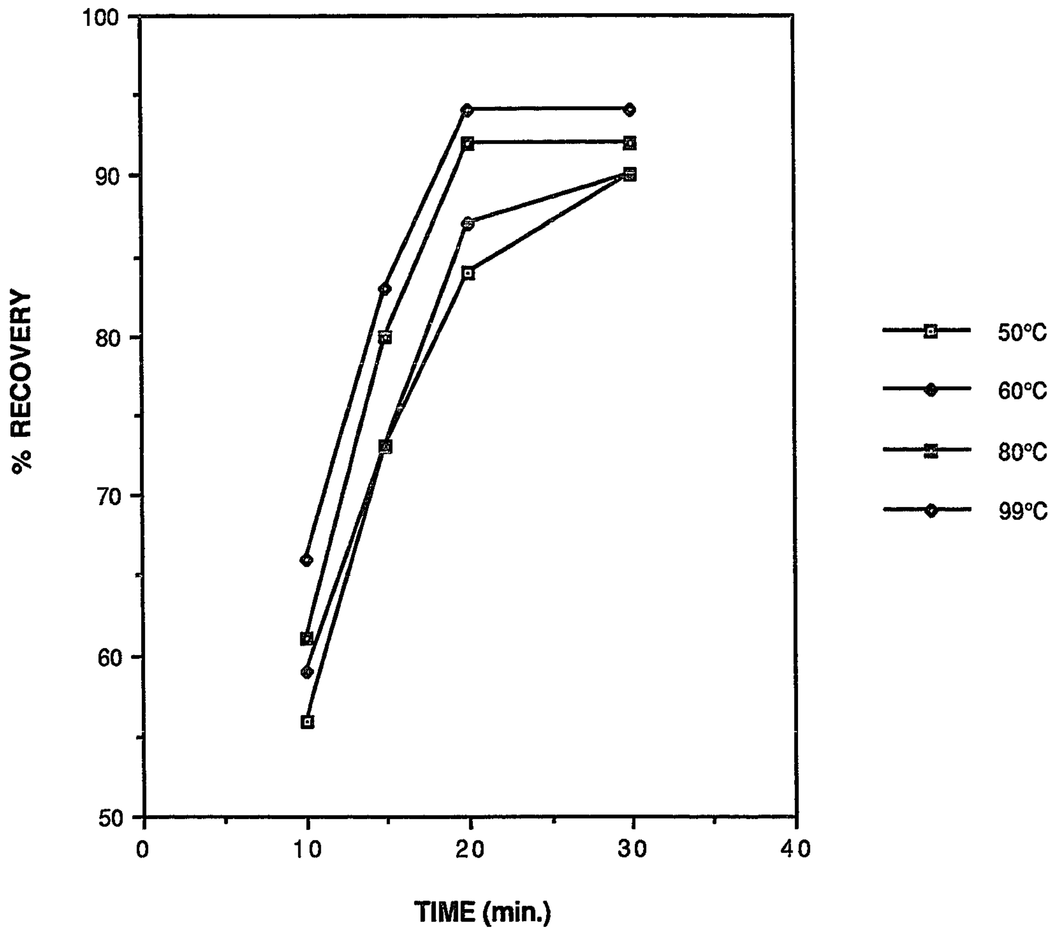


FIGURE 12
EXTRACTION STUDY OF IRGANOX 1010 (6000 psi)

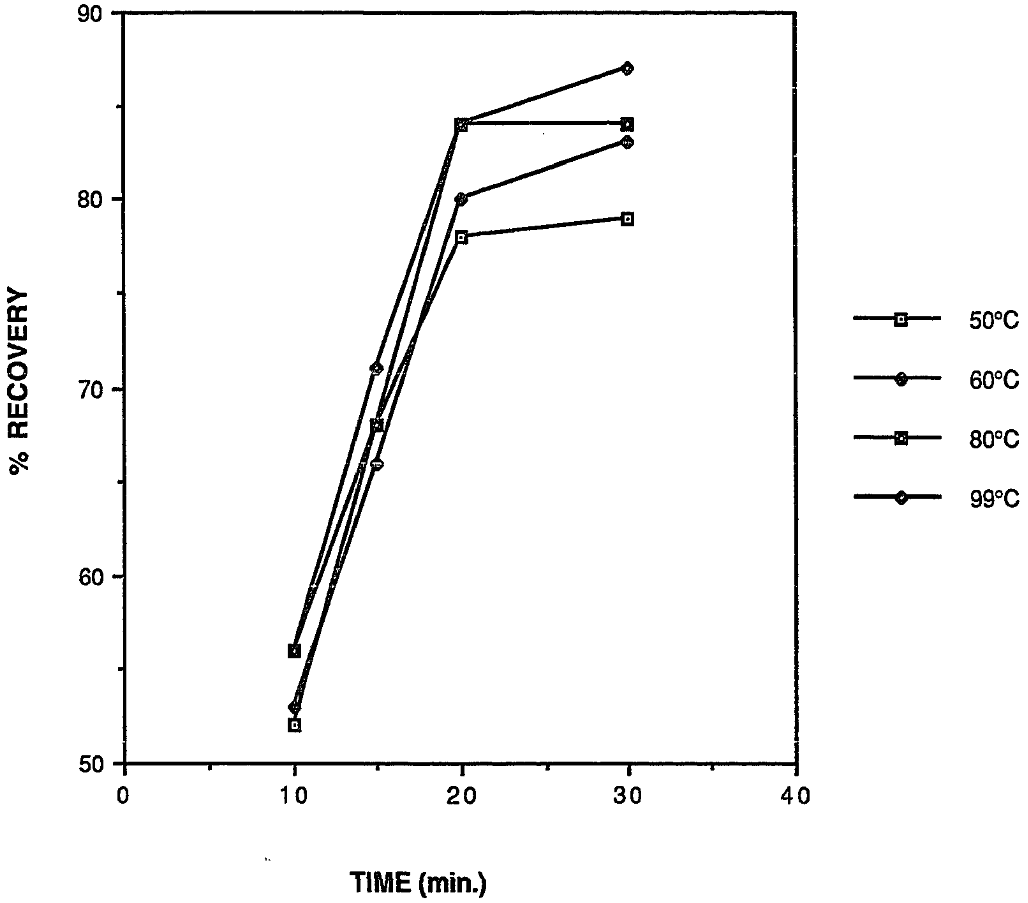


FIGURE 13
EXTRACTION STUDY OF IRGANOX 3114 (8000 psi)

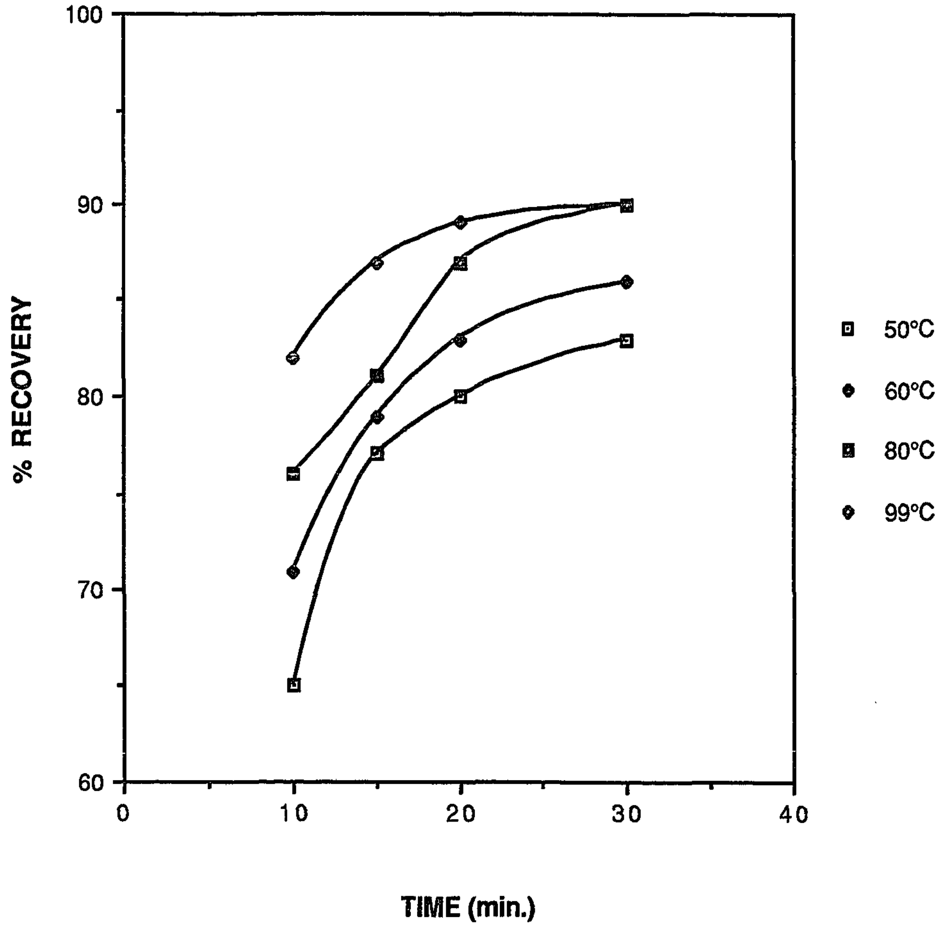


FIGURE 14
EXTRACTION STUDY OF IRGANOX 3114 (7000 psi)

