

Modification of the Collection Solvent to Enhance Liquid Trapping Efficiencies After Supercritical Fluid Extraction

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Abstract

A series of experiments is performed to determine the effect of adding a modifier to the collection solvent when using liquid trapping with direct restrictor immersion after supercritical fluid extraction. The addition of a modifier to the collection solvent allows the trapping efficiencies of a polarity test mix obtained at higher temperatures to approach those obtained at lower temperatures. Collection pressurization is found to increase both the recovery and precision for all analytes. The selection of both modifier and collection solvent is discussed, with emphasis on changing the physical properties (surface tension, viscosity, and boiling point) of the collection solvent.

Introduction

A successful supercritical fluid extraction (SFE) method can be considered to occur in at least 2 steps, both of which must be optimized. In the first step, the analyte is solubilized by the supercritical fluid (SF), moves from the matrix to the bulk fluid, and is swept out of the extraction vessel. The second step involves collecting or trapping the analyte for some type of further analysis. During this collection step, the SF containing the analyte decompresses from pressures of 75–600 atm down to atmospheric pressure. To accomplish this decompression, the volume expands from approximately 1 mL of the SF to approximately 500 mL of gas. During the decompression, there is ample opportunity for the analyte to be lost through volatilization or aerosol formation and vented to the atmosphere.

Several types of trapping devices are used in SFE. A solid sorbent, either inert or active, such as a chromatographic packing material, can be placed at the end of the restrictor. In this technique, the gas (normally CO₂ or CO₂ with organic modifier) is expected to pass through the sorbent while the analyte is deposited on the sorbent. After the extraction is complete, the analyte is typically eluted from the sorbent with a suitable sol-

vent. An advantage of this method is the use of small volumes (0.5–2.0 mL) of solvent to elute the analyte, resulting in fairly concentrated solutions for identification and quantitation. Drawbacks include the inability of a single sorbent to quantitatively trap a wide variety of polarities (1,2), the necessity of raising trap temperature when organic modifiers are used (3), and the finite capacity of the solid phase employed (4). To overcome some of these limitations, many researchers use a liquid trap in tandem after the solid phase trap, so that the trapping temperature can remain low. In this way, if the analyte is eluted from the solid trap by the organic modifier of the extraction fluid, it will pass into the liquid trap. Also, if the solid trap capacity is exceeded, the analyte is simply captured in the liquid solvent.

The other widely used trapping method uses a conventional liquid. There are 2 distinct types of liquid trapping. The first, common in the Dionex (Sunnyvale, CA) systems, involves the decompression of the fluid onto a transfer tube, where some of the nonvolatile analytes are expected to precipitate. There is a liquid collection solvent situated under the transfer tube to collect any analyte that may still be in aerosol form. This type of trapping would probably be more correctly referred to as a tandem trapping system, with the transfer tube representing an inert solid sorbent. This type of trapping is also seen on newer Isco (Lincoln, NE) systems, where decompression occurs at the top of the restrictor barrel, and the barrel itself serves as the transfer tube. In addition to this type of liquid trapping, there is a second method involving direct immersion of the restrictor into the collection solvent. This method of trapping occurs on the Isco 3560 used for this study. In this type of trapping system, the loss of analyte solubility in the extraction fluid as it expands to a gas, as well as the increased solubility of the analyte in the collection solvent, are taken advantage of in order to achieve high trapping efficiencies.

Yang et al. (5) compared the solvent and sorbent trapping of volatile petroleum hydrocarbons after extraction from soil. They found that both the solid sorbent and liquid trapping systems could effectively trap BTEX (benzene, toluene, ethylbenzene, and xylenes) at greater than 90% recovery. They also found that

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solid sorbents could quantitatively trap normal hydrocarbons of lower molecular weight (hexane) better than solvent trapping (heptane for pressurized collection, octane for nonpressurized collection). They used an Isco system with the restrictor immersed in the collection solvent. Approximately half of the solvent volume (7 mL) was required using trap pressurization as was required without trap pressurization (15 mL) for similar recoveries.

Ashraf-Khorassani et al. (6) compared collection efficiencies in an empty vial, a liquid-filled collection vessel, and a cryogenically cooled adsorbent trap for several PAHs. Recoveries into the empty collection vial were no greater than 23%, whereas the liquid collection method resulted in recoveries no greater than 38%. Reduction of the liquid CO₂ flow rate to less than 1 mL/min did not improve the recoveries for the empty vial but resulted in quantitative (> 90%) recovery in the liquid trap. Only methylene chloride was investigated for the solvent trap, and only two flow rates, 0.9 and 2.0 mL/min, were used.

