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Stir Bar Sorptive Extraction: Capacity and Competition Effects

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ABSTRACT
The determination of volatile and semivolatile analytes 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 and wastewater analysis, beverages and other consumer products. SBSE uses a thick film (0.5mm) polydimethylsiloxane phase on the stir bar to concentrate nonpolar analytes from polar matrices. One of the benefits of the high PDMS phase volume compared to SPME fibers, for example, is increased capacity. Additionally, the PDMS acts as an immobilized liquid phase that concentrates sample by absorption, rather than adsorption. This, coupled with the high capacity, minimizes or eliminates competition and displacement effects from high concentration matrix components often seen when other extraction techniques are used.

Physical capacity of the Gerstel Twister stir bar was determined gravimetrically by concentrating hexadecane from aqueous isopropanol solutions. Under optimal conditions,

the stir bar absorbed milligram quantities of hexadecane. From a practical perspective, the highest analyte concentration that still provides a linear calibration response could be defined as the working capacity of the stir bar. For typical analytes, this upper limit was found to be in the ppm range.

To assess competition and displacement effects, model compounds including a pesticide mix and methyl esters were extracted from water with Twister or SPME in the presence of up to 5 ppm limonene. Under these conditions, the most polar analytes showed the greatest reduction in peak area when extracted with SPME. Detection limits determined for model compounds showed a 10 to 25-fold advantage of the increased capacity of the Twister phase compared to SPME.

Introduction

The need for simpler, faster, more reliable sample preparation techniques continues to grow with the increasing demand for lower detection limits in more complex sample matrices. SBSE is a robust sample preconcentration technique that avoids many of the issues and interferences so often found with other extraction techniques. Key to the performance advantage of the stir bar is the thick film PDMS phase that acts as an immobilized liquid during aqueous extractions.

As interest in quantitative analysis with Twister stir bars increases, questions about stir bar capacity and performance relative to SPME often are raised. At issue most often are factors that affect the reliability of calibration and quantitation in real-world samples. Because the stir bar extraction format is being applied to such a wide range of complex sample matrices, there is need to better define the effect of other matrix components on the stir bar extraction efficiency. The purpose of this study is to help define Twister extraction capacity and clarify issues relating to matrix effects as they affect quantitative analysis.

Experimental

Instrumentation. All analyses were performed on a GC (6890, Agilent Technologies) with either mass selective detection (MSD) or flame ionization detection (FID). Both instruments were equipped with Thermal Desorption units (Figure 1) with autosamplers (TDS2 & TDSA, Gerstel) and PTV inlets (CIS4, Gerstel).

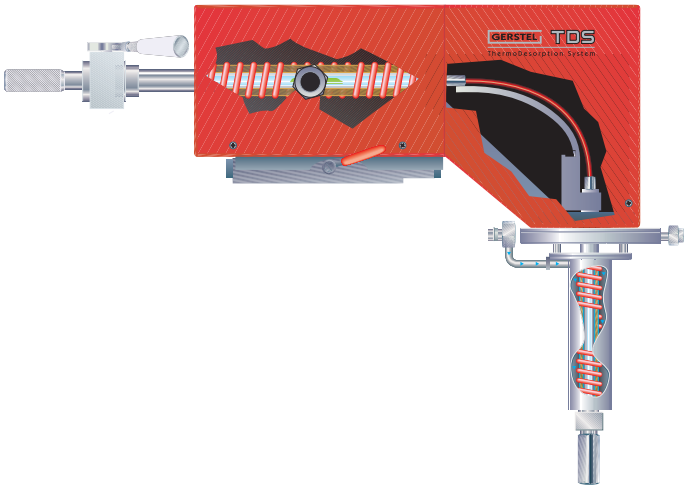

Figure 1. Gerstel TDS 2 ThermoDesorption System.

Analysis Conditions.