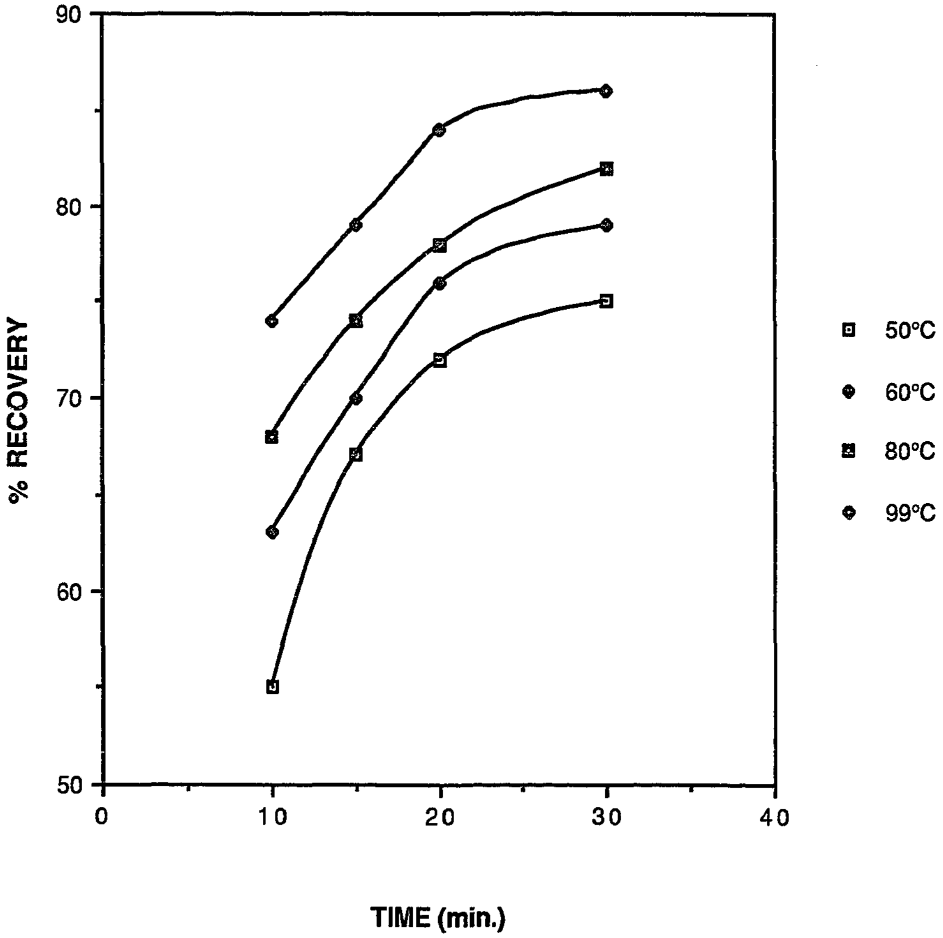


FIGURE 15

EXTRACTION STUDY OF IRGANOX 3114 (6000 psi)

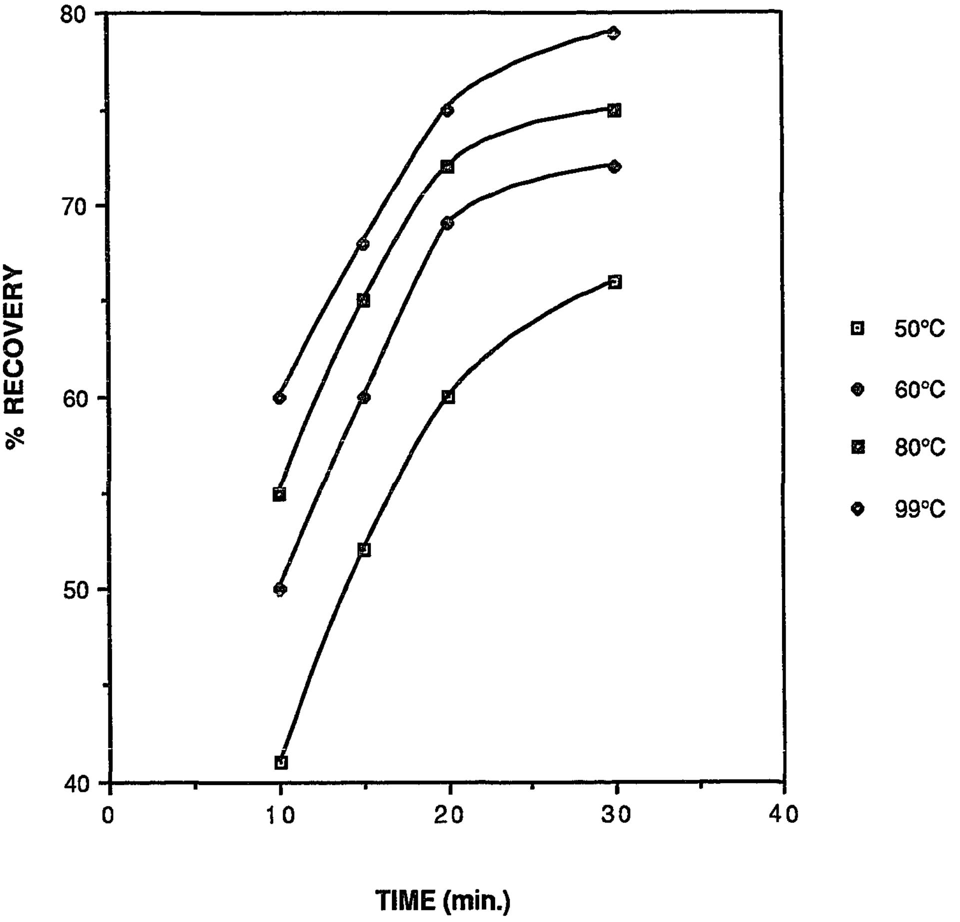


FIGURE 16
EXTRACTION STUDY OF IRGAFOS 168 (9000 psi)

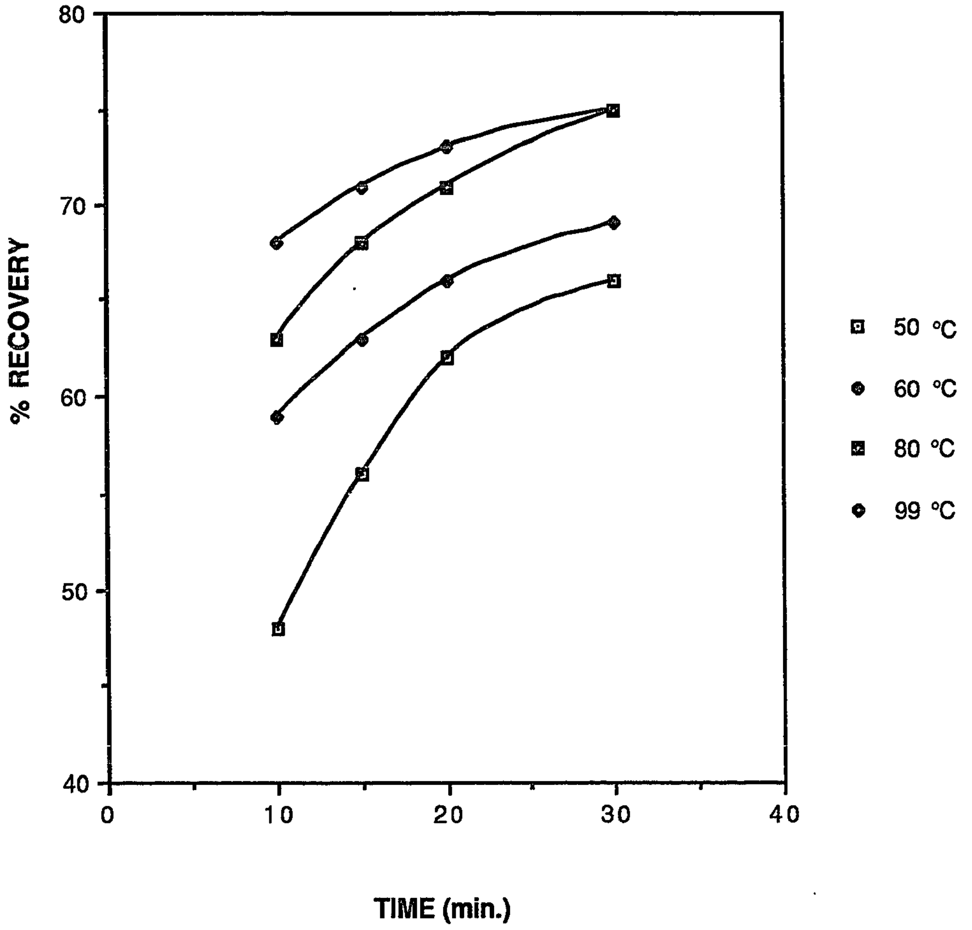


FIGURE 17
EXTRACTION STUDY OF IRGAFOS 168 (8000 psi)

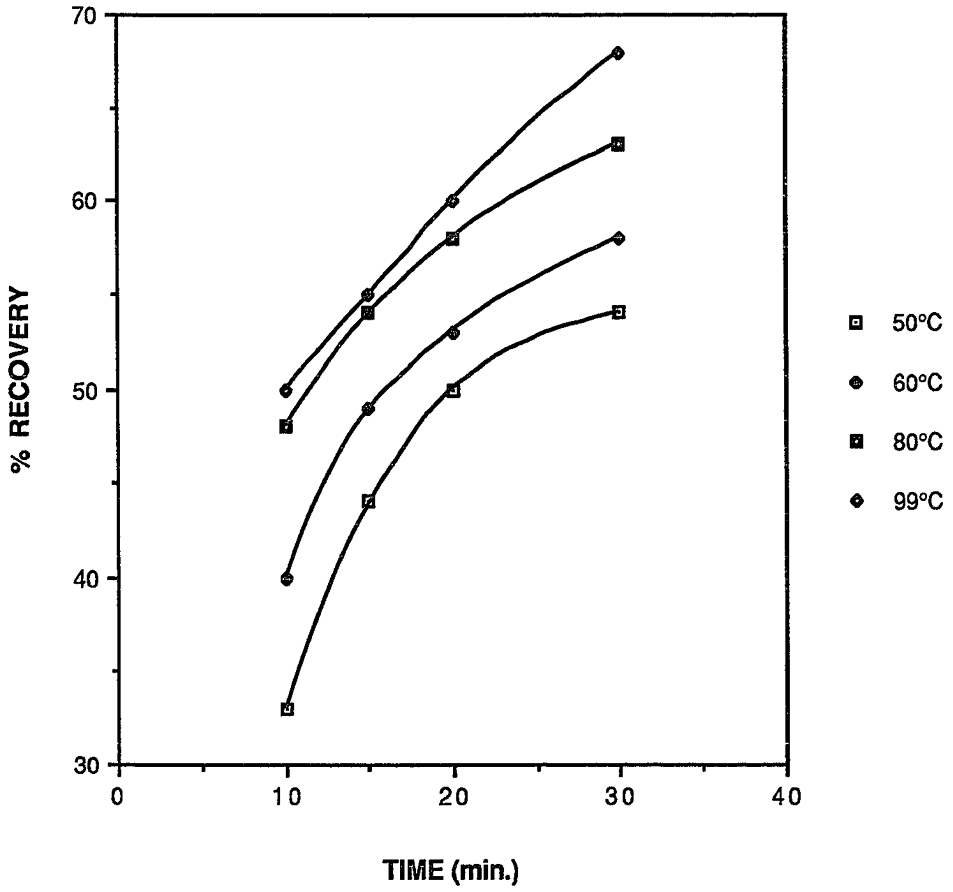


FIGURE 18
EXTRACTION STUDY OF IRGAFOS 168 (7000 psi)