Langenfeld et al. (7) performed an extensive study on the effects of collection solvent parameters and extraction cell geometries on SFE efficiencies. A mixture of 66 compounds of a wide range of polarities were extracted and trapped into one of 5 organic solvents (methylene chloride, chloroform, acetone, methanol, or hexane). The height of the collection solvent, volume of the solvent, and effect of collection temperature on trapping efficiencies were all investigated. They found that temperature control of the collection vessel at 5°C provided the best recoveries. When addressing the effect of the collection solvents, they concluded that the boiling point of the solvents did not appear to be important and that methylene chloride was the best solvent, whereas hexane was the worst for these analytes and conditions.

A thorough study of the Dionex liquid trapping method was performed by Thompson et al. (8). They found that when using unmodified CO₂ as an extraction fluid, the only media capable of quantitatively trapping (> 90% recovery) a test mixture of varying polarities (acetophenone, 2-naphthol, naphthalene, decanoic acid, tetracosane, and *N,N*-dimethylaniline) were mixed collection solvents. However, when using CO₂ modified with 1–8% methanol, toluene, or acetonitrile, a pure collection solvent was surprisingly necessary, because mixed solvents failed to achieve quantitative recoveries (9). Hexane was seen to be the best overall solvent, with poor recoveries seen only when 8% toluene was the modifier. In other words, the trapping process appreciably changed with the addition of modifier to the extraction fluid.

Wenclawiak et al. (10), using a Dionex system, found that trapping was analyte-dependent and that the addition of inert material such as glass beads to the collection solvent resulted in greater precision and higher recoveries when trapping hexachlorocyclohexane. The addition of these beads resulted in an increased residence time in the collection solvent, which was thought to favor exchange of the analyte from the CO₂ phase to the collection solvent. On the other hand, Porter et al. (11), using the same trapping design, found that the addition of steel shot, glass beads, or glass wool or the use of a stirring bar during collection actually decreased recoveries.

Previous work performed in our laboratory with liquid trap-

ping (12) found that the choice of pure collection solvent had a greater impact on collection efficiencies than the collection temperature, collection pressurization, restrictor temperature, or extraction flow rate when trapping fat-soluble vitamins. By choosing relatively similar analytes, any differences caused by polarity or volatility were minimized. It was found that the viscosity and surface tension of the collection solvents appeared to be the most important physical properties influencing collection efficiencies. If one thinks of the bubble formation occurring during the decompression in terms of fluid dynamics, the factors affecting the size of the bubble (smaller bubbles favoring the analyte partitioning into the collection solvent) would include extraction flow rate, density, viscosity, and surface tension of the collection solvent (13).

The goal of the present study was to investigate the effect of the addition of a modifier to the collection solvent (resulting in a binary fluid) on the collection efficiencies of compounds of varying polarities and volatilities (Figure 1) given a fixed set of (nonoptimized) extraction conditions. Methylene chloride and hexane were the collection solvents, and the added modifier was either methanol or *n*-propanol. Some physical properties of both the collection solvents and modifiers are shown in Table I. The addition of a modifier to the collection solvent induces small changes in the physical properties of the solvent that can change trapping efficiencies. Studying the addition of the modifier to a collection solvent will allow the prediction of trapping differ-

