GLOBAL ANALYTICAL SOLUTIONS

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AppNote 3/2002

Stir Bar Sorptive Extraction from Food Simulating Solvents: Preliminary Studies

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KEYWORDS
Food packaging, food simulants, SBSE

ABSTRACT
The FDA requires that any food-contact materials that may reasonably be expected to migrate into food must conform to existing regulations or be included in a petition proposing a new regulation. Alternatively, a no-migration status can be established by showing the packaging component is not detectable in food with a method with a LOD typically in the 1-50 ppb range. Since determination of trace component migration into complex food matrices is extremely difficult if not impossible, the FDA has established acceptable food simulating solvents to use for migration testing. These solvents (water, 3% acetic acid, 10% ethanol and 95% ethanol) comprise much simpler matrices and minimize the potential for interference. Simpler matrix notwithstanding, developing reliable analytical methods for low ppb LOD can be a formidable challenge.

Stir Bar Sorptive Extraction (SBSE) followed by thermal desorption GC has been shown to provide excellent detection limits for nonpolar analytes in the low ppb - ppt range. Polar matrix components such as ethanol and acetic

acid do not partition into the PDMS phase on the stir bar, minimizing potential interference during analysis. This technique is therefore compatible with the FDA specified food simulating solvents.

Model compounds spanning a wide polarity range were spiked into the food simulating solvents, extracted by SBSE using Gerstel Twister stir bars, and recovered by thermal desorption GC. The presence of solvents in the sample matrix reduced analyte recovery in the stir bar, with the largest effect seen for compounds with octanol:water partition coefficients less than 500. Since partitioning into the PDMS phase is proportional to the octanol/water partition coefficient and predictable, these results provide guidelines for the types and polarities of analytes amenable to this technique.

Introduction

In recent years the sophistication of food packaging materials has increased dramatically, including the development of multilayer laminate films, microwaveable containers, and coatings for rigid containers. Potential indirect food additives originating in the packaging material include residual monomers, plasticizers, antioxidants, decomposition products, and catalyst residues. For new food-contact materials that are not covered by existing regulation, a no-migration position can be established by showing the packaging component is not detectable in food with a method with a LOD typically in the 1-50 ppb range.

When designing appropriate food migration testing protocols, particularly for plastic packaging materials, guidelines for the conditions and duration of exposure are found in 21 CFR 177 in the FDA Code of Federal Regulations. Recommendations relating to testing protocols and data to be submitted as part of a petition for indirect food additives are also detailed in a document available from the FDA, Office of Premarket Approval, Center for Food Safety and Applied Nutrition [1].

For aqueous, acidic and low-alcohol foods 10% ethanol is now the recommended food simulant. In cases where this solvent may be expected to underestimate extraction levels, water and 3% acetic acid are preferred extraction solvents. For fatty foods, corn oil or synthetic food oils are the preferred solvents. In cases where analysis in oils is impractical, 50% or 95% ethanol are acceptable alternatives. Although these are much simpler matrices and minimize the potential for interference, developing reliable analytical methods for low ppb LOD can be challenging.

For analytes where GC is the preferred analytical tool, high water content solutions are problematic for direct liquid injection. Alternative approaches to eliminate matrix interference such as headspace GC will typically not provide the necessary detection limits. Recent publications demonstrated the utility of SPME for determining readily extracted compounds such as pesticides from all but the fatty food simulant [2,3]. Interference from ethanol and other extractables in the sample coupled with the limited capacity of the SPME fiber can prevent successful SPME method development.

Stir Bar Sorptive Extraction (SBSE) followed by thermal desorption GC has been shown to provide detection limits in the low ppb- ppt range for nonpolar analytes. Polar matrix components such as ethanol or acetic acid do not partition significantly into the PDMS phase on the stir bar, minimizing potential interference during analysis. This technique can potentially expand the range of compounds for which methods can be developed, and provide lower detection limits where necessary, such as for potential carcinogens.

Methyl esters were used as model compounds spanning a wide polarity range. Food simulating solvents were spiked at ppb levels and extracted by SBSE using Gerstel Twister stir bars. Recovery from the solutions was determined by thermal desorption GC. Since partitioning into the PDMS phase is proportional to the octanol/water partition coefficient and predictable, these results provide guidelines for the types and polarities of analytes amenable to this technique. To verify the predictions, a range of compounds often present in plastic packaging materials were spiked into the food simulants at low µg/L (ppb) levels and determined by SBSE and thermal desorption GC.

