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Qualitative Analysis of Coconut Water Products using Stir Bar Sorptive Extraction Combined with Thermal Desorption-GC/MS

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Abstract
This study shows the analysis of several commercially available coconut water products using a GC/MS system equipped with a versatile autosampler and sample preparation robot capable of performing a wide range of standard sample introduction techniques including thermal desorption. A fast and efficient analysis method based on stir bar sorptive extraction (SBSE) in combination with thermal desorption -GC/MS was developed for the determination of flavor compounds, pesticides, antioxidants, compounds migration from packaging materials, and off-flavors in coconut water.

Introduction
Coconut water is a clear isotonic solution made from young coconuts. It is a popular drink in tropical regions, and is currently gaining popularity in the US as a sports and health drink due to its high mineral and potassium content and antioxidant properties. Antioxidant properties of foods have been linked to many different classes of compounds including polyphenols, acids, aldehydes, esters, and aromatic compounds. Many of these can be found in coconut water.

The purpose of the work presented here was to investigate and document the usefulness of stir bar sorptive extraction

(SBSE) in combination with thermal desorption and GC/MS for the determination various classes of compounds in coconut water including antioxidants, residual pesticides and herbicides, plasticizers that might migrate from the food packaging used, flavor compounds, and potential off flavors.

A fast and efficient analysis method based on stir bar sorptive extraction (SBSE) in combination with thermal desorption -GC/MS was developed for the analysis of coconut water based on the GERSTEL MultiPurpose Sampler (MPS) in combination with the GERSTEL Thermal Desorption Unit (TDU) and a programmable temperature vaporizer (PTV) inlet, the GERSTEL CIS 4. The GERSTEL TDU is a highly flexible thermal desorber that can accommodate both liquid and solid samples as well as adsorbent tubes and Twister stir bars placed in TDU liners. Sample introduction in combination with Stir Bar Sorptive Extraction (SBSE) is shown in Figure 1. An enhanced view of a Twister inside a TDU liner is shown in Figure 2.

Figure 1. GERSTEL MultiPurpose Autosampler (MPS) with GERSTEL Thermal Desorption Unit (TDU) setup.

Figure 2. GERSTEL Twister in TDU tube.

This system provides the user with the ability to perform thermal desorption, direct thermal extraction and Stir Bar Sorptive Extraction (SBSE) using the GERSTEL Twister. The use of the Twister in combination with this configuration helps minimize or eliminate the use of solvents for extraction, while reducing sample preparation time, and minimizing the need for sample preparation equipment when performing GC/MS analysis.

Experimental

Instrumentation. Analyses were performed on a 7890 GC combined with a 5975C Inert XL MSD with triple axis detector (Agilent Technologies). The GC/MS system was configured with a Cooled Injection System (CIS 4) PTV-type inlet, Thermal desorption Unit (TDU) and MultiPurpose Sampler (MPS) with 10 μL ATEX syringe (All GERSTEL).

Analysis conditions.

TDU:	splitless	
	35°C, 720°C/min, 280°C (3 min)	
PTV:	splitless (1.2 min)	
	-120°C (0.2 min), 12°C/sec,	
	275°C (3 min)	
Column:	30 m Rxi®-5Sil MS (Restek),	
	d_i = 0.25 mm	d_f = 0.25 μm
Pneumatics:	He, constant flow (1.2 mL/min)	
Oven:	40°C (1 min), 10°C/min,	
	300°C (3 min)	
MSD:	Full scan, 50-450 amu	

Standard preparation. A stock solution of 20 organophosphorus pesticides was prepared at a concentration of 100 ng/mL in hexane. The pesticide standard was diluted to obtain a concentration of 1 ng/mL in 10 mL coconut water.

Sample preparation. Coconut water samples were purchased at a local store. 10 mL samples of undiluted coconut water were pipetted into 10 mL vials. A conditioned Twister was added to each vial. The vials were screw capped, and the samples stirred at room temperature for 90 minutes. Twisters were rinsed with water, dried and placed in an empty TDU tube. The TDU tube was capped with a transport adapter and placed into a 98 position VT-98t tray.