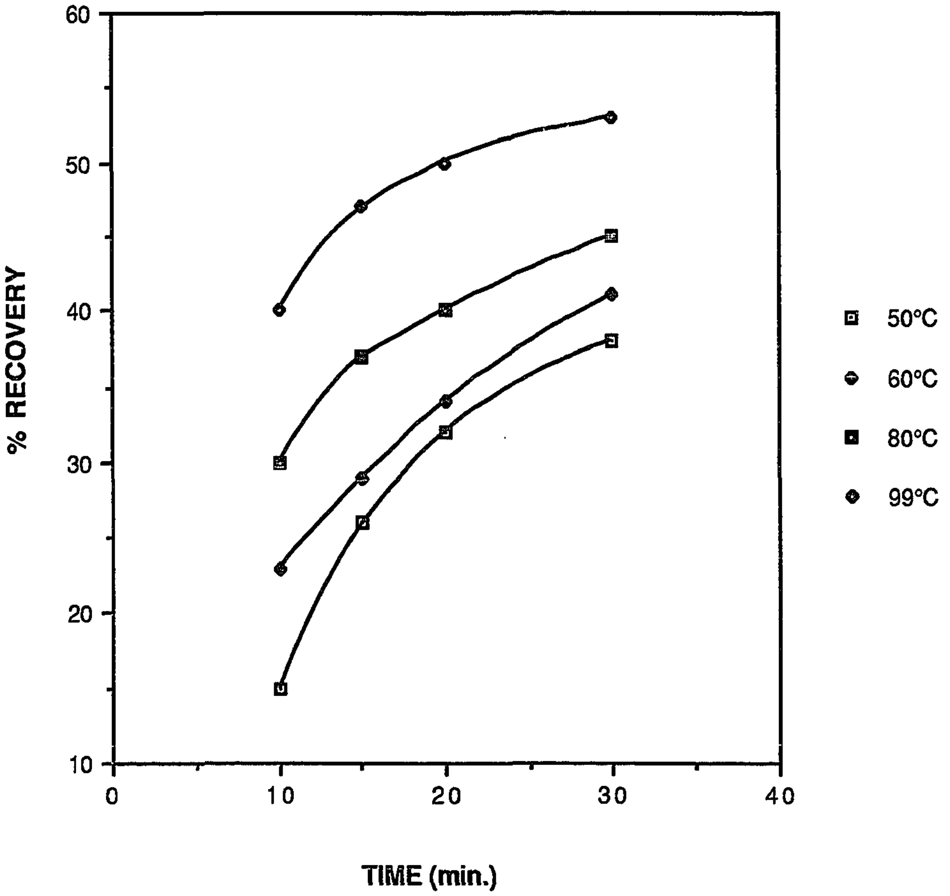


FIGURE 19
EFFECT OF PRESSURE ON SFE OF SPIKED PLASTICS ADDITIVES

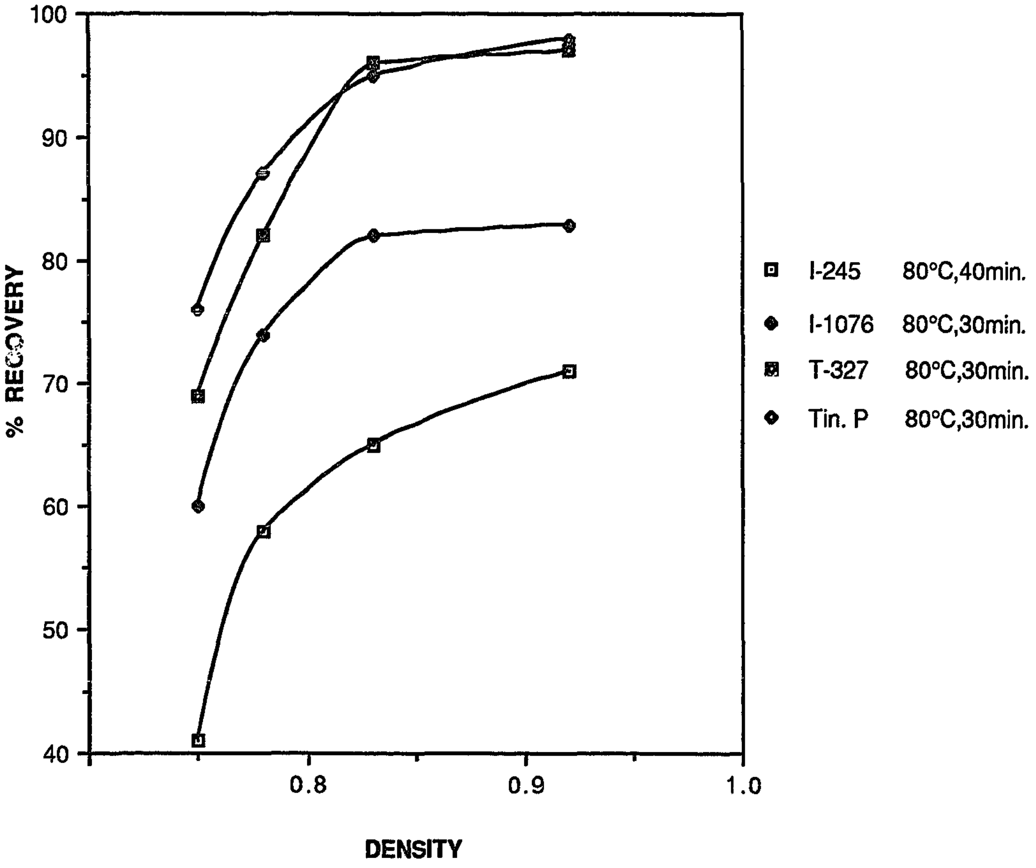


FIGURE 20
EFFECT OF TEMPERATURE ON SFE OF SPIKED PLASTICS ADDITIVES

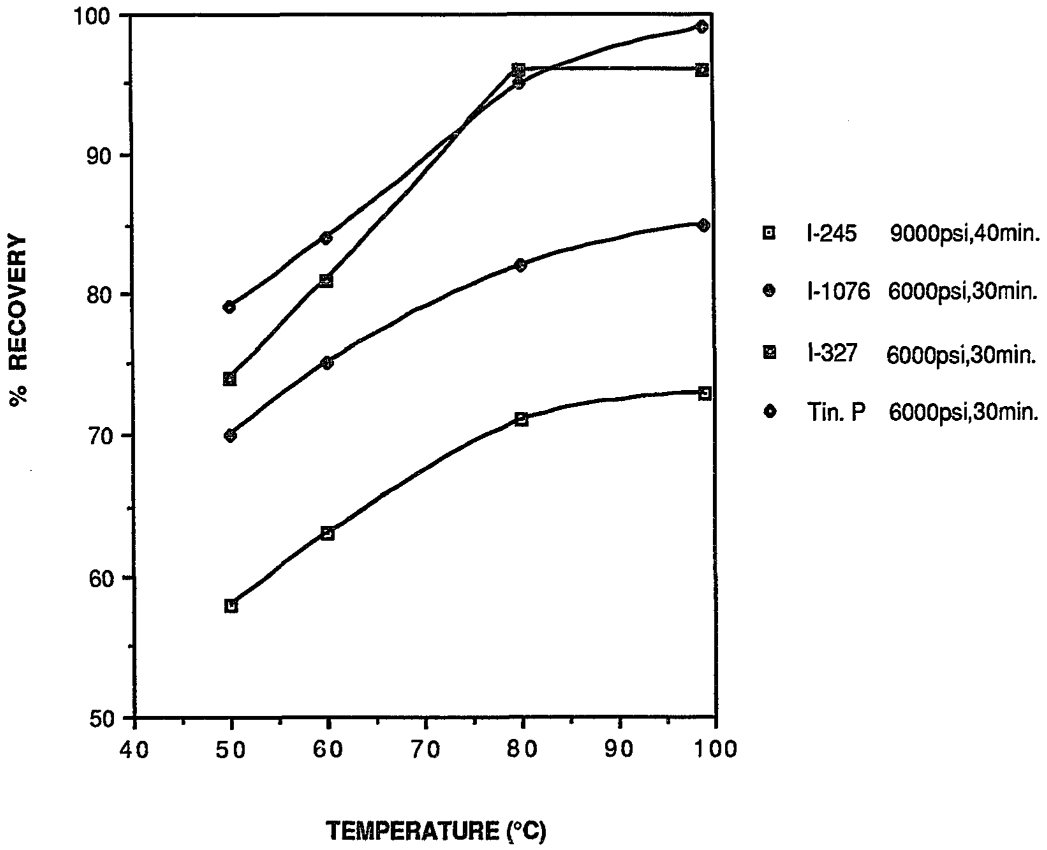


TABLE 10

OPTIMUM EXPERIMENTAL CONDITIONS
(6000 psi, 80°C, 20 min.)

Additives	% Recoveries (spikes)	RDS
Irganox 245	70	±6%
Tinuvin P	95	±6%
Tinuvin 327	96	±7%
Irganox 1076	82	±11%

RDS = relative standard deviation
n = 3

TABLE 11

OPTIMUM EXPERIMENTAL CONDITIONS

Additives	(Commercial Polypropylene) % Recoveries	RDS
Irganox1010[a]	98	±5%
Irganox3114[b]	90	±8%
Irgafos168[c]	75	±6%

a- (8000 psi, 100°C, 30 min.)
b- (8000 psi, 80°C, 30 min.)
c -(9000 psi, 80°C, 30 min.)
RDS = relative standard deviation
n = 3

Samples of the commercial polypropylene containing the additives were ground using an electric coffee grinder. The ground material was sieved, and those particles passing 24 mesh (701μm), 60 mesh (250μm) and 80 mesh (177μm) sieves were extracted. One gram of each fraction was placed in the extraction chamber to be extracted for 30 minutes at pressures between 8000-9000 psi and temperatures ranging from 80°C to 99°C. Results which are averages of three runs are given in Table 12.

STUDIES OF OTHER EXTRACTION TECHNIQUES

To compare SFE with other methods of extraction, the commercial plastic containing Irganox 1010, Irganox 3114 and Irgafos 168 was extracted using Soxhlet and dissolution extraction methods.

TABLE 12

STUDY OF EFFECT OF PARTICLE SIZE ON EXTRACTION OF IRGANOX 1010, IRGANOX 3114, IRGAFOS 168

	PARTICLE SIZE (PS)-% RECOVERY (±RSD)*			
COMPOUND	PS<177µm	177µm<PS<250µm	250µm<PS<701µm	PS>701µm
Irganox 1010[a]	98±5	84±7	52±5	22±6
Irganox 3114[b]	90±8	79±6	43±5	18±5
Irgafos 168[c]	75±6	61±5	35±6	10±4

a- 8000 psi, 100°C, 30 min.
b- 8000 psi, 80°C, 30 min.
c- 9000 psi, 80°C, 30 min.
PS- particle size
*RSD = % relative standard deviation
n = 3

a) SOXHLET EXTRACTION *(108)*

One gram of each plastic was Soxhlet extracted in 250 ml methylene chloride for 5, 10, 15, and 24 hours separately. For each time indicated, the extraction was terminated and the extracted solution was evaporated to dryness on a rotary evaporator and then redissolved in 5 ml of THF. This solution was then filtered through a 0.05μm Teflon filter, concentrated to 1 ml, and analyzed by HPLC/UV. The result for each time from each sample is documented in Table 13; the results are averages of two extractions each.

b) DISSOLUTION METHOD *(80)*

This method involves refluxing one gram each of the samples in 25 ml of toluene to dissolve it. Each sample was refluxed for 3, 4, 6, and 8 hours separately. Methanol (75 mL) is then added through the top of the condenser to precipitate the polymer. The additives remain in solution. The solution is filtered through a 0.05 μm Teflon filter, concentrated and analyzed by HPLC/UV. Each extraction is repeated twice and the results are indicated in Table 14.