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).

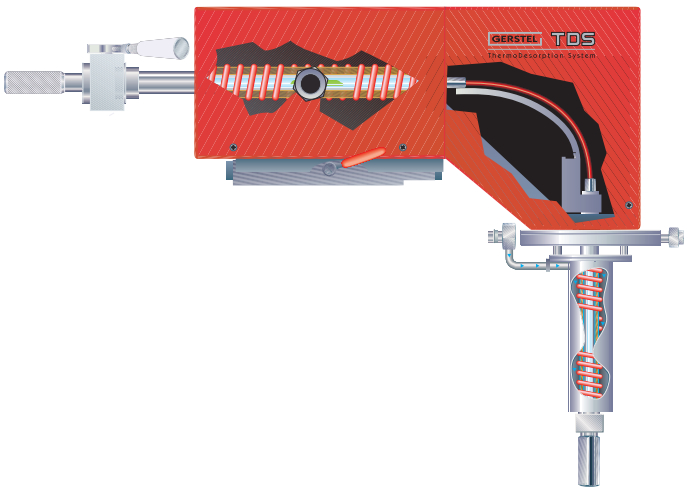

Figure 1. Gerstel TDS 2 ThermoDesorption System.

Analysis Conditions.

Column:	30m HP-5 (Agilent),
	d_i= 0.25mm, d_f= 0.25mm
Pneumatics:	He, P_i= 9.01 psi (MSD),
	P_i= 13.2 psi (FID)
	Constant flow = 1.2 mL/min
Oven:	40°C (2 min), 10°C/min,
	280°C (5 min)
PTV	split ratio 30:1
	250°C

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 see figure legends
	-120°C, 12°C/s, 280°C (3 min)

Sample Preparation.

Twister extraction. Samples were prepared at either 1.0, 50 or 100 µg/L in 10 mLs of H_2O, 10% ethanol, 95% ethanol and 3% acetic acid. The samples diluted into 95% ethanol were further diluted 1:10 in HPLC grade H_2O prior to extraction. 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.

Results and Discussion

Predicting Analyte Recovery from Food Simulants. One of the benefits of using a PDMS phase for sample extraction is that analyte partitioning from water is proportional to the octanol:water partition coefficient (Kow). This allows an estimation of analyte recovery from aqueous solution, and predictions of the approximate detection limits that will be achievable from a given sample size.

The presence of other organic solvents during the extraction can be expected to reduce analyte partitioning into the PDMS phase. The magnitude of the effect will be related to the polarity and concentration of the solvent, and the polarity of the analytes of interest. Since previous studies suggested SBSE with the Gerstel Twister was effective for samples containing alcohol [4], we expected that the food simulants 3% acetic acid and 10% ethanol would be directly amenable to Twister extraction. The fatty food simulant 95% ethanol, on the other hand, can be diluted 1:10 reducing the ethanol concentration to 9.5%.

To estimate the effect the presence of the food simulant will have on analyte recovery, we chose a series of short-chain methyl esters spanning a wide polarity range (Table 1). The octanol:water partition coefficients were estimated using a software program

Table 1. Methyl ester & target compound data.

Model compounds	Target compounds	Log Kow	Est. recov. [%]
	Butanal	0.82	1.6
	Pentanal	1.31	4.7
Methyl butyrate		1.36	5.2
	Hexanal	1.80	13
Methyl pentanoate		1.85	14
Methyl hexanoate		2.34	34
	Methyl salicylate	2.60	49
	Diethyl phthalate	2.65	52
Methyl heptanoate		2.85	63
Styrene		2.89	65
	Benzophenone	3.15	77
Methyl octanoate		3.32	83
Methyl nonanoate		3.81	94
Methyl decanoate		4.30	98

(KOWIN, Syracuse Research Corp., North Syracuse, NY) that uses “fragment constant” methodology to predict log(Kow). The estimated percent recovery was based on the predicted analyte distribution at equilibrium between the aqueous and PDMS phases. Sample volume was 10 mL, and PDMS volume was estimated at 24 µL.