Column:	30m HP-5 (Agilent), d_i= 0.25mm, d_f= 0.25mm
Pneumatics:	He, P_i= 9.0 psi (MSD), P_i= 13.3 psi (FID) Constant flow = 1.2 mL/min
Oven:	40°C (2 min), 10°C/min, 250°C (5 min) for Methylesters 60°C (1 min), 10°C/min, 150°C (1 min), 15°C/min, 300°C (5 min) for Pesticides 40°C (2 min), 4°C/min, 70°C (1 min) for BTEX

Twister desorption

TDS 2	splitless, 20°C, 60°C/min, 250°C (5 min)
PTV	0.2 min solvent vent (50 mL/min), split ratio 20:1, 30:1 or splitless -120°C, 12°C/s, 280°C (3 min)

MPS2 / SPME

Fibers	50/30µm DVB/Carboxen/PDMS 100µm PDMS
Equilibration	60°C (15 min)
Extraction	60°C (15 min)
PTV	1.2 min splitless 220°C or 250°C

Sample Preparation

Gravimetric analysis. Twister stir bars were weighed prior to immersion in the test solutions. A Twister stir bar was added to 10 mL each test solution (1% isopropanol, 30% isopropanol, 100% hexane, and 1000 ug/mL hexadecane in 30% isopropanol) and the samples stirred at room temperature 1-4 hours. After

extraction the Twister was removed, dried briefly and re-weighed.

Methyl esters. Methyl esters ranging from C4-C10 were prepared at a concentration of 50 µg/L or 250 µg/L in HPLC grade H_2O containing 10% ethanol or limonene at concentrations of 500, 1000 and 5000 µg/L. Each level was prepared in duplicate.

Pesticides. A pesticide evaluation mix containing Aldrin, Endrin, 4,4' DDT, and Dibutyl chlorendate was prepared at a concentration of 10 µg/L (Twister study) and 50 µg/l (SPME study) in HPLC grade H_2O containing limonene at concentrations of 50, 100, 250, 500 and 1000 µg/L. Each level was prepared in duplicate.

Detection Limit Studies. A model compound mix was prepared containing hexanal, methyl salicylate and benzophenone (each at 10ug/L), methyl heptanoate (5ug/L) and limonene (1ug/L) in HPLC grade water. Each sample was extracted in duplicate. Detection limits were estimated by comparing the resulting analyte peak to baseline noise levels in the elution time window.

Twister extraction. 10 mL of sample were transferred to a 10 mL headspace vial. A Twister was added and the samples stirred at room temperature for 90 minutes. After extraction the Twister was removed, rinsed, dried and placed into a thermal desorption tube for analysis.

SPME. 9 mL of sample was transferred to a 10 mL headspace vial. The analytes were extracted directly utilizing immersion SPME with agitation for 15 minutes.

Results and Discussion

Gravimetric Capacity. Recent studies show the distribution of nonpolar analytes between aqueous and silicone (PDMS) phases correlates with the octanol: water partition coefficient (Kow). For a given system, recovery of analytes from aqueous solution will be in part determined by the aqueous and PDMS phase ratios. A typical 100 µm PDMS SPME fiber has a phase volume of about 0.5 µL. The Twister uses a thick 0.5 mm PDMS film with a phase volume of about 24 µL as the absorptive phase on the magnetic stir bar. This thick film should provide much higher capacity for extracting materials from aqueous solution.

To assess the maximum physical capacity of the Twister PDMS phase, stir bars were weighed before and after exposure to various solutions. Polar solvents like short chain alcohols and water are not expected to partition significantly into the PDMS phase. Nonpolar species (hexane and hexadecane) will partition strongly into the PDMS phase. The results in Table 1 show that weight gain from control solutions (1% and 30% isopropanol) is minimal. Soaking the stir bar in hexane to saturate the PDMS phase gives an indication of the maximum capacity that the phase can physically hold.

The hexadecane sample in 30% isopropanol is a more realistic test of the capacity of the stir bar to extract nonpolar compounds from polar solution. The presence of isopropanol was needed to solubilize hexadecane, although it will reduce the partitioning of the hexadecane into the PDMS. Even in the presence of 30% isopropanol the stir bar absorbed 2 milligrams of hexadecane. To put this in perspective, a typical GC injection of 1 µL of a 2 ppm sample contains 2 nanograms of material.

Table 1. Twister gravimetric study results.

Solution	Twister weight gain
1% Isopropanol	0.3 mg
30% Isopropanol	0.3 mg
100% Hexane	12 mg
1 mg/mL C16 in 30% Isopropanol	2.0 mg

Linear Range. Perhaps a more practical way to express the capacity of the stir bar is to describe the maximum linear dynamic range. If the stir bar was used to extract a very concentrated sample as described in the gravimetric experiment above, the GC column and detector under normal operating conditions would be severely overloaded. Under conditions commonly used to obtain low (ppb) detection limits, the upper concentration limit that provided linear detector response is about 1 ppm (Figure 2). This typically corresponds to a few hundred nanograms of analyte on-column, and also tends to be near the solubility limit for these nonpolar compounds in water.

