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AppNote 1/2000

A Novel Extraction Technique for Aqueous Samples: Stir Bar Sorptive Extraction

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INTRODUCTION

The analysis of organic compounds in aqueous environmental, biomedical, food and fragrance matrices is normally performed after extraction and enrichment of the solutes from the matrix (drinking water, waste water, body fluids, beverages,...). Most used sample preparation methods are based on liquid-gas extraction or equilibrium (purge and trap, headspace), liquid-liquid extraction or solid phase extraction (SPE).

During the past years, miniaturisation has become a dominant trend in analytical chemistry. Typical examples of miniaturisation in sample preparation techniques are micro liquid-liquid extraction (in-vial extraction), ambient static

headspace and disk cartridge SPE. In combination with state-of-the-art analytical instrumentation, this resulted in faster analysis, higher sample throughput, lower solvent consumption, less manpower in sample preparation while maintaining or even improving sensitivity.

Some 10 years ago, a new micro-extraction method was developed by Arthur and Pawliszyn [1], namely solid-phase micro-extraction (SPME). Extraction of organic compounds from aqueous samples or from a gas phase using the polydimethylsiloxane (PDMS) sorbent as extraction medium was already described by different groups in the mid 80s using open tubular traps coated with thick PDMS films. Extraction using PDMS media is based on sorption instead of adsorption. Sorptive enrichment offers several advantages over adsorption processes, as described by Baltussen et al [2]. These advantages include predictable sorption, absence of displacement effects, inertness and faster and milder desorption. Practical limitations (low sample capacity, low breakthrough volumes,..), however, limited the applicability of PDMS coated open tubular traps. SPME, on the other hand, is a very simple and fast technique. A relative thin layer of PDMS (7-100 µm) on the outside of a needle device is used as extraction medium. After sorption, the compounds are thermally desorbed in a GC inlet or liquid desorbed in an LC inlet. In contrast to PDMS coated open tubular traps, SPME is by nature an equilibrium technique, based on the partitioning of the solutes between the silicone phase and the aqueous (and/or gas) matrix.

Recent studies [3-5] have correlated this equilibrium with octanol/water distribution coefficients ($k_{(o/w)}$). These studies demonstrated that for solutes with low $k_{(o/w)}$ (k<10000) low recoveries are obtained. This is mainly due to the phase ratio between the aqueous and PDMS phase. The amount of PDMS used in SPME is typically in the order of 0.5 µL or less, thereby limiting the enrichment on the PDMS fiber.

Based on these observations, a new approach using stir bars coated with PDMS was recently developed [2]. In this approach, 50-300 µL PDMS coatings are used. Consequently, the sensitivity is increased by a factor of 100 to 1000. Complete recovery is possible for solutes with $k_{(o/w)}$ larger than 500. Solutes with $k_{(o/w)}$ from 10 to 500 can also be analysed using calibration as is done in SPME. This technique is called stir bar sorptive extraction (SBSE).

PDMS coated stir bars are now commercially available (Twister™, Gerstel GmbH). Magnetic stirring rods are incorporated in a glass jacket and coated with a 1 mm layer of PDMS. Two Twisters are available : 10 mm L x 3.2 mm o.d. and 40 mm L x 3.2 mm o.d. PDMS coated stir bars. Typically the 10 mm stir bars are used for 1-50 mL sample volumes and the 40 mm stir bars are used for 100-250 mL sample volumes.

**Figure 1.** Gerstel Twister.

EXPERIMENTAL

Sample preparation. Sample extraction is performed by placing a suitable sample amount (typically 10 mL) in a vial, adding a stir bar and stirring during 30-120 min. After extraction, the stir bar is introduced in a glass thermal desorption tube (4 mm i.d. x 187 mm L), placed in a thermal desorption unit and thermally desorbed. Desorption temperatures are application dependant and are between 150-300°C during 5-15 min. Alternatively liquid desorption can be used.