Figure 2 shows a typical chromatogram of the C4-C10 ester test mix extracted from 10% ethanol with a Twister stir bar. For comparison, it is overlaid with the same ester mix, spiked onto a Tenax TA adsorbent tube where no discrimination due to PDMS partitioning occurs. This mix contains equal concentrations of all esters therefore ideally all peak areas should be the same. The slight reduction in the early peaks in the Tenax TA control sample is due to more difficulty in trapping the lower boiling esters during desorption.

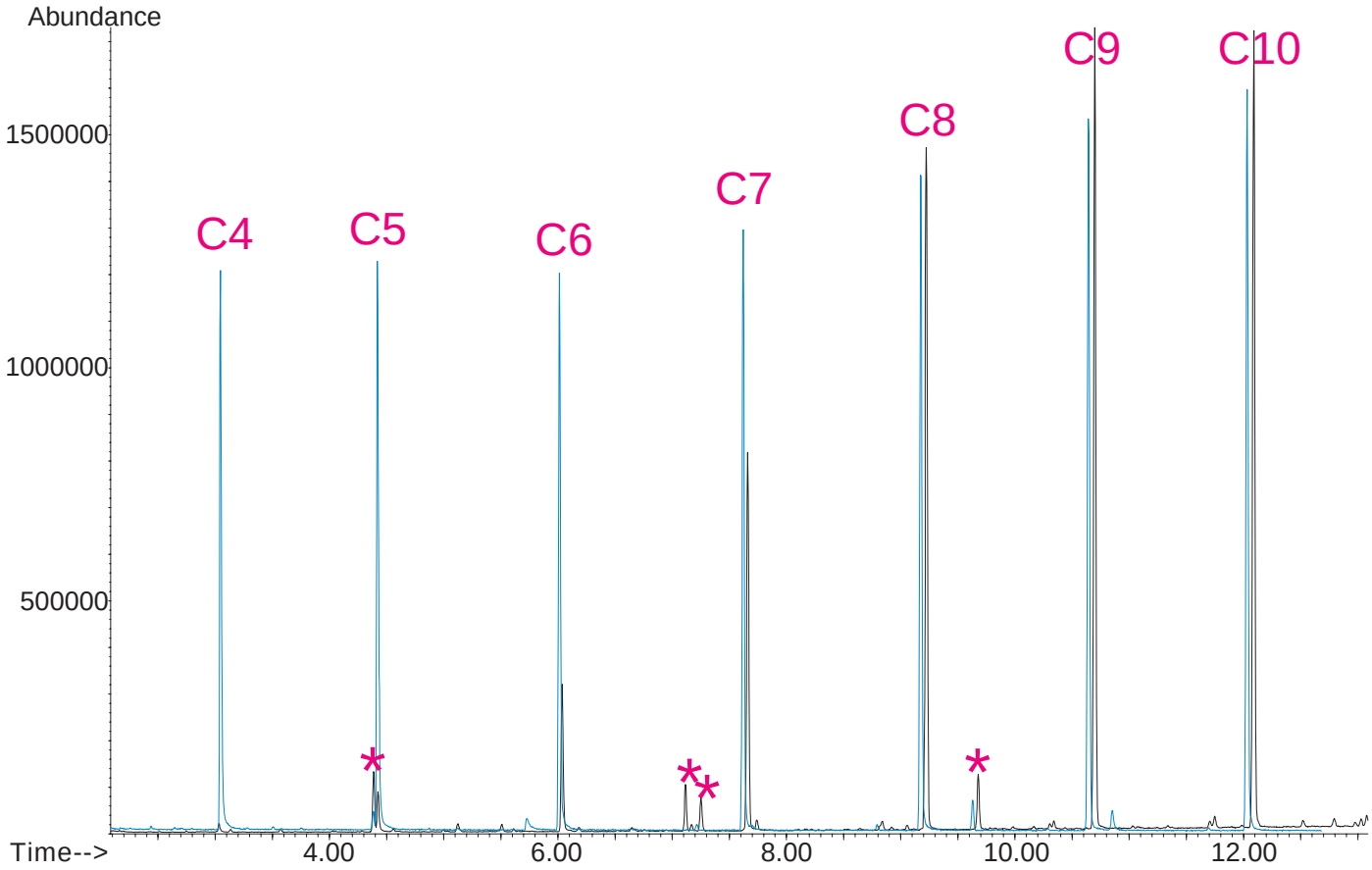

Figure 2. Total ion chromatogram of 50 µg/L methyl esters extracted from 10% ethanol by SBSE, 30:1 split. Peaks indicated by (*) are typical siloxane peaks from Twister PDMS phase. Control (blue): overlay of esters spiked onto Tenax TA adsorbent tube.

