Screening of Pesticide Residues in Water by Sequential Stir Bar Sorptive Extraction-Thermal Desorption with GC/MS

Application Note

Food

Authors

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Abstract

The performance of sequential stir bar sorptive extraction (sequential SBSE) in combination with thermal desorption (TD)-GC/MS for screening of pesticide residues in water was described. Compared to conventional SBSE, sequential SBSE provides more uniform enrichment over the entire polarity and volatility range for organic pollutants at ultra trace levels in water. Sequential SBSE consists of an SBSE performed first on a 5-mL sample without modifier using one stir bar, then on the same sample after addition of 30% NaCl using a second stir bar. After extraction the two stir bars are placed in a single glass desorption liner and are thermally desorbed simultaneously. The presence of pesticide is elucidated with a retention time locked GC/MS method (RTL-GC/MS). Screening of pesticides at the ng/L level in river water samples was successfully carried out with sequential SBSE-TD-RTL-GC/MS operated in the scan mode.

Agilent Technologies

Introduction

The determination of pesticide residues in environmental samples, such as water, soil, and agricultural products, has been a major subject for many years. This is because of their potential risk for human health, persistence and tendency to bio-accumulate. For water samples, analytical methods usually include extraction and enrichment steps for determining pesticide residues at very low levels (<sub-µg/L). Therefore, miniaturized methods such as solid phase micro-extraction (SPME) and stir bar sorptive extraction (SBSE) were introduced because they are simple, solvent-free techniques that allow extraction and concentration in a single step. [1,2]. These sorptive extraction methods have been successfully applied to the determination of organic compounds in various sample matrices, such as water, soil, food, and biological fluid [3-5]. These methods also provide enhanced sensitivity because the extracted fraction (on a fiber or on a stir bar) can be introduced quantitatively into a GC system by thermal desorption. In addition, the enrichment factor for SBSE is higher than that of SPME because of the 50-250 times larger volume of extraction phase on the stir bar. Several authors indicated that the SBSE method allows high recovery and an extremely low limit of detection (LOD) at the sub-ng/L level, particularly for some solutes having hydrophobic characteristics [4, 5]. In 2008, Ochiai et al, developed an SBSE procedure termed sequential SBSE for exhaustive enrichment of organic pollutants in aqueous samples. This procedure is performed sequentially for one aliquot under two extraction conditions using two stir bars [6]. The technique counters the difficulty in recovering both hydrophobic and hydrophilic compounds. This new approach produced a remarkable improvement in recoveries for a set of 80 pesticides (log $K_{o/w}$: 1.70-8.35) in water, 82-113% for the majority and less than 80% for only five hydrophilic compounds.

This application note describes the performance of sequential SBSE-thermal desorption (TD) in combination with retention time locked (RTL)-GC/MS for the screening of pesticide residues in water.

Experimental

Instrumentation

Analyses were performed with a GERSTEL TDU thermal-desorption unit equipped with a MPS 2 auto-sampler (Gerstel) and a CIS 4 programmed temperature vaporization (PTV) inlet (Gerstel) installed on an Agilent 7890 GC with an Agilent 5975 Series GC/MSD triple-axis detector (TAD).

Sequential SBSE-TD-RTL-GC/MS

For the first SBSE, five milliliters of water sample were transferred to 10 mL headspace vials. A stir bar (Gerstel Twister; 24 µL of PDMS) was added and the vial was sealed with a screw cap. SBSE of several samples was performed simultaneously at room temperature (24 °C) for 60 min while stirring at 1500 rpm. After the first extraction, the stir bar was removed with forceps, dipped briefly in Milli-Q water, dried with a lint-free tissue, and placed in a glass thermal desorption liner. The glass liner was temporarily placed and stored in a sealed sample tray of the MPS 2. For the second extraction, 30 % NaCl was dissolved in the sample. Then, a second stir bar was added and the vial was capped again. The second extraction was performed under the same conditions as the first extraction. After the second extraction, the stir bar was removed with forceps, dipped briefly in Milli-Q water, dried with a lint-free tissue, and placed in the glass liner which contained the first SBSE stir bar. Finally, the glass liner was placed in the thermal desorption unit. No further sample preparation was necessary. Figure 1 shows the experimental setup of sequential SBSE.

