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Stir Bar Sorptive Extraction: Enhancing Selectivity of the PDMS Phase

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Abstract
The analysis of volatile and semivolatile compounds in aqueous solutions using stir bar sorptive extraction (SBSE) as the extraction step is gaining acceptance in a wide variety of application areas including water, beverages and other consumer products. It has been shown to be simple, sensitive and often can eliminate cumbersome solvent extraction or other sample preparation steps.

Efficiency of analyte partitioning into the polydimethylsiloxane (PDMS) phase on the stir bar parallels the distribution of the analyte between octanol and water as described by the octanol-water partition coefficient K_{ow}. The PDMS phase used for most SBSE is therefore well suited for extraction of nonpolar analytes. There is interest in enhancing the selectivity of this technique to allow analysis of more polar analytes, or to simplify the background from complex matrices.

Strategies have been developed to provide additional control of the partitioning of analytes into the PDMS phase during SBSE. Parameters such as sample pH, salt content and the presence of solvents during extraction can be used to enhance the extraction efficiency of a range of analytes including polar compounds. The very high capacity of the SBSE phase allows the use of solvent back extraction prior to thermal desorption to selectively reduce the background interference from complex sample matrices.

Introduction

When speaking of SFC, Robert Stevenson (American Lab Editor) once said "We all know the stages of development of a technique: wild enthusiasm followed by a period of disillusionment arising from the challenge of unsolved problems. This is followed by despair as the commercial firms leave the field while the research leaders solve the problems."

Since SBSE using PDMS was introduced commercially a year ago, it has shown great potential to simplify sample preparation, achieve exceedingly low detection limits, and extract even complex matrices with high levels of non-volatile compounds. Any disillusionment seems to arise from the desire for an additional polar phase able to extract more polar compounds from a broader range of complex samples.

This report addresses some of the perceived limitations on the use of PDMS for extraction of analytes, including polar compounds, from complex samples with high levels of GC-unfriendly components. Perhaps development of SBSE will follow a new path to acceptance, avoiding the pitfalls of some of its predecessors.

Experimental

Instrumentation. All analyses were performed on a GC (6890, Agilent Technologies) with either mass selective detection or flame ionization detection. Both instruments were equipped with Thermal Desorption units with autosamplers (TDS2 & TDSA, Gerstel) and PTV inlets (CIS4, Gerstel).

Sample Preparation. All samples were diluted 10 fold (unless noted) in water or solvent. For back extractions, a Twister was added to aqueous samples and extracted for one hour with stirring at room temperature. The Twister was removed, rinsed and back extracted for another hour in a 10ml vial containing fresh solvent. Details of the extractions are given in the figures and text.

For acidification, a 1M solution of phosphoric acid was added dropwise to the scotch sample to a pH of 2. Sulfuric acid was used to acidify the SVOC sample test mix to pH <2. A 0.1M solution of sodium bicarbonate was added dropwise to the hand soap sample to a pH of 8. The samples were extracted with a Twister stir bar for one hour immediately following pH adjustment. After extraction or back extraction, the Twister was removed, rinsed with water, and placed into a thermal desorption tube for analysis.

Analysis Conditions.

TDS 2	splitless, 20°C, 60°C/min, 250°C (5 min)
PTV	0.2 min solvent vent (50 mL/min), split ratio 30:1 -120°C, 12°C/s, 280°C (3 min)
Column:	30m HP-5 (Agilent), d_i= 0.25mm, d_f= 0.25mm
Pneumatics:	He, P_i= 92.0 kPa for FID, He, P_i= 62.5 kPa for MSD, Constant flow = 1.2 mL/min
Oven:	40°C (2 min), 10°C/min, 280°C
Oven (SVOC):	40°C (4 min), 20°C/min, 50°C (3.25 min), 12°C/min, 290°C (6 min), 20°C/min, 325°C

Results and Discussion

Sample pH adjustment. Ionized organic species such as carboxylic acids, phenols, and amines will not readily partition into the nonpolar PDMS phase. Sometimes this selectivity is desirable if the ionized species would otherwise interfere with the analysis.

Partitioning of ionizable organic compounds into the PDMS phase on a Twister stir bar can be controlled by adjusting the sample pH before extraction. Lowering the pH to protonate acids and phenols will enhance the extraction of these compounds into the Twister phase. Figure 1 shows a scotch whiskey sample diluted 1:10 in water with (A) or without (B) acidification prior to extraction with a Twister stir bar. The acidified sample shows the presence of C10 and C12 acids not seen in the sample without pH adjustment. Only a very small C8 acid peak is seen despite the large C8-ester peak, indicating the acids do not result from acid hydrolysis.