TABLE 13

SOXHLET EXTRACTION OF IRGANOX 1010, IRGANOX 3114 AND IRGAFOS 168 (<177μm)

	% Recovery (±RSD)* at different time intervals		
TIME (hr.)	Irganox1010	Irgafos168	Irganox 3114
5	42±5	48±6	35±4
10	59±4	56±4	49±6
15	73±5	78±4	71±5
24	95±6	92±5	88±5

*RSD = % relative standard deviation
n = 2

TABLE 14

DISSOLUTION STUDY OF IRGANOX 1010, IRGANOX 3114, IRGAFOS 168

	% Recovery (±RSD)* at different time intervals		
TIME (hr.)	Irganox1010	Irgafos168	Irganox 3114
3	79±4	72±7	81±3
4	86±3	83±4	83±4
6	94±5	86±6	85±5
8	96±2	92±6	88±4

*RSD = % relative standard deviation
n = 2

SOXHLET EXTRACTION AND SFE COMBINED

After Irganox 1010, Irganox 3114, and Irgafos 168 were extracted by SFE at their optimum conditions (Tables 10 & 11), the plastics were Soxhlet-extracted with 250 ml each of methylene chloride for 24 hours to determine if any additional material could be recovered. The opposite process was also carried out with sample that had been previously Soxhlet extracted to determine if additional material could be recovered. Results which are averages of 2 runs each are given in Table 15.

TABLE 15

COMBINATION OF SOXHLET AND SFE

COMPOUND	% RECOVERY (±RSD)*			
	SFE	SOXHLET[a]	SOXHLET[b]	SFE[c]
Irganox 1010	98±5	0.05±2	98±6	0
Irganox 3114	90±5	0.02±1	86±5	5±4
Irgafos 168	75±6	19±4	91±6	0

a, Soxhlet with methylene chloride for 24 hr. after SFE
b, Soxhlet with methylene chloride for 24 hour
c, SFE after Soxhlet

SFE conditions: - Irganox 1010- 8000 psi, 99°C, 30 min.
Irganox 3114- 8000 psi, 80°C, 30 min.
Irgafos 168- 9000 psi, 80°C, 30 min.

*RSD = % relative standard deviation
n = 2

SOLUBILITY STUDIES

The solubility of the additives in supercritical carbon dioxide were studied to gain an insight as to why the additives are soluble in carbon dioxide. The procedure was done by loading approximately one gram each of Irganox 1010, Irganox 3114, Irganox 245, Irgafos 168 and Tinuvin P into the extraction chamber. A relatively large amount was chosen in order to ensure saturation of the supercritical carbon dioxide in the extraction chamber. Equilibrations were made in the pressure range of 6000-9000 psi at 80-100°C with a 30 min. equilibration time. A Chromosorb trap was used. Each compound was extracted at six different temperature-pressure combinations and each combinations were repeated three times. A Tygon tube (2' X 1/4") was connected to the end of the Chromosorb trap and the volume of depressurized carbon dioxide measured by displacement of carbon dioxide-saturated water in a one liter volumetric flask. The extract eluted from the trap with methylene chloride was diluted to 100 ml to prevent overloading the HPLC column, and was then quantitated by HPLC/UV. The volume of carbon dioxide collected at room temperature and atmospheric pressure was converted to STP conditions. Assuming ideal gas behavior, the number of moles of carbon dioxide and the mole fraction of compound in CO_2 were calculated. Results which are averages of three runs are given in Tables 16-25.

TABLE 16

SOLUBILITY OF TINUVIN P (at 99°C)

PRESSURE(psi)	RECOVERY(mg)	VOLUME OF CO_2(L)	MOLE FRACTION
9000	32	18	18×10^{-5}
8000	25	17	17×10^{-5}
6000	19	16	13×10^{-5}

TABLE 17

SOLUBILITY OF TINUVIN P (at 80°C)

PRESSURE(psi)	RECOVERY(mg)	VOLUME OF CO_2(L)	MOLE FRACTION
9000	26	17	14 $X10^{-5}$
8000	21	16	14 $X10^{-5}$
6000	17	15	12 $X10^{-5}$

TABLE 18

SOLUBILITY OF IRGANOX 1010 (at 99°C)

PRESSURE(psi)	RECOVERY(mg)	VOLUME OF CO_2(L)	MOLE FRACTION
9000	85	18	9 $\times 10^{-5}$
8000	54	17	7 $\times 10^{-5}$
6000	43	16	6 $\times 10^{-5}$

TABLE 19

SOLUBILITY OF IRGANOX 1010 (at 80°C)

PRESSURE(psi)	RECOVERY(mg)	VOLUME OF CO_2(L)	MOLE FRACTION
9000	62	17	6×10^{-5}
8000	38	16	5×10^{-5}
6000	24	15	3×10^{-5}

TABLE 20

SOLUBILITY OF IRGANOX 3114 (at 99°C)

PRESSURE(psi)	RECOVERY(mg)	VOLUME OF CO_2(L)	MOLE FRACTION
9000	35	18	6×10^{-5}
8000	18	17	3×10^{-5}
6000	12	16	2×10^{-5}

TABLE 21

SOLUBILITY OF IRGANOX 3114 (at 80°C)

PRESSURE(psi)	RECOVERY(mg)	VOLUME OF CO_2(L)	MOLE FRACTION
9000	20	17	3×10^{-5}
8000	10	16	2×10^{-5}
6000	5	15	1×10^{-5}

TABLE 22

SOLUBILITY OF IRGAFOS 168 (at 99°C)

PRESSURE(psi)	RECOVERY(mg)	VOLUME OF CO_2(L)	MOLE FRACTION
9000	15	18	3×10^{-5}
8000	8	17	2×10^{-5}
6000	5	16	1×10^{-5}

TABLE 23

SOLUBILITY OF IRGAFOS 168 (at 80°C)

PRESSURE(psi)	RECOVERY(mg)	VOLUME OF CO_2(L)	MOLE FRACTION
9000	7	17	1 $X10^{-5}$
8000	4	16	.9 $X10^{-5}$
6000	1	15	.3 $X10^{-5}$

TABLE 24

SOLUBILITY OF IRGANOX 245 (at 99°C)

PRESSURE(psi)	RECOVERY(mg)	VOLUME OF CO_2(L)	MOLE FRACTION
9000	14	18	3×10^{-5}
8000	8	17	2×10^{-5}
6000	4	16	1×10^{-5}

TABLE 25

SOLUBILITY OF IRGANOX 245 (at 80°C)

PRESSURE(psi)	RECOVERY(mg)	VOLUME OF CO_2(L)	MOLE FRACTION
9000	6	17	1×10^{-5}
8000	4	16	$.9 \times 10^{-5}$
6000	.8	15	$.2 \times 10^{-5}$

DISCUSSION

According to the results in Table 3-8, It is seen that both silica and Florisil give quantitative trapping of all the plastics additives studied, although Chromosorb W is best for Irganox 245. The fact that Chromosorb W is better suited for Irganox 245 than silica is a bit peculiar. Both silica and Chromosorb W have the same chemical nature in that their surface consists of a network of siloxane and silanol groups which can hydrogen bond to solutes. Furthermore, Irganox 245 has the same functional groups as Irganox 1010 and, therefore, should give similar recoveries. Perhaps Irganox 245 is adsorbed onto some reactive sites on silica but Irganox 1010 does not because of steric hindrance.

In determining the efficiency of trapping for the traps used, no compounds were detected when the depressurized carbon dioxide was allowed to dissolve in methylene chloride in the Erlenmeyer flask. This shows that the traps used were efficient.

OPTIMUM EXPERIMENTAL CONDITIONS

SFE recovery depends on four experimental parameters: pressure, temperature, particle size and equilibration time. Knowledge of these conditions is essential in determining with precision, the percentage of additives in commercial plastics.

The results in Figures 10-20 show that recovery increases with temperature and pressure. Tables 10 & 11 show the maximum percentage recovery at defined pressures, temperatures, and time for the additives. Irganox 1010, Irgafos 168 and Irganox 3114 can be quantitatively extracted within 30 min as indicated in Table 10. From the shapes of the above figures, it is seen that given the same time, the rate of increase in % recovery of Irganox 1010 is faster than the other additives. This indicates that supercritical carbon dioxide interacts more strongly with Irganox 1010 than with the other additives.

The above results can be explained in terms of the physicochemical properties of supercritical carbon dioxide. Diffusion of SCF-CO_2 is affected by temperature and pressure.

Diffusion plays a particularly important role in SCF extraction. If the rate-limiting step (or the largest mass-transfer resistance) of a separations process is the transfer of a material from the surface of a solid to the solution phase, then a gas-like diffusivity would enhance diffusion in an extraction carried out with a supercritical fluid, relative to an extraction carried out with a liquid solvent. However, if the extraction is occurring from within a nonporous particle such as a polymer, internal solid-phase diffusion will govern the overall rate of mass transfer *(2)*. In this case, interparticle-phase SCF diffusion will have little or no effect on the rate of mass transfer.

In certain systems, polymers can absorb a supercritical fluid and swell (*2*). The swelling initially increases linearly with pressure but at higher pressures, the rate of swelling reaches a limiting value. Polymers swollen with supercritical fluid lose some of the properties of the rigid, solid state (*2*). In this case, the rate of extraction is limited by the intraparticle diffusion of extract through the absorbed supercritical fluid carbon dioxide. This change in matrix accounts for the relative ease of extraction of the polymer additives.

EFFECT OF PARTICLE SIZE

The effect on the percentage recovery of the polypropylene particle size is given in Table 12. This study was done to determine if on the analytical scale, the additives could be extracted from the commercial polypropylene as supplied in 1/8 inch pellets. However, it is clear that the extra step of grinding is necessary in order to achieve quantitative recovery.

This result was interesting and important since it was able to contribute to the solution of a real industrial extraction problem. While I was doing this study, my mentor, Dr. Locke, was contracted by Dr. Minnich from Mobay Corporation in Pittsburgh, PA who was having problems using SFE to extract a mold release agent, pentaerythritrol tetrastearate, from polycarbonate resin. The results of this study were communicated to Dr. Minnich, who was able to increase percentage recovery by 50% using higher carbon dioxide pressures and finely ground samples instead of whole pellets.

