

Analysis of Extractive Properties of Homogeneous Polymers Using Immobilized Liquid Extraction and GC-MS

by

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Introduction

Classical methods for extracting organic compounds from aqueous samples are generally based on either liquid/liquid extraction or liquid/solid extraction employing solid phase extraction (SPE) disks or cartridges. More recently, methods have been introduced using non-extractable homogeneous sorptive polymers as extraction media. Solid Phase Micro Extraction (SPME), Stir-Bar Sorptive Extraction (SBSE), and Immobilized Liquid Extraction (ILE) have employed this technique.

In this study, we evaluated the extractive properties of polydimethylsiloxane (PDMS), as well as diphenyl and trifluoropropyl siloxanes and siloxane blends using the ILE method. ILE shares many fundamental principles with traditional liquid-liquid extractions (LLE). In traditional LLE, a compound partitions between two immiscible liquid phases, usually an aqueous sample and an organic solvent, based on its affinity for each of the liquids. ILE separations are very similar; however, the 'organic solvent' is instead a thin layer of polymer (immobilized liquid) that is coated on the surface of an ILE device.

ILE Caps were used in this study. The septum of each ILE Cap is coated with a thin layer of non-extractable homogeneous sorptive polymer which acts as the extraction medium. A sample is directly exposed to the immobilized polymer to allow analytes to partition from the sample into the polymer. Analytes which partition into the polymer (immobilized liquid) are desorbed into a small amount of GC solvent and may be analyzed immediately.

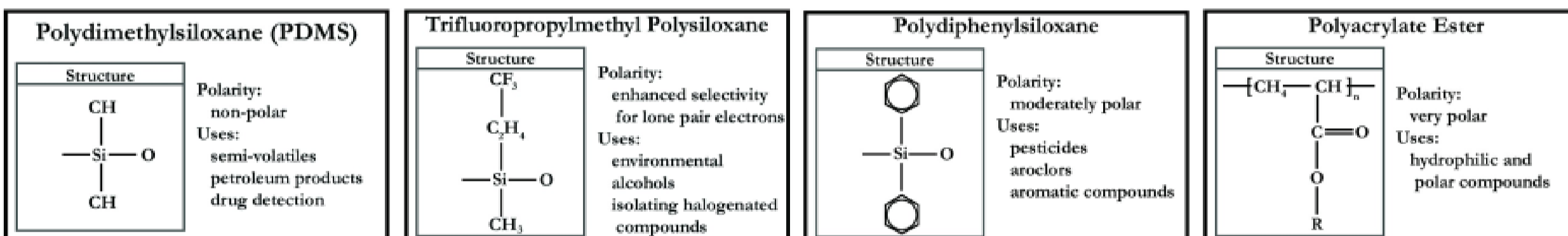
This study investigates and evaluates extraction efficiency, enhancing or altering selectivity, solvent phenomena and effects, and discusses other characteristics associated with a variety of applications and extracting phases. Applications investigated in this analysis include the extractions of pesticides, PCBs, phenols and semivolatiles from water and more complex matrices like juice or whole fruit, as well as biological applications including the extraction of drug metabolites.

Materials & Methods

Instrumentation

Sample extracts were prepared with Wohleb Scientific, Inc. 24mm Immobilized Liquid Extraction (ILE) Caps. Each ILE cap septum is coated with a 254 micron thick layer of homogenous polymer, resulting in a 61 μ L extracting phase. The following polymer phase compositions were evaluated and compared in a variety of applications:

- (a) Polydimethylsiloxane (PDMS)
- (b) Polydiphenylsiloxane
- (c) 50% Polydimethylsiloxane / 50% Trifluoropropylmethyl Polysiloxane
- (d) 90% Polydimethylsiloxane / 10% Acrylate Ester
- (e) 90% Polydiphenylsiloxane / 10% Acrylate Ester
- (f) Nitrile Rubber