The short-chain esters do not partition as strongly into the stir bar as the long-chain esters, giving lower initial extracted mass. As long as partitioning and trapping are reproducible, normal calibration routines correct for these differences between analytes.

Figure 3 shows a comparison of the recovery of the esters from 50 µg/L solutions in water and the three food simulating solvents. The longer chain esters are nearly unaffected by the presence of the organic solvent, whereas recovery of the shortest chain esters from the food simulants is reduced by 50% or more. In the case of 95% ethanol, the methyl butyrate was undetectable under our test conditions. Based on these results, it appears that esters from methyl hexanoate (log Kow = 2.34) and higher will be well recovered from food simulating solvents.

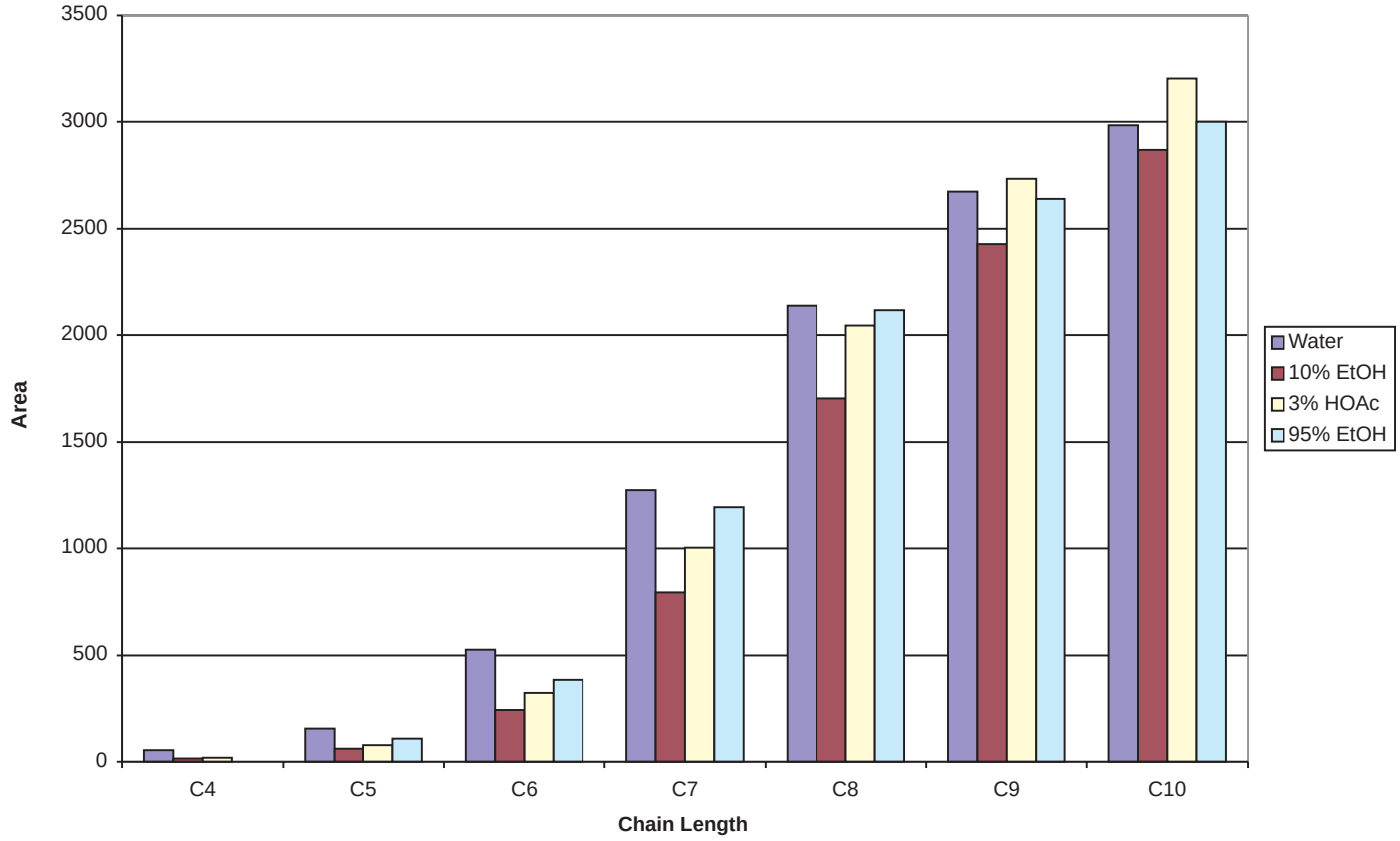

Figure 3. Recovery of C4-C10 methyl esters from food simulating solvents. Note: 95% ethanol peak area x 10 for comparison.

Target compound recovery. To test this conclusion, we selected a list of target compounds with octanol:water partition coefficients spanning the critical region identified in the methyl ester model study (Table 1). These compounds are typical of species that might be monitored as potential indirect food additives from plastic packaging materials.

Figure 4 shows an example chromatogram obtained after extraction from 10% ethanol for the target compounds with log Kow values greater than 2.34. Note that the size of the peaks obtained correlates with expectations based on the log Kow: methyl salicylate and diethyl phthalate are similar, styrene slightly larger, and benzophenone substantially larger due to higher recovery. All peaks are easily detectable at the 50 µg/L level. Figure 5 shows an extracted ion chromatogram of the same sample mix at 1 µg/L, illustrating the potential to achieve much lower detection limits, if necessary.