DIFFUSION STUDY

A study was done to determine the diffusion of the additives as a function of time and particle size. Crank *(120)* formulated useful equations based on the following argument:

Consider a spherical particle of radius, a immersed in supercritical carbon dioxide. The particle is not in contact with other particles, that is, diffusion occurs in each particle independently, with no interparticle diffusion. The additive or solvated additive moves out of the particle with diffusion coefficient, D.

The problem can be parametized as:

$$dc/dt = D\ [\{d^2c/dr^2\} + \{2/r\}\{dc/dr\}] \qquad (1)$$

If the sphere is initially at a uniform concentration C_1 of the additive, and the surface concentration of carbon dioxide is maintained constant at C_0, the solution is :

$$(C-C_1)/(C_0-C_1) = 1 + 2a/\pi r \sum_{n=1} (-1)^n \sin(n\pi r/a) \exp(-Dn^2\pi^2 t/a^2) \qquad (2)$$

For the system,

$C(r,0) = C^*$ $\quad 0 < r \leq a$ $\quad$ initial concentration in sphere

$C(a,t) = 0$ $\quad$ surface concentration

a = radius of particle

r = radial coordinate

It can be found from the above formulation that:

$$C(r,t)/C^* = (2a/\pi r) \sum (-1)^{n+1}/n \sin(\pi n r/a) \exp(-n^2 D \pi^2 t/a^2) \quad (3)$$

The total amount of diffusing additive leaving the sphere at time t is given by

$$M_t/M = 1-(6/\pi^2) \sum_{n=1}^{\infty} 1/n^2 \exp(-Dn^2\pi^2 t/a^2) \quad (4)$$

where M_t = the amount which has left the sphere

M_∞ = the initial amount in the sphere

M_t/M_∞ = F (a,t) which is the fractional amount extracted from particle of radius a, after t seconds.

Using a one term expansion:

$$\{1-F(a,t)\}\, \pi^2/6 = \exp(-D\pi^2 t/a^2) \quad (5)$$

or,

$$\ln\{1-F(a,t)\} = \ln(6/\pi^2) - D\pi^2 t/a^2 \quad (6)$$

Equation 6 suggests that if a plot of ln [1-F(a,t)] versus time for a range of particle sizes, a, a straight line with slope of $-D\pi^2/a^2$ and a common intercept, ln $[6/\pi^2]$ should result. Alternatively, a plot of ln [1-F (a,t)] versus $1/a^2$ for various times should linear with a slope of $D\pi^2t$. From these plots, the diffusion coefficient can be determined.

The data for Irganox 1010, Irganox 3114, and Irgafos 168 in polypropylene of particle sizes, <177 µm and 177-250 µm at 10, 15 and 30 minutes were used. Plots of ln [1-F(a,t)] versus time are shown in Figures 21-23. The data for Irgafos 168 and Irganox 3114 were normalized to account for the fact that the maximum recoveries, 75% and 90% were obtained even after exhaustive (one hour) extraction. Thus, the data for these two compounds were taken as a percentage of the maximum recovery. Straight lines were obtained for all the graphs which showed that the proposed model was reasonable.

There are slight deviations from the anticipated intercept, -0.50, except for Irganox 3114 for which the intercepts are -0.30 and -0.48 for particle sizes <177 µm and 177-250 µm, respectively (Table 26). To account for the differences in intercept, one may assume that the particles are not spherical in the supercritical