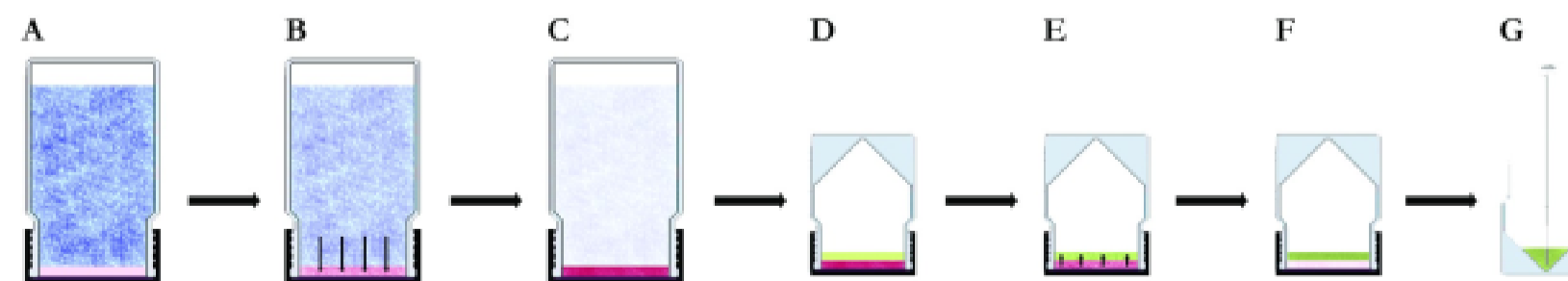
Method

For each extraction, an ILE Cap is placed on a sample-containing vessel in which the sample is spiked with known quantities of one or more analytes. A small aliquot of methylene chloride or another co-solvent is optionally added to each sample to enhance or improve selectivity and partitioning of analytes from the sample into the polymer (this co-solvent extraction step is described and evaluated in greater detail in the discussion section). The sample-containing vessel is agitated by a mechanical wrist-shaker, or another appropriate method, such that the immobilized solvent (polymer) comes in repeated contact with the sample, thus allowing analytes to partition from the sample into the polymer. Agitation disrupts a boundary layer which forms at the sample-polymer interface, thereby reducing the amount of time required for analytes to partition to equilibrium.

Upon completion of the extraction, the analyte-laden cap is removed from the sample vessel and placed on a high recovery vial containing a small amount of GC solvent. This vessel is agitated for a short period of time to accelerate analyte desorption from the polymer into the GC solvent. The resultant extract is analyzed by gas chromatography coupled with mass spectrometry.

ILE Cap Procedure

- A - Sample vessel is inverted to directly expose sample to immobilized solvent (polymer)
- B - Analytes partition from sample to polymer
- C - Analytes have partitioned to equilibrium
- D - Analyte-enriched ILE Cap is removed from sample vessel and placed on vial containing a small amount of GC solvent
- E - Analytes desorbed from polymer into solvent
- F - Analytes have fully desorbed into solvent
- G - Remaining solvent extract is analyzed by GC-MS



Results, Interpretations and Conclusions

Non-polar polymers exhibit similar extractive properties to traditional extraction solvents. A commonly used extractive polymer is polydimethylsiloxane (PDMS). It has been experimentally shown that PDMS exhibits polarity and extractive properties similar to n-octanol. Thus, hydrophobic compounds partition between an aqueous matrix and PDMS with a partition ratio approximately equal to K_o/w . Figure 1 displays the MS response of a series of relatively non polar herbicides with Log P between 3.0 and 4.9 that were extracted with a range of polymer phases.

When predicting the extractive behaviors of more complex extractive elastomers, an analyst may base his predictions on such characteristics as the elastomer's functional groups. For example, an analyst might expect a polydiphenylsiloxane elastomer to display enhanced partitioning for aromatic compounds due to pi bonding potential -- a similar effect to extracting with toluene. One might also expect that a trifluoropropyl phase would provide enhanced ability to extract compounds with lone pairs of electrons. This trend can be seen in Figure 1, which shows that napropamide is extracted most efficiently by a trifluoropropyl siloxane blend.

