Headspace Solid-Phase Dynamic Extraction (SPDE) and GC/MS/MS for the determination of Amphetamines and Synthetic Designer Drugs in Hair Samples

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INTRODUCTION

During the past few years solid-phase microextraction (SPME), discovered and developed by Pawliszyn and co-workers (1), has emerged as a versatile solvent-free alternative to conventional liquid-liquid extraction and solid-phase extraction procedures. SPME in conjunction with GC-MS analysis has been employed for a variety of organic compounds, especially of volatile and semi-volatile agents using the headspace technique. The main disadvantages of SPME are the fragility of the fused silica and the unprotected stationary phase coating on the outer surface of the fibre when extended through the syringe needle. The limited flexibility regarding surface area and film thickness is another problem of SPME. There were several efforts to overcome these disadvantages. All attempts aimed at developing a device with the coating on the interior of a needle or capillary instead of a fibre. The advantages are greater capacity, higher extraction speed and stability of the device. A technique using internally coated hollow needles was described by Murphy (2). In 1997 an inside needle capillary adsorption trap (INCAT) technique was developed (3).

The solid-phase dynamic extraction (SPDE) developed by Chromtech (Idstein, Germany) in 2000 is the first commercially available inside-needle device. It uses coated stainless steel needles (8 cm) with a 50 µm film of polydimethylsiloxane (PDMS) and 10 % activated carbon (BGB Analytik, Anwil, Switzerland). A diagram of a SPDE device in comparison with a SPME fibre is given in Fig. 1. The volume of the stationary phase of the SPDE needle is approximately 5.99 mm³ compared to a 100 µm PDMS SPME fibre with 0.94 mm³. SPDE was successfully applied to the analysis of pesticides in water by Lipinski (4).

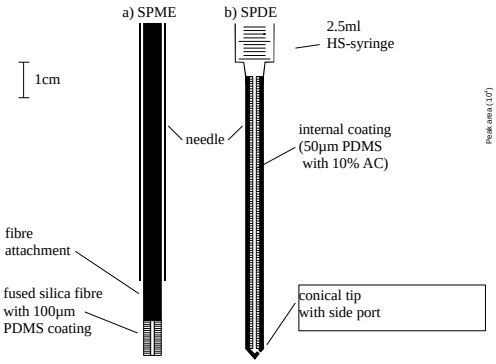

Fig. 1: Schematic representation of the SPME device (a) in comparison to the SPDE device (b)

EXPERIMENTAL

The hair samples were washed for 5 min in deionised water, petroleum benzine and dichloromethane, respectively. Ten mg of hair, 1 mL NaOH (10 M) and 80 µL internal standard mixture (deuterated analytes, 250 ng/mL) were placed into a 10 mL headspace vial. A second vial was filled with 25 µL MBTFA and sealed in the same way. The fully automated SPDE procedure using a CTC Combi PAL autosampler is shown in Fig. 2.

The following SPDE specific parameters were successively optimised: temperature of agitator and headspace syringe, number of filling cycles for extraction and derivatisation, speed of aspirating the syringe for extraction and desorption, flush gas volume for desorption, predesorption time in GC injection port and desorption temperature (Fig. 3).

For analysis an Agilent model 6890 Series Plus gaschromatograph in combination with a Bear Kodiak 1200 GC/MS/MS Triple Quadrupole masspectrometer and a CTC-Combi-PAL-Autosampler were used (Chromtech, Idstein, Germany).

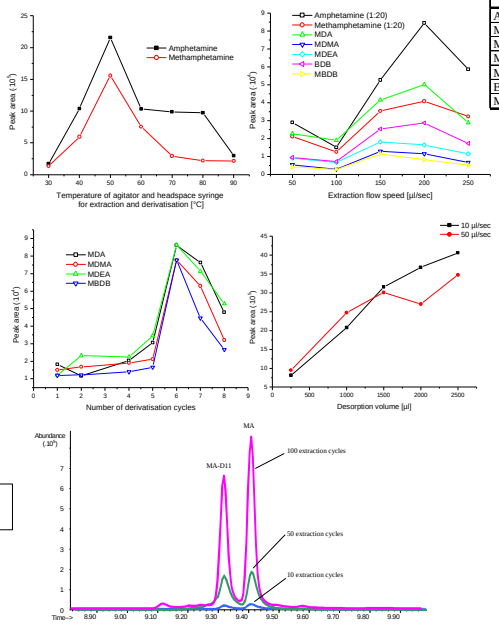

Fig. 3: Optimisation of the SPDE procedure

RESULTS AND DISCUSSION

By routine analyses of authentic samples no interferences were observed. Peak purity and selectivity are ensured. Further validation data are demonstrated in Tab. 1. As shown in Fig. 4 the sensitivity was increased by using the triple quadrupole MS/MS-mode (B) in comparison to single quadrupole MS-SIM (A). The limits of quantitation and detection were markedly enhanced compared to SPME or SPDE with conventional GC/MS, e.g. the limits of MDA were lowered tenfold (5,6). Regarding the validating data, the procedure is sensitive, selective and reproducible.

A large advantage of the SPDE technique in relation to SPME is the robustness of the capillary. It is nearly impossible to damage the SPDE device mechanically in contrast to the fragile SPME fibres. The SPDE capillary lasted more than twice the time of an SPME fibre. The absolute extraction yield with SPDE was 50% higher compared to a SPME fibre.

