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Elimination of Polar Matrix Components Prior to GC Analysis using Stir Bar Sorptive Extraction (SBSE)

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ABSTRACT
Analysis of samples containing polar matrix components such as water, glycols, sugars or surfactants by gas chromatography has usually required extensive cleanup such as liquid/liquid extraction, solid phase extraction or distillation. Some polar matrix components like acetic acid or ethanol are highly volatile and difficult to eliminate using traditional sample preparation techniques. Poor analyte peak shapes, interference from large matrix peaks or even column degradation result if some matrix components are introduced into the GC.

Stir bar sorptive extraction [1] using a Polydimethylsiloxane (PDMS) phase on the stir bar prior to GC analysis can eliminate major interference from these polar matrix components. The PDMS selectively extracts nonpolar analytes, discriminating against the polar matrix components present in the sample at even percent levels or higher. Samples that contain high levels of interfering compounds like surfactants and emulsifiers that usually form emulsions when attempting organic solvent extractions can be analyzed directly by SBSE.

Examples include separation of flavor and fragrance components in balsamic vinegar and alcoholic beverages, and analysis of fragrances and other additives in consumer products like soaps and detergents. Trace additive analysis in new and used antifreeze further demonstrates the versatility of SBSE for sample preparation prior to GC analysis.

INTRODUCTION

The analysis of organic compounds in consumer products, foods, biomedical and other complex matrices is normally performed after extraction and enrichment of the solutes from the matrix. Common matrix components that often give rise to sample preparation problems include acids, alcohols, glycols, surfactants, and polymeric emulsifiers and wetting agents. Traditional approaches to sample preparation are based on liquid-gas extraction or equilibrium (purge and trap, headspace), liquid-liquid extraction using solvents compatible with GC analysis, or solid phase extraction (SPE).

Headspace and purge and trap methods are usually limited to lower boiling volatiles and are relatively low sensitivity techniques. Purge and trap in particular is problematic with matrices prone to foaming. Liquid-liquid extractions can require large volumes of organic solvents, are labor-intensive, solvents may interfere with determination of some compounds or create emulsions, and waste disposal is costly. SPE disks and cartridges can be plugged by suspended solids, high-level matrix components can displace analytes, and dilution by solvents used to recover analytes can reduce sensitivity.

Stir Bar Sorptive Extraction (SBSE) with the Gerstel Twister™ uses a nonpolar PDMS immobilized liquid phase coated onto a magnetic stir bar to selectively concentrate nonpolar compounds from aqueous (or other polar) matrices. Studies have shown [2-4] the distribution of nonpolar compounds between an aqueous and silicone phase correlates with the octanol-water partition coefficient K_{ow}. Tabulated values of octanol-water partition coefficients can span 8 orders of magnitude, therefore they are often referred to as the logarithm, or pK_{ow}. Software programs are also available (Syracuse Research Corp.) that can be used to estimate pK_{ow} for compounds based on their structures. If the pK_{ow} for an analyte is relatively high, the efficiency of extraction from a sample can be predicted. Likewise, if the pK_{ow} of a matrix component is low it will not interfere with SBSE based on a PDMS phase.

Elimination of water. The most ubiquitous polar matrix compound complicating GC analysis is water. Water has a very high vapor expansion volume (approximately 1000x) which necessitates small volume injections into hot inlets to prevent overloading. Water does not wet the common nonpolar GC column phases and can therefore degrade peak shape of other analytes. High levels of water can interfere with detection or even extinguish the flame on a FID.

The PDMS phase on the Twister stir bar does not absorb water, therefore eliminating the problems noted above. All of the following examples and discussions focus on elimination of additional polar matrix components found in the aqueous samples. For many sample types, dilution or dispersion into water actually improves sample handling and extraction using Twister stir bars.

EXPERIMENTAL

Instrumentation. All analyses were performed on a GC (6890, Agilent Technologies) with mass selective detection (5973, Agilent Technologies) equipped with a Thermal Desorption unit with autosampler (TDS2 & TDSA, Gerstel) and a PTV inlet (CIS4, Gerstel). Inlet conditions were optimized for both liquid injection and SBSE.

Analysis Conditions.

Column:	30m HP-5 (Agilent), d_i= 0.25mm, d_f= 0.25mm
Pneumatics:	He, P_i= 62.7 kPa, Constant flow = 1.2 mL/min
Oven:	40°C (2 min), 10°C/min, 280°C (5 min)
PTV	250°C, split ratio 30:1

Twister desorption.