FIGURE 21
EFFECT OF PARTICLE SIZE ON DIFFUSION IN IRGAFOS 168

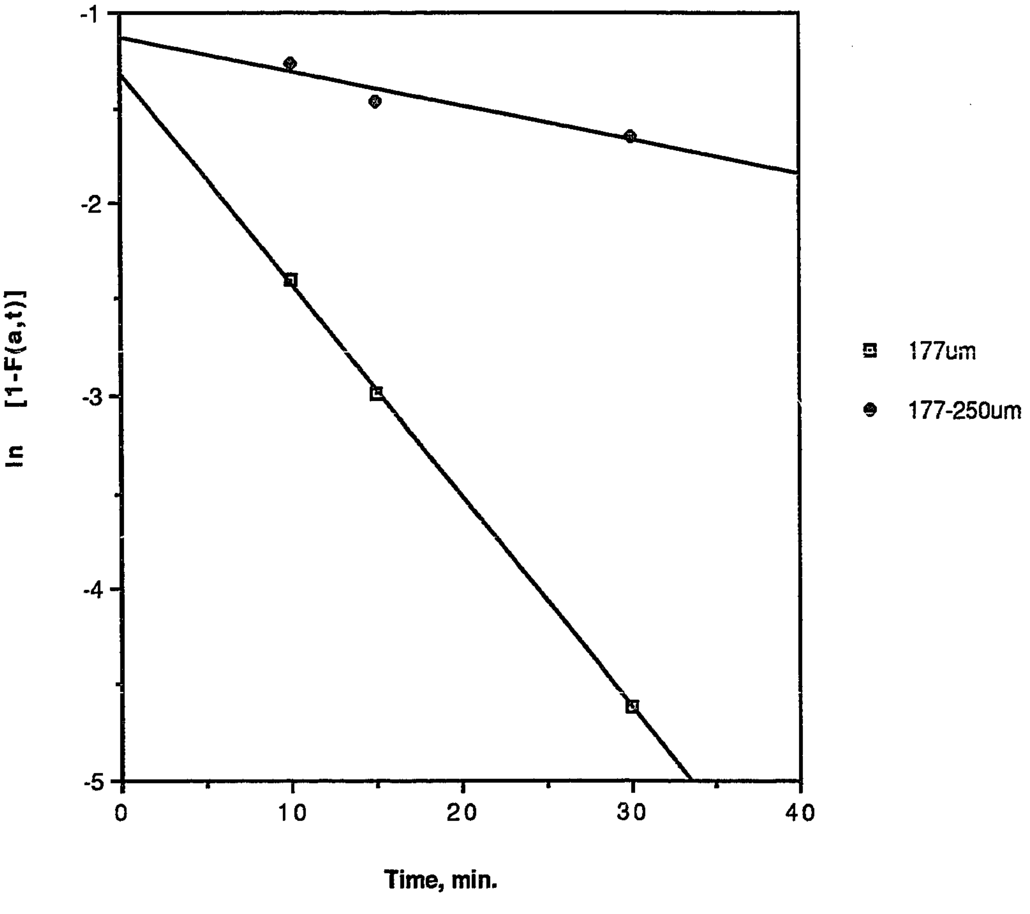


FIGURE 22
EFFECT OF PARTICLE SIZE ON DIFFUSION IN IRGANOX 1010

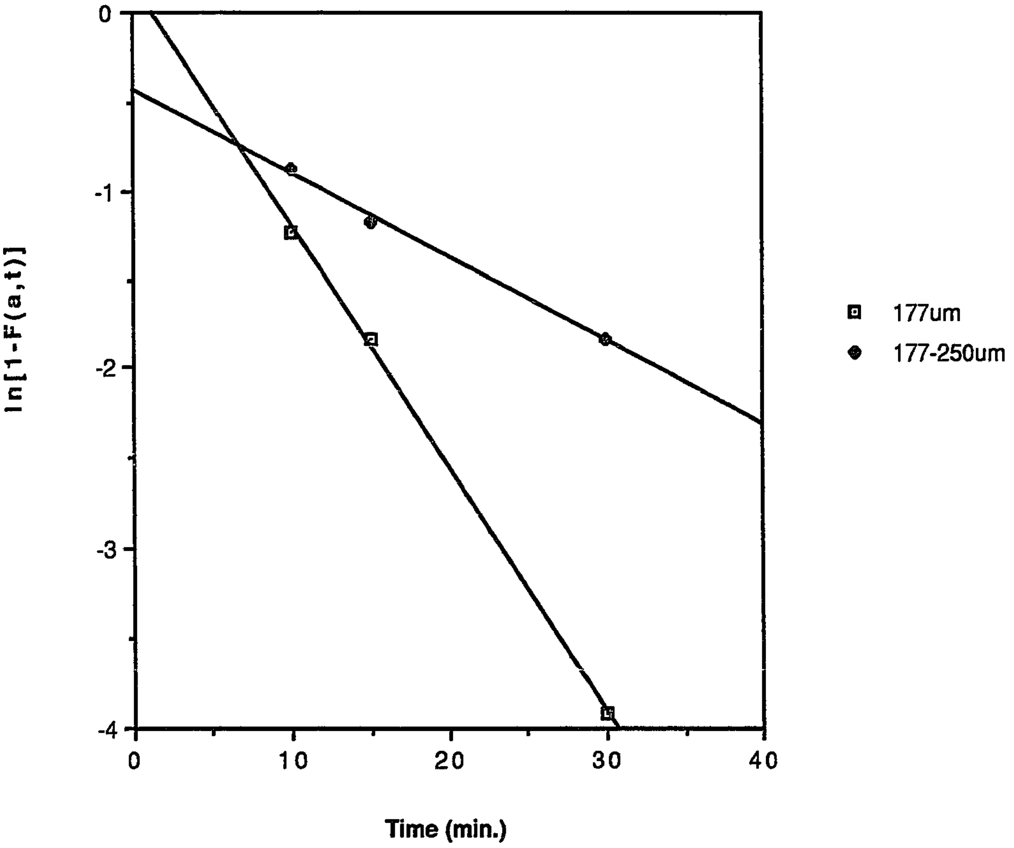


FIGURE 23
EFFECT OF PARTICLE SIZE ON DIFFUSION IN IRGANOX 3114

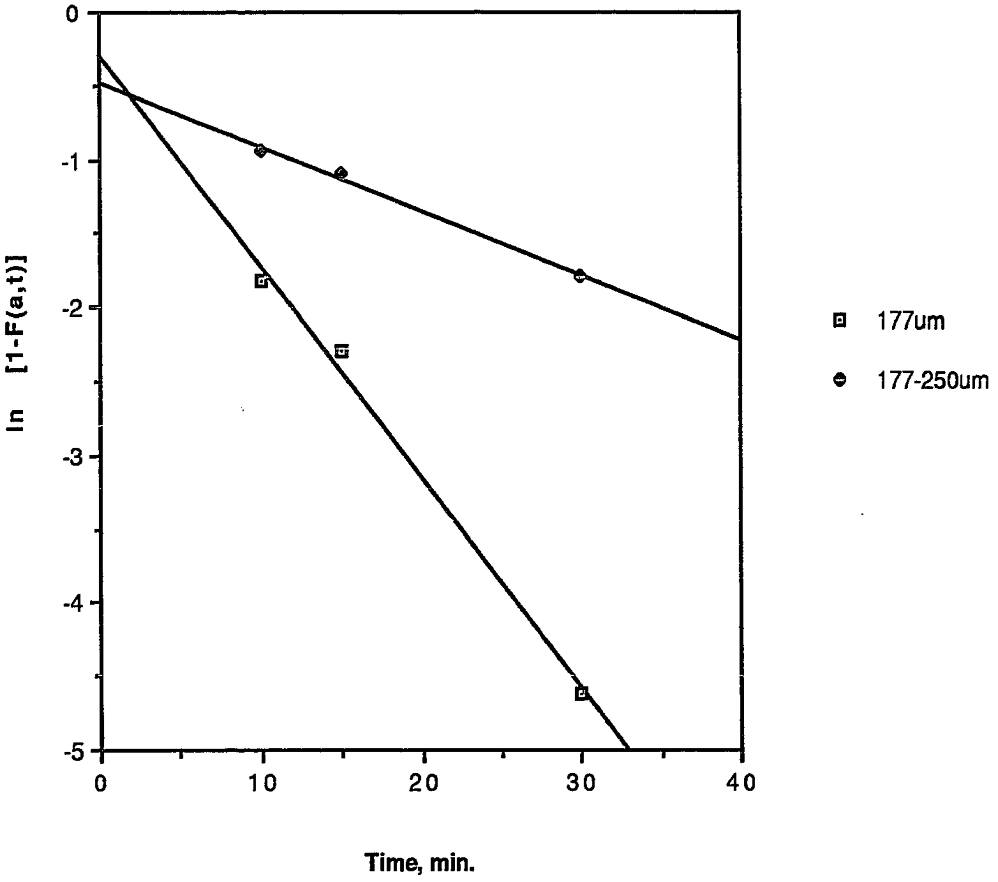


TABLE 26

DIFFUSION STUDY OF COMMERCIAL POLYPROPYLENE

ADDITIVE	INTERCEPT		DIFFUSION COEFFICIENT (cm^2/s)	
	<177μm	(177-250)μm	<177 μm	(177-250)μm
I-1010	0.15	-0.43	3.01×10^{-6}	2.99×10^{-6}
I-3114	-3.02	-0.48	2.72×10^{-6}	2.75×10^{-6}
I-168	-1.32	-1.14	1.13×10^{-6}	1.14×10^{-6}

where I-1010 is Irganox 1010
I-3114 is Irganox 3114
I-168 is Irgafos 168

phase, as was assumed in the model. Furthermore, the sizes of the particles are not precisely known.

The derived diffusion coefficients are given in Table 26 which shows that Irganox 1010 has the largest value. The differences in diffusion coefficient are usually related to the size and shape of a molecule. Irganox 1010 being like a cross is probably more spherical and smaller in size than the other compounds. Irgafos 168 is trigonal pyramidal with the lone pairs of the phosphorus at right angles to the plane of the molecule. In this type of arrangement, the molecule is more spread out and bulky, and may be more likely to have some chemical interaction with the matrix. Most likely, the shape of the molecule is maintained throughout the supercritical phase, because unlike nitrogen, phosphorus compounds do not invert rapidly.

MECHANISM

There are four possible mechanisms to describe the diffusion of the additives and carbon dioxide from the polymer. One is that there is free diffusion of carbon dioxide by itself. However, the diffusion coefficient of carbon dioxide in this case is 10^{-3} *(121).* Furthermore, the polymer would not dissolve in carbon dioxide to produce a single phase, and if it did, the extraction chamber would be covered with dissolved polymer which was not the case.

Another approach would be to assume that the additives diffuse out to the surface of the plastic and then get picked up by the carbon dioxide on the outside: this produces the driving force for other additive molecules to diffuse to the surface and be removed. If this were the case, then the expected diffusion coefficient would be around 10^{-14} cm^2/s, a value quite reasonable for diffusion in glassy polymers *(122,123)*. Furthermore, it has been stated that molecules incorporated into a polymer, require for their diffusion a co-operative movement by the micro-Brownian motion of several monomer units, i.e. the so-called polymer segment to take place *(124)*. This implies that the rate of diffusion of an organic substance in a polymer, and hence the diffusion coefficient of such a system is primarily controlled by the mobility of the polymer segmental unit. For any diffusion to occur, the polymer has to expand its surface area by absorption of small molecules into the system and this would enhance the micro-Brownian motion segmental units. This effect increases the average interchain distance and thus weakens the molecular interaction between neighboring polymer molecules.

Based on these requirements, it is highly improbable for the additives to diffuse out of the polymer unaided.

A more practical interpretation of the mechanism is that carbon dioxide diffuses into the polymer, the additive gets dissolved in the carbon dioxide and the polymer is then swollen by the carbon dioxide solution of the additive *(125, 126)*. This theory has been well supported by other studies and the value of the diffusion coefficients obtained are very close to the value calculated in this study. The diffusion coefficient of trichloroethylene (TCE) in polyvinylchloride (PVC) was 10^{-7} cm^2/sec, *(127)* and the diffusivity of carbon dioxide in polystyrene (PS), PVC, and polymethylmethacrylate (PMMA) are in the range of 10^{-6} to 10^{-7} cm^2/sec., typical for carbon dioxide in rubbery polymers *(126,128)*. This shows that the rate of diffusion of the solvated additive in this study is not greatly different from the diffusion coefficient of carbon dioxide itself. Recent studies have shown that carbon dioxide under high pressure swells and cause significant plasticization resulting in substantial decreases in the glass transition temperature of polymers *(129, 130)*. Carbon dioxide is more effective in lowering the glass transition temperature than are ordinary solvents, presumably because of its small molecular size and high mobility. Internal stresses may be set up when a vapor diffuses into a polymer. It may be assumed that the inner, unswollen part of the solid will exert a compression force on the outer, swelling part, while the swollen part will exert, on the unattacked region, a force which tends to expand the solid *(124)*. These compression and expansion forces change as sorption and desorption proceeds, since the concentration distribution in the solid changes with time and since the polymer chains tend to relieve these stresses by changing their conformations.

The sorption and desorption of carbon dioxide in many polymers appear to follow Fickian kinetics at all pressures studied and the transport kinetics seem to provide evidence that these polymers are plasticized into the rubbery state in the presence of supercritical carbon dioxide *(127)*. The transport of compressed carbon dioxide in polymers have been studied *(126)*. PVC samples had been exposed to organic additives and carbon dioxide under pressure. It was found that compressed carbon dioxide accelerates the absorption of many high molecular weight additives into PVC. Upon the release of pressure, the carbon dioxide rapidly diffuses out of the PVC, leaving the additive trapped in the polymer to diffuse at the normal rate for the polymer/additive binary system. Since the rate of diffusion of a species adsorbed is equal to the rate desorbed, the system just described is similar to the desorption of additive in polypropylene studied in this research. It was stated that the absorption and desorption data for the PVC/CO_2/additive system showed a pronounced effect of carbon dioxide pressure on the rate of the additive diffusion in the carbon dioxide-accelerated transport of additives in polymers.

Another way of describing the mechanism involves the approach toward an equilibrium distribution of the three components (polymer, additive, and carbon dioxide) among the phases present. The polymer and the additives have low solubility in carbon dioxide. Thus the system consists of a carbon dioxide-swollen polymer-rich phase and essentially pure carbon dioxide *(126)*. At high pressures the micro-Brownian motion of polymer molecules is sufficiently active to enable equilibrium to be reached rapidly *(124)*. The chains in any volume element of the polymer may take up almost instantaneously an equilibrium conformation consistent with the sorbed state when carbon dioxide diffuses into the solid. This means that at any instant and at any point in a polymer which is absorbing carbon dioxide, the polymer molecules realize an equilibrium conformation corresponding with the instantaneous concentration there. It may seem logical to assume that the additives are partitioned between the two phases, followed by the rapid desorption of the carbon dioxide. As a result the concentration of the additive desorbed or absorbed by the polymer will depend upon the relative solubility of the additive in the polymer-rich and carbon dioxide phases.

The fact that the additives diffuse to the surface and are removed, accounts for the fact that as the particle size is decreased by grinding, the diffusion distance is shortened, and for the same extraction time, the percentage recovery increases.

Another way of accounting for the dependence of recovery on particle size can be described in terms of diffusion time (Δt) where the additive is diffusing out of the particle. For a spherical particle,

$$\Delta t \sim R^2\tau/\varepsilon D_{12}$$

where R = radius of the particle

τ = tortuosity within the spherical pellet

ε = porosity

D_{12} = molecular diffusion coefficient

The values for tortuosity and porosity are normally in the range of 2 -20 and 0.4-0.5, respectively, and D_{12} has a magnitude of 10^{-6} cm^2/sec. for a particle of 1mm radius [Welsh, 1983]. Hence, for this size particle, the characteristic diffusion time is less than one hour. For the same extraction time, the larger the particle, the poorer is the recovery because the additive has a longer distance to diffuse out.

COMPARISON OF SFE WITH OTHER METHODS OF EXTRACTION

It is seen in Tables 13 and 14 that Soxhlet extraction and the dissolution method gave recovery results comparable to those of SFE. However, it is clear that one of the advantages of SFE over Soxhlet is that of speed; a 30 min. extraction using SFE gave >90% recovery in most cases, whereas it took about 24 hours of Soxhlet extraction. In addition, there are no emulsions or other technical difficulties with supercritical extraction and fewer impurities in CO_2 than in ordinary solvents. Furthermore, SFE has the advantage over Soxhlet of exclusion of light and air, which is especially important for the extraction of antioxidants and light stabilizers; these react with oxygen and photolyze, respectively. Finally, increased governmental regulation of common but toxic industrial solvents has made nontoxic, environmentally acceptable supercritical fluids such as carbon dioxide attractive as alternative solvents. SFE proves to be the method of choice for the extraction of plastics additives.

Both Soxhlet and SFE methods, as mentioned above (Table 15), gave comparable percentage recoveries, except for Irgafos 168, which gave a higher percentage recovery by Soxhlet. As stated before, the groups that are available for solvent interaction on Irgafos 168 are methyl groups, which may make the compound behave like a hydrocarbon. The fact that the solvent, methylene chloride, is of similar polarity, would result in stronger solute-solvent interactions, and, thus, a higher yield of this additive when the Soxhlet method of extraction is used. This would also be true for the other additives which have methyl carbons for interaction. Although supercritical fluid extraction has the advantage of speed, Soxhlet extraction can be used as an alternative method of extraction of these additives.

SOLUBILITY

Tinuvin P is most soluble in carbon dioxide, followed by Irganox 1010 and Irganox 3114: Irgafos 168 and Irganox 245 have the lowest solubility. Tinuvin P has the highest solubility, which could be linked to its basic heterocyclic nitrogen group which could form an acid-base complex with carbon dioxide. This type of behavior was also seen in the study of the solubility of acridine and anthracene in supercritical carbon dioxide *(131)*. Acridine is more soluble than anthracene which was explained by the fact that acridine is an organic base and the increased solubility in carbon dioxide is due to an acid-base complex *(131)*.