Reconditioning of stir bars was done after use by soaking in Milli-Q purified water and a mixture of methylene chloride-methanol (1:1) for 24 h each. Stir bars were then removed from the solvent and dried on a clean surface at room temperature for 1 h. Finally, the stir bars were thermally conditioned for 30 min at 300 °C in a flow of helium. Typically, 30 extractions could be performed with the same stir bar.

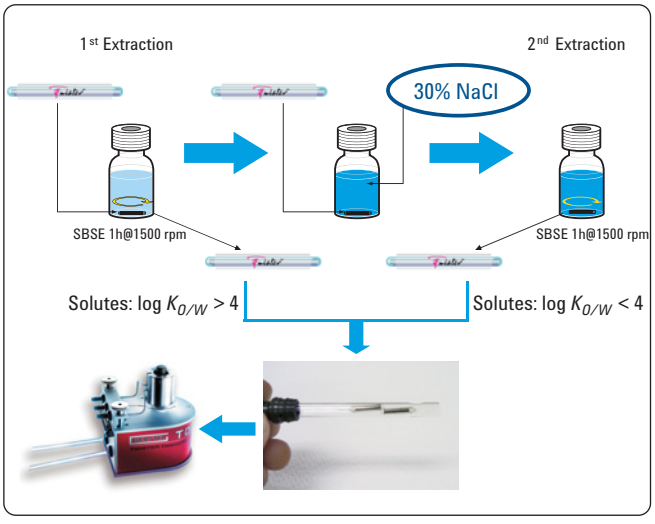

Figure 1. Experimental setup of sequential SBSE

The two stir bars were thermally desorbed by the thermal desorption unit (TDU) with 50 mL/min desorption flow. Desorbed compounds were cryo-focused on quartz wool packed liner in the PTV inlet for subsequent GC/MS analysis. The analytical conditions are summarized in Table 1.

Table 1 Analytical conditions

Stir bar	GERSTEL Twister; 24 µL PDMS
Sequential SBSE	5 mL sample volume 60 min extraction for each SBSE Non-modifier for 1st SBSE 30 % NaCl for 2nd SBSE 1500 rpm stirring speed
TDU	Splitless 50 mL/min desorption flow 40 °C (0.2 min); 720 °C/min; 280 °C (5 min)
PTV	Quartz wool packed liner Splitless –100 °C (0.5 min); 12 °C/s; 280 °C (hold)
Column	30 m × 0.25 mm id × 0.25 µm Agilent HP-5ms
RTL	Chlorpyrifos methyl locked to 15.59 min.
GC Oven	70 °C (2 min); 25 °C/min; 150 °C; 3 °C/min; 200 °C; 8 °C/min; 300 °C (2 min)
MSD	Scan mode Scan: m/z 58-510; 3.2 scans/s

Results and Discussion

Figure 2 shows a comparison of the recoveries of SBSE without modifier, SBSE with 30% NaCl, and sequential SBSE for representative pesticides with various log $K_{o/w}$ values in natural water spiked at 500 ng/L. The recoveries for solutes with log $K_{o/w}$ of less than 4.0 dramatically increased with salt addition, for example, for pirimicarb (carbamate; log $K_{o/w}$: 1.70), fenobucarb (carbamate; log $K_{o/w}$: 2.79), and pacrobutrazol (other; log $K_{o/w}$: 3.36), the recovery increased from 15% to 74%, 41% to 90%, and 31% to 95%, respectively. However, recovery for solutes with log $K_{o/w}$ of more than 4.0 drastically decreased, for example, for terbufos (organophosphorus; log $K_{o/w}$: 4.24), pyridaben (other; log $K_{o/w}$: 5.47) and permethrin 1.2 (pyrethroid; log $K_{o/w}$: 7.43), the recovery decreased from 89% to 68%, 100% to 57%, and 101% to 54%, respectively. In contrast with conventional SBSE with or without salt addition, the sequential approach could eliminate the negative effect of the salt for solutes with log $K_{o/w}$ of more than 4.0, while maintaining increased recovery for hydrophilic solutes with salt addition, resulting in high recovery. Therefore, using sequential SBSE, results in higher sensitivity for a wide range of solutes with different polarities.