TDS 2	splitless, 30°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)

Liquid extraction. All samples (1gm) were extracted in 2mls of either ethyl acetate or methylene chloride (details in figures). For the detergent and hand soap samples, it was necessary to add 2mls of water and wait up to 3 days to break the emulsion. 1ul of sample was removed from the organic layer and injected into the hot GC inlet.

Twister extraction. All sample types were diluted 10 fold in water unless noted. A Twister was added and samples were extracted for one hour with stirring at room temperature. The Twister was removed, rinsed in water, dried and placed directly in a conditioned thermal desorption tube for analysis.

RESULTS AND DISCUSSION

Elimination of acid interference. The presence of acids in aqueous samples can strongly interfere with or prevent determination of other sample components. Acids may be naturally occurring, or may be added during sample preparation. Introduction of inorganic acids into the GC can lead to creation of active sites

in the inlet, deterioration of the column, and damage to sensitive detectors. Organic acids can elute with typical shark-fin peak shape on many nonpolar GC columns, interfering with nearby compounds.

Balsamic vinegar of Modena (6% acidity) is made by fermentation and barrel aging of cooked Trebbiano grape must that results in a complex, fruity aroma. Determination of the components contributing to the flavor and aroma of the vinegar requires concentration of the flavors from the water and acetic acid matrix. Figure 1 shows a typical solvent extraction of balsamic vinegar with ethyl acetate compared to an extraction with Twister.
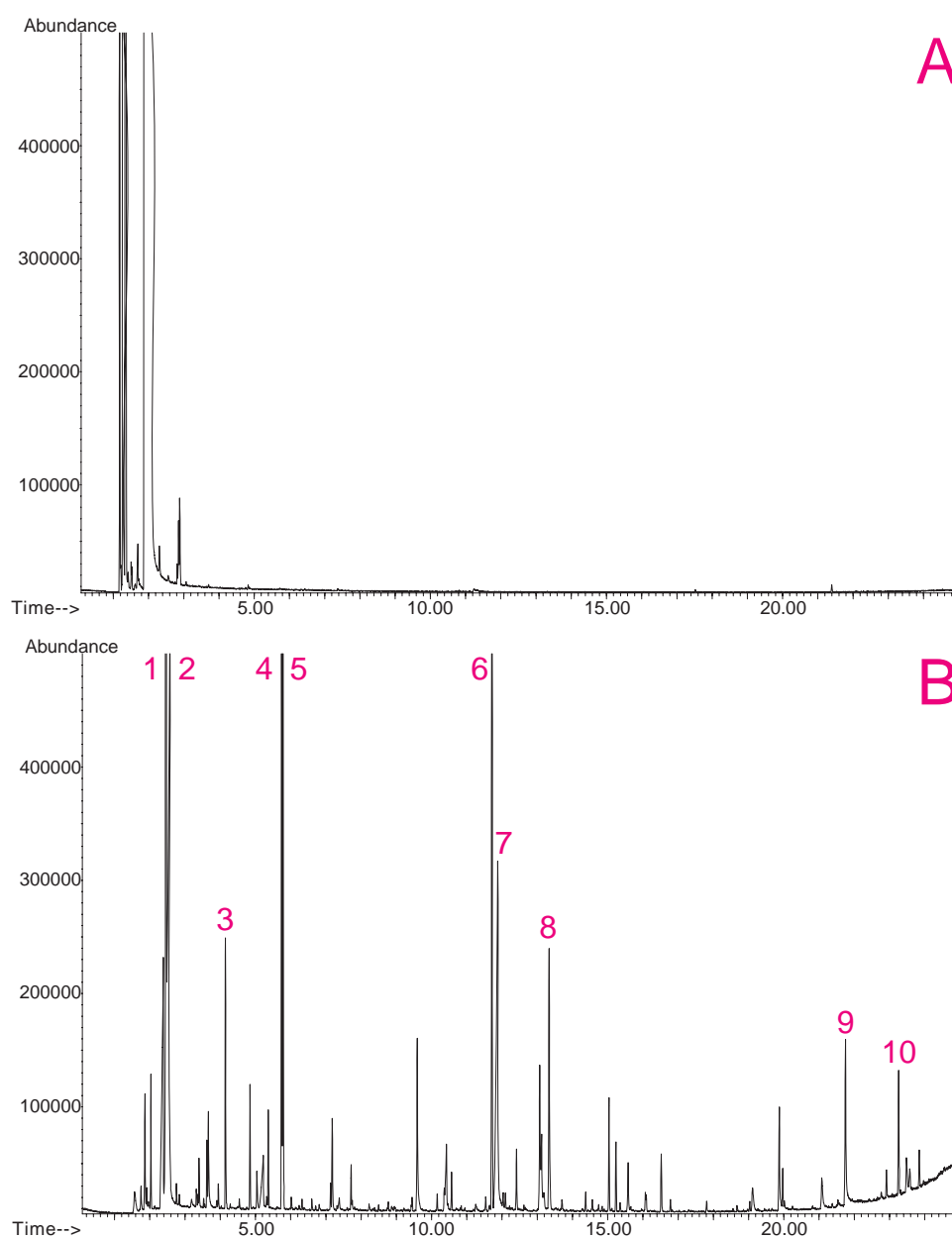

