



Over the past few years, stir bar sorptive extraction (SBSE) [1] using stir bars coated with polydimethylsiloxane (PDMS), has been successfully applied to trace analysis of organic compounds in various sample matrices such as water, soil, food, beverages and biological fluids [2-4]. The PDMS coated stir bars are commercially available from GERSTEL under the name Twister®. Several authors have indicated that SBSE provides high recovery and extremely low limits of detection (LOD) at the sub-ng/L level, particularly for hydrophobic solutes [2-4].

6 times faster screening of pesticide multi-residues in aqueous samples

Take Two!

SBSE can be performed in parallel on two aliquots of the same sample under different extraction conditions using two Twisters. Using this dual Twister approach, the two extractions can be optimized individually: For aqueous samples [6], one extraction can be optimized for hydrophilic solutes with salt addition [7, 8] and the other extraction can be optimized for more hydrophobic solutes with addition of an organic solvent such as methanol [9]. After extraction, the two Twisters can be simultaneously desorbed using a thermal desorption system. Dual SBSE has previously been proposed for multiresidue screening of pesticides in food samples such as vegetables, fruits and green tea [5].

SBSE methods involve batch sample preparation (parallel extraction of up to 60 samples on one stir-plate, typically for 1 hour) and sequential analysis (separation and detection); sample throughput is mainly determined by the separation step. SBSE methods can therefore

provide high sample throughput when combined with Fast GC.

A Fast GC system with direct resistive heating is commercially available in which a capillary column is enclosed in a resistively heated toroid-formed assembly (Low thermal mass GC [10]) The system is available under the name of Modular Accelerated Column Heater (MACH). The MACH system provides fast temperature programming rates combined with rapid cool-down and short equilibration times for shortest possible analytical cycle times. Using the MACH system, a maximal heating rate of 30 °C/s can be achieved, cool-down from 400 °C to 100 °C typically takes less than one minute [10]. The MACH system can be directly integrated with Agilent GC instruments to allow full use of conventional injectors, detectors, sampling systems, and software. We recently optimized and validated a dual

Twister method for both polar pesticides with low K_{ow} , and apolar pesticides with high K_{ow} , at very low levels (sub- $\mu\text{g/L}$) in aqueous samples. Dual Twister analysis was performed in combination with a MACH Fast GC/MS system and a quadrupole MS providing maximum



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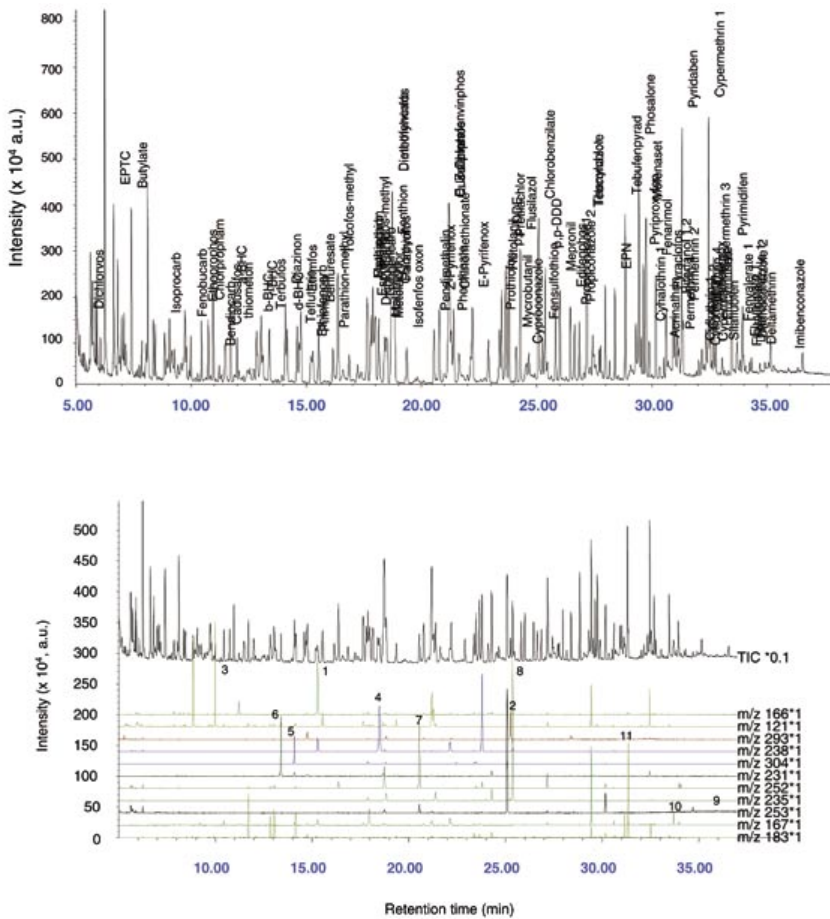
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sample throughput. The principle and potential of Dual Twister-Fast GC/MS is demonstrated in the following, using the determination of pesticides in river water and brewed green tea as examples.