Instrumentation. For thermal desorption a TDS-2 system (Gerstel GmbH) is used. The thermal desorption unit is mounted on a HP 6890 GC (Agilent Technologies, Wilmington, DE, USA) equipped with a CIS 4 PTV inlet. The desorbed solutes are cryofocussed in the PTV inlet. After desorption, the PTV is programmed to inject the solutes and the compounds are analysed on a capillary column.

RESULTS AND DISCUSSION

Stir bar sorptive extraction can be used for quality control of different consumer samples, including food, beverages, soaps, cosmetics, etc. A typical applications is the analysis of a fruit flavoured soft drink. 20 mL sample was placed in a headspace vial and extracted using a 10 mm stir bar during 60 min. The stir bar was then thermally desorbed at 240°C during 10 min in splitless mode. The desorbed solutes were cryofocussed in a CIS 4 PTV inlet at -150°C. After desorption the PTV was programmed to 300°C and the compounds were analysed on a 30 m x 0.25 mm i.d. x 0.25 µm Stabilwax column. Detection was done using MS in scan mode. The chromatogram is given below.

Abundance
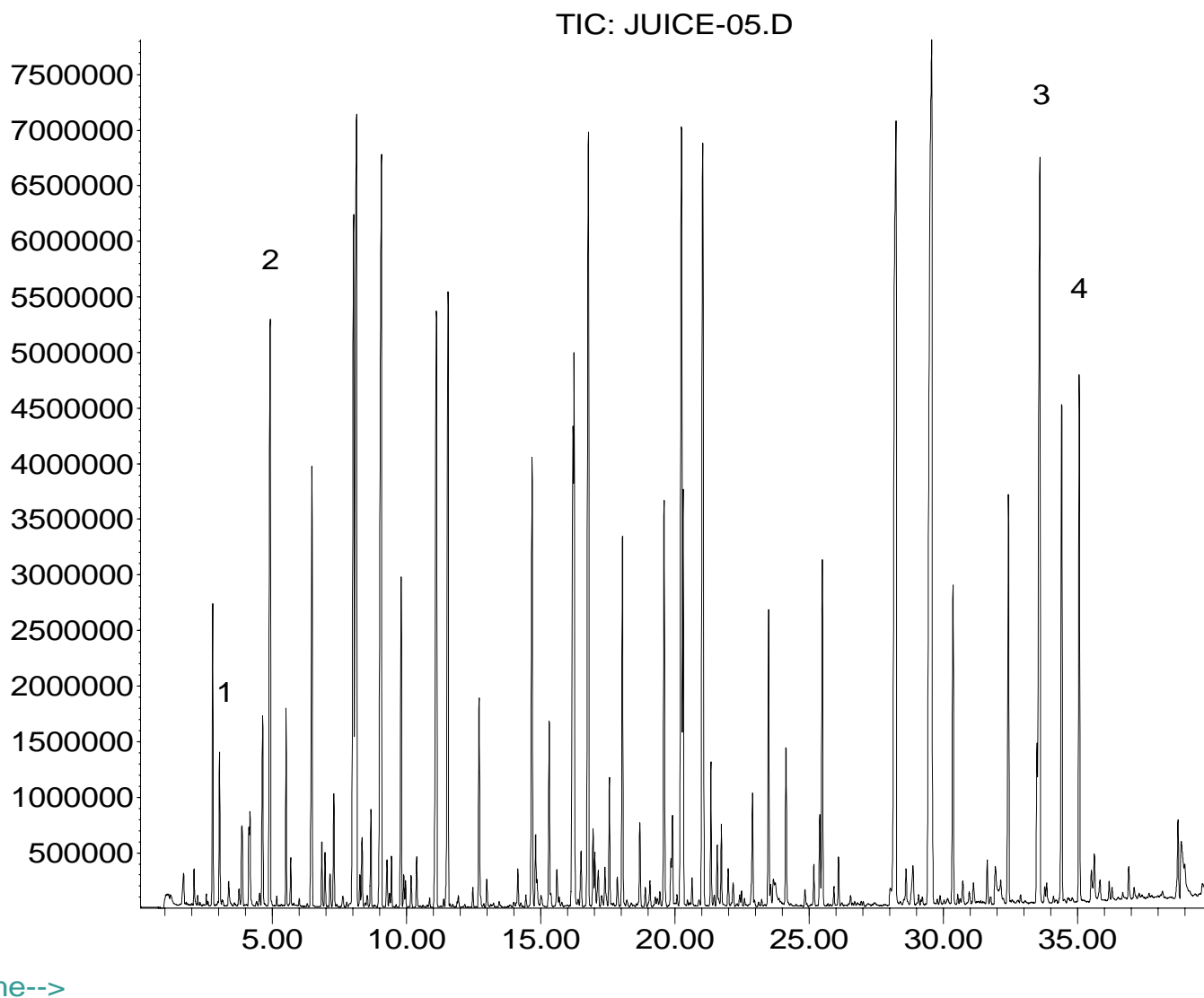
Figure 2. Analysis of multi-fruit soft drink by SBSE - thermal desorption - GC-MS (Peaks: 1.ethyl acetate, 2. butyl acetate, 3. γ-decalactone, 4. ethylcitrate).