Figure 1. Ethyl acetate (A) and Twister (B) extractions of Balsamic vinegar flavor and fragrance components. Peak identities: 1) ethyl acetate, 2) acetic acid, 3) isobutyl acetate, 4) isoamyl acetate, 5) 2-methyl-1-butyl acetate, 6) phenethyl acetate, 7) nonanoic acid, 8) butyl butyrate, 9) stearic acid, 10) androst-5-en-3-beta-ol.

Several of the esters easily seen in the Twister extraction are identified, whereas the ethyl acetate extraction gives no useful information about the flavor components. Since acetic acid has a very low solubility in PDMS (pK_{ow} = 0.09) no interference from the acetic acid is seen in the Twister extract.

Elimination of ethanol interference. Ethanol is present in alcoholic beverages in concentrations from 3-75% or more depending on the particular spirit. Ethanol is also a common diluent in flavor concentrates and extracts, and along with other short chain alcohols can be found in many consumer products.

Figure 2 shows the comparison of a direct 1ul injection of neat Scotch whiskey with a Twister extract of a 1:10 dilution in water. In the neat injection, the large ethanol peak and water combine to elevate the baseline and alter retention of compounds eluting in the first 6 minutes of the analysis. Only when the scale is greatly expanded can traces of long chain esters be seen. The Twister extraction readily shows the ester profile as well as several of the early eluting alcohols, with no significant interference from the small ethanol peak. Ethanol has low solubility in PDMS (pK_{ow} = -0.14).
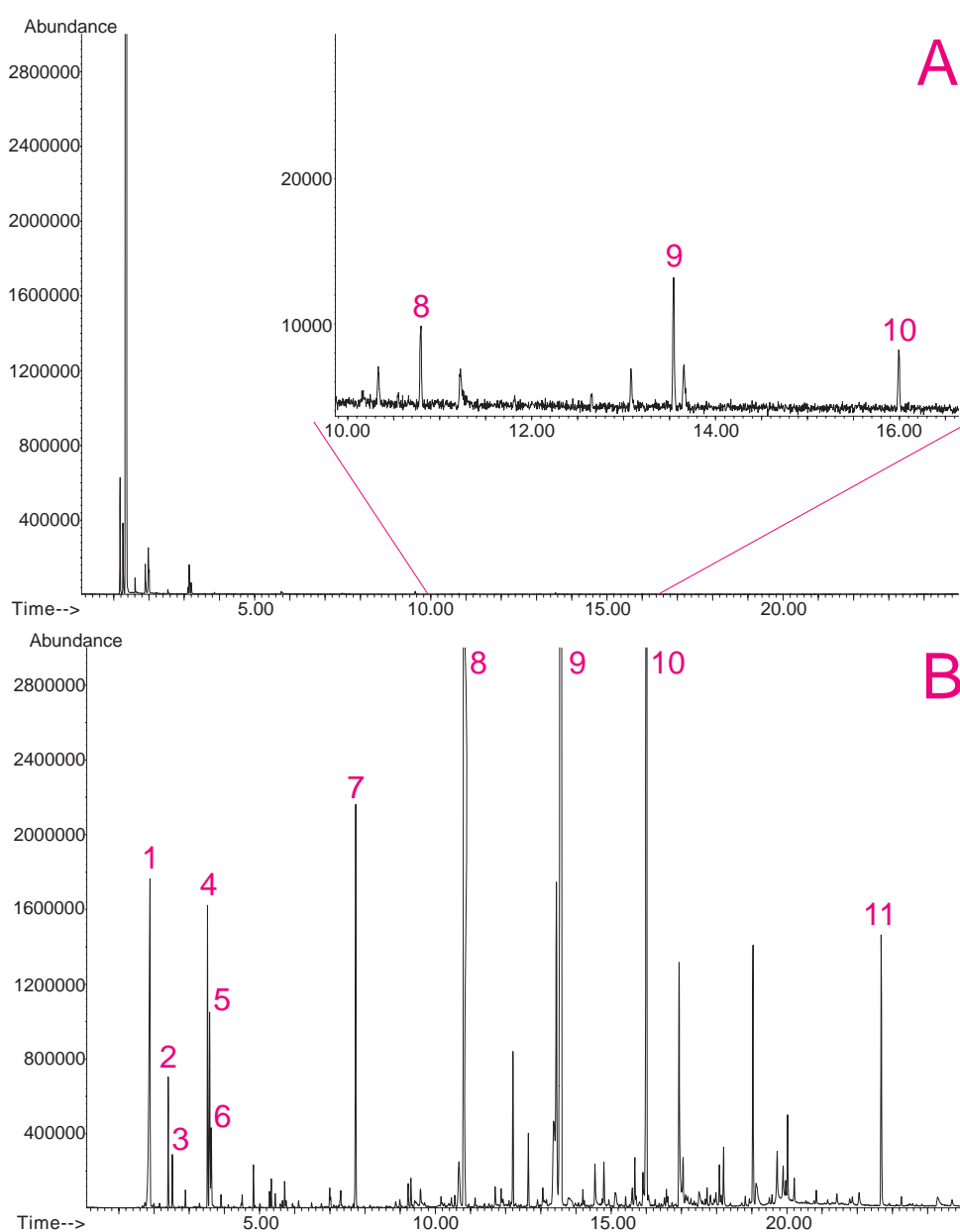