Note in the inset, the C12 acid peak in the acidified sample obscures several smaller peaks including farnesol, a fragrant alcohol. Also note the loss of several small acid-labile acetals (*) in the acidified sample.

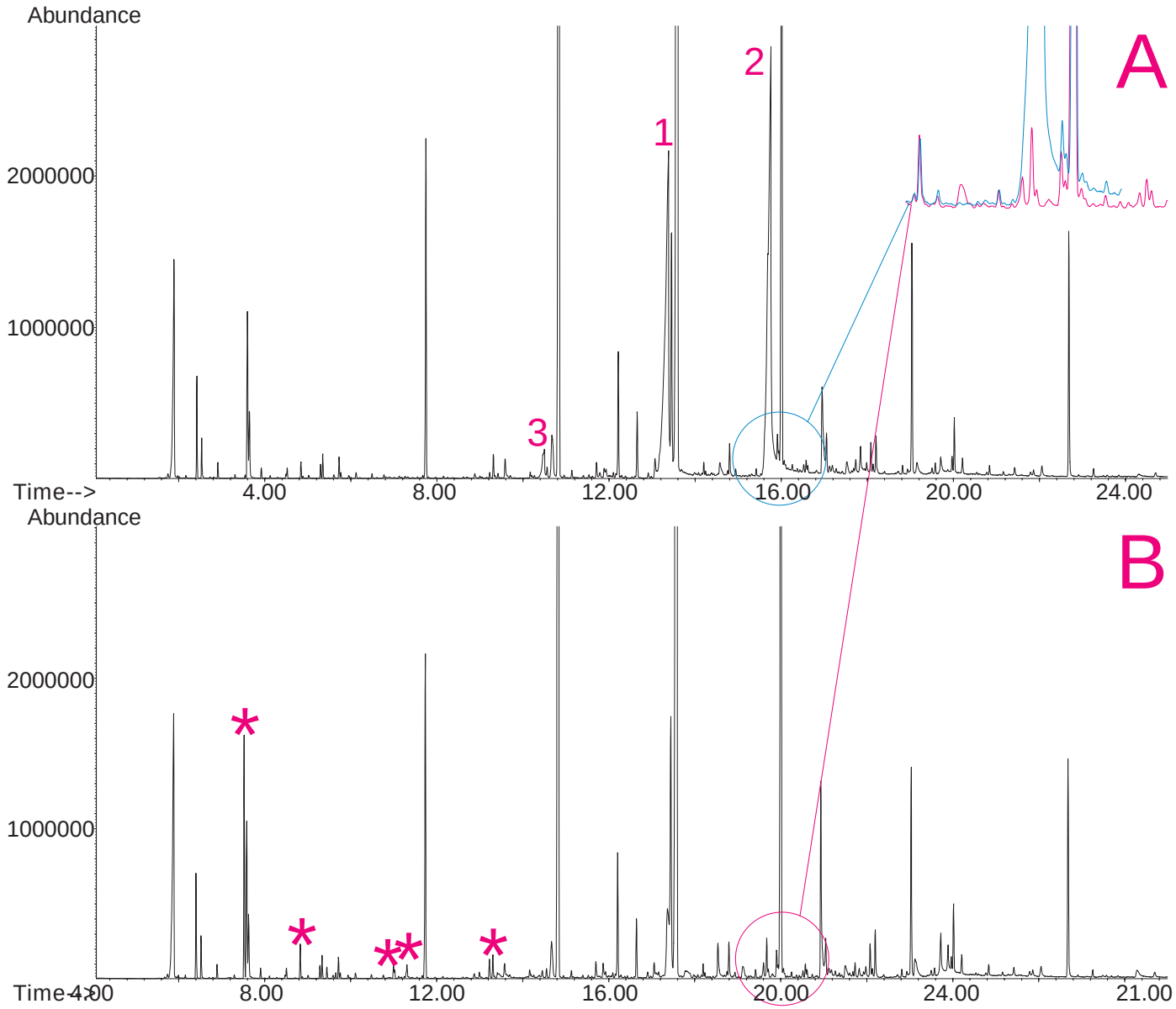

Figure 1. Twister extraction of scotch whisky (A) acidified to pH 2, (B) non-acidified. Peak identities: (1) C10 acid, (2) C12 acid (3) C8 acid.

Figure 2 shows a portion of a water sample spiked with 5-100ppm SVOC's. One aliquot was acidified to pH 2 with sulfuric acid (upper trace) while the second aliquot was not pH adjusted. The acidified sample shows the presence of four phenols in addition to the other SVOC's seen in both samples. Raising the pH to deprotonate amines to enhance extraction efficiency may be limited by increased siloxane background from the PDMS above pH 8.