While more volatile, Irganox 245 is less soluble than Irganox 1010 in carbon dioxide. Although they are structurally similar molecules, the degree of solubility could be related to hydrogen bonding interactions between carbon dioxide and hydroxyl groups.

The more hydroxyls in a molecule, the more sites for interaction, the more carbon dioxide molecules that are involved and the higher the solubility. This could explain why Irganox 1010, which has twice as many hydroxyl groups as Irganox 245, is more soluble in carbon dioxide. By way of comparison, it is interesting to note that when cholesterol is removed from butter using supercritical fluid extraction, fatty acids are also extraction *(132)*. The reason for this result was suggested to be the hydrogen bonding interaction of carbon dioxide with the hydroxyl groups of the molecules.

Irgafos 168 has methyl carbons and a phosphorus atom, but no hydroxyl groups. In this case, the type of interaction possible between carbon dioxide and phosphorus atom presumably tends to be weaker than a hydrogen-bonding type interaction. Furthermore, Irgafos 168 is trigonal pyramidal and the lone pairs of the phosphorus are exposed perpendicular to the molecule. This may cause the electron cloud of Irgafos 168 and carbon dioxide to repel each other, resulting in low solubility.

DENSITY BASED CORRELATION FOR SOLUBILITY OF ADDITIVES IN SUPERCRITICAL CO_2

Relatively extensive experimental data are required to develop sound designs for maximizing extraction and selecting the best conditions for a supercritical extraction process. Theory facilitates prediction, interpolation, and extrapolation of experimental data, and reduces experimental work.

Equations of state (EOS) are normally used to fit experimental data to binary interaction parameters*(2,133-136)*. However, significant errors have been encountered in the prediction, interpolation, and extrapolation of supercritical solubilities using cubic equations of state *(134)*.

The Peng-Robinson equation was applied to the solubility of naphthalene in supercritical ethylene *(133)* by fitting the binary interaction parameters to experimental data. Fractional errors were large in the pressure region in which solubility changes rapidly. Attempts to model other systems were less successful due to unreliable binary interaction parameters *(135)*. Ehrlich *(134)* compared experimental solubilities for n-heptane in supercritical ethane with values calculated using the Redlich-Kwong equation of state.

Because of the above shortcomings, Lee and Ellington *(135)* deduced an equation to satisfactorily correlate experimental data for solubility of solutes in supercritical fluids with the fluid density:

$$\log m = n \log \rho + C \qquad (7)$$

where m is the solubility, ρ is the density of the gas, and n and C are constants. This equation suggests that a plot of log (solubility) versus log (density) should be linear. Robin *(136)* proposed the above equation empirically in 1948, but it was not demonstrated experimentally until 1987 by Lee and Ellington. They used data of Tsekhanskaya *(137)* for naphthalene in ethylene and carbon dioxide; equation 7 successfully correlated the experimental data.

Equation 7 was used in this research to correlate the solubility of Tinuvin P, Irganox 3114, and Irgafos 168 in carbon dioxide. A plot of log (solubility) versus log (density) should yield a straight line. The International Union of Pure and Applied Chemistry (IUPAC) lists the density of carbon dioxide in tabulated form at various temperatures and pressures *(138)*. However, densities were not available at the experimental conditions used. As a result, a cubic equation of state was used to find the relevant densities. There are many equations of state that can be used to calculate density *(139-142)*, but the Peng-Robinson equation of state *(143)* gives result within 2% error. A computer program was written to determine the density of carbon dioxide using this equation of state. The following is an account of how the equations were used in the program to generate the density:

Consider the Peng-Robinson equation of state:

$$P = [RT/ (v-b)] - \{a(T)/ [v(v+b)+b(v-b)]\} \qquad (8)$$

where a is the interaction parameter; b is the volume excluded by intermolecular repulsive forces, and v is the molar volume.

Equation 8 can be rewritten in the form

$$Z3 - (1 - B)Z^{2} + (A - 3B^{2} - 2B)Z - (AB - B^{2} - B^{3}) = 0 \qquad (9)$$

where Z is the compressibility of a gas and its a measure of the deviation from ideality of the behavior of a real gas:

$$A = a(T)\ P/(R^{2}T^{2}) \qquad (10)$$

$$B = b(T)\ P/(RT) \qquad (11)$$

$$Z = Pv/(RT) \qquad (12)$$

The value of a(T) and b(T) can be found from the following equations:

$$a(T) = a(T_c) \,.\, \alpha(T_r, \omega) \tag{13}$$

$$b(T) = b(T_c) \tag{14}$$

where

$$a(T_c) = 0.45724\ (R^2T_c{}^2)/P_c \tag{15}$$

$$b(T_c) = 0.07780\ (RT_c)/P_c \tag{16}$$

$$\alpha^{0.5} = 1 + \kappa(1 - T_r{}^{0.5}) \tag{17}$$

where T_c is the critical temperature, P_c is the critical pressure, T_r (T/T_c) is the reduced temperature, and κ is a constant characteristic of each substance. This constant has been correlated with the acentric factor. The resulting equation is

$$\kappa = 0.37464 + 1.54226\omega - 0.26992\omega^2 \tag{18}$$

Thus, A and B can be calculated, and allow calculation of Z from equation 8. Z is the compressibility factor (cc/mole) which is inversely proportional to density. Solution of equation 9 yields three roots, Z1, Z2, and Z3. A large density corresponds to liquid, and the smaller density value is that of a gas. Therefore, because Z is inversely proportional to density, the largest positive root will correspond to the density of the vapor and the smallest positive root to the density of liquid carbon dioxide. The third root Z3, is either equal to Z1, Z2 or it is negative which is not physically acceptable.

In order to determine the density, that is the roots of the cubic equation 9, the Newton-Raphson method was used *(144)*. This method evaluates the function f(Z) (equation 9), and its derivative f'(Z) at an arbitrary point Z. This arbitrary point Z is a trial root which in this program is initially set equal to one, because Z for gases is usually approximately unity. The following, is the Newton-Raphson equation that is used to find the roots:

$$Z(NEW) = Z(OLD) - \{[f(Z(OLD))] / [f'(Z(OLD))]\} \qquad (19)$$

where Z(OLD) is the initial trial root, 1; f(Z(OLD)) is equation 9 evaluated at 1, and f'(Z(OLD)) is the derivative of equation 9 evaluated at 1. The answer obtained from equation 19 which is called Z(NEW) is compared to Z(OLD). If the difference between them is less than or is equal to 0.0001, then that value Z(OLD) is the first root. If the difference is more than 0.0001, then Z(NEW) becomes Z(OLD) and the program is iterated until the difference between Z(OLD) and Z(NEW) is 0.0001.

The second root is determined in the same way and it corresponds to the density of liquid carbon dioxide. The trial root or initial guess in this case is 0.01 because the density of liquid carbon dioxide is within this value. The third root is obtained by the expansion $(Z - Z1)(Z-Z2)(Z-Z3) = 0$ where the sum of the roots is equal to the coefficient of Z^2 in equation 9.

The density of carbon dioxide can now be obtained from the three roots of equation 9, Z1, Z2 and Z3. From equation 12,

$$\rho = (P/ZRT)\ (44.01)$$

where 44.01 is the molecular weight of carbon dioxide.

Plots of log solubility versus log solvent density were linear for Tinuvin P, Irganox 3114, and Irgafos 168 (Figures 24-26). The correlation coefficient is better than 0.96 for all the graphs which indicates that equation 7 successfully correlates the experimental data. Therefore, the equation can be used to interpolate and extrapolate the solubility of these compounds, and thus reduce experimental work.

The values of constant n and C in equation 7 for the solubility data are reported in Table 27. As indicated in this table, the values of n for Irgafos 168 and Irganox 3114 which are antioxidants are