Figure 3 shows the mass chromatogram (m/z 304) of diazinon (log $K_{o/w}$: 3.86) in 5 mL of natural water spiked at 20 ng/L. Excellent sensitivity (peak-to-peak S/N of 40) and a well defined mass spectrum were obtained for ng/L level samples even with the scan mode.

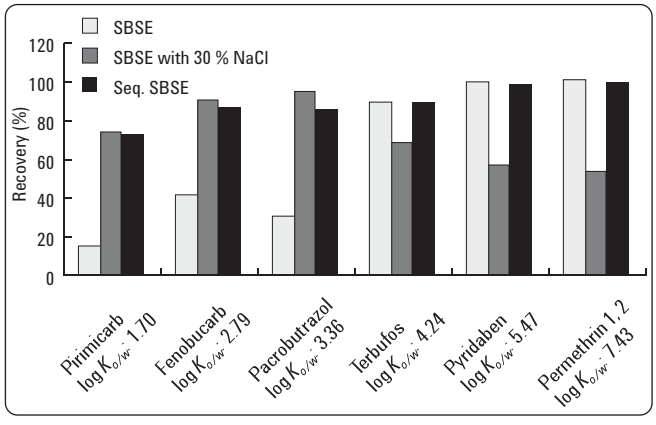

Figure 2. Comparison of the recovery of SBSE without modifier, SBSE with 30 % NaCl, sequential SBSE for representative pesticides with various log $K_{o/w}$ in natural water spiked at 500 ng/L.

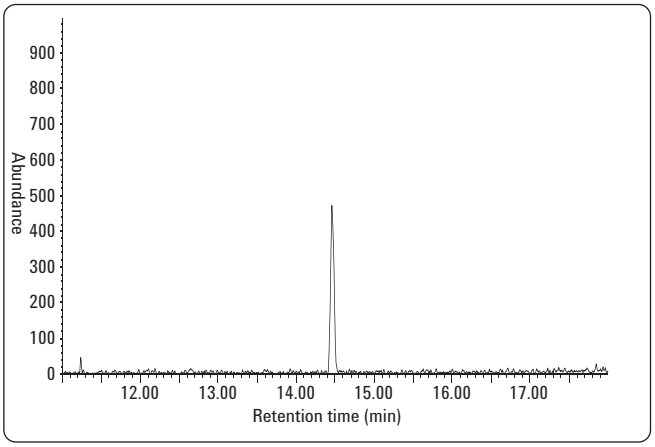

Figure 3. Mass chromatogram (m/z 304) of diazinon (log $K_{o/w}$: 3.86) in 5-mL natural water spiked at 20 ng/L.

Figure 4 shows a Wiley library search result, which obtained a match factor of 94.

RTL GC/MS method can eliminate many false positives and give more confidence in compound identification with not only mass spectral information but also locked retention times. Recently, Agilent updated the RTL pesticide library with 926 pesticides, endocrine disruptors, and related compounds [7]. For the present paper, the presence of pesticides in river water sample is elucidated automatically via the RTL screener in combination with the RTL library for 926 compounds.