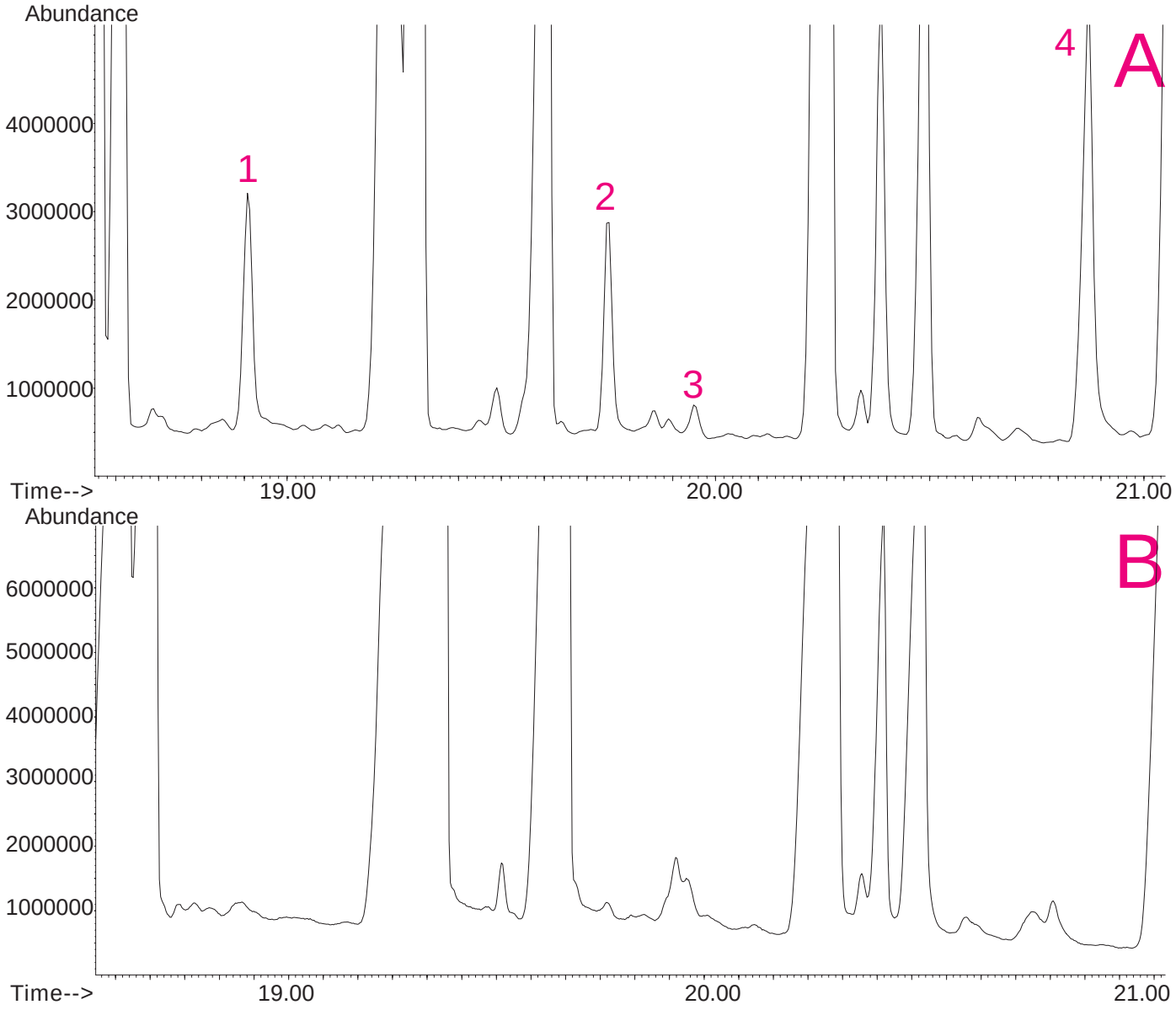

Figure 2. Twister extract of water spiked with semi-volatile organic compound (SVOC) mix. (A) acidified (B) non-acidified. Peak identies: 2,3,5,6-tetrachlorophenol (1); 2,4,6-tribromophenol (2); o-(o-bromophenyl)phenol (3); pentachlorophenol (4).

Twister back extraction with sodium bicarbonate. Some samples may contain matrix components that partition into the PDMS and interfere with an analysis. Figure 3 shows the Twister extraction of liquid hand soap dispersed in water. The large C12 acid peak could be obscuring other components. Back extracting the Twister stir bar in pH 8 sodium bicarbonate completely eliminates the C12 acid peak. In addition, losses of other peaks eluting in the 13 - 15 min window are seen. These compounds have relatively low pK_{ow} values (1.5-2.2) and are expected to readily back extract into water.