For more highly concentrated samples extracted using Twister, a higher split ratio can be used to avoid exceeding the dynamic range of the detector. In this case, the Twister can be shown to provide a linear range from low ppt to 100 ppm analyte concentration.

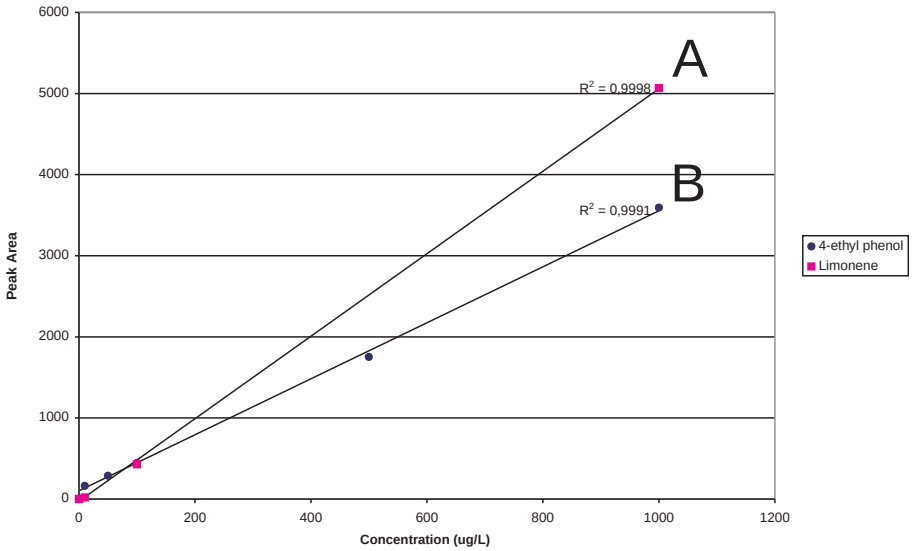

Figure 2. Twister calibration curves. A: limonene in water B: 4-ethyl phenol in wine.

Matrix Competition. One of the factors sometimes encountered when developing quantitative extraction methods is competition effects related to other matrix components. Samples can contain percent levels of solvents (ethanol, for example) that can alter distribution coefficients between the aqueous and extraction phase. Alternatively, samples can contain variable levels of other components that may compete with the analyte for adsorption sites, altering extraction efficiency.

Figure 3 shows the influence of polar solvents (methanol and acetonitrile) on limonene calibration curves prepared by Twister extraction. Limonene partitions well into PDMS (log Kow = 4.83) and is relatively unaffected by the presence of even 20% solvent.

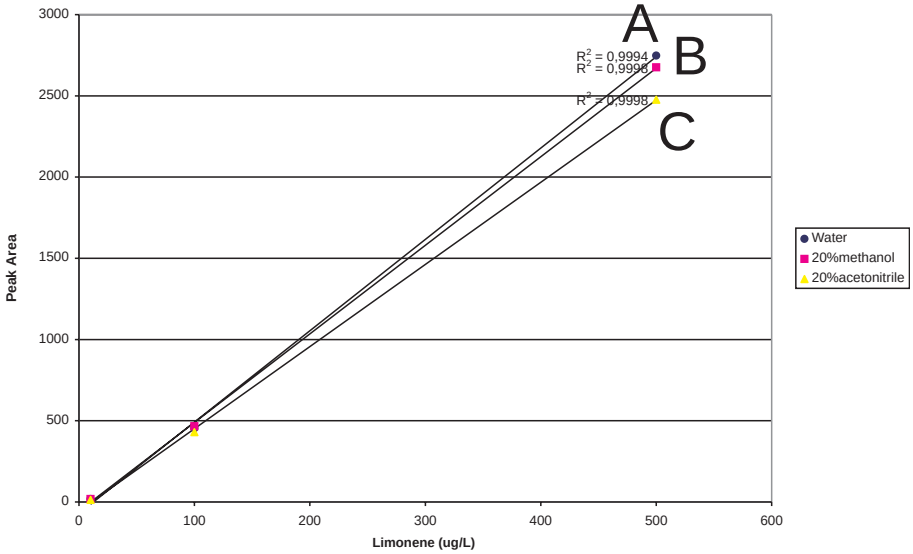

Figure 3. Twister calibration curves for limonene in water(A); 20% methanol (B) and 20% acetonitrile (C).