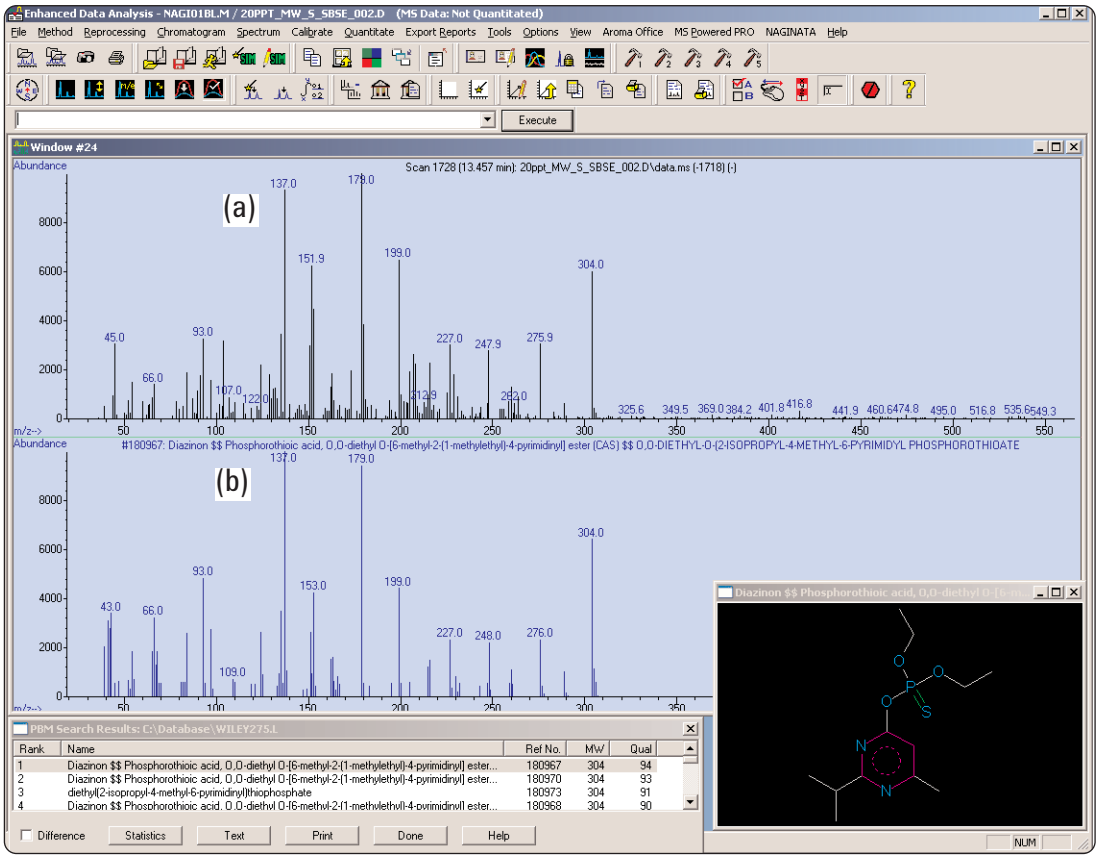

Figure 4. Wiley library search result of diazinon (log $K_{o/w}$: 3.86) in 5-mL natural water spiked at 20 ng/L. (a) Measured mass spectrum (b) Wiley library spectrum.

Figures 5 and 6 show the screener software windows for the positive detection and identification of symetryn (log $K_{o/w}$: 2.90) and pyributicarb (log $K_{o/w}$: 5.34) in Ayase river water sample. The ratio of four qualifier ions are measured and compared with those listed in the database. The software window also shows the deviation of measured retention time with the RTL value. After identification of these pesticides by the RTL screener, quantification was performed in six replicate analyses with standard addition calibration method. The determined concentrations were 240 ng/L (RSD: 2.9 %, n = 6) for symetryn and 25 ng/L (RSD: 8.9 %, n = 6) for piributicarb, respectively.