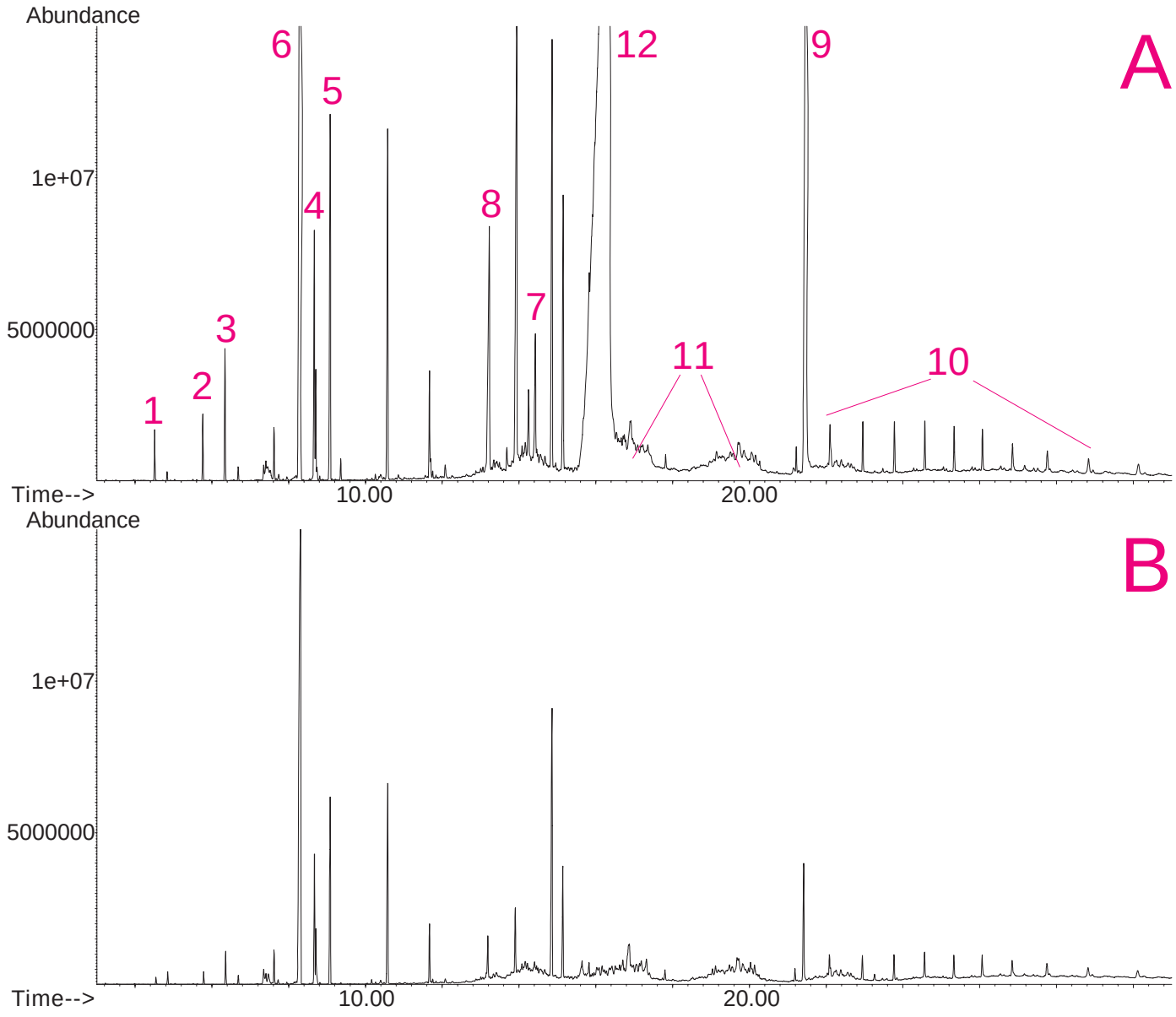

Figure 3. Twister extraction of liquid hand soap (A) and after back extraction at pH8 (B). Peak identities: 12) lauric acid, (9) Triclosan, (10) C20-C30 hydrocarbons, (11) polyoxyethylene alcohols or triglycerides, (6) limonene, (7) ethyl vanillin, (1-5) esters and (8) decalactone.

Sample dilution with organic solvents. Normally, concentrated samples like consumer products, beverages and synthetic flavors can be diluted at least 1:10 in water before extracting with the Twister stir bar. This can help reduce sample viscosity, reduce high solvent levels (e.g. ethanol in distilled spirits) and avoid overloading the PDMS phase.

