GLOBAL ANALYTICAL SOLUTIONS

GERSTEL

TechNote 5/2002

Design, Performance, and Applicability of a Newly Developed Sample Introduction System for Use with Stir Bar Sorptive Extraction (SBSE)

Andreas Hoffmann, Bita Kolahgar, Christian Heinz, Sascha Funke, Bernd Rose
Gerstel GmbH & Co. KG, Eberhard-Gerstel-Platz 1, D-45473 Mülheim an der Ruhr, Germany

Keywords
SBSE, Twister, Thermal Desorption

Abstract
The use of stir bar sorptive extraction (SBSE) as a technique to extract volatiles and semivolatiles from polar, especially aqueous matrices, has gained more and more acceptance in several application areas. Thermal desorption, analogous to SPME, has been found to be the most suitable technique to transfer the extracted analytes into an analytical system and make them accessible for gas chromatographic analysis.

PDMS-coated stir bars („Twister“) have much more stationary phase and consequently bigger outer dimensions compared to SPME-fibers. They do not fit into standard injection ports for thermal desorption as SPME-fibers do, therefore usually a thermal desorption unit is used for this purpose.

This type of unit is intentionally designed to desorb previously trapped analytes from porous polymer-packed sample tubes, or for thermal extraction of volatiles from solids. It works perfectly for Twister-desorption, but may simply be somewhat oversized if this is the only purpose.

This paper describes the design, performance and applicability of a new desorption unit especially designed for use with "Gerstel Twister". This unit is compatible with existing GC models and can be automated using a modified regular autosampler.

Introduction

Analyzing organic compounds in aqueous matrices of, for example, environmental, food, flavor, and fragrance samples has always been a challenge. Several sample preparation methods like liquid-liquid or solid phase extraction for semi-volatiles, as well as headspace and purge & trap techniques for volatiles have attempted to address that problem.

Several years ago Arthur and Pawliszyn [1] developed a technique called solid phase micro extraction (SPME). This equilibrium technique, based on partitioning of analytes between the aqueous/gaseous matrix and a silicone (PDMS) phase, could be correlated with the so called octanol/water partitioning coefficient Kow [2-4]. This coefficient was originally defined to give an approximation to a biotic lipid-water coefficient, and reflects the relative hydrophobicity of a compound. Using published Kow values [5-7], the extraction efficiency of a PDMS-coated device vs. an aqueous matrix can be easily predicted.

But this correlation also showed that with SPME low recoveries are obtained for compounds with an octanol/water partitioning coefficient below 10,000. A recently developed technique called stir bar sorptive extraction (SBSE) [8] addresses this problem by using much thicker coatings leading to an increase in sensitivity by a factor of 100 to 1000.

A magnetic stir bar coated with PDMS (commercially available as "Gerstel Twister") is added to an aqueous sample and stirred extracting the organic analytes. After extraction the stir bar is removed and placed in a thermal desorption tube for subsequent GC analysis.

Instrumentation

Stir bar design. The stir bars, commercially available as "GERSTEL-Twister", consist of a magnetic core which is sealed in glass and coated with a polydimethylsiloxane (PDMS)-layer (Figure 1).

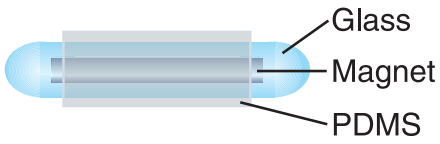

Figure 1. Twister Design.

They are available in 4 different dimensions: from a length of 10 mm and a phase thickness of 500µm with a PDMS volume of 27µl up to a length of 20 mm and a phase thickness of 1000µm, providing a PDMS volume of 126µl.

Thermal desorption. After extraction of analytes from a polar matrix like water the Twister is usually thermally desorbed and the analytes are cryofocused in a PTV inlet. For this purpose, a newly developed thermal desorption device, the so called TDU (Twister Desorption Unit) is used (Figure 2).

Figure 2. Twister Desorption Unit TDU.