FIGURE 24
SOLUBILITY OF TINUVIN P IN CARBON DIOXIDE

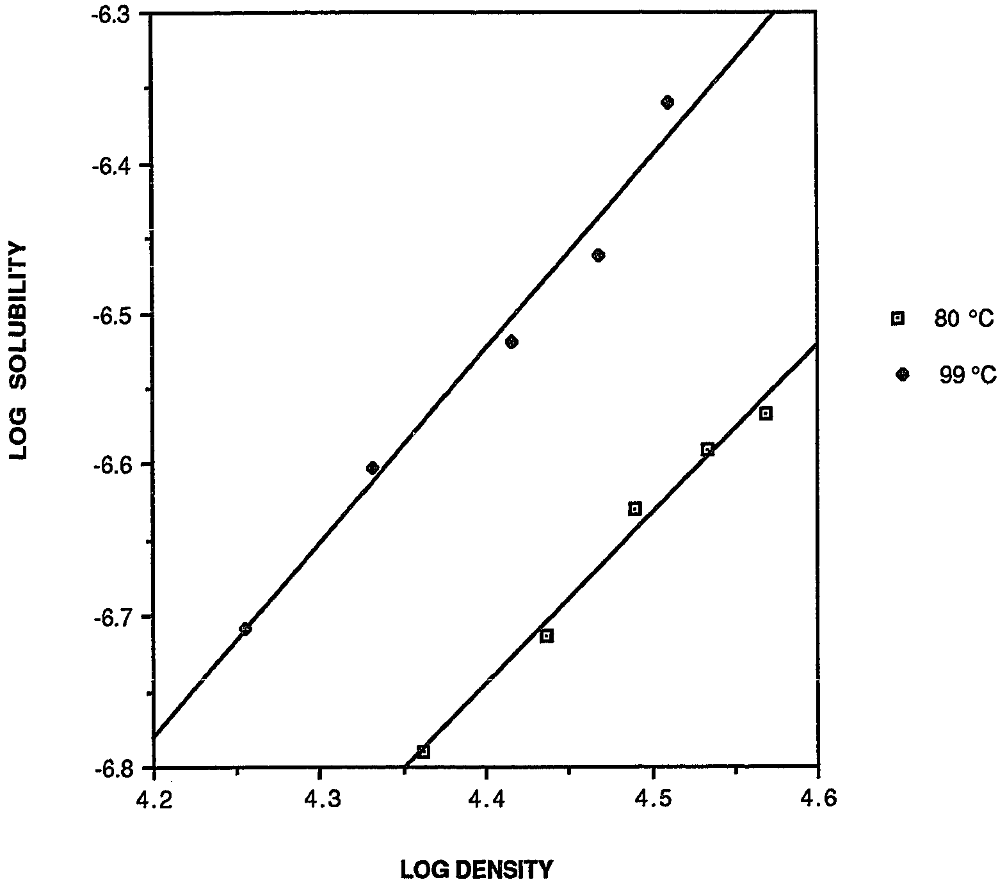


FIGURE 25
SOLUBILITY OF IRGAFOS 168 IN CARBON DIOXIDE

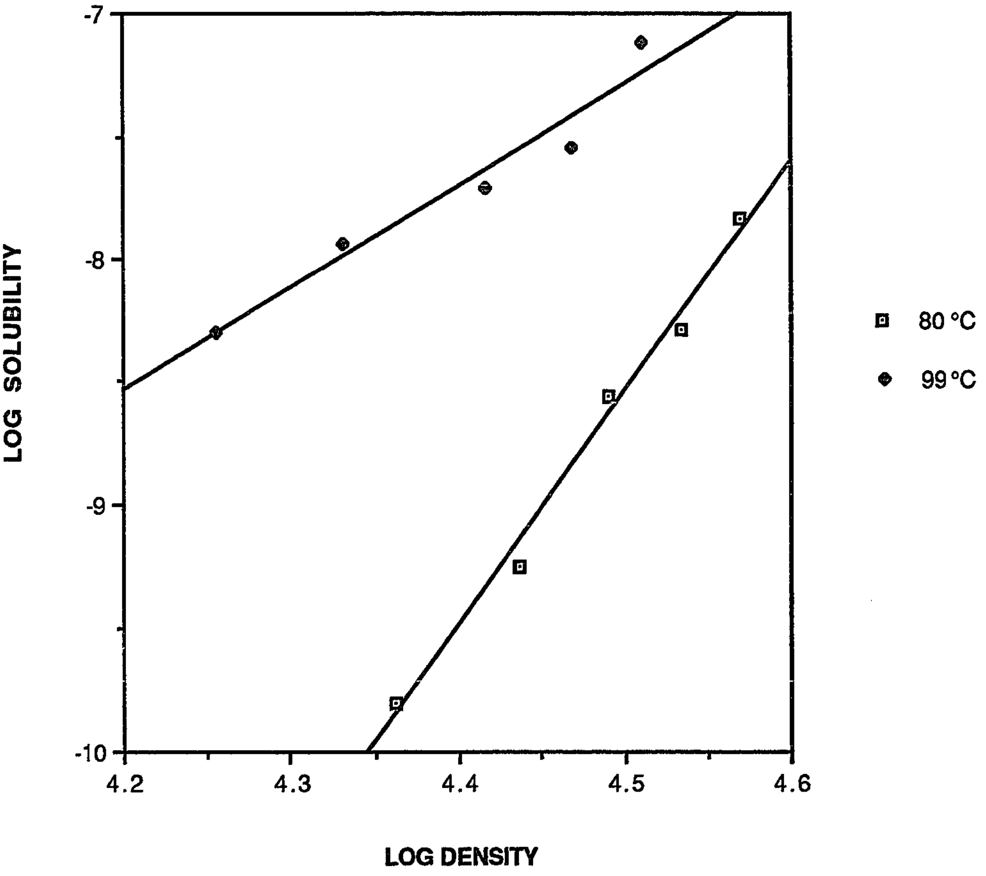


FIGURE 26
SOLUBILITY OF IRGANOX 3114
IN CARBON DIOXIDE

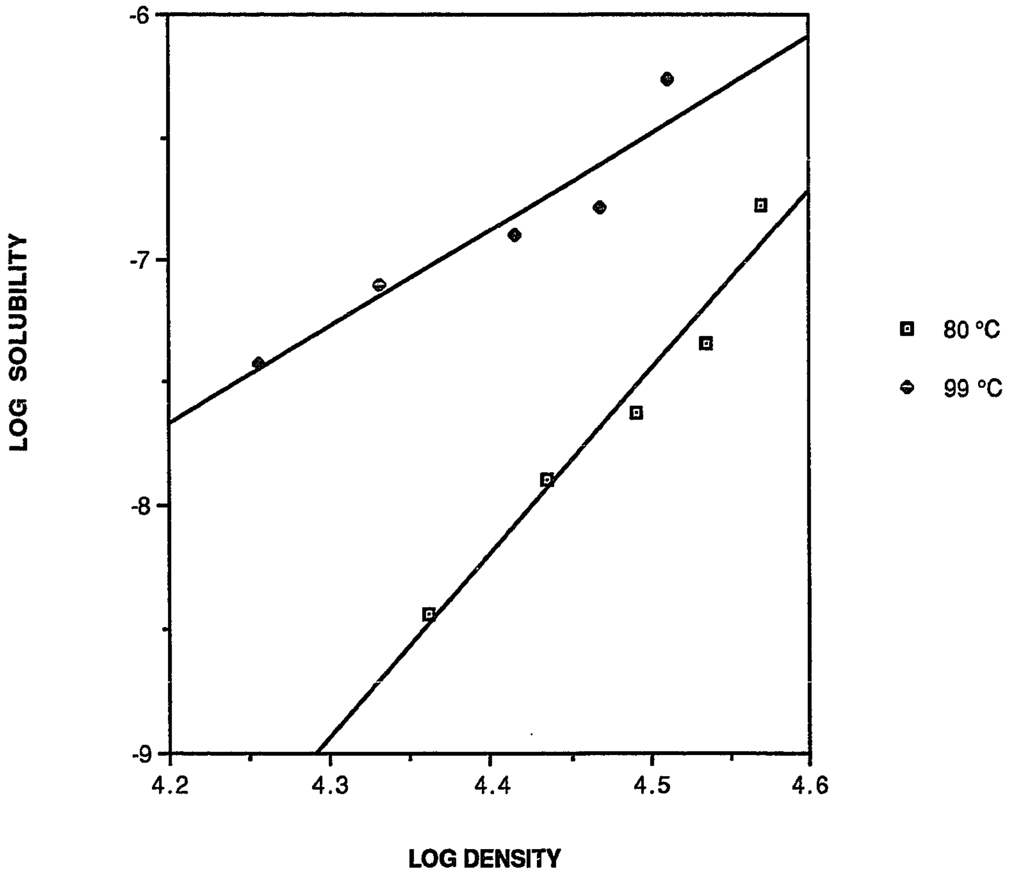


TABLE 27

SOLUBILITY DATA

COMPOUND	TEMPERATURE (°C)	SLOPE (n)	INTERCEPT (C)
Tinuvin P	99	1.28	-12.1
	80	1.12	-11.7
IRGANOX 3114	99	3.95	-24.3
	80	7.39	-40.8
IRGAFOS 168	99	4.16	-26.0
	80	9.41	-50.9

similar. Thus, this information may be used to predict the solubility of antioxidants in supercritical carbon dioxide.

APPENDIX A

```
1     REM Use consistent units of P (bar), T(K), R (=83.1408 bar-
          cubic cm/K mol).
2     REM Critical properties of carbon dioxide are:
3     REM PC = 73.748 bar; TC = 304.127K; Accen. Factor, W = 0.225
          Molecular weight = 44.01 g/mol.
4     REM File name is : PENGROB programmed by Evelyn A. Wolfe
10    REM This program solves cubic equation of state to find the
          density
20    REM Peng Robinson equation of state is used.
30    REM Program uses NEWTON-RAPHSON method to find the roots
40    REM There are three roots, Z1, Z2 and Z3.
50    REM Supply the critical properties of the fluid.
60    PRINT "CRITICAL TEMPERATURE = TC": INPUT TC
70    PRINT "CRITICAL PRESSURE = PC": INPUT PC
80    PRINT "ACCENTRIC FACTOR = W": INPUT W
90    REM Calculate the equation of state parameters
```

```
100  PRINT "GAS CONSTANT = R": INPUT R
110  RTP = (R*TC)/PC
120  AC = 0.45724*R*TC*RTP
130  BC = 0.0778*RTP
140  K = 0.37464 + 1.54226*W - 0.26992*(W^2)
150  REM "INPUT Pressure, P and Temperature, T of interest
160  PRINT "TEMPERATURE, T =": INPUT T
170  PRINT "PRESSURE, P =": INPUT P
180  PRINT"units of P: (1 = psia, 2 = atm, 3 = bar); U =": INPUT U
190  REM If the pressure is in psia use the conversion below
200  IF U = 1 THEN P = P/(14.7*0.987)
210  IF U = 2 THEN P = P/0.987
220  IF U = 3 THEN P = P
230  PRT = P/(R*T)
240  ALF = (1! + K*(1! - ((T/TC)^0.5)))^2
250  A = (AC*ALF*PRT)/(R*T)
260  B = BC*PRT
270  REM First trial root, Z = Z1
280  Z = 1!
290  GOSUB 580
```

```
300  IF ABS(ZNEW - Z(OLD)) < = 0.0001 THEN 340
310  Z(OLD) = ZNEW
320  GOTO 290
330  REM The first root is determined
340  Z1 = Z(OLD)
350  REM Trial the second root
360  Z = 0.01
370  GOSUB 580
380  IF ABS(ZNEW - Z(OLD)) < = 0.0001 THEN 420
390  Z(OLD) = ZNEW
400  GOTO 370
410  REM The second root is determined
420  Z2 = Z(OLD)
430  REM The third root is given by (Z - Z1)(Z - Z2)(Z - Z3) = 0.0
440  Z3 = (1 - B) - Z1 - Z2
450  REM The sum of the roots = the coefficient of Z^2 in the
          equation
460  REM Now calculate the density from Z = PV/RT or Density =
          P/ZRT
```

```
470  REM Use units of density in g/cubic cm by using molecular
         weight
480  D1 = (PRT*44.01)/Z1
490  D2 = (PRT*44.01)/Z2
500  D3 = (PRT*44.01)/Z3
510  PRINT "T ="; T: PRINT "P = "; P
520  PRINT TAB(3) "Z1 ="; Z1 TAB(5) "D1 = "; D1
530  PRINT TAB(3) "Z2 ="; Z2 TAB(5) "D2 = "; D2
540  PRINT TAB(3) "Z3 ="; Z3 TAB(5) "D3 = "; D3
550  PRINT "Do you want to try another T and P (Yes = 1, No = 2)":
     INPUT Q
560  IF Q = 1 THEN 160
570  END
580  REM Subroutine: NEWTON-RAPHSON method
590  REM PENG-ROBINSON EQUATION: Z^3 - (1 - B)Z^2 + (A - 3B^2 -
         2B)Z - (AB - B^2 - B^3) = 0
600  REM Derivative, DF of the equation: 3Z^2 - 2(1-B)Z + (A - 3B^2 -
         2B) = 0.0
610  F1 = (1 - B): F2 = A -3*(B^2) - 2*B: F3 = A*B - (B^2) - (B^3)
620  F = Z^3 - F1*(Z^2) + F2*Z - F3: DF = 3*(Z^2) - 2*F1*Z + F2
```

```
630   H = F/DF: ZNEW = Z(OLD) - H

640   RETURN
```

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