We have found that nonpolar analyte partitioning into the PDMS is not strongly affected by the presence of moderate levels (10-40%) of polar organic solvents like alcohols or acetone in the sample. We tested the influence of 0-40% methanol concentrations on the peak area for a 25ppb-limonene standard from a Twister extraction. Limonene (pK_{ow}=4.83) is a common nonpolar component in many beverages and consumer product fragrances that partitions well into PDMS. Less than 5% difference in peak area was seen for any measurement, even in 40% methanol.

Figure 4 shows 3-point calibration curves prepared for 10-500ppb limonene in water, 20% methanol or 20% acetonitrile. The curves in water and 20% methanol are virtually indistinguishable, and the curve in 20% acetonitrile shows less than 10% lower response compared to water. These results show that even significant levels of polar solvents like methanol (pK_{ow}= -0.63) or acetonitrile (pK_{ow}=-0.15) do not partition into the Twister PDMS and will not adversely affect results for strongly partitioning analytes.

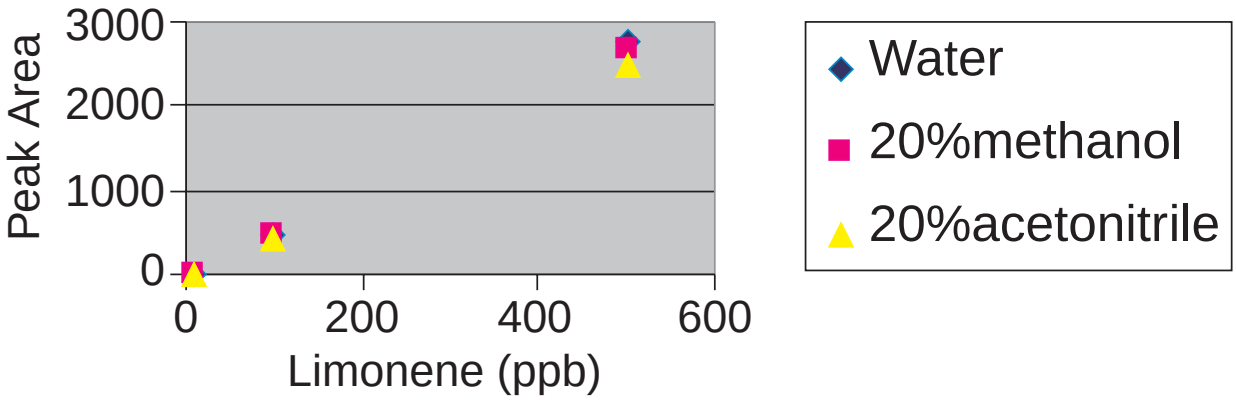

Figure 4. Limonene calibration curves. 10mL, Twister extraction, 30:1 split.

Figure 5 shows a Twister extraction of artificial coffee flavor diluted in water (5A) or 10% methanol (5C). A similar study was done for hand lotion (not shown). No significant differences were seen for either sample, even though the compounds present range widely in polarity. The insensitivity of limonene partitioning to the presence of solvent shown in figure 4 may apply generally to most compound types.

Sample back extraction with 10% methanol. Figure 5B shows the effect of back extracting the Twister stir bar in 10% methanol. Here we clearly see a selective reduction in peak area for many of the peaks, while others are nearly unaffected. It appears that compounds with pK_{ow} less than about 4.0 show a significant tendency toward back extraction into 10% methanol. Also, alcohols in both samples (such as linalool, dihydromyrcenol, and vanillin) are readily back extracted, perhaps due to high solubility in methanol.

One compound (α-pinene, pK_{ow}=4.27) was surprisingly easily back extracted despite its relatively high octanol-water partition coefficient. Since it is a bicyclic ring structure it may interact less strongly with the PDMS phase. The early elution of a-pinene on the HP5 GC column (coated with 5% phenyl PDMS) would be consistent with this hypothesis.