Figure 2. Neat injection (A) and Twister extraction (B) of Scotch whiskey flavor and fragrance components. Peak identities: 1) ethanol, 2) ethyl acetate, 3) isobutyl alcohol, 4) acetal, 5) 3-methyl-1-butanol, 6) 2-methyl-1-butanol, 7-10) C6-C12 esters, 11) acetyl tri-n-butyl citrate.

Elimination of surfactant and emulsifier interference. Many consumer products are complex formulations of surfactants, emulsifiers, lubricants, thickeners, and fragrance. Some of the most challenging to analyze by GC are soaps and detergents, which contain all of the above and more, in very high concentrations. Figures 4 and 5 show solvent extractions of dish detergent and liquid hand soap compared to extractions with Twister. Note the difference in scales in Figure 4. Although the chromatograms obtained by solvent extraction are similar to the chromatograms obtained using Twister, Figure 3 shows the typical emulsion problems associated with solvent extractions of these type products. Several days were needed to break the emulsions and in each case, the layer separation was still incomplete when sampling from the solvent layer was done.

In the dish detergent, among the classes of components extracted by Twister are fragrance [(1) limonene, (2) γ-terpinene, (3) α-terpinolene, (4) linalool, (5) citronellyl- (6) neryl- and (7) geranyl acetates]; (8) C12 and (9) C14 alcohols, and the antibacterial agent (10) Triclosan (pK_{ow} = 4.66). In the methylene chloride extract, additional late eluting compounds are seen that were not completely identified, although they appear to be long chain alcohol derivatives.