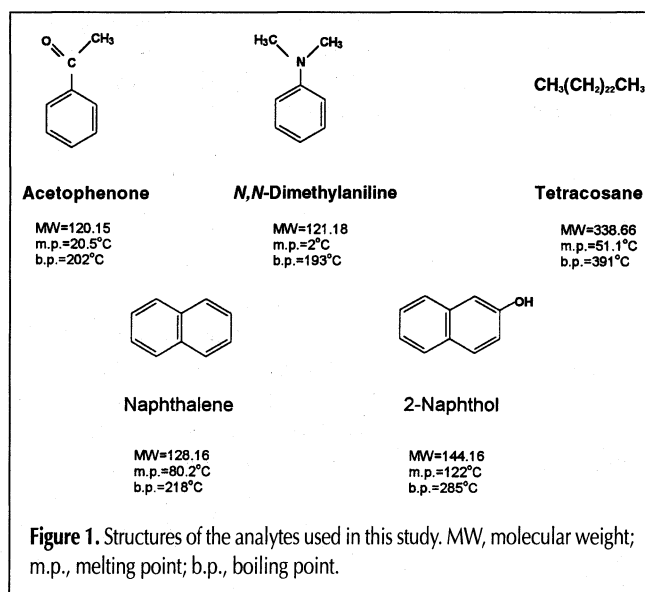


Table I. Physical Properties of the Collection Solvents and Modifiers

Identity	Boiling point (°C)	Density (g/mL)	Viscosity (cp, 20°C)	Surface tension (dynes/cm)
Methylene chloride	40	1.335	0.449	26.52
Methanol	65	0.792	0.754	22.60
Hexane	69	0.659	0.393	18.43
<i>n</i> -Propanol	97	0.802	2.256	23.78

ences that would result from the use of unmodified CO₂ versus modified CO₂. It was hoped that the addition of the collection solvent modifier could also help to overcome some common instrumental constraints, such as the lack of collection pressurization or collection temperature control.

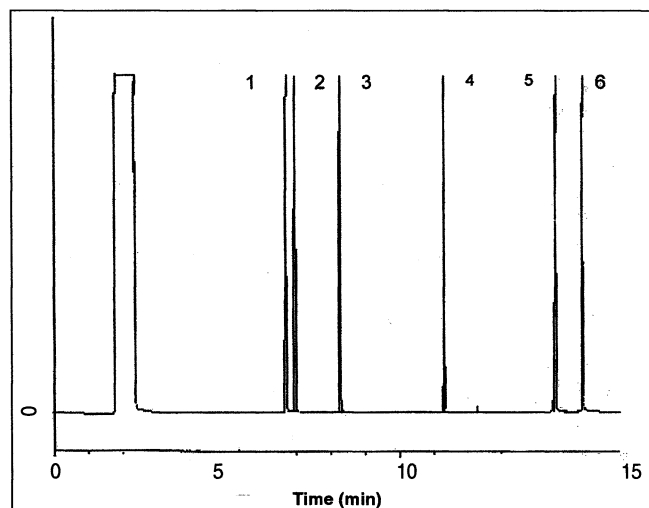


Figure 2. Representative gas chromatogram of the extracted polarity mix. Peaks: 1, acetophenone; 2, *N,N*-dimethylaniline; 3, naphthalene; 4, 2-naphthol; 5, pyrene (internal standard); 6, tetracosane.

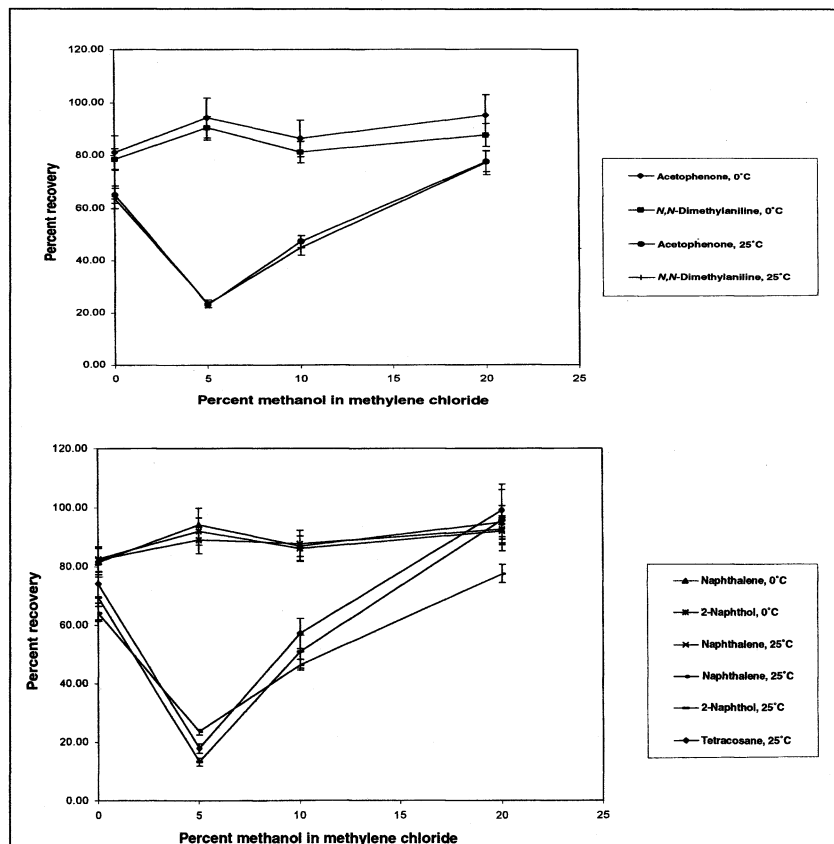


Figure 3. Effect of collection temperature on the recovery of polarity mix components: semivolatiles (A) and nonvolatile analytes (B). Conditions: nonpressurized collection, methanol modifier, methylene chloride collection solvent.