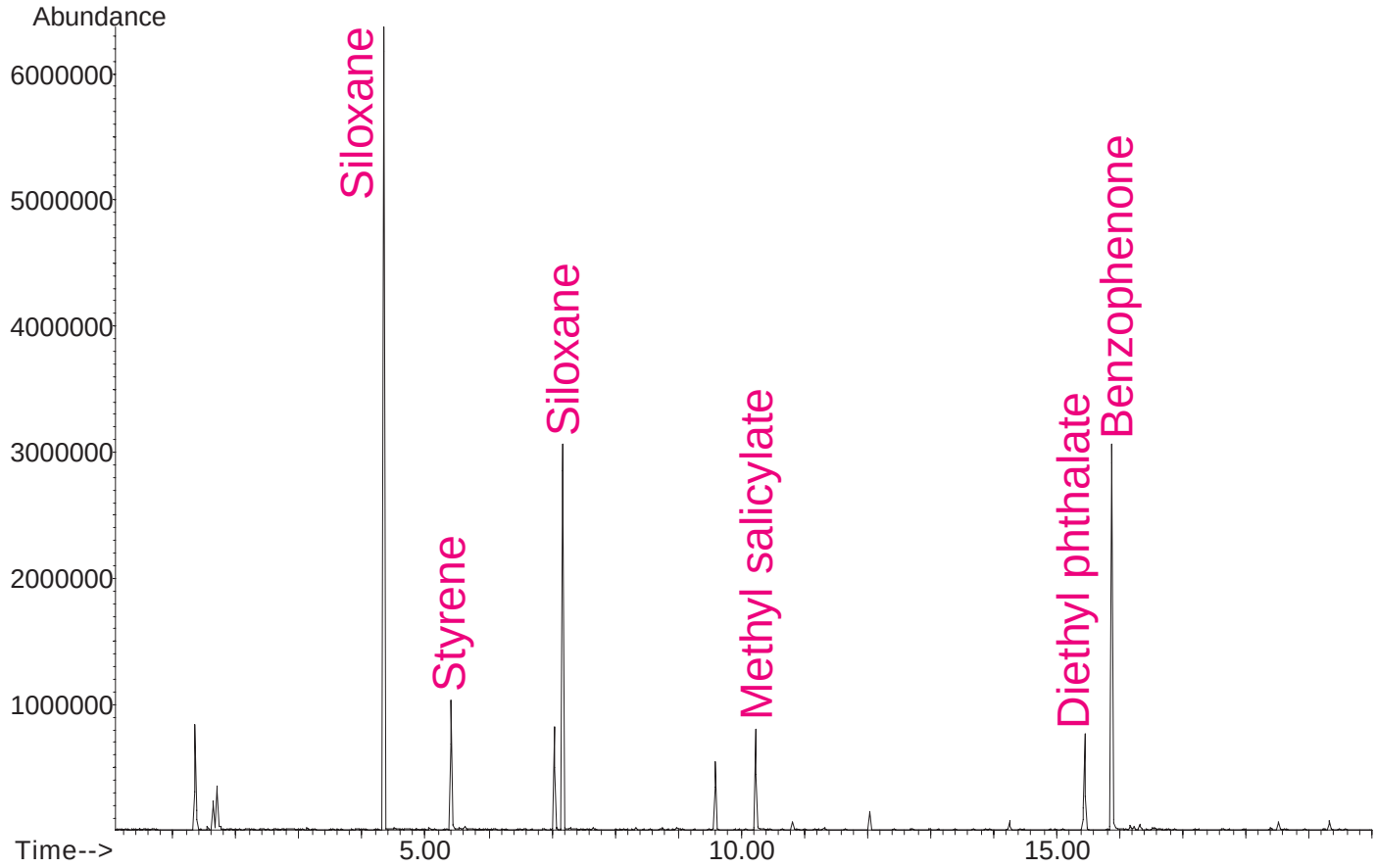

Figure 4. Total ion chromatogram of 50 µg/L target compounds extracted from 10% ethanol, 20:1 split.