When extracting acidic or basic compounds, it is often required that the pH of a sample be adjusted to ensure that compounds remain in their non-ionized form. There are, though, exceptions to this rule. Figure 2 shows extraction data for four herbicides extracted at neutral pH. The pKa for the triazines ranges from 1.7 to 4.3. The pKa of bromacil is 9.1. Compounds which are easily ionized, such as bromacil and atrazine, exhibit very low extraction efficiency on non-polar polymers at neutral pH. In contrast, simetryn, which is weakly ionizable, is partially extracted by the less polar PDMS and the trifluoropropyl phases, but not extracted well by the more polar diphenyl phase. Prometon, on the other hand, was extracted more efficiently by the diphenyl phase than the trifluoropropyl phase. All four compounds were efficiently extracted by the 90% PDMS / 10% acrylate ester copolymer phase.

In order for an elastomer to function as an extracting solvent, compounds of interest must be able to dissolve in the polymer. Because extractive elastomers are polymeric in nature, predicting extraction efficiency becomes more problematic as a polymer increases in complexity. Unlike simple solvent systems, immobilized liquids have a geometric structure. In addition to the simple solvent interaction, there are other factors that effect selectivity. These factors include polymer matrix geometry, polymer open-ness, backbone flexibility and cross link density. Additionally, analytes must be able to sufficiently diffuse through the elastomer, and a targeted compound's structure must be compatible with the polymer's interstitial spacing.

An example of a more complex polymer-compound interaction involves the extraction of phenols. A group of phenolic compounds were extracted from samples adjusted to pH 1.5 by a variety of elastomers to help demonstrate this phenomenon. Figure 3 shows how well each polymer was able to extract these compounds. Phenol is the only compound for which the nitrile phase had a strong affinity. Another example of a more complex interaction involves the addition of acrylate ester to the PDMS and diphenyl phases. The addition of acrylate ester to a PDMS polymer produces a more pronounced change in the phase polarity than the addition of acrylate ester to a diphenyl phase. This complex mechanism is illustrated in Figure 4. Metribuzin partitions poorly into the PDMS, trifluoropropyl, diphenyl and even the PDMS/acrylate ester phases. In contrast, metribuzin partitions relatively well into the diphenyl/acrylate ester phase.

Solvent Swelling and Co-solvent Extractions

A unique characteristic of extractive polymers is their ability to absorb many organic solvents. When directly exposed to these organic solvents, the immobilized polymers effectively act like a sponge, absorbing the solvent and any compounds which may be bound to the solvent. Every polymer has a swelling capacity specific to each solvent tested.

The phenomenon of solvent absorption permits an analyst to use a co-solvent to accelerate and enhance his extraction. To do so, the analyst must add an amount of water-immiscible solvent to a sample that is no greater than that which may be absorbed by the polymer. When a co-solvent is used to assist partitioning into the immobilized polymer, analytes are first rapidly sorped from a sample into the co-solvent, followed by concurrent sorption of the co-solvent and analytes into the polymer phase.

There are a few distinct advantages associated with this ability. First, both the rate and efficiency of the extraction are enhanced due to increases in both total solvent surface area and volume. Second, an analyst may alter his selectivity by strategically choosing an appropriate co-solvent/polymer combination to target or isolate certain compounds or compound groups. For example, a polar solvent will enhance the ability of polydimethylsiloxane to extract hydrophilic compounds.

Other Extractive Characteristics of Polymer Media

Extractive polymer media avoid many of the limitations associated with traditional extraction techniques. Problematic sample matrices that may otherwise result in lost samples or require additional preparative steps no longer present difficulty.