Experimental

Extraction

All extractions were performed using an Isco SFX 3560 SFE system with an automatic variable restrictor, where decompression takes place at the tip of the restrictor barrel. Carbon dioxide with helium headspace (~ 2000 psi) from Air Products and Chemicals (Allentown, PA) was used as the extraction fluid.

Approximately 14 grams of Ottawa Cement Testing Sand (Fisher Scientific, Houston, TX) was placed in a 10-mL Isco high-temperature crystalline polymer extraction vessel. The sand was used as received without performing clean-up steps or preliminary extractions. A spiking solution of acetophenone, *N,N*-dimethylaniline, tetracosane, naphthalene, and 2-naphthol (Fisher Scientific, Fairlawn, NJ) (~ 10 mg/mL of each) was prepared in high-performance liquid chromatography (HPLC)-grade methylene chloride from Fisher Scientific. A fresh spiking solution was prepared each week, wrapped in aluminum foil, and stored in a 4°C refrigerator to minimize the decomposition of the primary standard. A 100- μ L aliquot of the spiking solution was then introduced onto the sand to yield approximately 1 mg of each component. The methylene chloride was allowed to evaporate under ambient conditions prior to SFE. An internal standard solution of pyrene (~ 10 mg/mL) from Fisher Scientific was also prepared in methylene chloride.

All extractions were performed at an extraction chamber temperature of 80°C and a pressure of 340 atm, corresponding to a density of 0.88 g/mL. The restrictor temperature was held at 80°C and the liquid flow rate was 1.5 mL/min. The collection temperature, collection pressure, and collection solvent composition were varied. The volume of the collection solvent was held constant at 10 mL, there was no static extraction time, and the dynamic extraction time was 15 min. No solvent replenishment of the trapping solvent was performed to replace losses that occurred during the course of the extraction. The collection solvents were made by volume percent with HPLC-grade methylene chloride, hexane, methanol, and *n*-propanol, all from Fisher Scientific.

Extract analysis

After the extraction was completed, the collection vial was removed from the extractor, and additional collection solvent was added to approximate a volume of 10 mL. A 100- μ L aliquot of the internal standard solution was added next, and the solution was thoroughly mixed. To establish an equivalent 100% recovery, 100 μ L of the same spiking solution was added to an empty collection vessel, the volume was adjusted to 10 mL with the specific collection solvent being studied, and 100 μ L of the internal standard solution was added. The samples were sonicated for 5 min to remove any dissolved CO₂ prior to analysis. A portion of the solution was transferred to an amber autosampler vial for analysis. All extracts were

Results and Discussion

This work was conducted in 2 phases. The first phase of this work focused on determining whether the addition of a modifier to the collection solvent could overcome the effect of lowered collection temperature or collection pressurization. Although the Isco SFX 3560 system that was used for these extractions was capable of pressurizing the collection vessel and controlling the collection temperature down to -20°C through the use of an auxiliary coolant, it was recognized that many instruments available (especially the more basic models) do not present such advantages to the user. The second phase of the work focused specifically on the identity and concentration of the modifiers with each of the solvents.

Effect of collection temperature

For volatile and semivolatile analytes, lowering the temperature lowers the volatility of the analyte, directly leading to less compound loss (6). For the more nonvolatile analytes, a decrease in the collection temperature will usually result in a decrease in the solubility of the analyte in the fluid. Because the collection conditions in most extractions do not approach the solubility limit for the analytes, temperature is normally reduced as low as instrumentally possible. In this work, 25°C (relatively close to room temperature) and 0°C (easily obtainable with an ice bath) were chosen. In both cases, the collection vial was not pressurized. The target compounds were arbitrarily divided into semivolatile (acetophenone and *N,N*-dimethylaniline) and nonvolatile (naphthalene, 2-naphthol, and tetracosane) groups. Figure 3 compares the recoveries of the analytes at 0 and