Results and Discussion

Figure 3 shows total ion chromatograms of three brands of natural coconut water. The samples contain a wide array of ketones, aldehydes, acids, esters, and lactones. Good sensitivity was achieved for the identified compounds listed in the figure using full scan mode. The levels of octanoic, decanoic and dodecanoic acids varied significantly between the different brands of coconut water, as did some key flavor compounds such as isoamyl acetate and gamma-decalactone. The significant differences in acid content may be caused by differences in processing and storage or due to different types of coconuts used. The phthalates present were probably introduced through migration from packaging material.

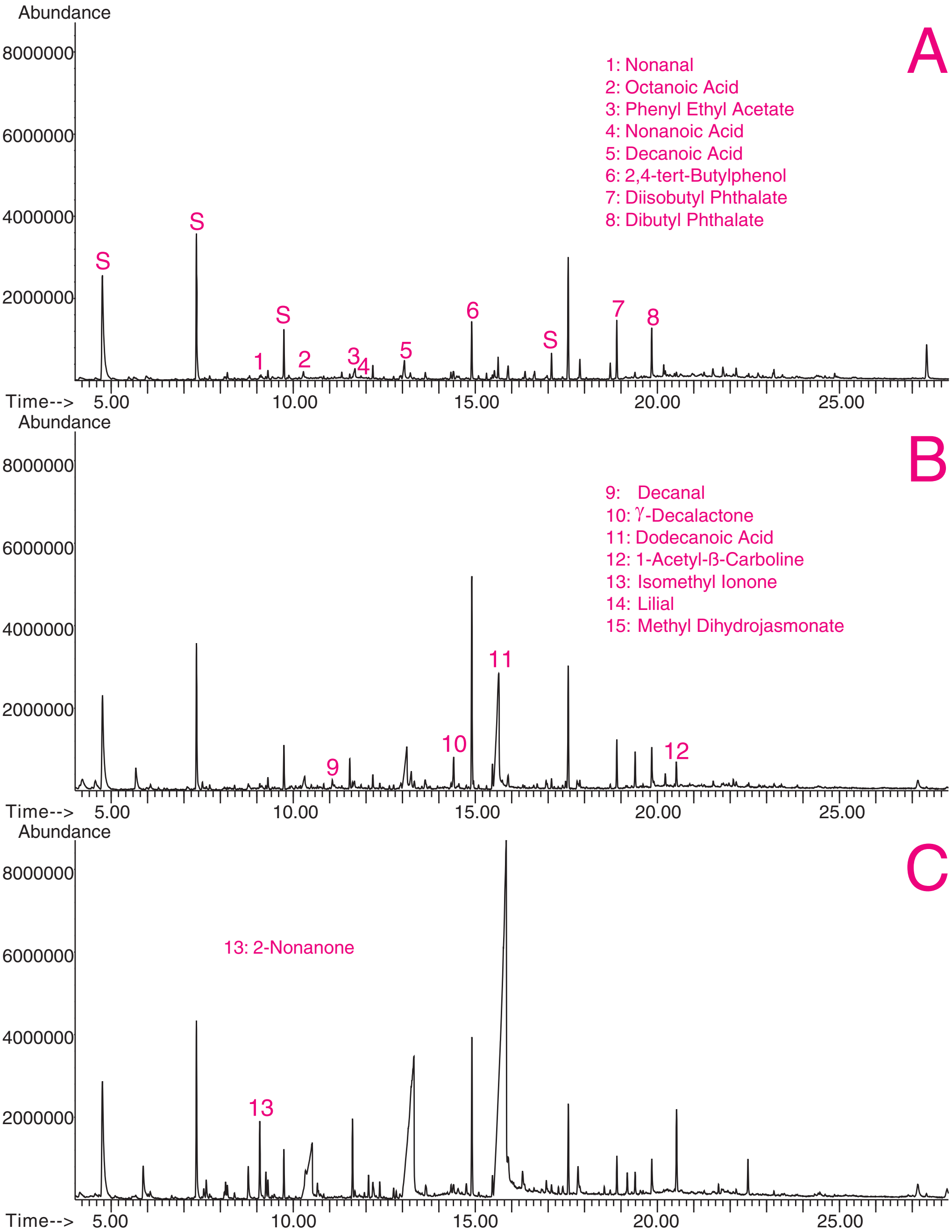

Figure 3. Total ion chromatograms resulting from SBSE of 3 brands of natural coconut water (A, B, and C).