Tab. 1: Extraction yield, limit of detection and quantitation (LOD/LOQ), precision, linear range and correlation coefficient of the calibration curves

				Precision		Regression line	
	Extraction yield [%]	LOD [ng/mg]	LOQ [ng/mg]	Intraday [%]	Interday [%]	Linear range [ng/mg]	correlation coefficient
Amphetamine	12.9	0.03	0.12	3.5	4.9	0.05-20	0.999
Methamphetamine	10.2	0.03	0.11	4.5	7.6	0.05-20	0.999
MDA	15.0	0.01	0.04	3.0	6.1	0.05-20	0.996
MDMA	16.7	0.03	0.10	1.4	3.7	0.05-20	0.999
MDEA	14.7	0.04	0.33	2.6	6.2	0.1-20	0.999
BDB	12.7	0.02	0.08	5.3	6.5	0.05-20	0.998
MBDB	11.6	0.03	0.11	1.9	3.6	0.05-20	0.998

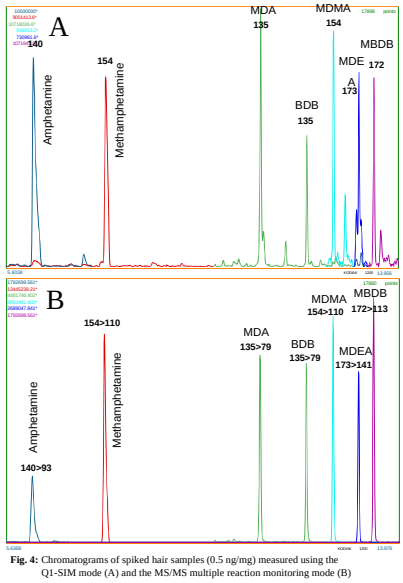

Fig. 4: Chromatograms of spiked hair samples (0.5 ng/mg) measured using the Q1-SIM mode (A) and the MS/MS multiple reaction monitoring mode (B)

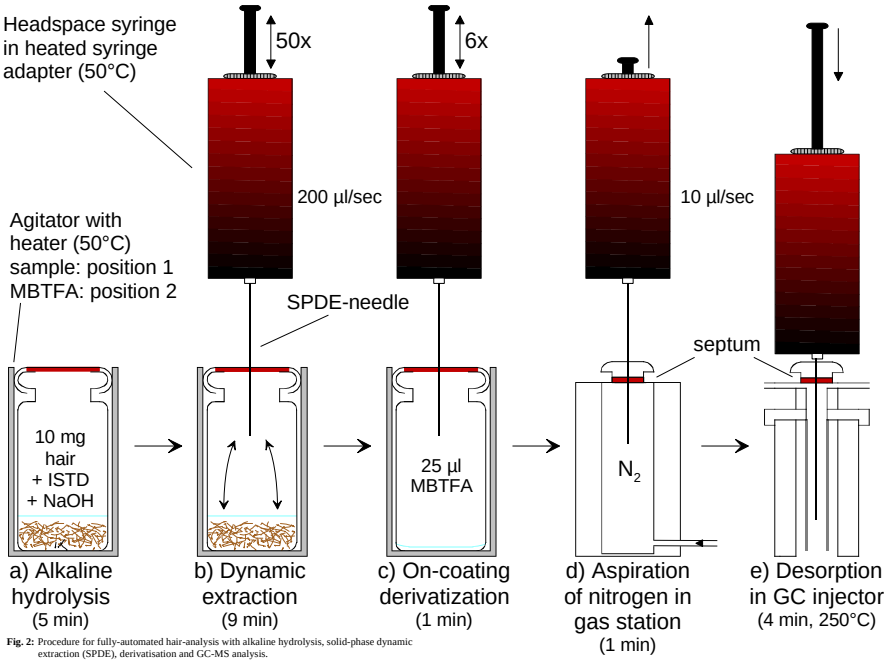

Fig. 2: Procedure for fully-automated hair-analysis with alkaline hydrolysis, solid-phase dynamic extraction (SPDE), derivatisation and GC-MS analysis.

CONCLUSIONS

The application of fully automated headspace solid phase dynamic extraction (HS-SPDE) with following GC/MS/MS for the determination of amphetamines and synthetic designer drugs in hair was tested. The method was successfully applied to the analysis of hair samples from drug consumers. The SPDE as a further development of SPME turned out to be equally suitable for the requirements of clinical and forensic toxicology regarding sensitivity and selectivity. The main advantages are the robustness of the device and the greater capacity.

ACKNOWLEDGMENTS

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REFERENCES

- Z. Zhang, J. Pawliszyn: Headspace solid-phase microextraction. Anal. Chem. 65 (1993) 843-852
- G.E. Murphy. United States Patent (1996) 5,565,622
- M.E. McComb, R.D. Oleschuk, E. Giller, H.D. Gesser: Microextraction of volatile organic compounds using the inside needle capillary adsorption trap (INCAT) device. Talanta 44 (1997) 2137-2143
- J. Lipinski: Automated solid phase dynamic extraction - extraction of organics using a wall coated syringe needle. Fresenius J. Anal. Chem. 369 (2001) 57-62
- F. Musshoff, H.P. Junker, D.W. Lachenmeier, L. Kroener, B. Madea: Fully Automated Determination of Amphetamines and Synthetic Designer Drugs in Hair Samples using Headspace Solid-Phase Microextraction and Gas Chromatography – Mass Spectrometry, J. Chromatogr. Sci. (2002) in press.
- F. Musshoff, D.W. Lachenmeier, L. Kroener, B. Madea: Automated Headspace Solid-Phase Dynamic Extraction for the Determination of Amphetamines and Synthetic Designer Drugs in Hair Samples, J. Chromatogr. A (2002) in press.