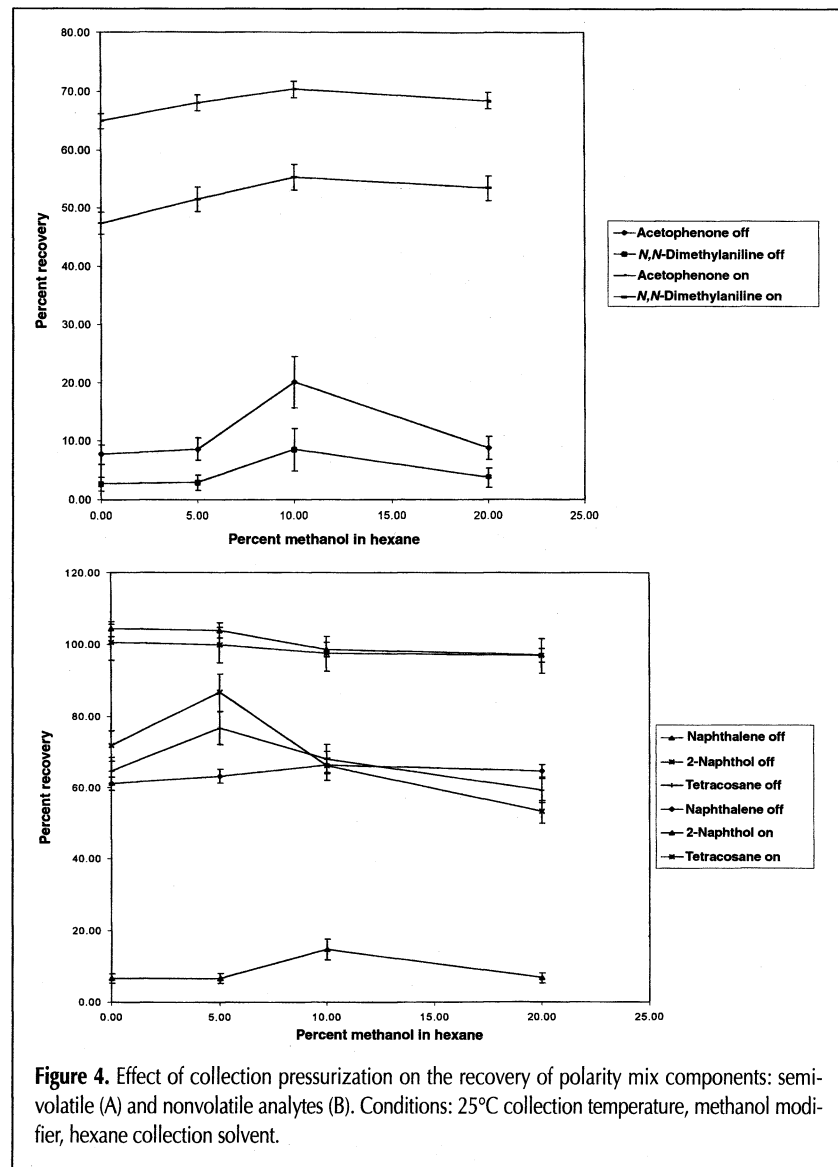


Figure 4. Effect of collection pressurization on the recovery of polarity mix components: semi-volatile (A) and nonvolatile analytes (B). Conditions: 25°C collection temperature, methanol modifier, hexane collection solvent.

analyzed using a Hewlett-Packard (Little Falls, DE) HP 5890 gas chromatograph equipped with a split/splitless capillary column inlet system that was maintained at 275°C . A $30\text{-m} \times 0.25\text{-mm}$ -i.d. ($0.25\text{-}\mu\text{m}$ df) DB-5 (J&W Scientific, Folsom, CA) fused-silica capillary column was used for the separation. Ultra-high-purity helium (Air Products and Chemicals) was used as the carrier gas at a flow rate of $\sim 2.5\text{ mL/min}$ (22 psi head pressure), and the flame ionization detector was maintained at 325°C . The employed temperature program contained an initial temperature of 50°C for 1 min, followed by a ramp to 140°C at 15°C/min , and 140°C was maintained for 1 min. A second ramp of 30°C/min was then used to raise the temperature from 140 to 300°C . The final temperature (300°C) was maintained for 3 min. For all of the extracts, $1\text{ }\mu\text{L}$ was injected using an HP 7673 (Hewlett-Packard) automatic injector in the splitless mode. A representative chromatogram of the extracted polarity mix components is presented in Figure 2.