Aqueous samples are often dirty, viscous or contain particulates. Extractive polymers are immune to clogging, and are not adversely affected by particulates or viscous samples. Additionally, analyte breakthrough is avoided because all reactions are brought to equilibrium. Furthermore, solvent emulsions do not form because the extracting phase is an immobilized liquid.

Extractions from biological samples often require additional preparative steps such as protein precipitation, pH adjustments or derivitization. Protein precipitation is not required because the polymers are immune to clogging. Extractive polymers do not erode in extreme pH conditions, so one can easily extract from both very acidic and very basic samples. Additionally, derivitization may be performed in situ, simultaneously with the back extraction (desorption) of analytes from the polymer phase.

Conclusions

The use of polymers as extractive media is a relatively new concept that shows promising potential for a variety of applications. The simplicity of both the technique and the reactions involved with the extraction, as well as the performance of the extraction media provide significant grounds to continue research in the science of using polymers as extraction media. As a wider range of polymers and polymer blends are evaluated for their extractive properties, the ability to easily extract specific compounds or compound groups most effectively and efficiently will be realized.

Figure 1

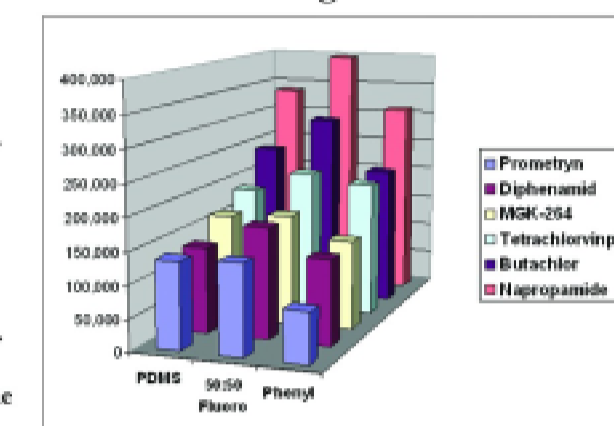


Figure 2

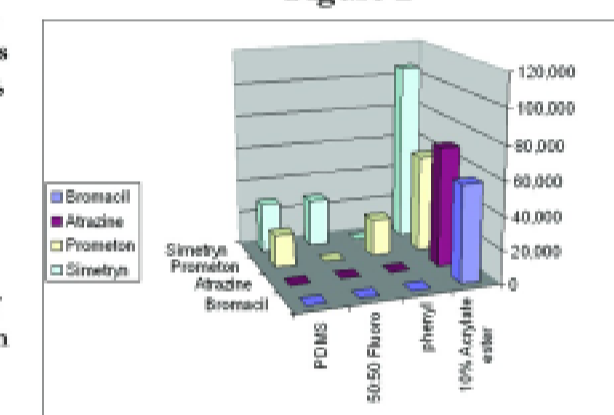


Figure 3

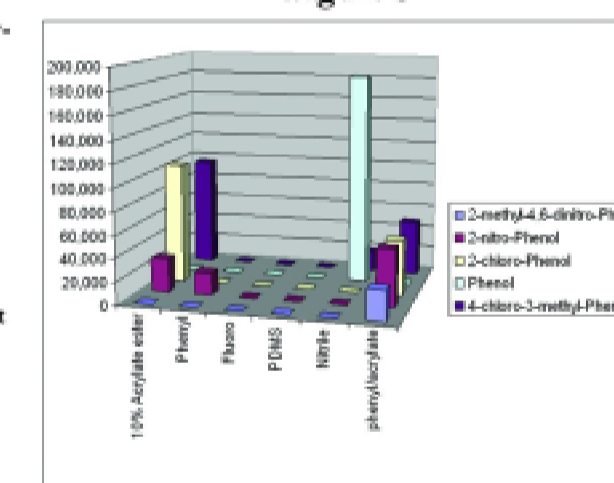


Figure 4

