

GLOBAL ANALYTICAL SOLUTIONS



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AppNote 5/2005

Application of Stir Bar Sorptive Extraction (SBSE) Coupled to Thermal Desorption GC-MS for Determination of Ultra-Trace Level Compounds in Aqueous Samples

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KEYWORDS

Sample preparation, aqueous sample, SBSE, thermal desorption, GC-MS.

INTRODUCTION

During the past decade, miniaturized and solvent-less sample preparation techniques based on sorptive extraction, e.g. solid phase micro-extraction (SPME), have proven to be simple, fast and environmentally friendly alternatives to LLE while maintaining or even improving sensitivity. In 1999, a new extraction technique known as stir bar sorptive extraction (SBSE) using stir bars coated with 50-300 μl of polydimethylsiloxane (PDMS) was developed by Baltussen et al. [1]. The advantage of SBSE is a higher enrichment factor combined with the application range and extraction mechanism of SPME.

The aim of this paper was to apply SBSE coupled to thermal desorption (TD)-GC-MS to determine ultra-trace level (sub-ng/L to ng/L) compounds in aqueous samples.

EXPERIMENTAL

A stir bar (Twister™; GERSTEL GmbH) coated with 24 µl of PDMS was used for SBSE. Aqueous samples and pre-conditioned stir bars were placed in 10-40 mL headspace vials. SBSE was simultaneously performed for 60-120 min at 25 °C during stirring at 1000 rpm. After extraction, stir bars were removed, rinsed with distilled water, dried with a lint-free tissue and placed in a glass TD tube. The TD-GC-MS analysis was performed with a GERSTEL TDS-2/A equipped with CIS-4 inlet and an Agilent 6890 GC with a 5973N MSD. The separations were performed on an HP-5MS (30 m x 0.25 mm i.d., 0.25 µm thickness). The mass spectrometer was operated in the SIM mode.

RESULTS AND DISCUSSION

Since SBSE is by nature an equilibrium technique, the extraction of solutes from the aqueous phase into the PDMS phase is controlled by the partitioning

coefficients. Recent studies have correlated this partitioning coefficient with the octanol-water distribution constant ($K_{o/w}$) [1]. The SBSE method allows limits of detection (LODs) at the sub-ng/L level, particularly for compounds having more hydrophobic characteristics with high $K_{o/w}$ values. This was illustrated by the ultra-trace analysis of off-flavor compounds, e.g. 2-methylisoborneol (MIB), geosmin and 2,4,6-trichloroanisole (TCA), in drinking water samples. The log $K_{o/w}$ values were 3.31, 3.57 and 4.00 for MIB, geosmin and TCA, respectively. Fig.1 shows the SIM chromatograms obtained by TD-GC-MS after 120-min SBSE of a natural water sample (40 mL) fortified at 1 ng/L. The method showed good linearity (0.2-100 ng/L, $r^2 > 0.9987$), recovery (93-104 %, fortified at 1 ng/L) and precision (RSD: 0.80-2.8 %, $n = 6$). The LODs were calculated to be 0.052-0.15 ng/L over 6 replicate analyses of the lowest-level calibration standard based on 3.36 times the standard deviation of the determination results. The method allowed determination of sub-ng/L or ng/L levels of the off-flavor compounds in raw and tap water with low RSDs (0.18-7.4 %, $n = 6$).