This unit is mounted and connected directly onto a PTV replacing the injector head. The PTV-liner rises into that of the TDU ("liner-in-liner" design) providing a totally inert sample transfer – a classical transferline is no longer needed (Figure 3).

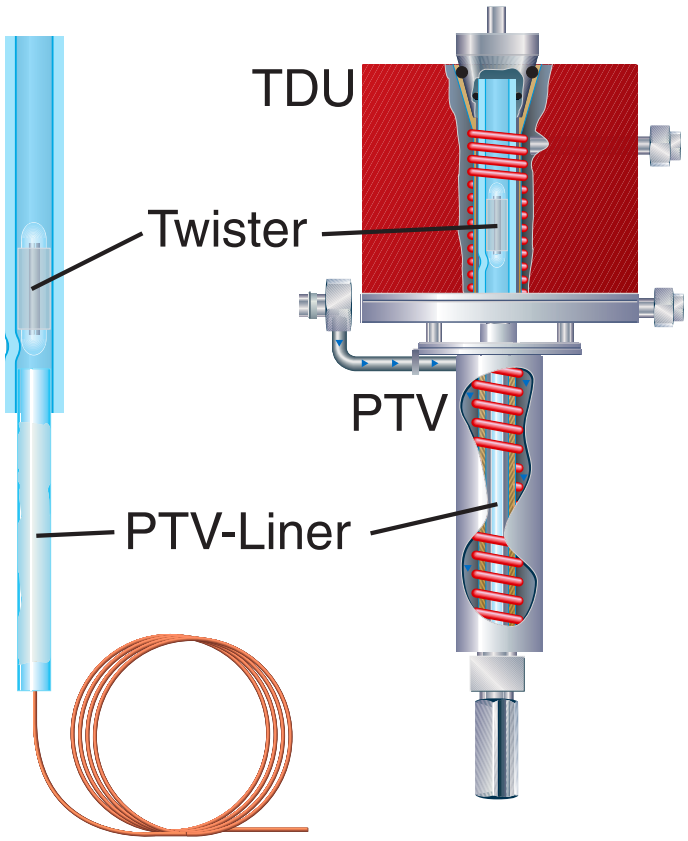

Figure 3. TDU attached to PTV, with „liner-in-liner“ concept.

Flow paths. A second split outlet is added to this “dual-stage” PTV allowing maximum flexibility for sample transfer. Figure 4 describes the flow path: here in a first step the Twister is desorbed splitless, but with high desorption flow into the liner of the PTV, where the analytes are cryogenically trapped; the split point is located behind the trapping point, so that no analytes are lost (Figure 4A). In a second step the split is switched to the TDU: now the split point is located before the trapping point; the analytes can be transferred splitless to the analytical column without any losses by ramping the PTV to the desired end-temperature (Figure 4B).

For the pneumatic system of the GC nothing has changed since there is still one carriergas-in line and one split-out line. The provided 3/2-way solenoid, which is agitated by the TDU-controller, gives way for either split 1 or split 2.