Experimental

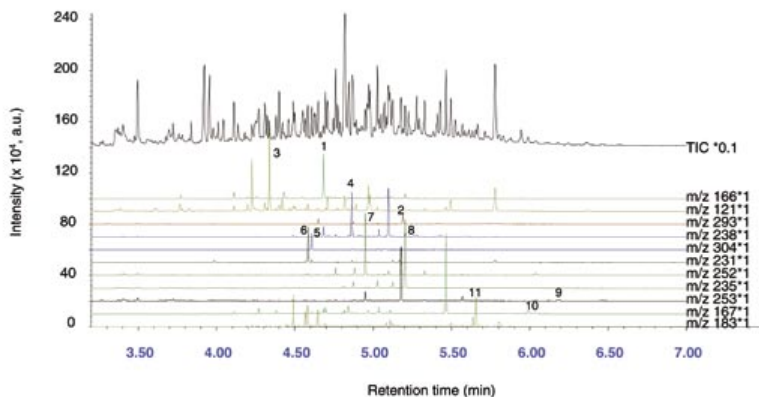
The dual Twister procedure works as follows: Two 20 mL aliquots of a sample, containing 30 % NaCl or 0-20 % methanol

Figure 1: Total ion chromatogram obtained by Dual SBSE-TD-RTL GC/MS of a river water sample spiked with 82 pesticides at 500 ng/L level.



- 1. Pirimicarb ($\log K_{ow} = 1.70$); 2. Fensulfotthion ($\log K_{ow} = 2.35$); 3. Fenobucarb ($\log K_{ow} = 2.79$); 4. Metolachlor ($\log K_{ow} = 3.24$);
- 5. Diazinon ($\log K_{ow} = 3.86$); 6. Terbufos ($\log K_{ow} = 4.24$); 7. Pendimethalin ($\log K_{ow} = 5.18$); 8. p,p-DDD ($\log K_{ow} = 5.87$);
- 9. Deltamethrin ($\log K_{ow} = 6.18$); 10. Cyhalothrin 1,2 ($\log K_{ow} = 6.85$); 11. Permethrin 1,2 ($\log K_{ow} = 7.43$);

Figure 2: Total ion chromatogram and some representative mass chromatograms obtained by Dual SBSE-TD-LTM GC/MS of a river water sample spiked with 82 pesticides at 500 ng/L level.