Each standard was injected 4 times to determine response factors. The extracts were injected, and their response factors were compared to those of the standards in order to calculate recoveries.

25°C when methylene chloride was the collection solvent and methanol was the collection solvent modifier. As seen in both instances, the addition of higher volumes of methanol to the methylene chloride collection solvent allows the collection efficiencies obtained at 25°C to approach those obtained at 0°C . Upon initial addition of the methanol (5%), the recoveries decrease at 25°C but changed very little for the 0°C collection. This decrease in collection efficiencies, followed by an increase as more modifier is added to the collection system, can be attributed to 2 competing phenomena: the solubility of the CO_2 in the collection fluid and the volatility of the collection solvent. Higher recoveries are obtained at the lower temperature because the CO_2 , carrying the analyte, is more soluble in the collection solvent than at higher temperatures. The lower temperature also minimizes collection solvent (and analyte) loss because of simple volatilization. Once higher levels (20%) of methanol are present in the collection solvent, the losses due to volatility at the high temperature are comparable to those seen at lower temperature. Simply decreasing the volatility of the collection solvent alone will not account for the observed behavior, because the collection efficiencies first decrease with the addition of the modifier and then increase as more mod-

ifier is added; the volatility of the collection solvent would decrease with the first addition of the modifier.

The same effect (an increase in collection efficiencies for all analytes as modifier is added) is seen at 25°C for a hexane trap with *n*-propanol modifier. However, no increases in collection efficiencies are seen when using either hexane with the methanol modifier or methylene chloride with *n*-propanol modifier. When hexane is modified with methanol, there is very little change in the overall volatility of the solution because of the similarity of the boiling points of the two liquids, and it affords no advantages during the trapping process. The case of methylene chloride modified with *n*-propanol is not explicable in terms of the decreased volatility of the collection solvent.

It can be seen that in some cases, increased (ambient) collection temperatures can be used if the collection solvent is modified so as to decrease its overall volatility, and collection efficiencies will be comparable to those obtained at subambient temperature.

Effect of collection pressurization

In order to determine the effect of pressurizing the collection vessel, the collection temperature was fixed at 25°C, which actually favored analyte loss. For cases in which hexane was the collection solvent, the reproducibility of the data for nonpressurized collection was much worse than for pressurized collection. This makes direct statistical comparison of the mean values difficult because of the unequal variances, but in both cases (methanol and *n*-propanol as modifier), pressurization of the collection vial resulted in higher recoveries for each analyte in the test mix. When *n*-propanol was the modifier, collection efficiencies improved as the modifier was added. This increase in collection efficiencies for both the pressurized and nonpressurized collection is shown in Figure 4.

For cases in which methylene chloride was the collection solvent, lower reproducibility was seen again for the nonpressurized collection. The pressurized collection proved to be superior with both methanol and *n*-propanol modifiers. In the case of *n*-propanol, addition of the modifier had no significant effect on the recoveries of any of the analytes. With methanol, however, even though the pressurized collection gave higher recoveries, addition of the methanol to the non-pressurized methylene chloride at 20% (v) resulted in higher recoveries than without modifier but still less than those obtained with pressurization. These data are shown for the nonpressurized 25°C recoveries in Figure 3.

In all instances investigated in this work, collection pressurization improved not only collection efficiencies for both semivolatile and nonvolatile analytes but also the reproducibilities for replicate trials. It appeared that pressurization of the collection vial exerted a greater effect on collection efficiencies than the addition of a modifier to the collection solvent.

Effect of modifier identity

For this study, the worst case scenarios were used, which were a collection temperature of 25°C and no collection pressurization. For the hexane-based collection solvents, the addition of methanol did not statistically enhance recoveries for any of the analytes. However, when *n*-propanol was the collection solvent modifier, recoveries were greatly enhanced, as seen in Figure 5. Although neither methanol nor *n*-propanol was soluble in hexane at the 20% (v) level, a 2-phase collection system did not diminish analyte recoveries and even increased them in the case of *n*-propanol. (Recoveries were determined based on a spiked standard treated in the same manner as the extracted samples. In these cases, only the hexane or methylene chloride phase was injected into the chromatograph, but any partitioning effect between the 2 liquids would be the same for the standard and samples.) The excess alcohol (after the hexane was saturated) tended to act in much the same manner as an inert solid particle in that it increased residence time in the collection solvent. Enhancement of the recoveries when *n*-propanol was the modifier was thought to be caused by the increased viscosity of the solution (in comparison to hexane alone, or hexane with methanol modifier) and the inclusion of the additional (immiscible) *n*-propanol in the collection vial. Both of these situations