Flavored coconut waters are also commercially available. Three flavored and one natural coconut water product, all from the same manufacturer, were purchased at a local store. The flavored coconut waters include as ingredients: Stevia leaf extract, black carrot extract, beta-carotene, grape juice, as well as “natural flavors”. Figure 4 shows the total ion chromatograms for three flavored and natural coconut water. The major flavor ingredients are clearly seen as major peaks in the respective chromatograms. In the grape-berry flavored drink, methyl anthranilate and dimethyl anthranilate impart the grape flavor. In the cranberry-grapefruit water, ethyl cinnamate and nootkatone contribute to the berry and grapefruit flavors, respectively. In the lemon-lime flavored water, several terpenes, such as limonene and linalool, contribute to the flavor. All three flavored coconut waters contain triethyl citrate, commonly added as a stabilizer. Several other compounds, such as osthol, auraptene, and isopimpinellin, are most likely from the plant extracts added to these products.

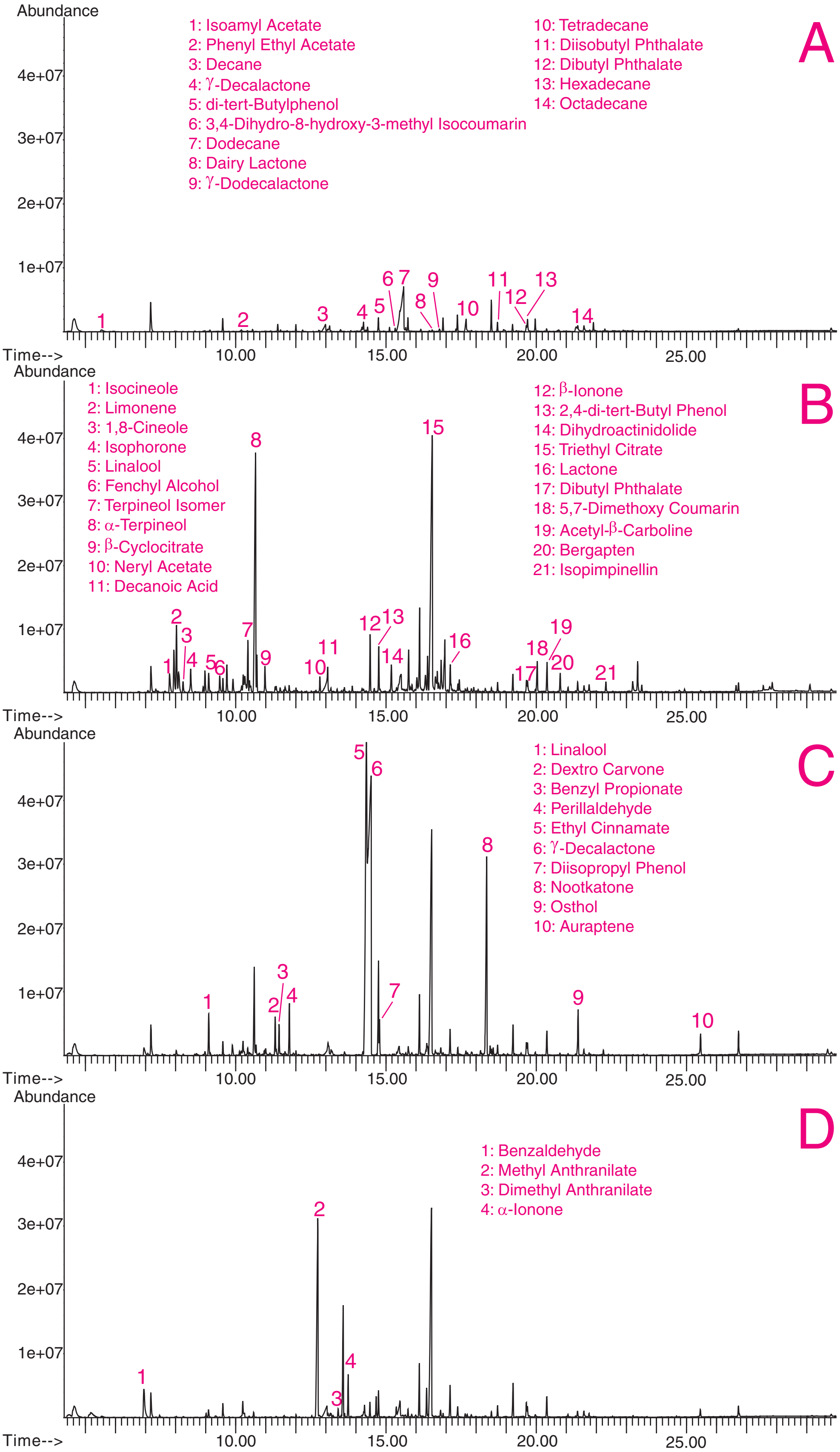

Figure 4. Total ion chromatograms of four types of coconut water. A: natural, B: lemon-lime flavored, C: cranberry-grapefruit flavored, D: grape-berry flavored.

SBSE is a powerful extraction technique for compounds with a high octanol to water partition coefficient (log kow). For compounds with lower octanol/water partition coefficients, techniques such as salting out or pH adjustment can enhance extractability. Figure 5 shows the total ion chromatograms of the berry flavored coconut water extracted with and without the addition of 30% NaCl. An increase in response can be seen for several classes of compounds extracted in the coconut water containing 30% NaCl.

