GLOBAL ANALYTICAL SOLUTIONS

GERSTEL

AppNote 7/2004

# Stir Bar Sorptive Extraction-Thermal Desorption-Capillary GC-MS applied for Analysis of Amphetamine Derivatives in Biological Fluids

Alexander Vedenin, Vladimir Suvorkin, Ekaterina Kachur
*InterLab Inc., Vadkovsky Lane 1,*
*127055 Moscow, Russia*

## Abstract

Stir bar sorptive extraction (SBSE) is a novel sample preparation technique that can be used for the enrichment of solutes from biological matrices. The principle and operation of SBSE for enrichment of pharmaceutical drugs and its derivatives – phenylalkylamines and amphetamines included into the list of pharmaceutical drugs, psychotropic compounds and its precursors, subjects to the control in Russia .

## Introduction

Stir bar sorptive extraction (SBSE) is a novel sample preparation technique for the enrichment of organic compounds from aqueous samples. 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)

A magnetic stir bar coated with PDMS is added to a liquid sample and stirred extracting the organic analytes. After extraction the stir bar is removed, rinsed with DI water, briefly blotted dry on a clean paper tissue to remove residual water droplets and placed in thermal desorption tube for subsequent GC analysis.

SBSE in combination with thermal desorption on-line coupled to capillary gas chromatography-mass-spectrometry, the technique proved to be very versatile and sensitive for the analysis of a wide range of drug substances.

The object of the investigation was samples of urine that contain derivatives – phenylalkylamines and amphetamines. Preliminary concentration of target components was evaluated by a Polarizing fluoroanalysis method and has made for amphetamine, methamphetamine- 3ppm; for MDA, MDMA and 4-methyl-thioamphetamine- 230 ppb.

## EXPERIMENTAL

*Procedure for urine samples.* Urine sample (20 ml) was poured into 40 ml headspace vial. The experiment optimized the amount of $Na_2SO_4$ added to the sample to salt out the analytes to increase recovery. The stir bar containing 24 µl PDMS was stirred in the sample for 60 min at 1000 rpm. After sampling, the stir bar is removed, rinsed with DI water, briefly blotted on a clean paper tissue to remove residual water droplets. The "Twister" was finally put in an empty special glass liner for thermal desorption.

*Instrumentation.* Analyses were performed on a GC (Agilent 6890N) equipped with mass selective detection (MSD) (Agilent 5973N). Systems were equipped with a PTV inlet (CIS, Gerstel), Thermal Desorption Unit (TDU, Gerstel).

After extraction of analytes from the biological matrix the "Twister" is thermally desorbed and the analytes are cryofocused in a PTV inlet. For this purpose, a newly developed thermal desorption device so-called TDU is used. 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 (Figure 1).