- 1. Pirimicarb ($\log K_{ow} = 1.70$); 2. Fensulfotthion ($\log K_{ow} = 2.35$); 3. Fenobucarb ($\log K_{ow} = 2.79$); 4. Metolachlor ($\log K_{ow} = 3.24$);
- 5. Diazinon ($\log K_{ow} = 3.86$); 6. Terbufos ($\log K_{ow} = 4.24$); 7. Pendimethalin ($\log K_{ow} = 5.18$); 8. p,p-DDD ($\log K_{ow} = 5.87$);
- 9. Deltamethrin ($\log K_{ow} = 6.18$); 10. Cyhalothrin 1,2 ($\log K_{ow} = 6.85$); 11. Permethrin 1,2 ($\log K_{ow} = 7.43$);



respectively, were transferred to two 20 ml vials. A Twister was added to each vial and stirred for 60 min. The two Twisters were then simultaneously desorbed using a GERSTEL TDU thermal desorption system, programmed from 40 °C (1 min) at 720 °C/min to 280 °C (5 min) in splitless mode. The desorbed compounds were cryo-focused in a GERSTEL CIS 4 PTV inlet at -100 °C. The CIS 4 inlet, operated in splitless mode, was then programmed at 720 °C/min to 280 °C (5 min), thus transferring the analytes to the capillary column. The separation was performed on a DB-5 column (10 m x 0.18 mm i.d., 0.18 μm film thickness, Agilent Technologies), which was coiled and packaged tightly together with a heating wire, a sensor, and ceramic fibers in the MACH column module (wide format, 5 inch module). The column was connected to the GC inlet with a 1 m long, 0.32 mm i.d. fused deactivated silica capillary and to the MS detector with a 1m long, 0.18 mm i.d. fused deactivated silica capillary, using



< 12 %, n = 5). The compounds could be determined using a standard addition calibration method. A brewed green tea sample was found to contain pirimiphos-methyl ($K_{O/W} = 4.20$; 10 ng/L, RSD 7.8 %) and tebuconazole ($K_{O/W} = 3.89$; 240 ng/L, RSD 8.1 %).

Conclusion

Dual Twister Fast GC/MS was successfully applied to fast screening of pesticide multiresidues in aqueous samples. The proposed method has many practical advantages, for example high sensitivity, good linearity, remarkable precision and high sample throughput. Also, the method allowed the determination of ng/L levels of pesticides in river water and brewed green tea samples with very low Relative Standard Deviation in the range from 7.8 to 12 %.

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press-fit connectors on both sides. The column temperature was programmed from 40 °C (2 min) at 75 °C/min to 300 °C (2 min). Helium was used as carrier gas. The carrier gas pressure was programmed from 82 kPa (2 min) at 36 kPa/min to 207 kPa (held for 2 min), keeping the carrier gas approximately at a constant flow rate of 1.1 mL/min. The host GC oven (Agilent 6890 GC) and the MSD interface were kept at a constant temperature of 250 °C. The mass spectrometer (Agilent 5975 MSD) was operated in scan mode using electron-impact ionization (electron-accelerating voltage: 70V). The scan range was set from m/z 58 to 510 and sampling rate of zero, resulting in scan rate of 10.83 scan/s.

Results and Discussion

Figure 2 shows the total ion chromatogram (TIC) and some representative mass chromatograms obtained by Dual Twister-Fast GC/MS of spiked river water samples. 82 pesticides – organochlorine,

carbamate, organophosphorous, pyrethroid and others – spiked at 500 ng/L could be clearly determined. The method showed good linearity over the range 25–1000 ng/L ($r^2 > 0.9900$) and low LOD (< 10 ng/L; signal-to-noise ratio of 3:1) for most of the target pesticides. Using this method, the first and last compounds to elute were dichlorvos with a retention time of 3.722 min and imibenconazole with a retention time of 6.519 min, respectively. For comparison, the same compounds have retention times in conventional GC-MS analysis with retention time locking (RTL) of 5.829 min and 35.930 min, respectively, a factor of 5.5 longer for imibenconazole using the conventional RTL method, as seen in figure 1.

For river water samples, although fenobucarb ($K_{O/W} = 2.79$) and diazinon ($K_{O/W} = 3.86$) were present at ultra trace levels (16 and 4.9 ng/L, respectively), well defined mass chromatograms were obtained without interference from matrix compounds at acceptable precision (RSD

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