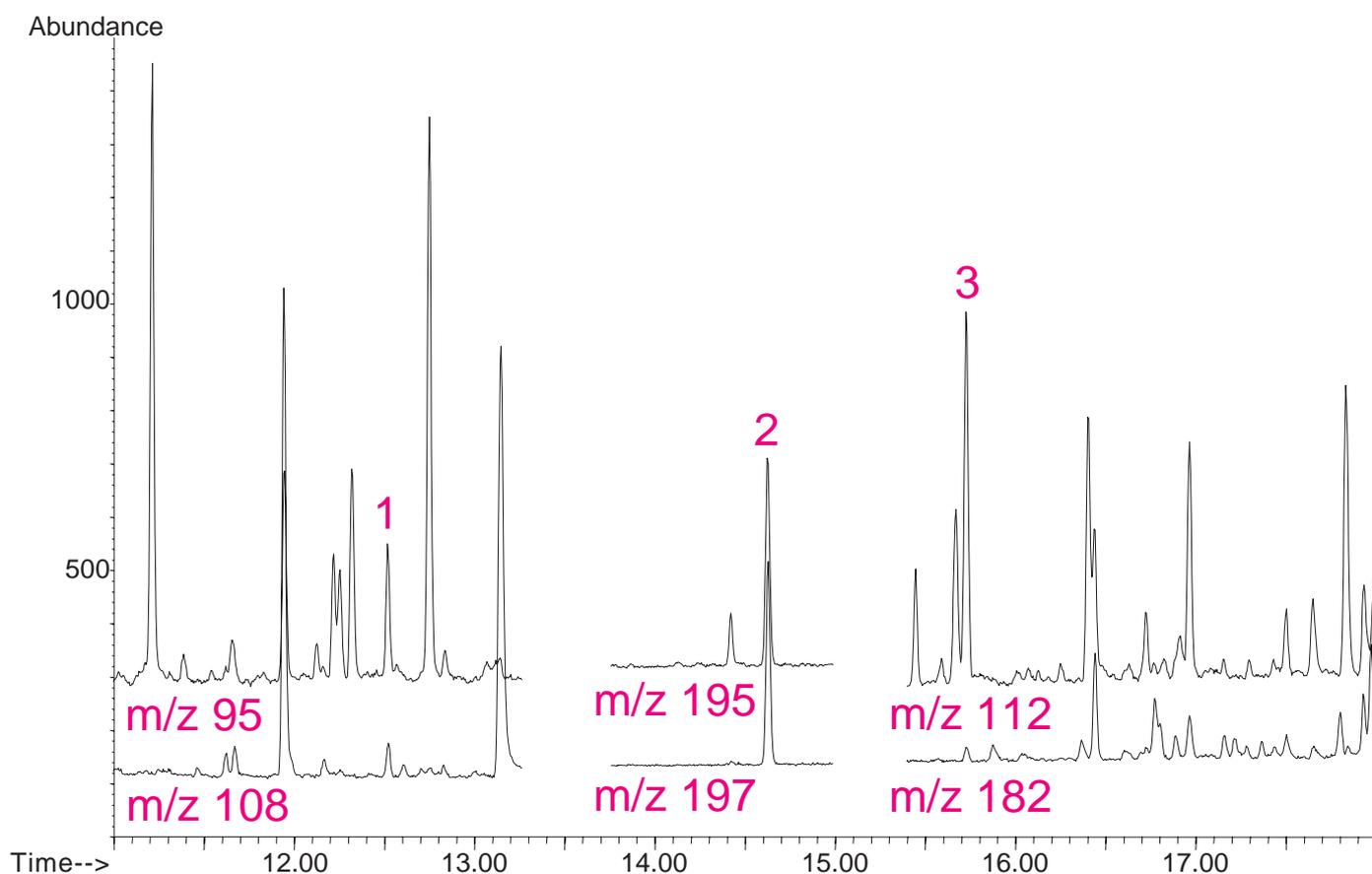


Figure 1. SIM chromatograms obtained by SBSE-TD-GC-MS of fortified natural water spiked at 1 ng/L. 1: MIB, 2: TCA, 3: Geosmin.

SBSE can also be applied to ultra-trace analysis of alkylphenols and bisphenol A in river water. For the present study, SBSE with in-situ derivatization (acetylation) using anhydrous potassium carbonate (K_2CO_3) and acetic anhydride was performed. Conversion of phenolic compounds into acetyl derivatives can improve not only chromatographic analysis but also sample enrichment in the PDMS phase because of an increase in the $\log K_{O/W}$ values (3.74-6.28). Fig. 2 shows the SIM chromatograms obtained by TD-GC-MS after 60-min SBSE with in-situ acetylation of a

natural water sample (10 mL) fortified at 50 ng/L. The method showed good linearity (1-1000 ng/L, $r^2 > 0.9981$), recovery (85-106 %, fortified at 10 ng/L) and precision (RSD: 3.0-11 %, $n = 6$). The LODs were calculated to be 0.11-3.6 ng/L by 6 replicate analyses of natural water samples fortified at 0.2-10 ng/L based on 3.36 times the standard deviation of the determination results. The method allowed determination of ng/L levels of 4-tert-octylphenol, nonylphenol and bisphenol A in river water.