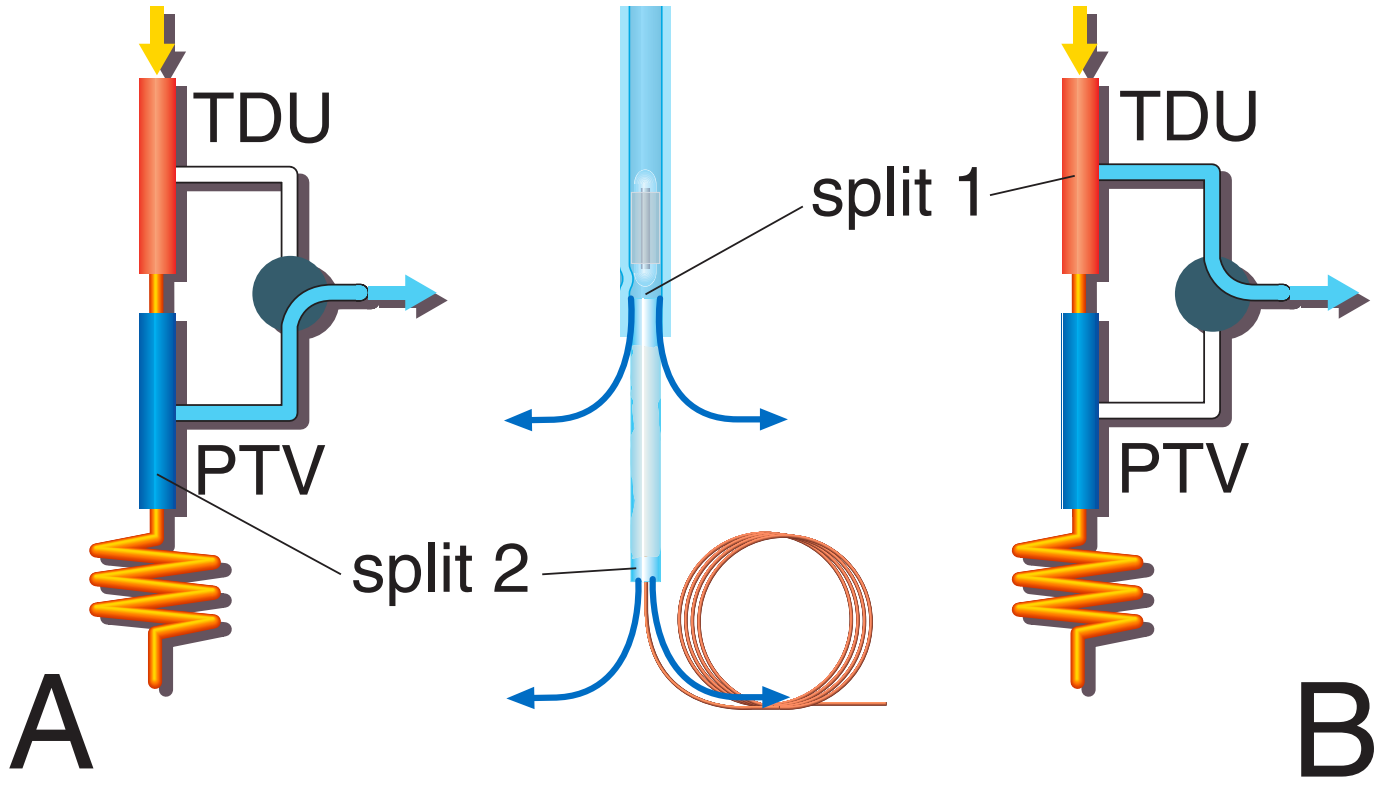

Figure 4. Flow paths of the instrumental setup with split point locations, TDU splitless mode (A), PTV splitless mode (B).

Twister introduction. Every Twister is placed in its own liner which itself is afterwards attached to a locking cone (Figure 5). This cone works as seal and also as transport adapter allowing easy introduction into and removal from the TDU. This entire Twister-liner setup is exchanged for every analysis preventing any cross-contamination and at the same time allowing full automation of the entire system.

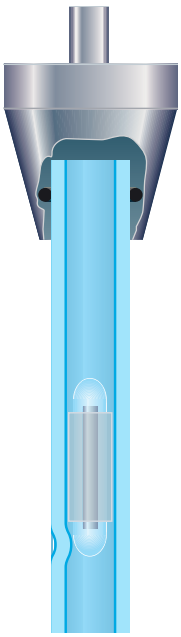

Figure 5. Liner with Twister and locking cone.

Automation. Twister-liners consisting of liner, Twister and locking cone/transport adapter, are placed in a specially designed tray where they are stored safely through the airtight seal of the adapter avoiding the risk of sample loss or contamination. For analysis an MPS 2 autosampler, equipped with a newly designed Twister-holder (Figure 6) picks a liner, inserts it into the TDU, and returns it to the tray when analysis is complete. Figure 7 shows the entire procedure.