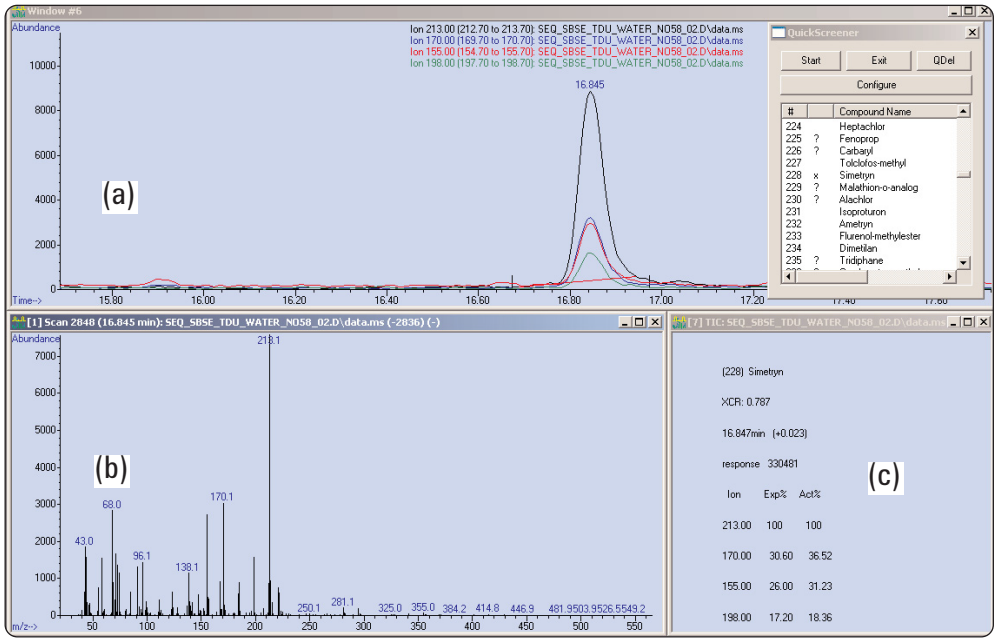

Figure 5. Results screener window of the positive identification of symetryn (log $K_{o/w}$: 2.90) in Ayase river water (a) Mass chromatograms (m/z 213, 170, 155 and 198) (b) Measured mass spectrum (c) Expected and measured relative ion abundance ratio and deviation of the RTL value.

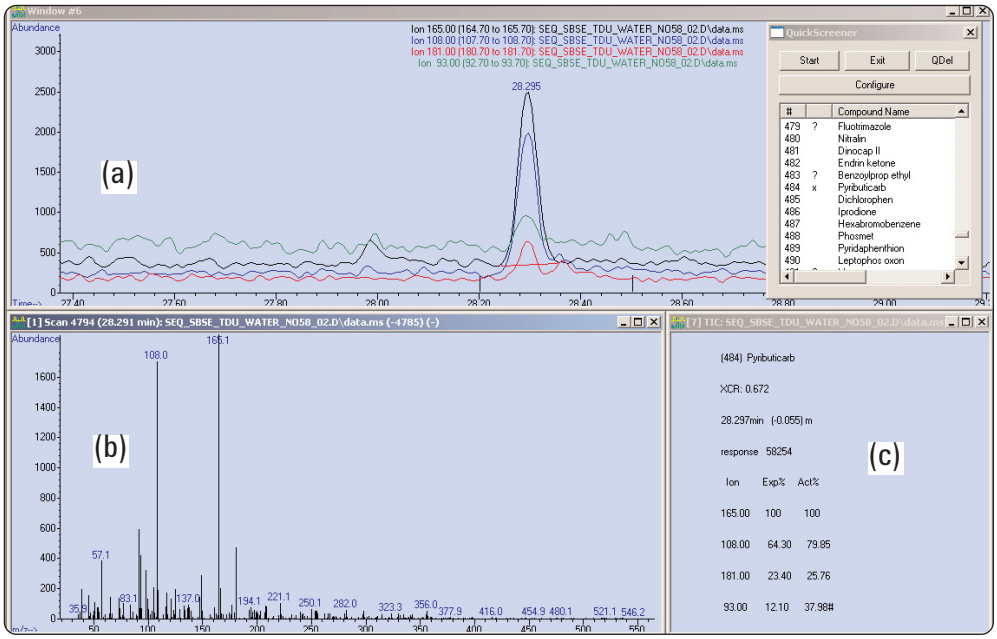

Figure 6. Results screener window of the positive identification of pyributicarb (log $K_{o/w}$: 5.34) in Ayase river water (a) Mass chromatograms (m/z 165, 108, 181 and 93) (b) Measured mass spectrum (c) Expected and measured relative ion abundance ratio and deviation of the RTL value.

Conclusion

The combination of sequential SBSE, thermal desorption and RTL GC/MS operated in the scan mode can provide a very powerful system to screen wide range of pesticide residues at ultra trace levels in water.

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