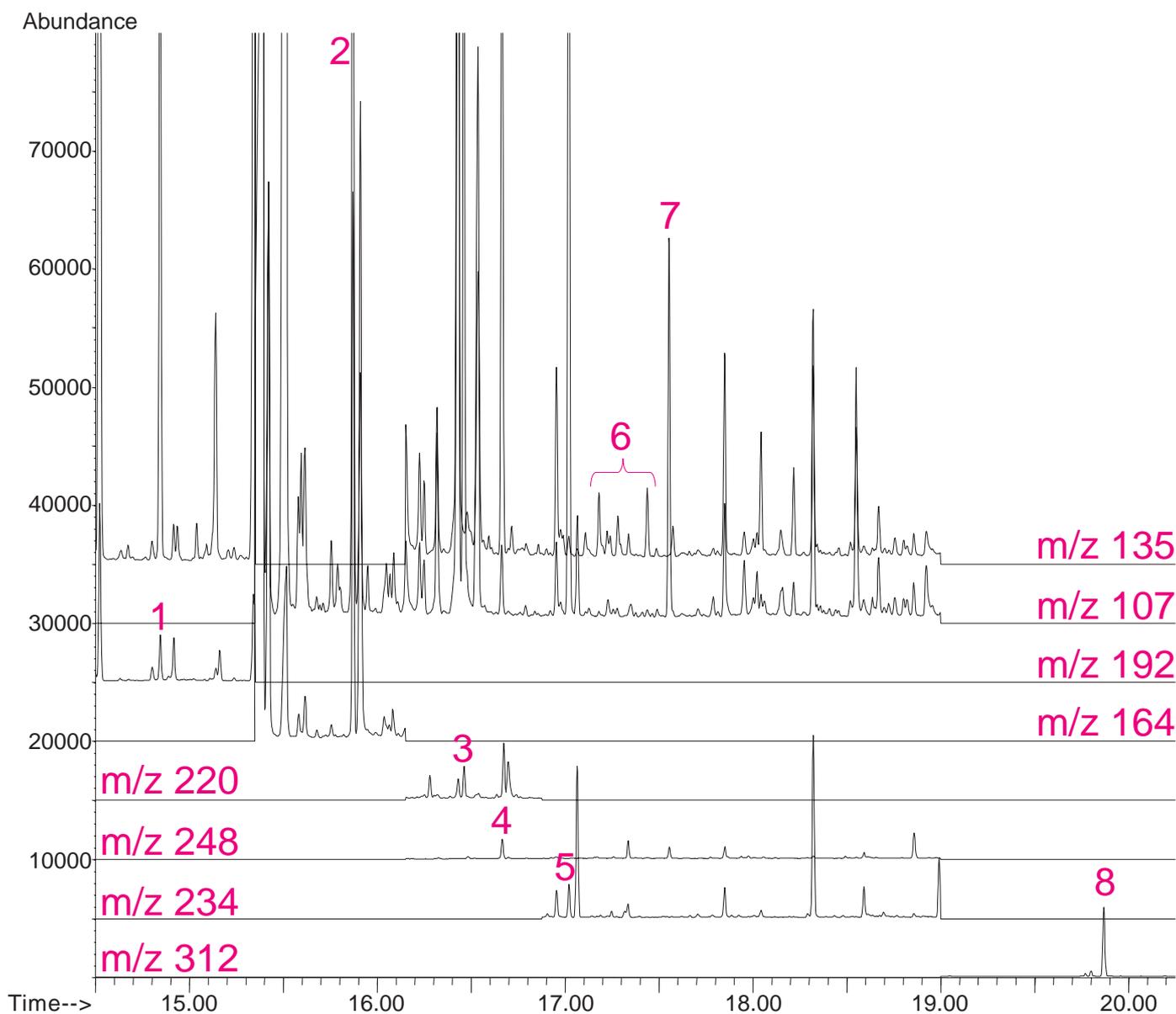
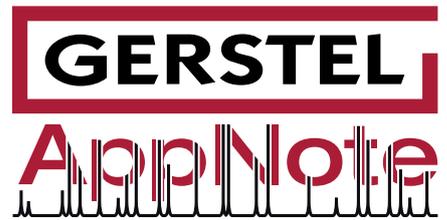


Figure 2. SIM chromatograms obtained by SBSE with in-situ acetylation and TD-GC-MS of fortified natural water spiked at 50 ng/L. 1: 4-tert-Butylphenol, 2: 4-n-Pentylphenol, 3: 4-n-Hexylphenol, 4: 4-tert-Octylphenol, 5: 4-n-Heptylphenol, 6: Nonylphenol isomers, 7: 4-n-Octylphenol, 8: Bisphenol A.

REFERENCE

- [1] E. Baltussen, P. Sandra, F. David, C. Cramers, J. Microcol. Sep. 11, 737-747 (1999).



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