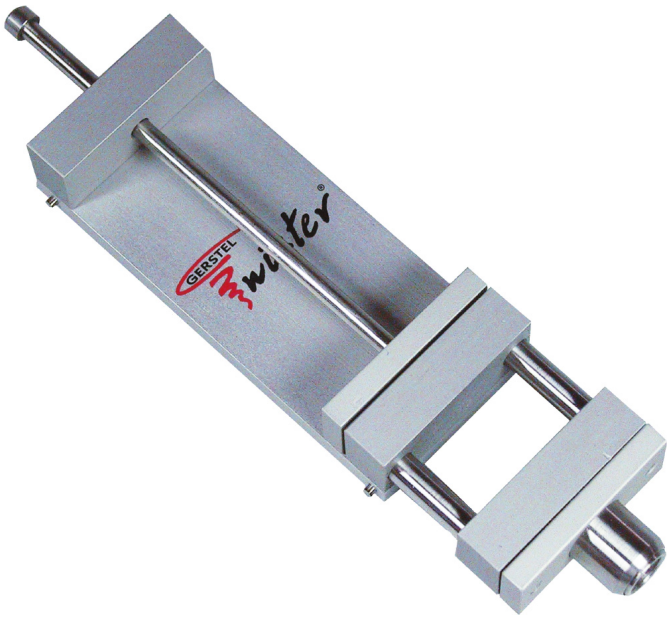

Figure 6. Twister-holder for use with MPS 2.