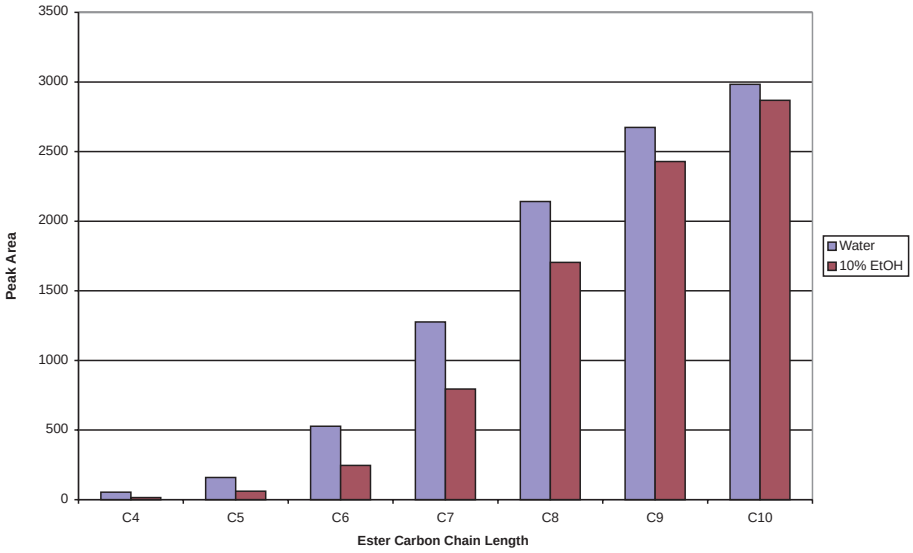

Figure 4. Effect of ethanol on Twister extraction of methyl esters.

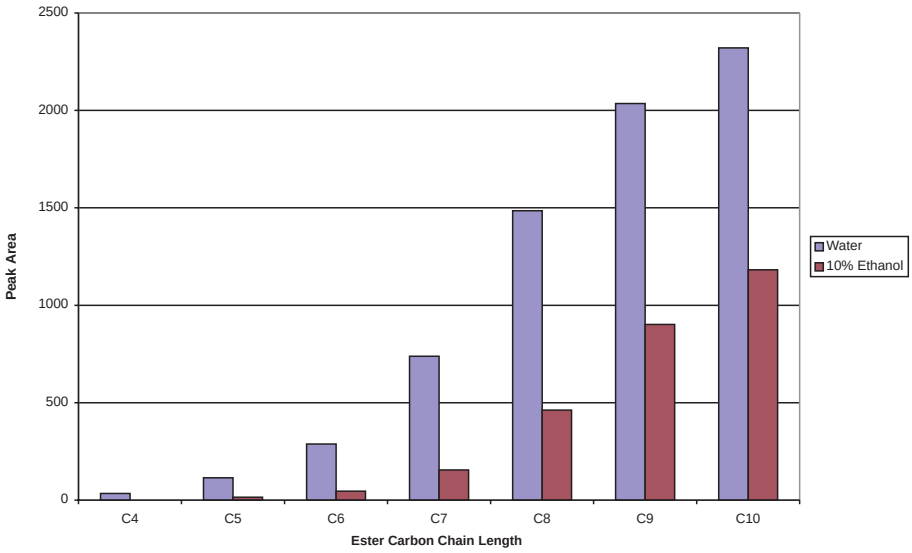

Figure 5. Effect of ethanol on SPME extraction of methyl esters. Fiber: DVB/Carboxen/PDMS.

Figures 4 and 5 illustrate the influence of ethanol on recovery of esters from aqueous solution using Twister or SPME. The C4-C10 methyl esters have octanol:water partition coefficients spanning 3 orders of magnitude (log Kow 1.36 – 4.30) and include short chain esters that will not partition as strongly as limonene into PDMS. For Twister extraction, recovery of the longer chain esters shows minimal influence of ethanol, whereas recovery of the short chain esters can be significantly reduced. For the DVB/Carboxen/PDMS SPME fiber, recovery of all esters is significantly reduced in the presence of 10% ethanol.