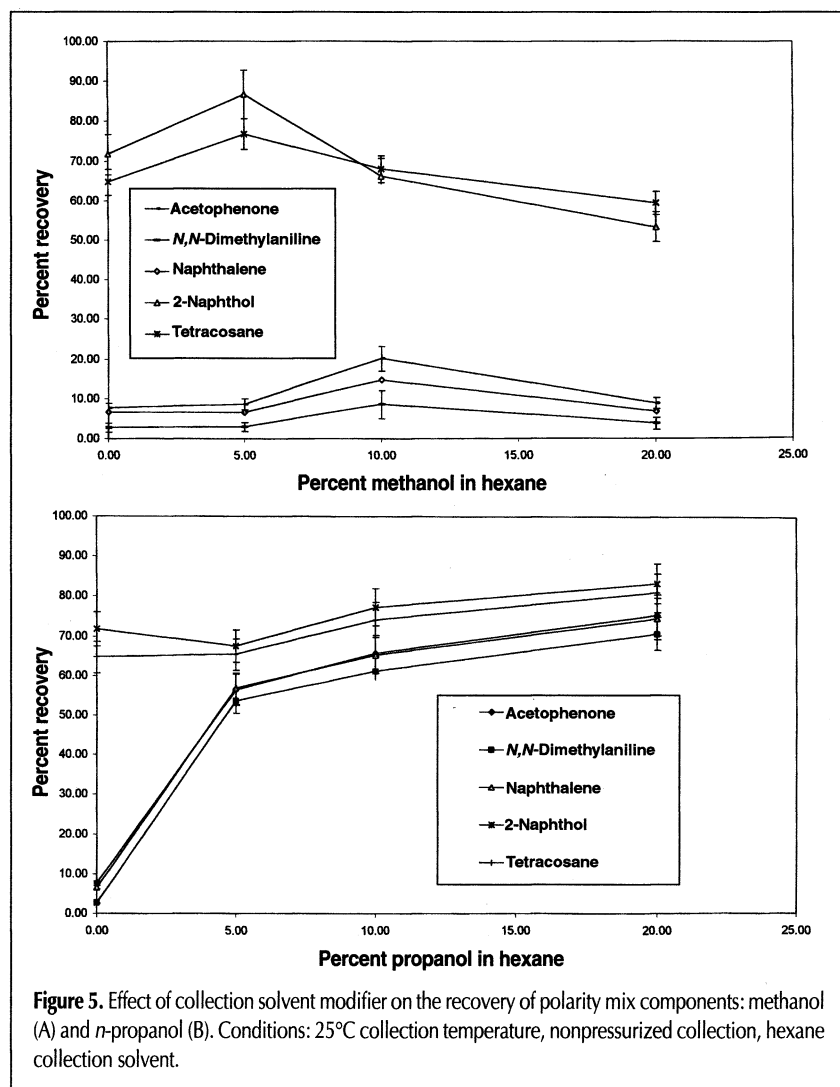


Figure 5. Effect of collection solvent modifier on the recovery of polarity mix components: methanol (A) and *n*-propanol (B). Conditions: 25°C collection temperature, nonpressurized collection, hexane collection solvent.

caused an increase in the time the CO₂-analyte bubbles spent in the collection solvent.

For the methylene chloride-based solvents, the addition of *n*-propanol resulted in no significant change in the collection efficiencies for any of the analytes. The addition of methanol resulted in significantly improved recoveries only for tetracosane and 2-naphthol and only at the 20% level. The reasons for this occurrence are unclear.

Effect of collection solvent identity

Finally, if the collection solvent itself is considered, when the modifier was the same, a much more pronounced effect was seen with hexane than with methylene chloride when *n*-propanol was

the modifier. These data are illustrated in Figure 6, and the results can be attributed to the ability of the *n*-propanol to function in several ways to modify the collection fluid. The volatility of the collection fluid is decreased, the viscosity is increased, and the immiscible *n*-propanol droplets act to change the flow path, thus increasing the residence time of the analytes. Apparently, an increase in fluid polarity is not important, because the same general trend was seen for all of the analytes regardless of their polarity.