Figure 3. Emulsion formed during solvent extraction of liquid hand soap.
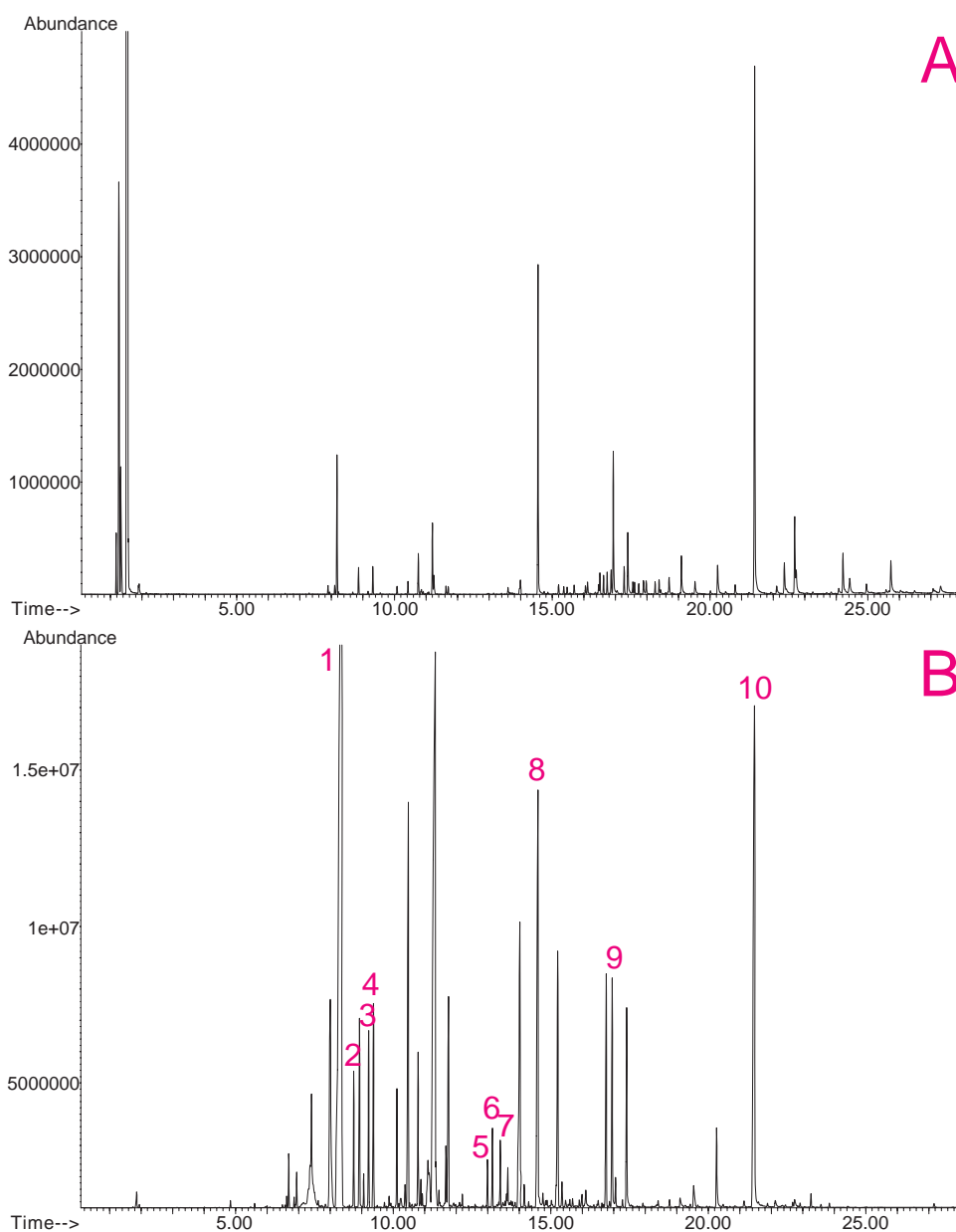

Figure 4. Comparison of methylene chloride and Twister extractions of antibacterial dish detergent compon-