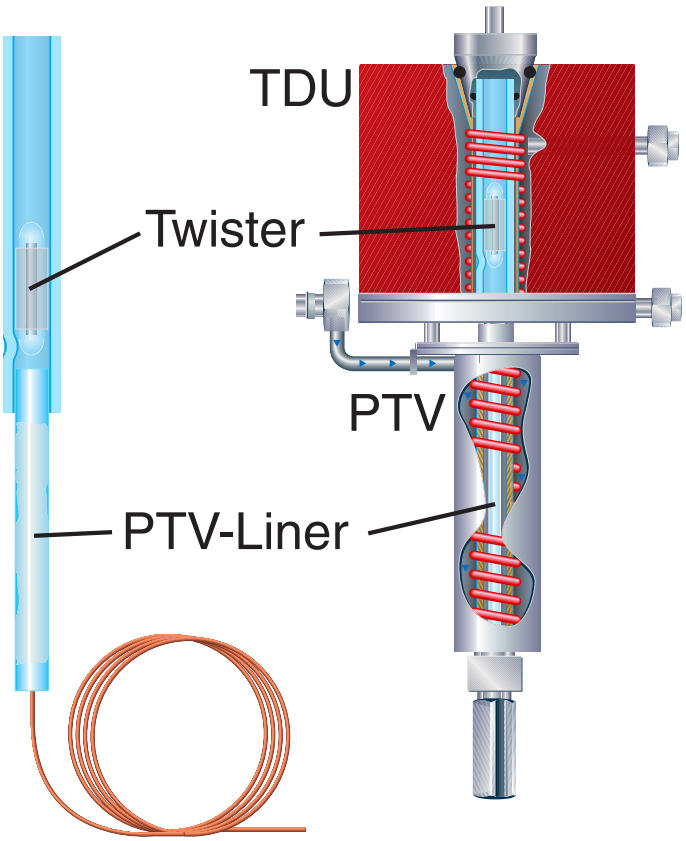


**Figure 1.** TDU attached to PTV, with „liner-in-liner" concept.

The stir bar was thermally desorbed in the splitless mode using the following desorption temperature program: 30°C, 720°C/min to 280°C (5min). The desorbed solutes were cryofocused in the CIS-4 at -25 °C. After a stir bar desorption, the PTV inlet was programmed to 280°C at 12°C/s and held for 5 min. Injection was done in the splitless mode. The compounds were separated on a capillary column HP-5MS (30m long x 0.25mm i.d. x µm 0.25) using helium carrier gas. The oven was programmed from 70°C (2min) to 280°C at 15°C/min (10 min). GC/MS data was acquired in scan mode scanning from 40 to 550 amu at 2.89 scan/s.

## Results and Discussion

Figures 2 and, 3 show the experimental total ion chromatograms obtained from the urine samples containing compounds -phenylalkylamines and amphetamines .