The chromatogram shows excellent peak shapes and resolution. Peaks ranging from the very volatile esters (ethyl acetate, butyl acetate) to semivolatiles (gamma-decalactone, ethylcitrate) are identified.

Another example of quality control is the analysis of coffee. The same analytical conditions were used, except that the column effluent was split between the MSD detector and a pulsed FPD detector. The PFPD allows very sensitive detection of sulfur compounds. The chromatogram shows excellent peak shapes and resolution. In the PFPD trace, several sulfur compounds are detected, ranging from dimethyldisulfide to substituted thiophenes.
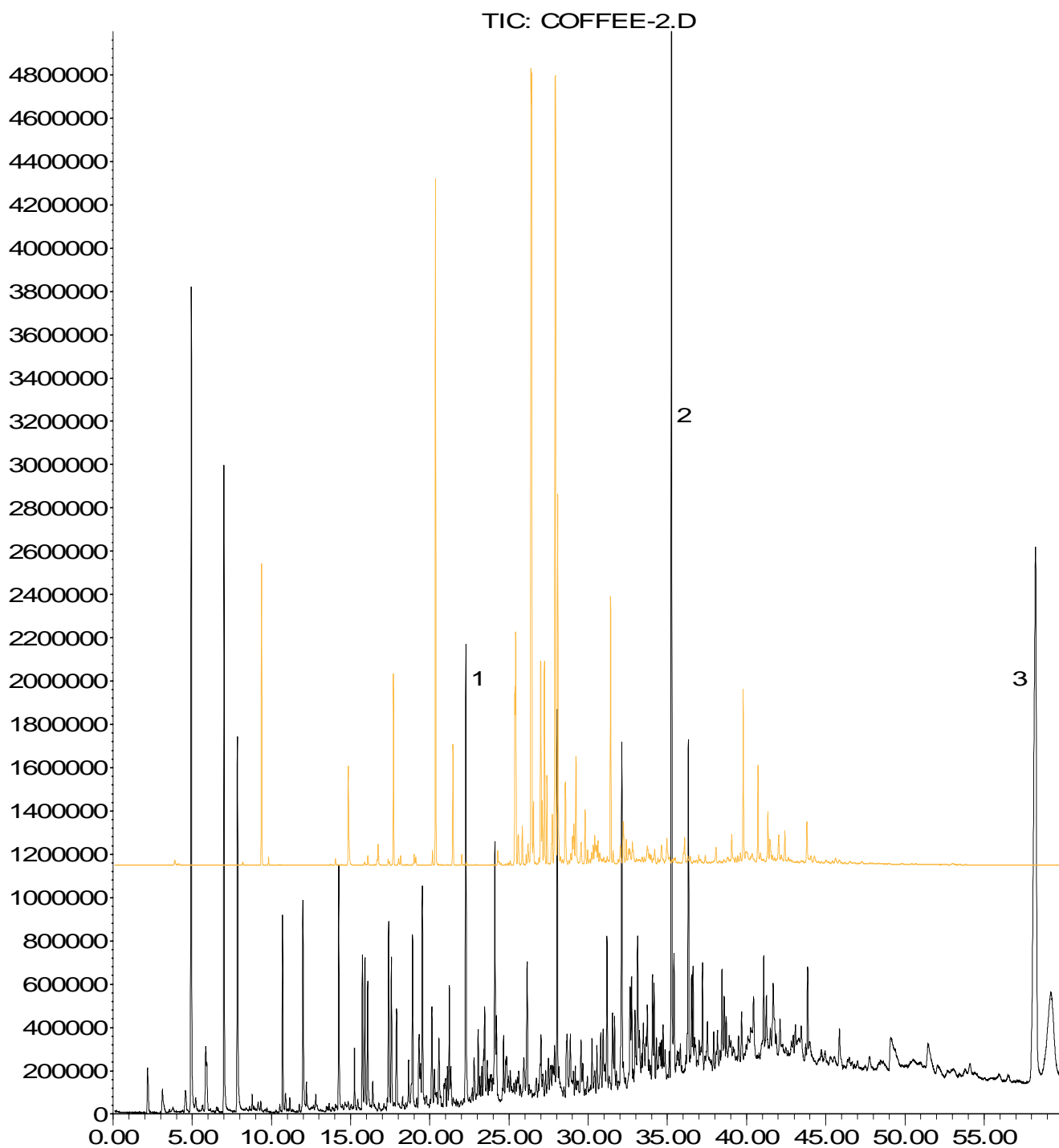
Abundance