In the hand soap, the major component classes seen include the soap (8) lauric acid, the antibacterial (9) Triclosan, (10) C20-C30 hydrocarbons, and a poorly defined series of peaks (11) likely to be polyoxyethylene alcohols or triglycerides. Fragrance components (6) limonene, (7) ethyl vanillin, (1-5) esters and decalactone were easily seen in the Twister extraction.
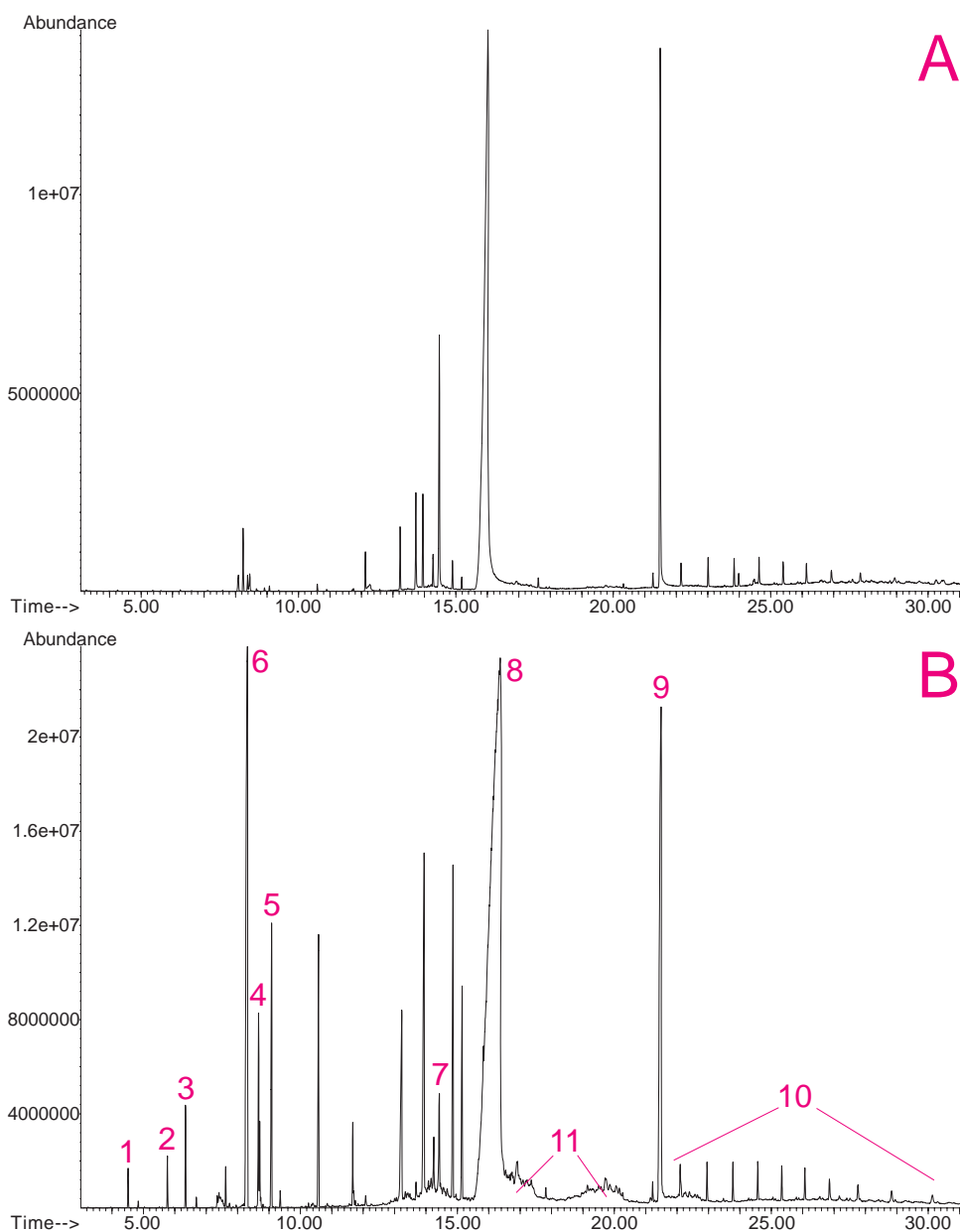

Figure 5. Comparison of ethyl acetate and Twister extractions of antibacterial liquid hand soap components.

Elimination of ethylene glycol interference. Automobile antifreeze consists largely of ethylene glycol with trace additives serving as antifoamers and corrosion inhibitors. A methylene chloride extract gave virtually no information about trace components in the new antifreeze, while the Twister extract shows a wide range of compounds present including even styrene, which is likely extracted from the storage container. No significant interference was seen from ethylene glycol (pK_{ow} = -1.2) or diethylene glycol (pK_{ow} = -1.47), the only compounds seen in the methylene chloride extraction (Figure 6).