Conclusion

In agreement with our previous work, it was found that the choice of collection solvent is immensely important in achieving the effective liquid trapping (direct restrictor immersion) of analytes. The addition of a modifier to the collection solvent allowed for the use of higher trapping temperatures to trap semivolatile and non-volatile analytes. This should allow trapping systems to be operated under ambient conditions instead of subambient temperatures. Collection pressurization makes a significant difference at higher collection temperatures, which is most profound when trapping the more volatile analytes (acetophenone and *N,N*-dimethylaniline). Collection vial pressurization exerts a greater effect on collection efficiencies than the addition of a collection solvent modifier, thus pressurization is highly recommended. Though pressurizing the collection vial in the Isco 3560 system used in this study is quite easy, for less sophisticated systems, this may be quite an instrumental constraint.

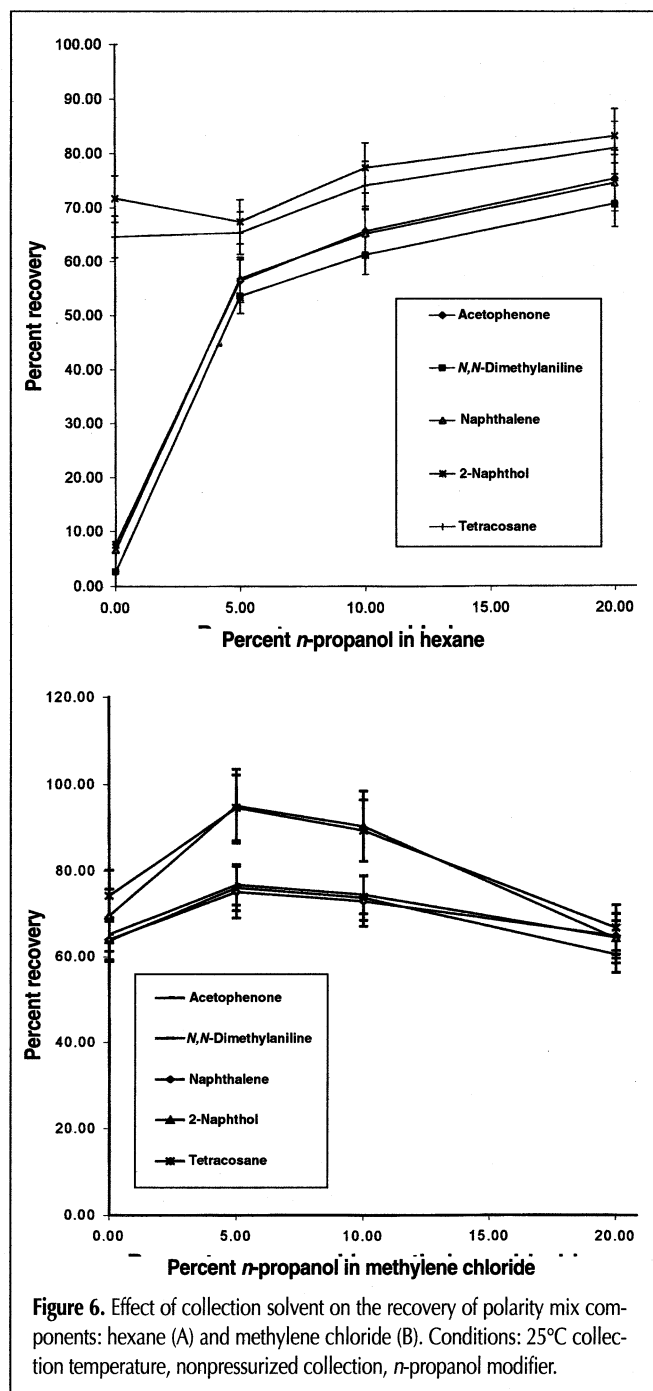
Changing the viscosity and surface tension of the collection solvent can also change trapping efficiencies. This is an important point that must be considered when trapping in a pure collection solvent after extraction has been performed with a modified fluid. The collection efficiency will continually change during the course of the extraction with the addition of the extraction fluid modifier, which will also act to modify the collection solvent. This modification of the collection solvent can be either beneficial or detrimental to the collection process. This indicates that the choice of SFE trapping parameters can be as important as the choice of extraction parameters.

Acknowledgments

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