Figure 3. Analysis of brewed coffee by SBSE - thermal desorption - GC-MS/PFPD. (Peaks : 1.5-methylfurfural, 2. p.vinylguaiacol, 3. caffeine). The sulfur trace detected by the PFPD is given in yellow.

Stir bar sorptive extraction can also be applied to trace analysis of contaminants. This is illustrated by the analysis of pesticide residues in wine. A blank wine sample (dry white wine) was spiked at the 10 ppb level with a mixture of organochlorine pesticides. 25 mL of the sample was placed in a 40 mL vial and extracted with a 10 mm stir bar during 40 min while stirring at 1400 rpm. After sorption, the stir bar is transferred to a thermal desorption tube and extracted at 300°C during 10 min in a TDS-2 system. The solutes were cryofocussed in an HP-PTV inlet of a HP 6890 GC at -50°C. The separation was carried out on a 30 m x 0.25 mm i.d. x 0.25 µm HP-5 MS column. The oven was programmed from 70°C (2min) to 150°C at 25°C/min, to 200°C at 3°C/min and to 280°C at 8°C/min. Detection is done using a HP G2350A Atomic Emission Detector.
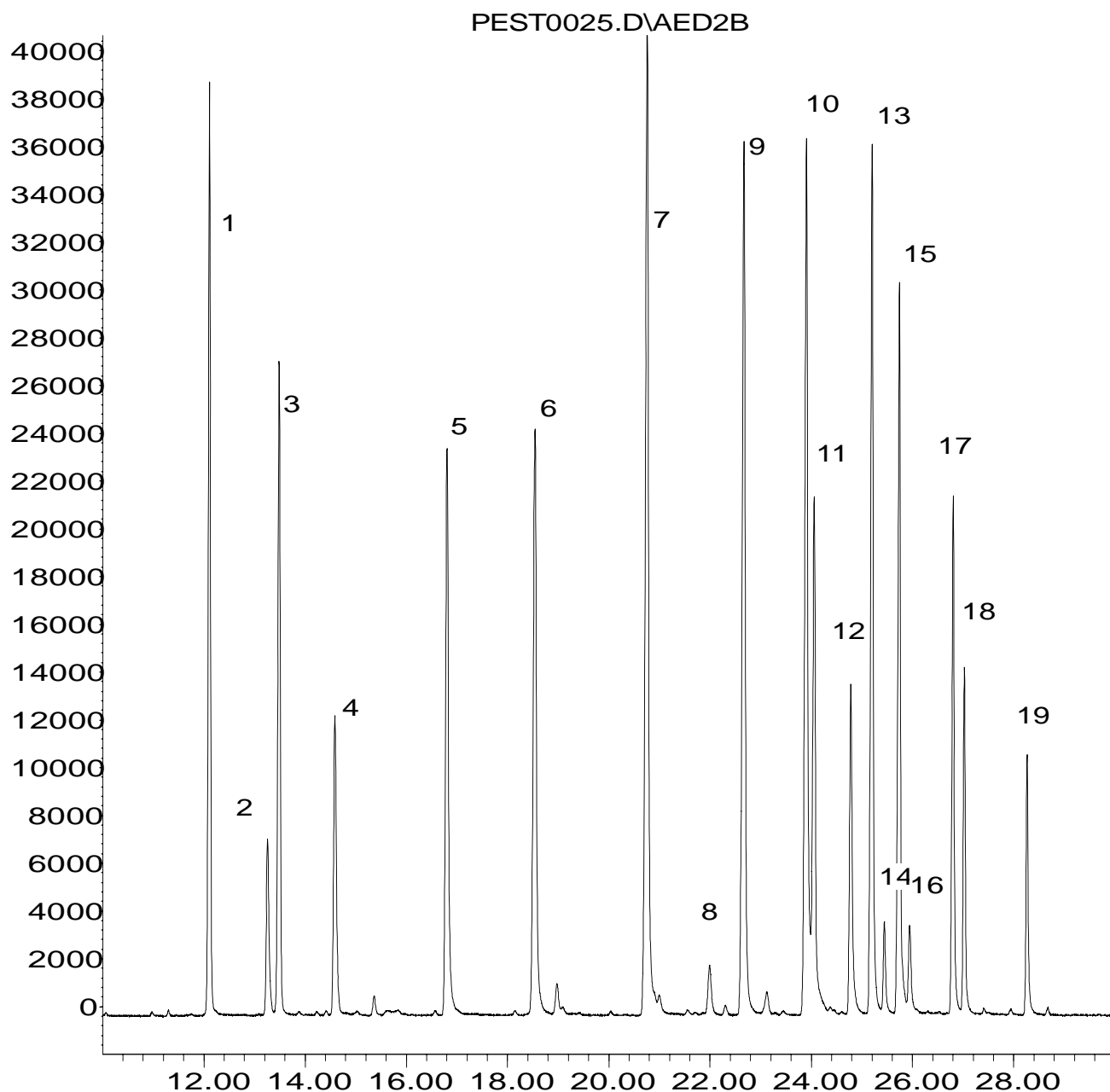

Figure 4. Analysis of wine sample spiked with 10 ppb organochlorine pesticides by SBSE - thermal desorption - GC-AED (Peaks: 1. α-HCH, 2. β-HCH, 3. γ-HCH, 4. δ-HCH, 5. Heptachlor, 6. Aldrin, 7. Heptachlorepoxide, 8. Procymidone, 9. Endosulfan I, 10. Dieldrin, 11. DDE, 12. Endrin, 13. Endosulfan II, 14. Chlorpropylate, 15. DDD, 16. Endrin aldehyde, 17. Endosulfan sulphate, 18. DDT, 19. Endrin ketone).