Another type of competition can occur where trace analysis is attempted in the presence of other strongly absorbed matrix components. Figure 6 shows that if the analytes are strongly enough retained they will not show significant displacement from either Twister or SPME fibers even in the presence of up to 1 ppm limonene. Both 4,4'-DDT, (DDT) log (Kow = 6.79) and dibutyl chlorendate (DBC), log (Kow = 7.25) have octanol:water partition coefficients at least 2 orders of magnitude higher than limonene.

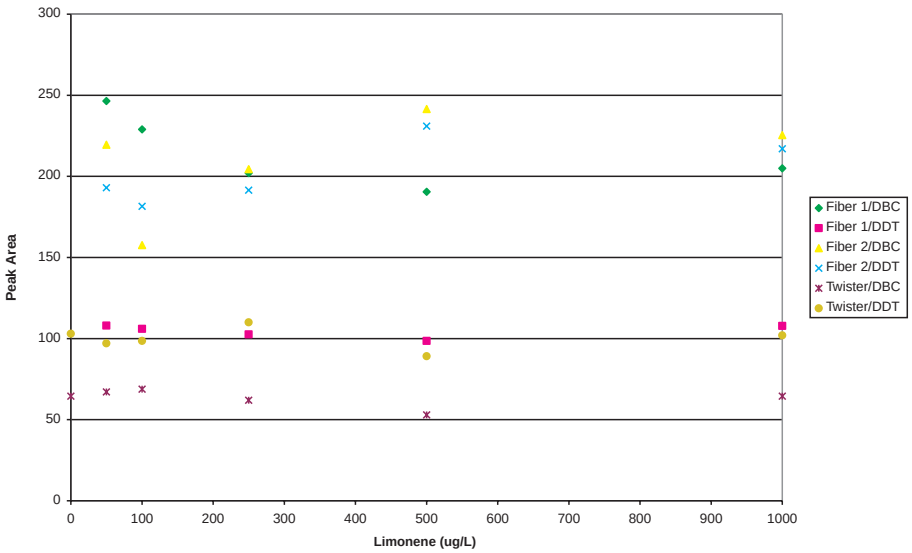

Figure 6. Effect of strongly retained matrix component (limonene) on pesticide extraction by Twister or SPME. Fiber 1, DVB/Carboxen/PDMS; Fiber 2, 100 µm PDMS; Twister, 0.5 mm PDMS; PTV: splitless for both Twister and SPME. Note: sample concentration 50 ppb (SPME) and 10 ppb (Twister).

For analytes that are much less strongly retained, the presence of a competing, strongly retained analyte can affect analyte recovery.

For Twister extraction, methyl ester recovery was reduced by only 10-20% in the presence of up to 5 ppm limonene (Figure 7).

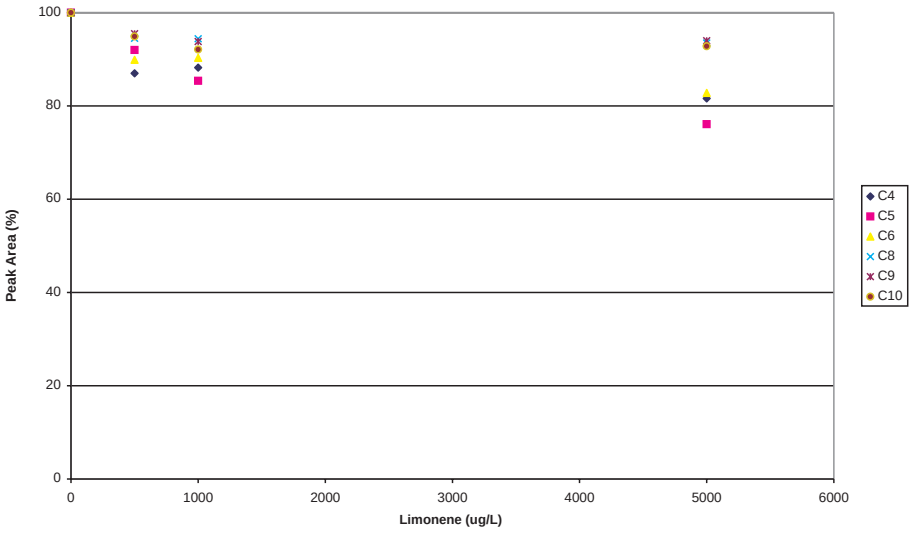

Figure 7. Effect of strongly retained matrix component (limonene) on methyl ester extraction by Twister.