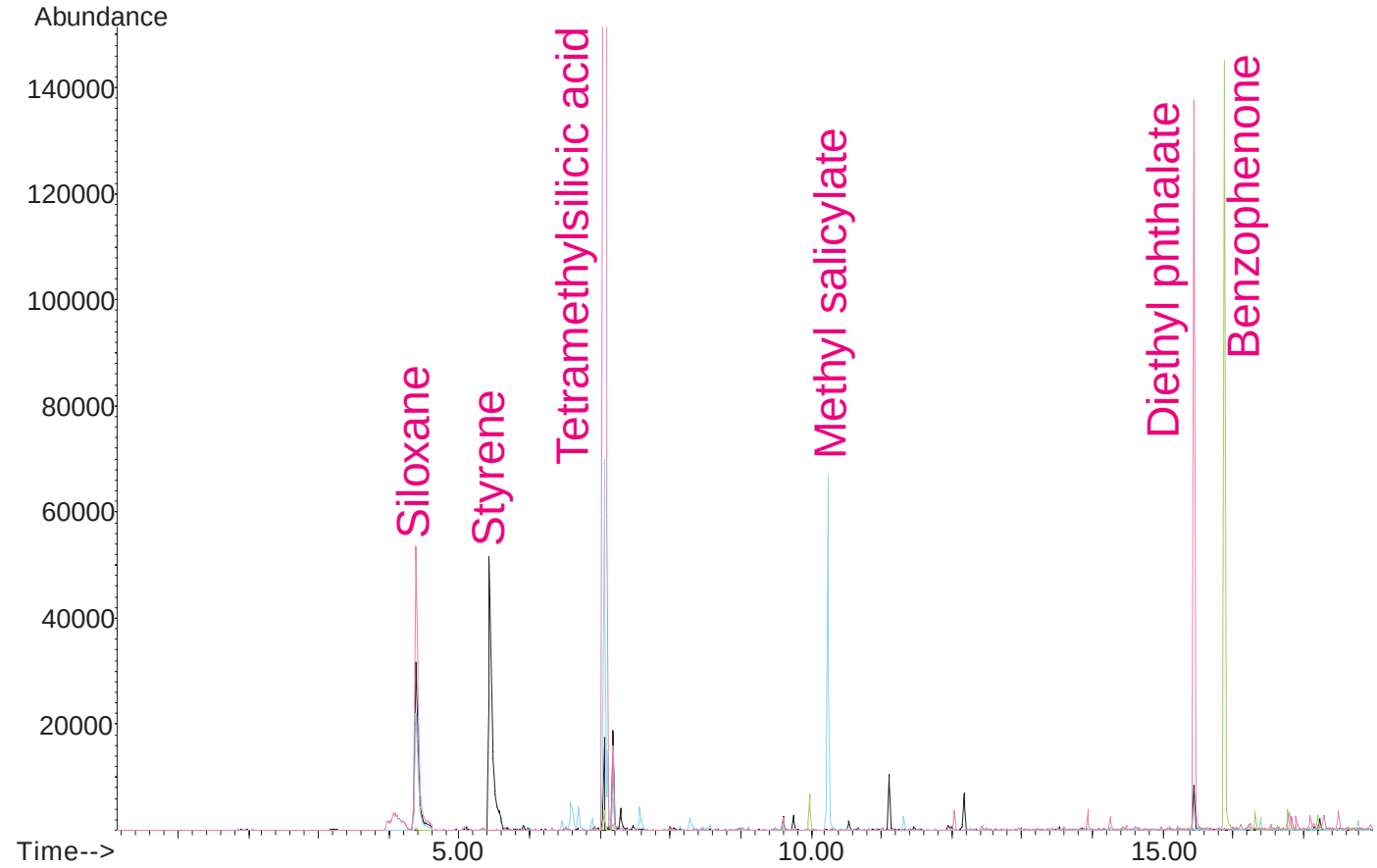

Figure 5. Extracted ion chromatogram of 1 µg/L target compounds extracted from 10% ethanol by SBSE, splitless.

Figure 6 shows an overlay of chromatograms obtained after extraction from water, 10% ethanol and 3% acetic acid for the target compounds with log Kow values lower than 2.34. These relatively polar compounds were not detectable when spiked at ppb levels into 95% ethanol and diluted 1:10 to reduce the ethanol concentration to <10%. Pentanal and hexanal are readily detectable at 100 µg/L in both water and 10% ethanol, but butanal is barely detectable in water and undetectable in either 10% ethanol or 3% acetic acid. Background interference from esters in the 3% acetic acid solution were problematic, and prevented the direct determination of hexanal.