Secondly a real (non-spiked) sample was analysed under the same conditions. In this sample, an important peak is detected in the chlorine trace at 21.93 min. Using the retention time locking pesticide library, this peak was identified as procymidone, a fungicide frequently used in grape cultivation.
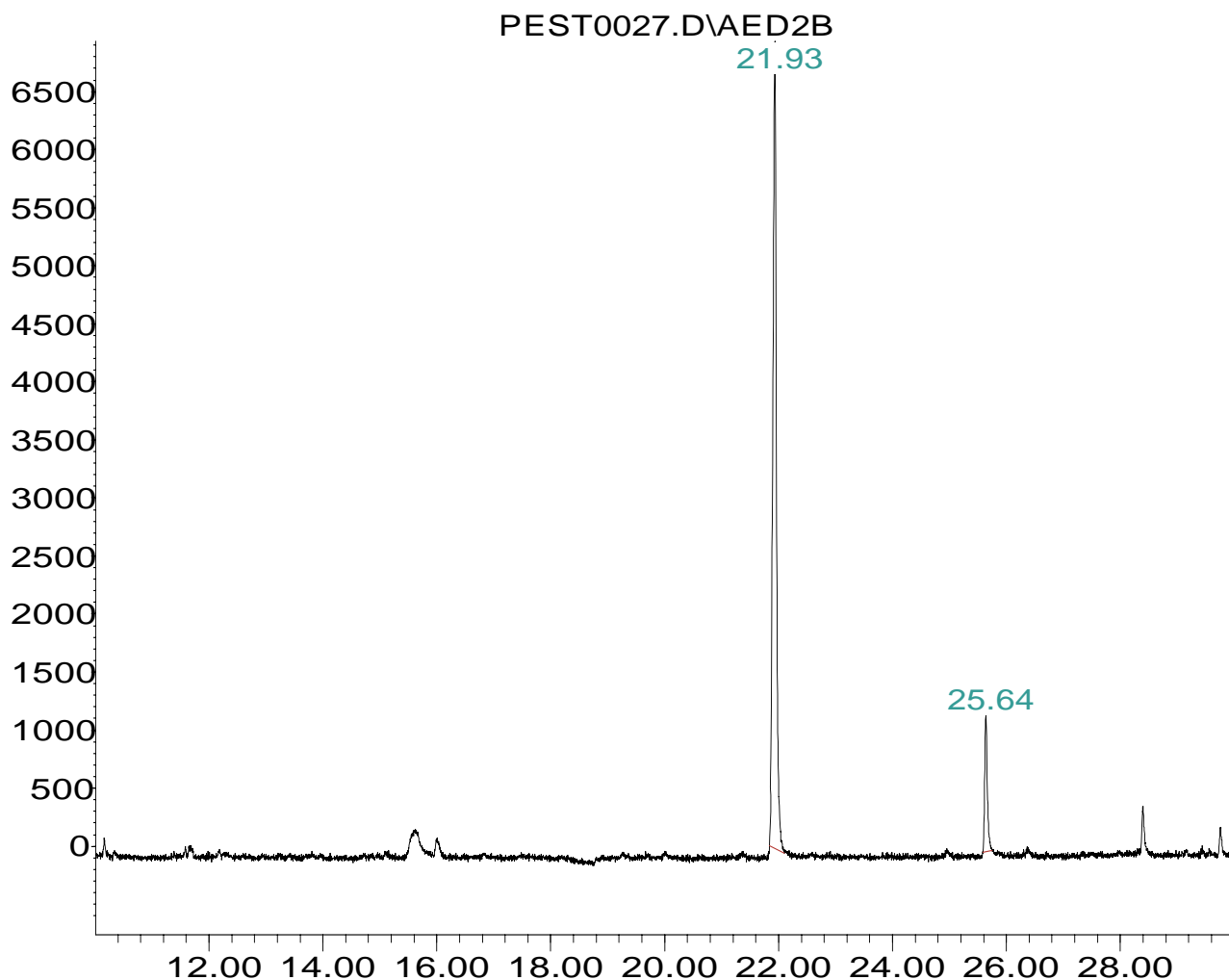
Figure 5. Analysis of a white wine sample by SBSE - thermal desorption - GC-AED.

CONCLUSIONS

Stir bar sorptive extraction is a powerful technique for the extraction and analysis of organic compounds in aqueous matrices. The system can be used for fast quality control of food and fragrance samples and for trace analysis in environmental, food and biomedical samples.

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