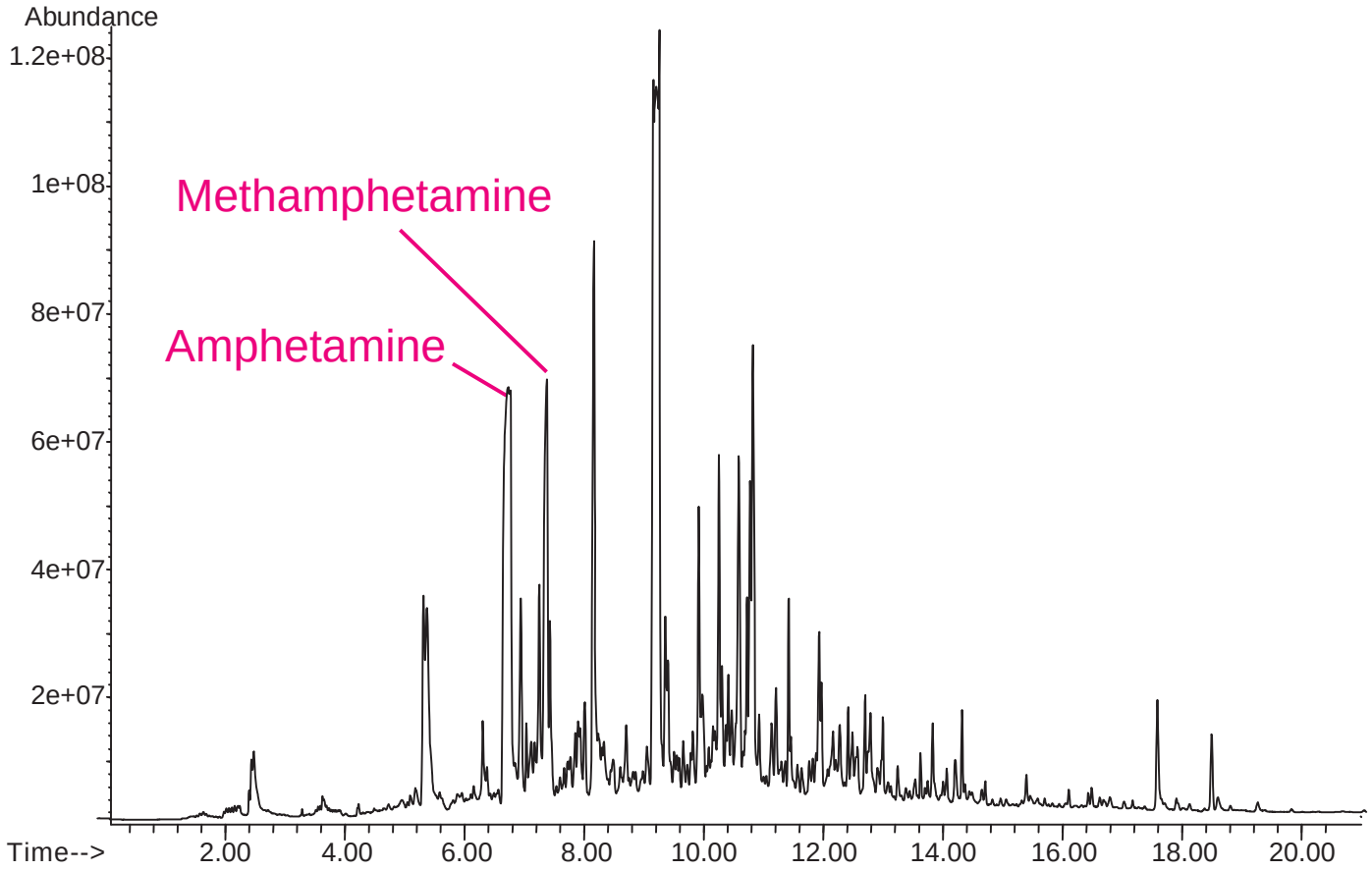


**Figure 2.** Total ion chromatogram of the SBSE-TD-capillary GC-MS analysis of urine sample contains amphetamine and methamphetamine.

Examination of the obtained chromatograms shows, that the majority of the peaks corresponding to the target compounds, are overloaded considering the response of the MSD, and the absolute amount of the extracted substances under study at the given level of concentration in experiment goes outside the limit of linear dynamic range for the MSD. It testifies to effective extraction of derivatized phenylalkylamine from a biological matrix by using SBSE and enables detection of target components at lower levels of concentration. In these preliminary studies the stir bar was thermally desorbed in the splitless mode; however split injection may be preferred to reduce the mass of compound injected into the column, with the purpose of obtaining correct quantitative results without overloading the response of the detector.