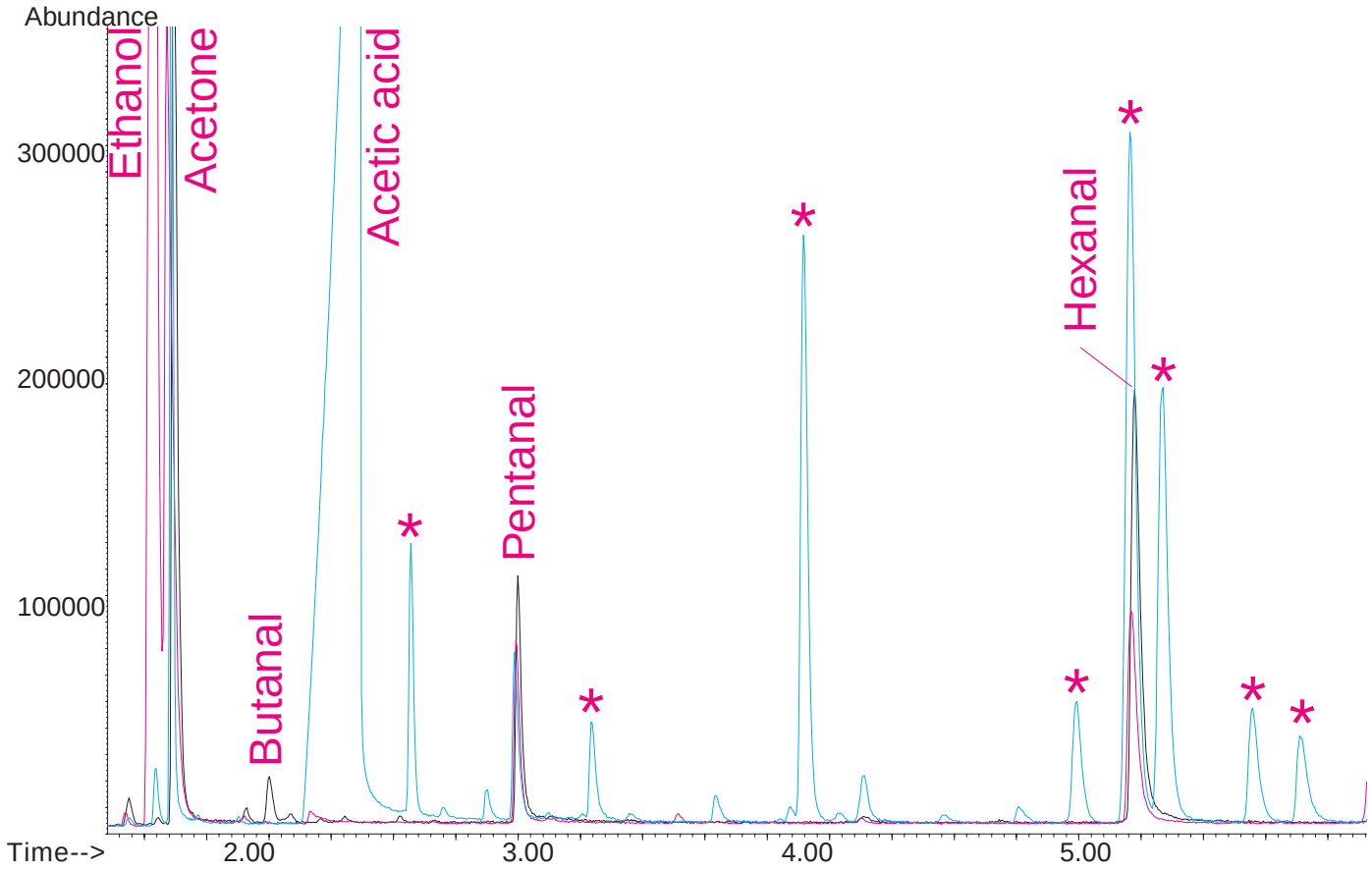

Figure 6. Overlay of total ion chromatograms of 100 µg/L short chain aldehydes extracted from water, 10% ethanol and 3% acetic acid by SBSE, 20:1 split. Oven program: 40°C (5 min), 10°C/min (180°C). Peaks with (*) are background ester contaminants in acetic acid.

Detection Limits and Precision. Table 2 summarizes the approximate detection limits obtained from water and food simulants for the compounds tested.

To illustrate the reproducibility of Twister extraction from food simulants, analytes were spiked at levels indicated in Table 2. 10 mL aliquots were extracted with different Twister stir bars for 90 minutes at room temperature. Precision was generally excellent with %RSD typically less than 4%. Styrene gave the highest, but still reasonable, variability in all simulants tested.

Table 2. Results- Detection limits and precision.

Compound	DL (estimated)[µg/L]				Precision [%RSD]			
	Water	10% EtOH	3% HOAc	95% EtOH	Water	10% EtOH	3% HOAc	95% EtOH
Butanal	50	250	250	2500				
Pentanal[1]	10	50	50	500		5.2		
Methyl butyrate[2]	5	20	20	200	4.2			
Hexanal[1]	1	4	4	40		6.7		
Methyl pentanoate[2]	1	4	4	40	1.4			
Methyl hexanoate[2]	1	2	2	20	1.3			
Methyl salicylate[3]	1	2	2	20	1.4	2.1	4.6	5.2