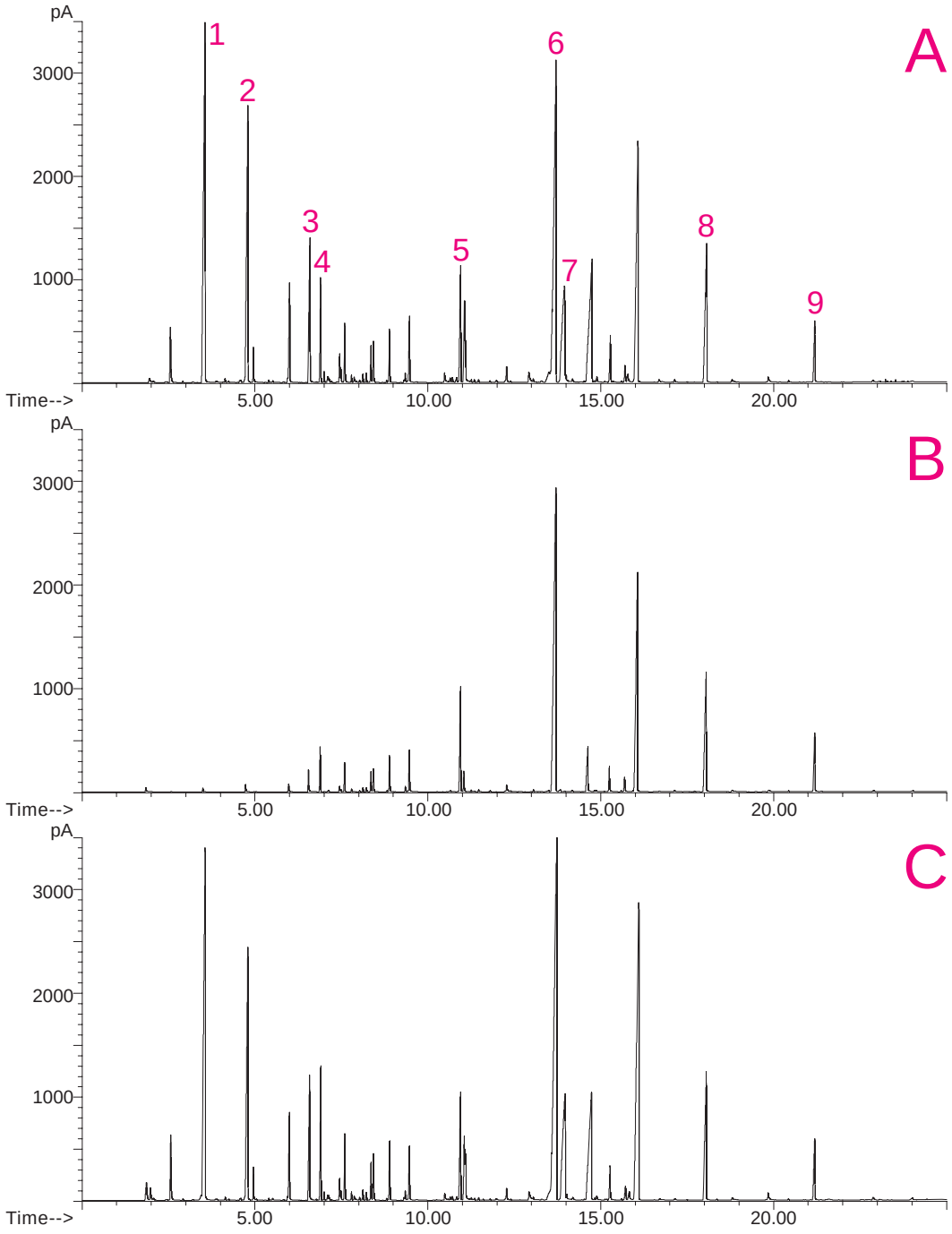

Figure 5. *Twister extraction of artificial coffee flavor diluted 1:10 in (A) water (C) 10% methanol. (B) Back extraction of Twister with 10% methanol. Peak identities: (1) ethyl propionate, (2) ethyl butyrate, (3) pentyl acetate, (4) α-pinene, (5) ethyl octanoate, (6) ethyl decanoate, (7) vanillin, (8) benzyl benzoate, (9) benzyl cinnamate.*

Sample dilution with acetonitrile. Acetonitrile and similar polar solvents that are miscible with both water and fat may enhance partitioning of very nonpolar compounds in the PDMS phase. Figure 6 shows the recovery of a variety of compounds from artificial coffee flavor diluted with 10, 30 or 50% acetonitrile in water. The data were normalized as percent of the maximum peak area recovered to eliminate the influence of the absolute size of the peak. It is clear that compounds with very high octanol:water partition coefficients (pK_{ow} >5.5) are relatively poorly recovered when extracted with Twister directly from water. As the acetonitrile concentration in the sample increases, recovery of compounds like C16-C18 esters increases significantly until a maximum is seen near 30% acetonitrile. Acetonitrile may disrupt micelle structures or eliminate competing adsorption on vessel surfaces. 50% acetonitrile appears to extract most compounds from the PDMS phase.