Used antifreeze shows a large increase in silicone polymer fragments, a more prominent benzothiazole peak (a possible corrosion inhibitor base) and interestingly, a peak identified as menthol. Qualitative comparison of the odor in the headspace of the new and used antifreeze confirmed the presence of a menthol-like aroma in only the used antifreeze.
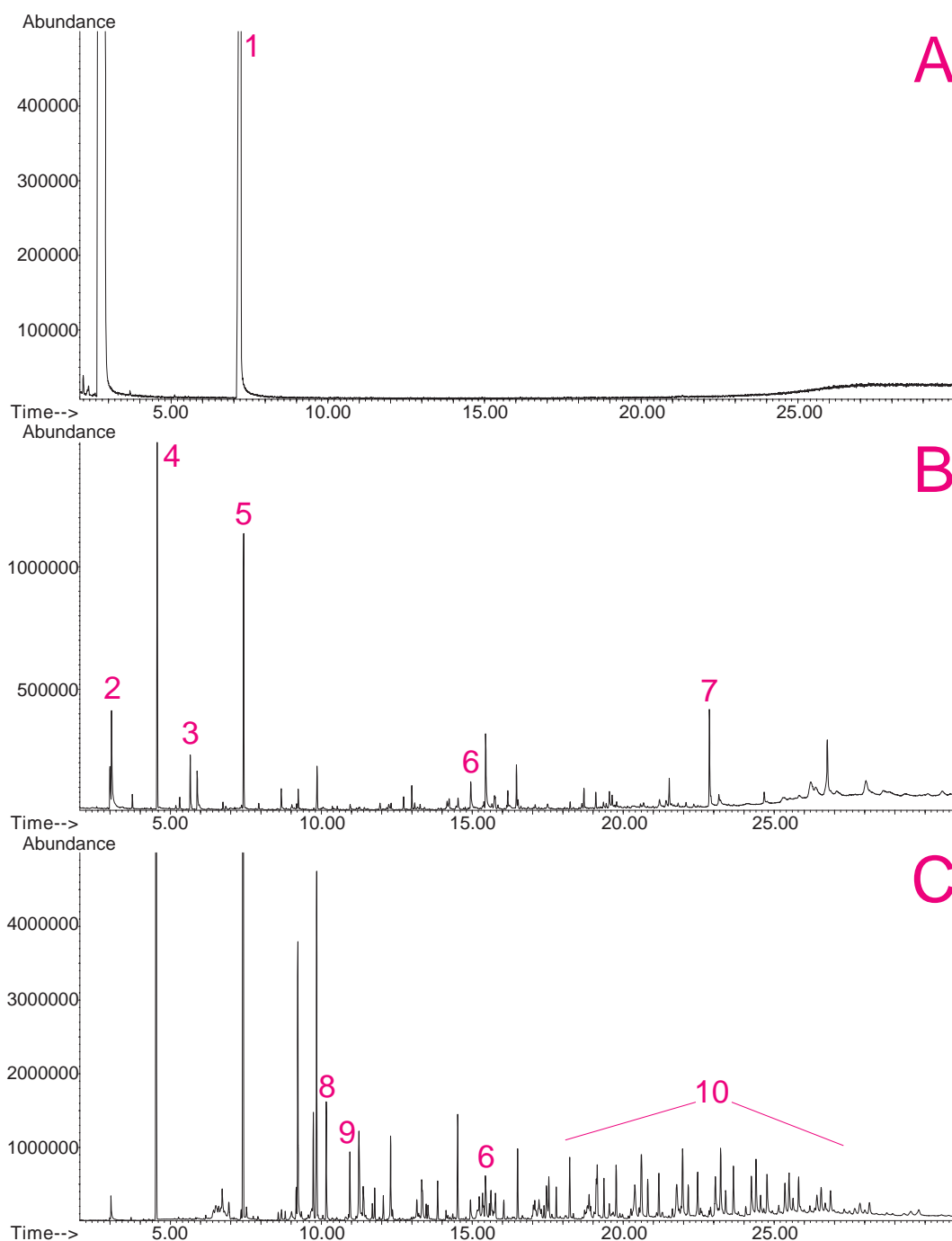
Figure 6. Methylene chloride extract of fresh antifreeze (A), Twister extract of new antifreeze (B) and Twister extract of used antifreeze (C). Peak identities: 1) diethylene glycol, 2) ethylene glycol, 3) styrene, 4,5) siloxanes, 6) tolyl isocyanate, 7) 3-(4-methoxyphenyl)-2-propenoic acid, 2-ethylhexyl ester, 8) menthol, 9) benzothiazole, 10) silicone.

CONCLUSIONS

The PDMS phase on the Gerstel Twister stir bar selectively extracts nonpolar compounds from polar matrices, eliminating interference from polar compounds such as short chain organic acids, alcohols, and glycols.

The Gerstel Twister showed no significant interference from polar species in soaps and detergents, indicating the PDMS phase also appears to discriminate against large nonionic surfactants and charged detergents. Elsewhere we demonstrate that the partitioning of weakly charged species such as carboxylic acids and phenols can be controlled by pH adjustment.

The probability of a compound partitioning into the PDMS phase can be readily predicted based upon the known or calculated octanol-water partition coefficient.

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