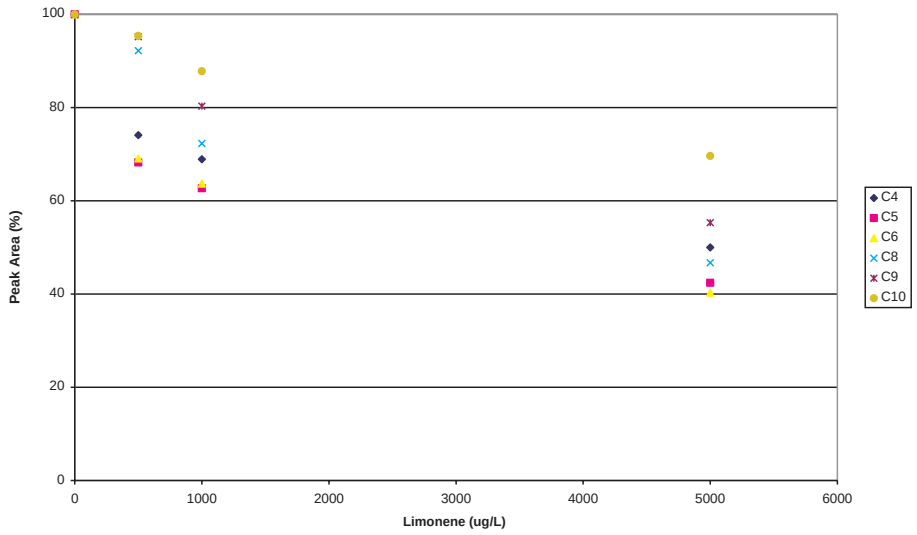

Figure 8. Effect of strongly retained matrix component (limonene) on methyl ester extraction by SPME (DVB/Carboxen/PDMS).

Longer chain esters were less strongly affected than shorter chain esters. For the DVB/Carboxen/PDMS SPME fiber competition from limonene was much more pronounced, with recovery reduced by 50-60% for all but the C10 methyl ester (Figure 8).

Table 2. Detection limits (ug/L) in water.

Compound	Twister	SPME	
		100µm PDMS	DVB/Carboxen/PDMS
Methyl salicylate	0.2	3.2	1.3
Hexanal	0.1	1.1	0.68
Methyl heptanoate	0.06	1.5	0.45
Benzophenone	0.04	1.0	1.0
Limonene	0.01	0.31	0.17

Detection Limits. The PDMS phase volume on the Twister stir bar is about 40 times larger compared to a 100um SPME fiber, therefore raising the possibility of achieving lower detection limits. For the most comprehensive comparison, we also used the DVB/Carboxen/PDMS SPME fiber since it is found to provide better detection limits than the PDMS fiber in some cases. We therefore determined the best detection limits (s/n = 3) for five model compounds using all three liquid immersion techniques. Table 2 summarizes the best detection limits we achieved using GC/FID. In general, we found detection limits using Twister 10-25 times lower than those possible using either SPME fiber.

Conclusions

The standard Twister stir bar is capable of extracting milligram quantities of nonpolar analytes from aqueous solution. The typical linear calibration range, however, is from low pg/mL (ppt) to low µg/mL (ppm) levels.

The presence of 10% ethanol in the sample during SPME extraction reduced recovery of all model compounds tested. When using Twister extraction under similar conditions there was some reduced recovery of polar analytes and minimal effect on recovery of nonpolar analytes.

The presence of other components in the sample can reduce extraction efficiency for less strongly extracted analytes. The magnitude of this effect was shown to be greater on SPME fibers than for Twister extraction. This suggests Twister extraction will be more reliable than SPME for analysis of samples with variable background.

Detection limits for liquid extractions using Twister were found to be 10-25 times lower than the best detection limits achievable using either the 100um PDMS or 50/30 DVB/Carboxen/PDMS SPME fiber in liquid immersion mode.

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