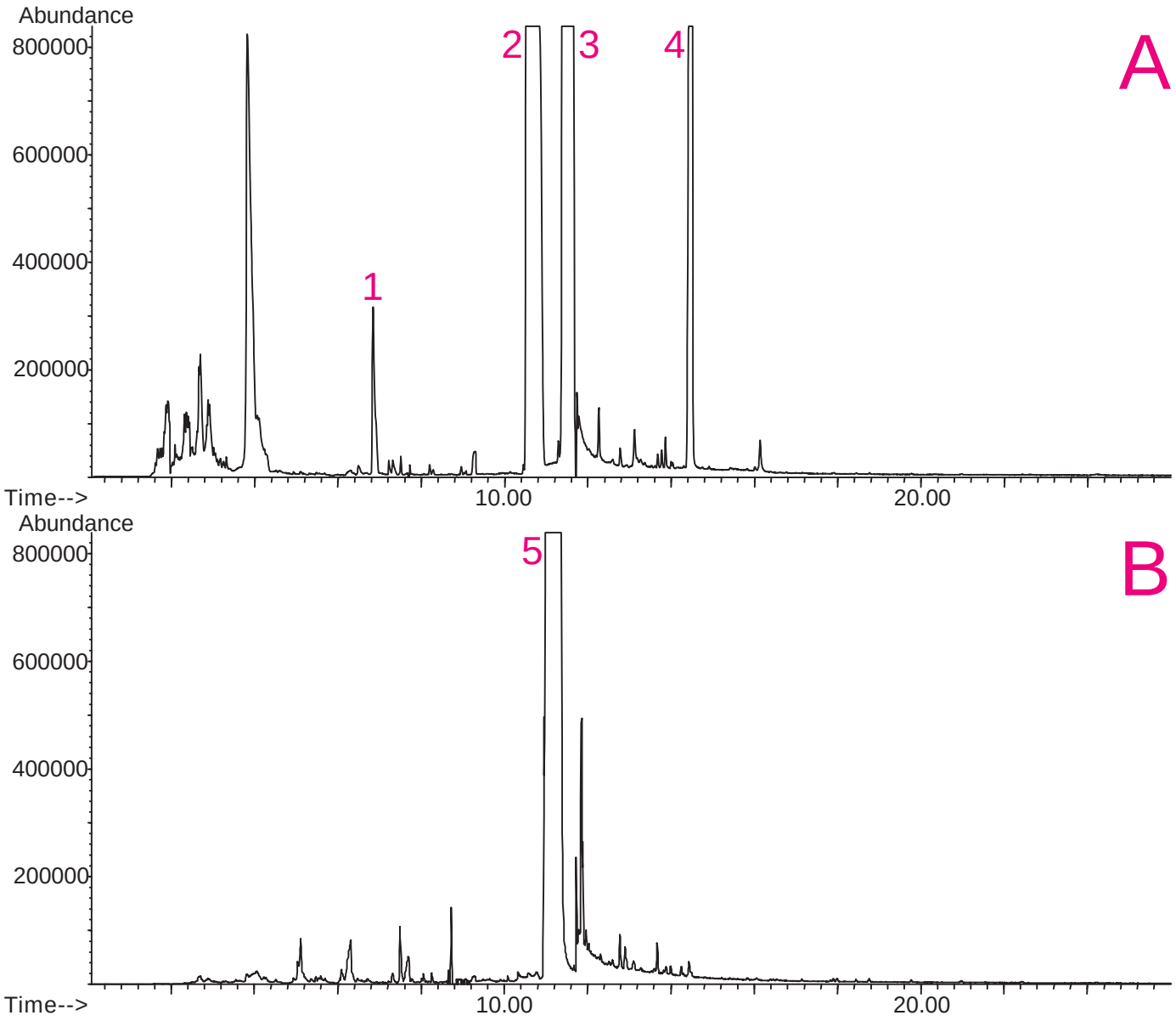


**Figure 3.** Extracted ion chromatogram of the SBSE-TD-capillary GC-MS analysis of urine samples:
A) at 44 m/z: 1. Amphetamine (6.84 min); 2. MDA (10.56 min); 3. 4-Methyltioamfetamine (11.56 min); 4. 4-Methyltioamfetamine AC (14.42 min);
B) at 58 m/z: 5. MDMA (11.06min).

## Conclusion

Stir Bar Sorptive Extraction is an effective technique for extracting pharmaceutical drugs and derivatives from biological matrices. SBSE in combination with thermal desorption- capillary gas chromatography provides a very versatile tool for the analysis of organic solutes in biological fluids. This technique allows avoiding the use of hazardous organic solvents and subsequent steps to concentrate the extracts. The "Twisters" used in the study were reused over 50 times with no apparent degradation in performance. This extraction technique can be combined with other analytical method advances to allow miniaturization, provide maximal simplification of extraction, improve sample throughput, and increase productivity of processing of samples in laboratories.

G L O B A L  A N A L Y T I C A L  S O L U T I O N S


**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**
Level 25, North Tower
One Raffles Quay
Singapore 048583
☎ +65 6622 5486
🖷 +65 6622 5999
@ SEA@gerstel.com
🌐 www.gerstel.com

**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