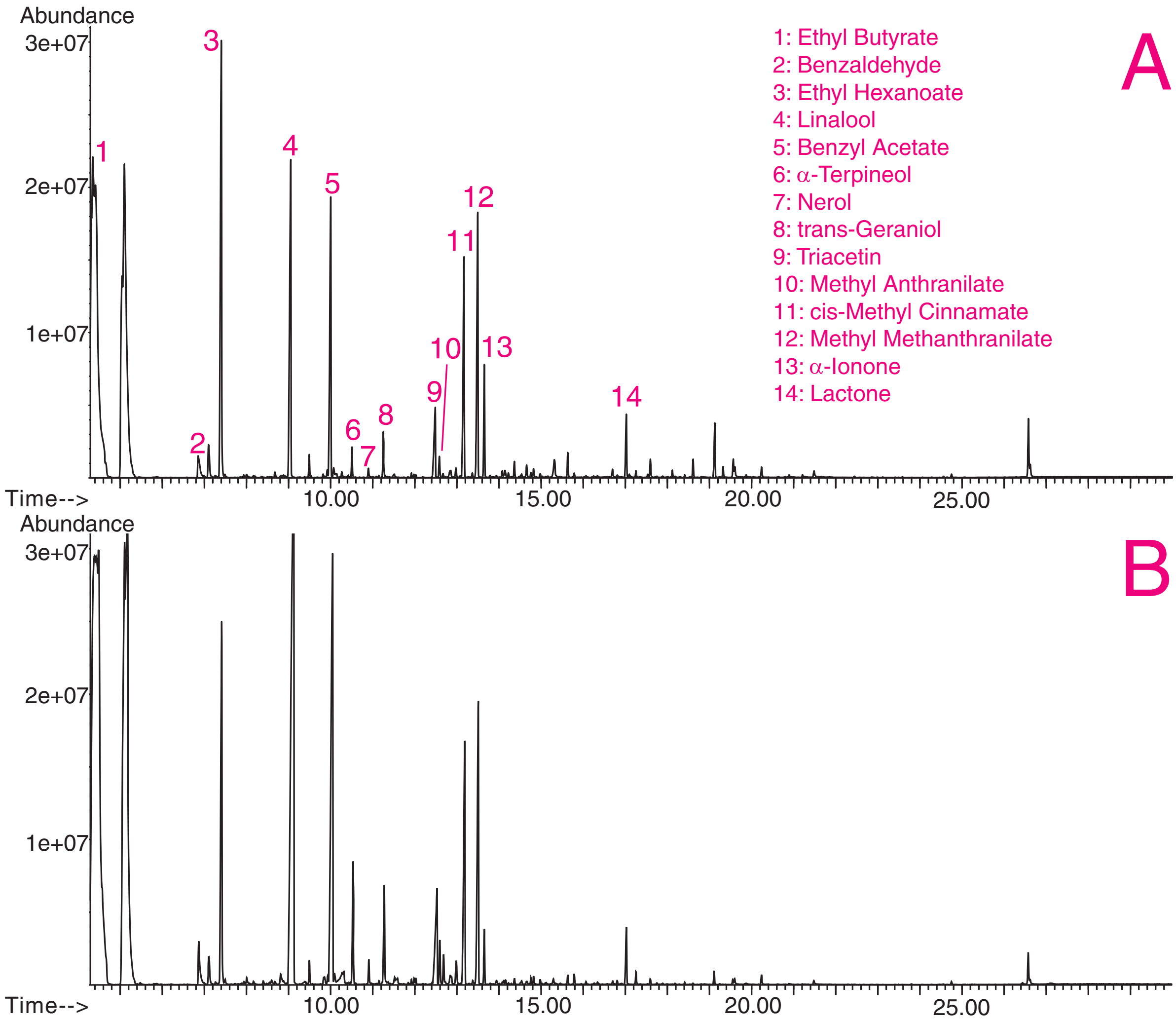

Figure 5. Total ion chromatograms of berry flavored coconut water with 30% NaCl (B) and without NaCl (A).

Food safety is an increasing concern for consumers. Migration of compounds from packaging materials, residual pesticides and herbicides, and other compounds causing off-odor/flavors or potential health risks are of interest. To demonstrate the applicability of SBSE for this type of analysis, a mix of twenty pesticides was spiked into the coconut water. Figure 6 shows an overlay of three replicates of the total ion chromatograms of natural coconut water spiked with 1 ppb pesticides. The sensitivity and precision of the analysis was good. The inset shows an enhanced view for Disulfoton. The results are listed in Table 1. The % RSDs for n=3 ranged from 2.5-17%.

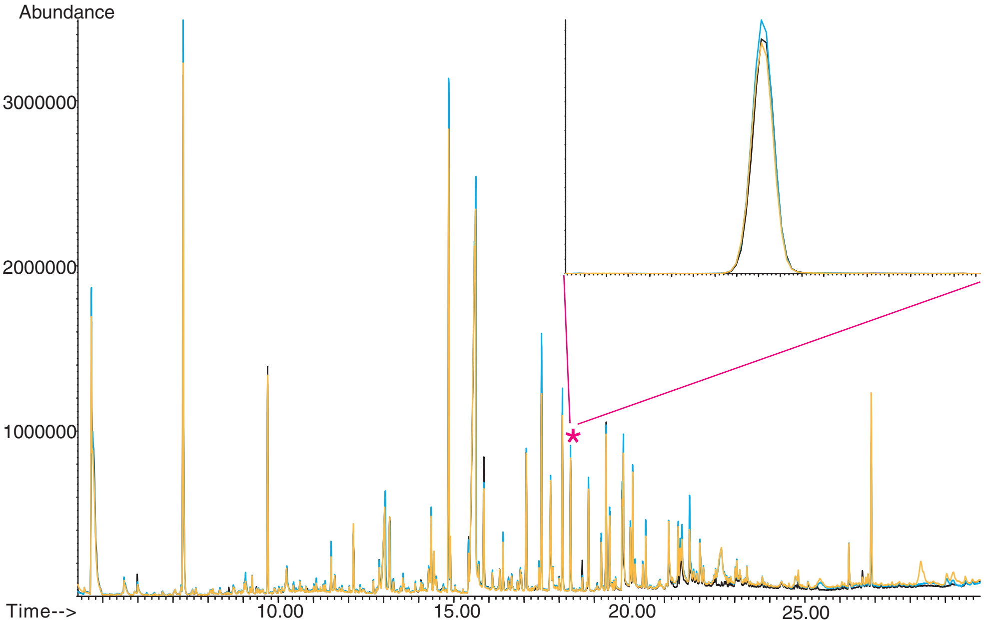

Figure 6. Overlay of six replicate total ion chromatograms following individual SBSE extractions of natural coconut water spiked with 1 ppb organo-phosphorous (OP) pesticides.

To achieve more mass on column and better sensitivity, the Multi-Desorption Mode feature within the GERSTEL Maestro software was used, desorbing and concentrating analytes from multiple Twisters for each GC/MS run. The number of desorptions performed is defined by selecting a vial range in the Chemstation Sequence table. To illustrate the benefit of using this technique, multiple samples of coconut water spiked to a level of 1 ppb with the pesticide mix were extracted using SBSE. Four Twisters were subsequently desorbed in multi-desorption mode. The resulting GC/MS chromatogram compared with the GC/MS chromatogram from the desorption of a single Twister. The chromatograms are shown in Figure 7. A comparison of peak area ratios achieved are listed in Table 1. The expected four-fold increase in sensitivity is seen for most of the analytes, the peak area ratios range from 3.1 to 4.7.