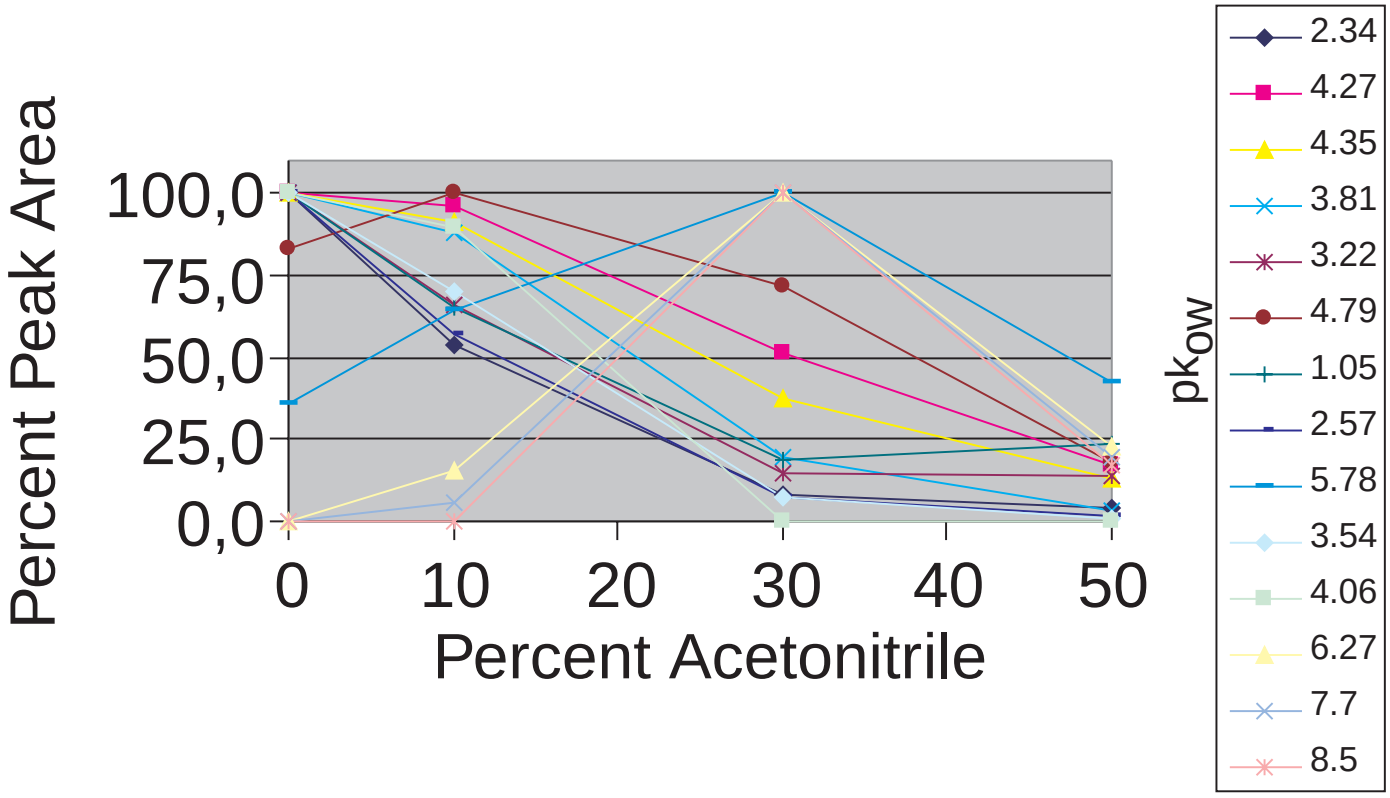

Figure 6. Recovery of analytes from artificial coffee flavor as a function of acetonitrile concentration in the sample.

Figure 7 shows the chromatograms from this set of experiments. Acetonitrile and propylene glycol are seen in the stir bar when the sample is diluted in 50% acetonitrile, suggesting at this point the PDMS begins to swell and the acetonitrile is able to carry polar compounds into the PDMS. The benefits of acetonitrile concentrations between 10% and 30% for recovery of very nonpolar analytes should be further investigated.

Back extraction with acetonitrile. Back extraction of the Twister stir bar with 10, 30 and 50% acetonitrile showed results similar to that seen for methanol. Acetonitrile concentrations between 10-30% appear to be most promising for future solvent selectivity studies.