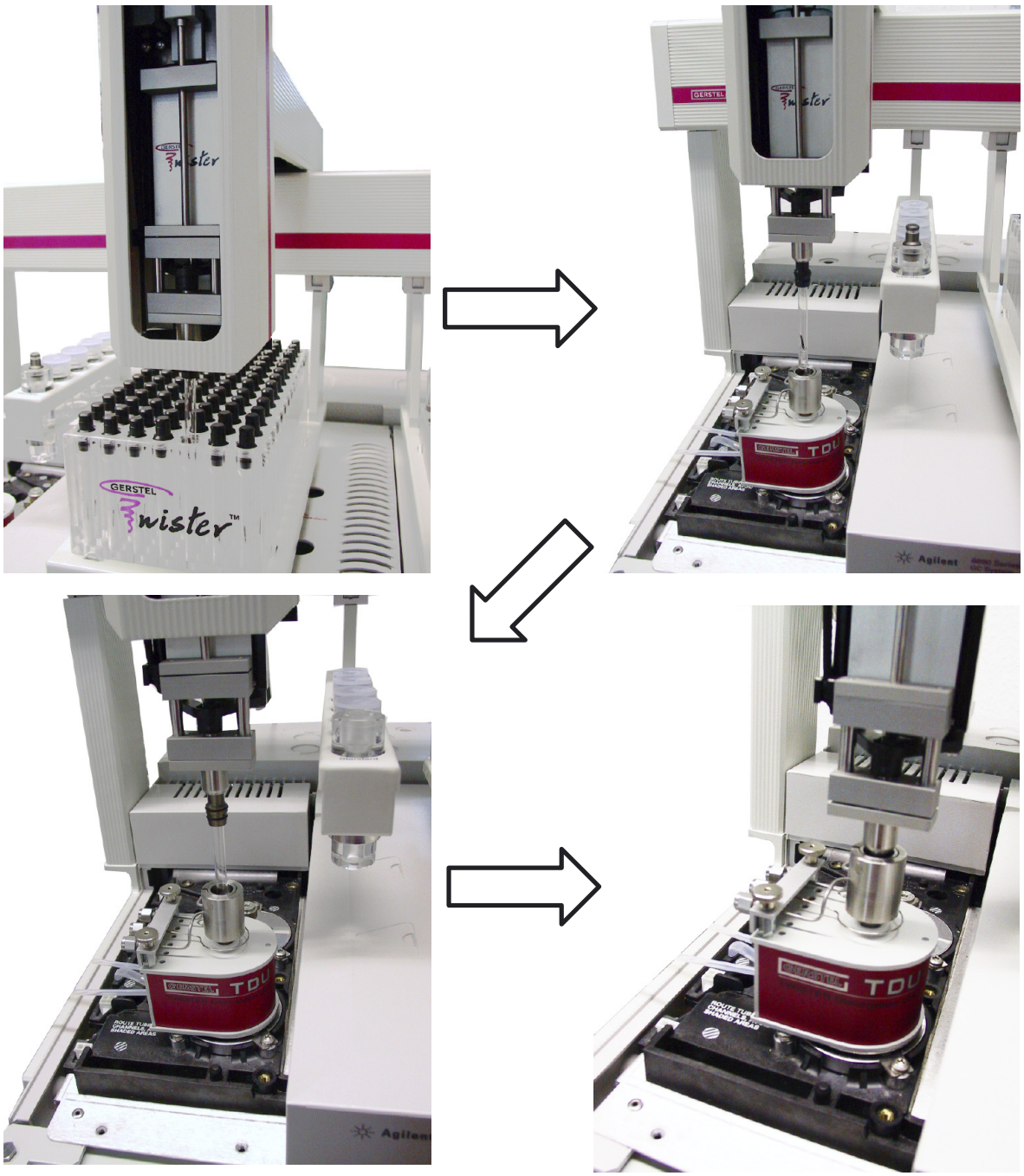

Figure 7. Automation.

References

[1] C.L. Arthur and J. Pawliszyn, J. Anal. Chem. 1990, 62, 2145-2148.

[2] J. Dugay, C. Miège and M.-C. Hennion, J. Chrom. A 1998, 795, 27-42.

[3] L.S. De Bruin, P.D. Josephy and J. Pawliszyn, Anal. Chem. 1998, 70, 1986-1992.

[4] J. Beltran, F.J. Lopez, O. Cepria and F. Hernandez, J. Chrom. A 1998, 808, 257-263.

[5] A. Leo, C. Hansch and D. Elkins, Chem. Rev. 1971, 71, 525.

[6] C. Hansch and A. Leo, Substituted Constants for Correlation Analysis in Chemistry and Biology, Wiley, New York 1979.

[7] C. Hansch and A. Leo, Log P and Parameter Database, a Tool for the Quantitative Prediction of Bioactivity, Pomona College Medicinal Chemistry Project, Comtex Scientific Corporation, New York 1982.

[8] E. Baltussen, P. Sandra, F. David and C. Cramers, J. Microcol. Sep. 1999, 11, 737.

GERSTEL GmbH & Co. KG
Eberhard-Gerstel-Platz 1
45473 Mülheim an der Ruhr
Germany
+49 (0) 208 - 7 65 03-0
+49 (0) 208 - 7 65 03 33
gerstel@gerstel.com
www.gerstel.com

GERSTEL Worldwide

GERSTEL, Inc.
701 Digital Drive, Suite J
Linthicum, MD 21090
USA
+1 (410) 247 5885
+1 (410) 247 5887
sales@gerstelus.com
www.gerstelus.com

GERSTEL AG
Wassergrabe 27
CH-6210 Sursee
Switzerland
+41 (41) 9 21 97 23
+41 (41) 9 21 97 25
swiss@ch.gerstel.com
www.gerstel.ch

GERSTEL K.K.
1-3-1 Nakane, Meguro-ku
Tokyo 152-0031
SMBC Toritsudai Ekimae Bldg 4F
Japan
+81 3 5731 5321
+81 3 5731 5322
info@gerstel.co.jp
www.gerstel.co.jp

GERSTEL LLP
10 Science Park Road
#02-18 The Alpha
Singapore 117684
+65 6779 0933
+65 6779 0938
SEA@gerstel.com
www.gerstel.com

GERSTEL (Shanghai) Co. Ltd
Room 206, 2F, Bldg.56
No.1000, Jinhai Road,
Pudong District
Shanghai 201206
+86 21 50 93 30 57
china@gerstel.com
www.gerstel.cn

GERSTEL Brasil
Av. Pascoal da Rocha Falcão, 367
04785-000 São Paulo - SP Brasil
+55 (11)5665-8931
+55 (11)5666-9084
gerstel-brasil@gerstel.com
www.gerstel.com.br

Awarded for the active pursuit of environmental sustainability