Diethyl phthalate[3]	1	2	2	20	2.9	3.5	7.6	8.5
Methyl heptanoate[2]	1	1	2	10	1.6			
Styrene[3]	1	1	2	10	7.7	5.4	11.8	8.8
Benzophenone[3]	0.5	1	1	10	1.1	2.1	3.0	5.2
Methyl octanoate[2]	0.1	0.1	0.1	1	2.4			
Methyl nonanoate[2]	0.1	0.1	0.1	1	3.0			
Methyl decanoate[2]	0.1	0.1	0.1	1	3.6			

For precision data: [1] 100 µg/L, n = 4; [2] 100 µg/L, n = 5; [3] 50 µg/L, n = 7

CONCLUSIONS

- Octanol:water partition coefficients (Kow) are widely used to estimate lipophilicity of organic compounds. When performing Twister extractions, the Kow can also be used to estimate analyte recovery and approximate detection limits in water.
- Compounds with log (Kow) greater than 2.3 can typically be detected at 1 ppb or lower in water. Detection limits in moderately polar food simulants (10% ethanol and 3% acetic acid) will be approximately 2x higher for compounds with log(Kow) <2.3.
- Detection limits in fatty food simulants (95% ethanol) will be at least 10x higher than in water due to the need to dilute the sample 10-fold to reduce ethanol concentration to <10%.
- Excellent precision can be obtained using Twister extraction from food simulants; typical %RSD should be <5%.

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