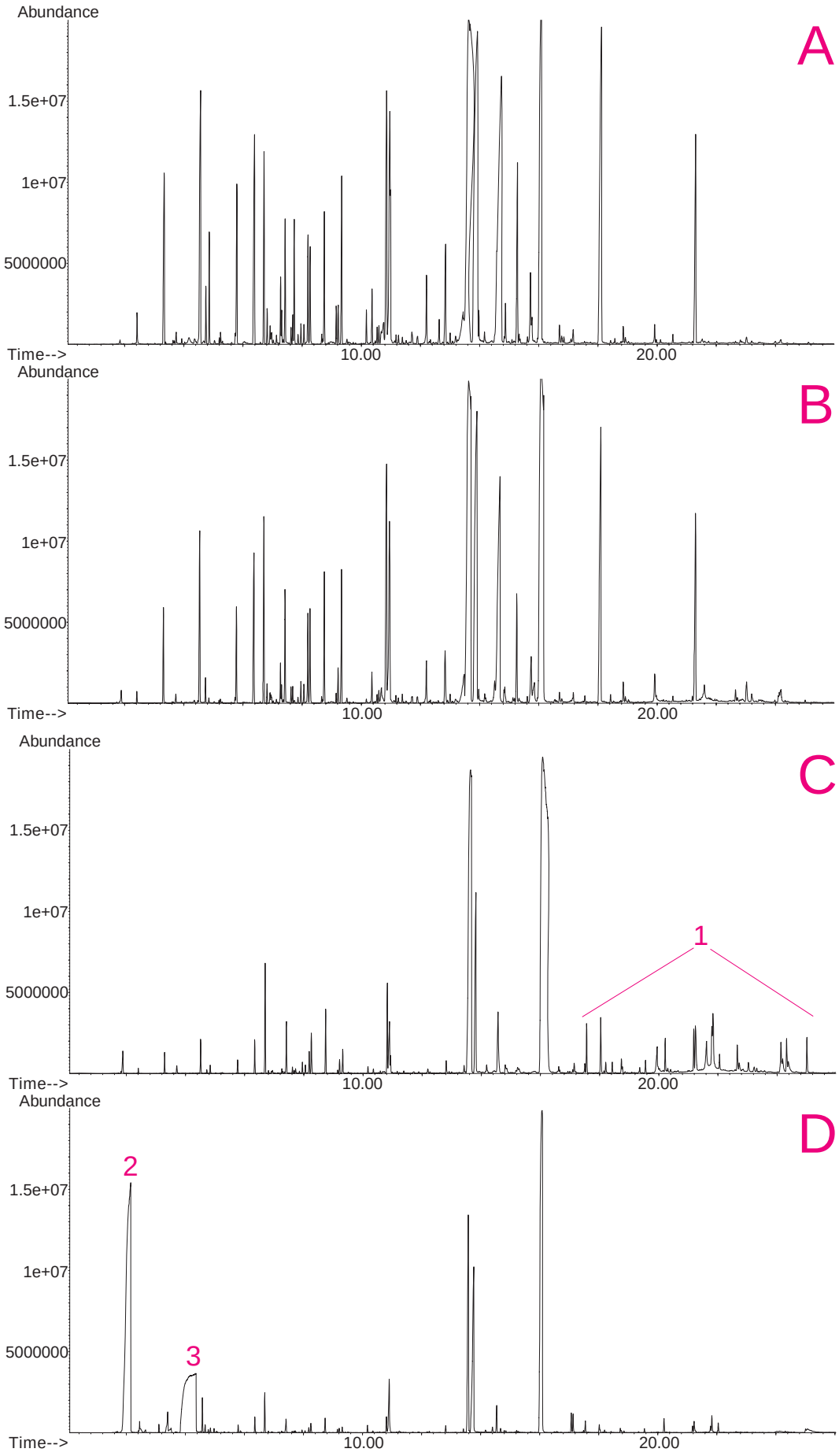

Figure 7. Twister extractions of artificial coffee flavor diluted 1:10 with A) water B) 10% acetonitrile C) 30% acetonitrile D) 50% acetonitrile. Peak identities: (1) C16-C18 esters, (2) acetonitrile, (3) propylene glycol.

Conclusions

Adjusting sample pH to 2 with acid can enhance PDMS partitioning and improve recovery of phenols and carboxylic acids with Twister stir bars. Adjusting sample pH to 8 may have similar benefit for some basic species. Back extracting the Twister stir bar in pH 8 sodium bicarbonate can eliminate unwanted acidic compound partitioning into the stir bar. This may also be used to neutralize the stir bar after extraction of strongly acidic solutions.

Methanol concentrations from 10-40% can be used to dilute samples prior to Twister extraction without significantly decreasing partitioning of most compounds into PDMS. Other polar solvents (ethanol, acetone) show similar behavior. Back extracting the Twister stir bar with 10-30% methanol may selectively reduce or eliminate interference from polar compounds and alcohols.

Acetonitrile concentrations from 10-30% may be used to dilute samples to enhance extraction of very nonpolar compounds (>C16). Back extraction with similar solutions can selectively remove some interfering compounds from complex matrices.

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