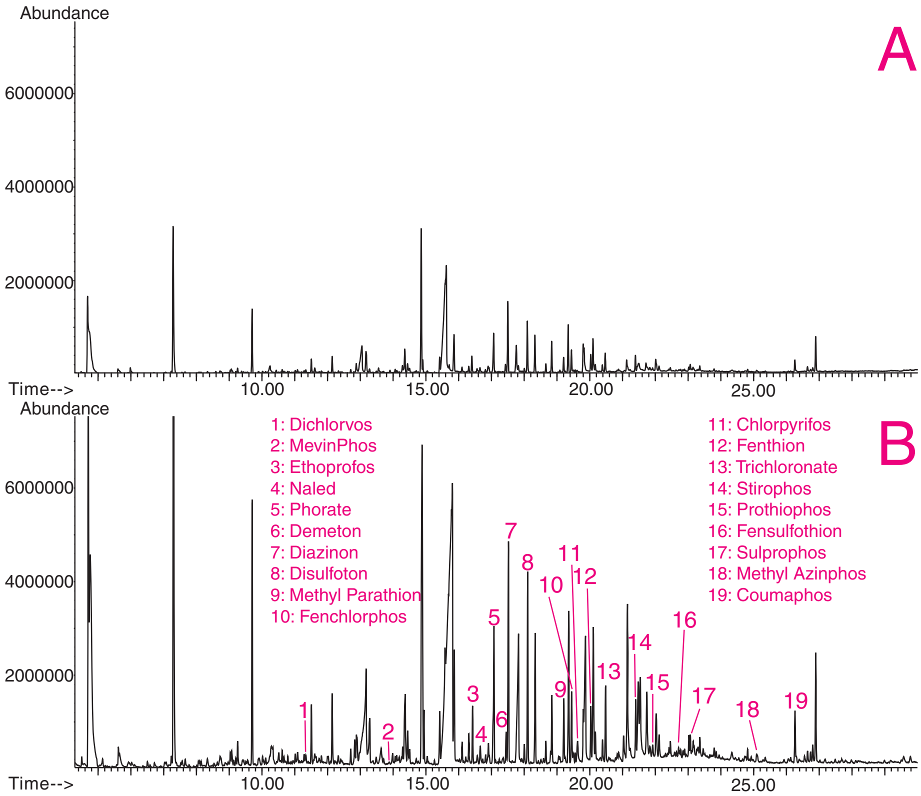

Figure 7. Stacked view of total ion chromatograms resulting from the desorption of one (A) and four Twisters (B) following extractions of coconut water samples spiked with pesticides at the 1 ppb level.

Table 1. %RSDs and ratios between the peak areas resulting from Multi-Desorption mode with four Twisters and from single Twister desorption for each GC/MS run. Sample: natural coconut water spiked with 1 ppb OP pesticides

Compound	Quant Ion	RSD [%]	Area Ratio
Dichlorvos	109	16.7	4.7
Ethoprophos	158	9.4	3.6
Phorate	121	2.4	1.5
Diazinon	179	3.9	3.6
Disulfoton	88	4.4	3.4
Methyl parathion	109	8.9	4.5
Fenchlorphos	285	4.5	3.2
Chlorpyrifos	314	5.0	3.3
Fenthion	278	4.6	4.2
Trichloronate	109	7.5	3.1
Stirophos	329	4.3	4.0
Prothiophos	309	4.5	3.5
Sulprofos	322	4.4	3.6
Methyl Azinphos	160	5.5	3.8
Coumaphos	362	3.3	4.4

Conclusions

Stir Bar Sorptive Extraction (SBSE) provides an easy and reliable method for extraction of coconut water beverages and similar samples for subsequent introduction of a range of analytes into GC/MS using thermal desorption. The GERSTEL MPS/TDU/CIS combination provides a versatile platform for this purpose. Stir bar sorptive extraction (SBSE) shows good precision and sensitivity for the analysis of contaminants, flavor constituents, and other compound groups found in “natural” drinks.

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