Supporting Information

Quantitative Silylation Speciations of Primary Phenylalkyl Amines, Including Amphetamine and 3,4-Methylenedioxyamphetamine Prior to Their Analysis by GC/MS

Borbála Molnár[†,&], Blanka Fodor[†], Imre Boldizsár[‡], Ibolya Molnár-Perl[†]*

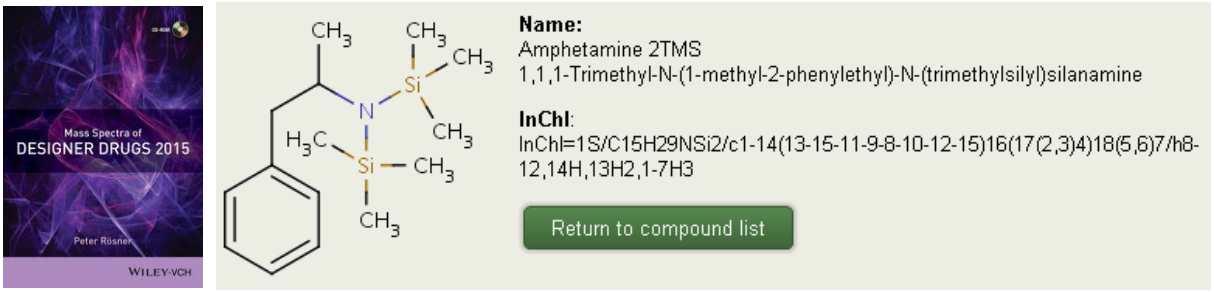
Institutes of Chemistry[†] and Biology[‡], Departments of Analytical Chemistry[†] and Plant Anatomy[‡], L. Eötvös University, 1117, Pázmány Péter sétány 1/A-C, Budapest, Hungary; Doctoral School of Pharmaceutical Sciences[&], Semmelweis University, 1085, Üllői út 26, Budapest, Hungary

TABLE OF CONTENTS

The source and preparation background of the amphetamine ditrimethylsilyl (A-diTMS) spectrum in the NIST data basis

The A-diTMS spectrum's source

Coming back to the statement in the manuscript, here we gave details on the source of A-diTMS spectrum, found in the NIST library.
This spectrum was taken from the list of a separate spectrum library, authored by Peter Rösner, entitled "Mass spectra of designer drugs"[S1]



The preparation background of the A-diTMS derivative[S2]

E-mail, on corresponding author's request

From: i.molnar.perl@gmail.com
To: info@chemograph.de
Date: April 4, 2015 at 9:33 AM
Subject: request for analytical conditions

Dear Colleagues,
Undersigned I would be happy to know, the experimental conditions providing amphetamine-2TMS (reagent, solvent, catalyst, reaction time, temperature).
Many thanks in advance, kind regards,
ibolya molnár-perl

E-mail, with the answer

From: Steven.Luhn@bka.bund.de
To: i.molnar.perl@gmail.com
Cc: p.roesner@t-online.de
Date: April 7, 2015 at 9:04 AM
Subject: AW: request for analytical conditions

Good morning Dr. Molnar,
Dr. Roesner instructed me to give you a guide for the silylation of amphetamin.
GC-Conditions: Inlet Temp-250°C->Start Temp. 70°C->Ramp up at 10°C/min-> 300°C->5min. hold
Transfer-line 250°C; Column DB-1 or DB-5 for best results
Silylation with MSTFA (N-Methyl-N-(trimethylsilyl)trifluoroacetamide) and Pyridin as catalyst.
Your GC-MS-System must be conditioned by 3-5 injections with a mixture of CHCl3/MSTFA(3:1).
Your amphetamine-sample should be dry.->At a normal amphet.-sample use 0,1-0,5mg of your sample->mix it with 100µl MSTFA and 10µl Pyridin->store it for 10-to 15 min in a 70°C hot sand bath or another hot place and afterwards put it in a clean microvial->do not use another solvent->inject the mixture.
The amphetamine-TMS elutes after 7-10 min (big Peak, RI: 1566) and the amphetamin-TMS2(small Peak) 3-6 min later. Maybe you have to inject the solution for some more times to get good results.
For more questions write me an e-mail.
Good luck,
Greetings from Germany.
Steven Luhn

Sample preparation for derivatization prior to their GC-MS analysis

Ultrasound assisted solvent extraction followed by centrifugation of the freeze dried cactus (*Lophophora Williamsii*, Lem.)

0.002 g freeze dried cactus tissues, weighed with ± 0.001 mg uncertainty, were subjected to ultrasound assisted extraction with 2 mL methanol containing 10% hydrochloric acid, w/w (further on: methanol/HCl). Reactions were performed at 60 °C for 30 min, applying a reflux condenser. After centrifugation, solvent was quantitatively transferred to a 5 mL volumetric flask. The residue was extracted, centrifuged, then the solvent layer transferred again, 3 times, as before. Stock solution volume was completed to 5.0 mL, its aliquots (5 μL, 10 μL, 25 μL and 50 μL) were evaporated to dryness at 30 - 40 °C and derivatized.

Liquid/liquid extraction of urine

1 mL urine pipetted into a shaking funnel, was treated with 20 μL sodium hydroxide (10% w/v) and extracted with 1 mL dichloromethane. Subsequently the phases separation, solvent was transferred through a cartridge - covered with anhydrous sodium sulfate – into a 5 mL volumetric flask, containing 50 μL methanol/HCl. The entire procedure was repeated 3 times more. Stock solution volume was completed to 5.0 mL, its aliquots (250 μL, 500 μL) were evaporated to dryness at 30-40 °C and derivatized.

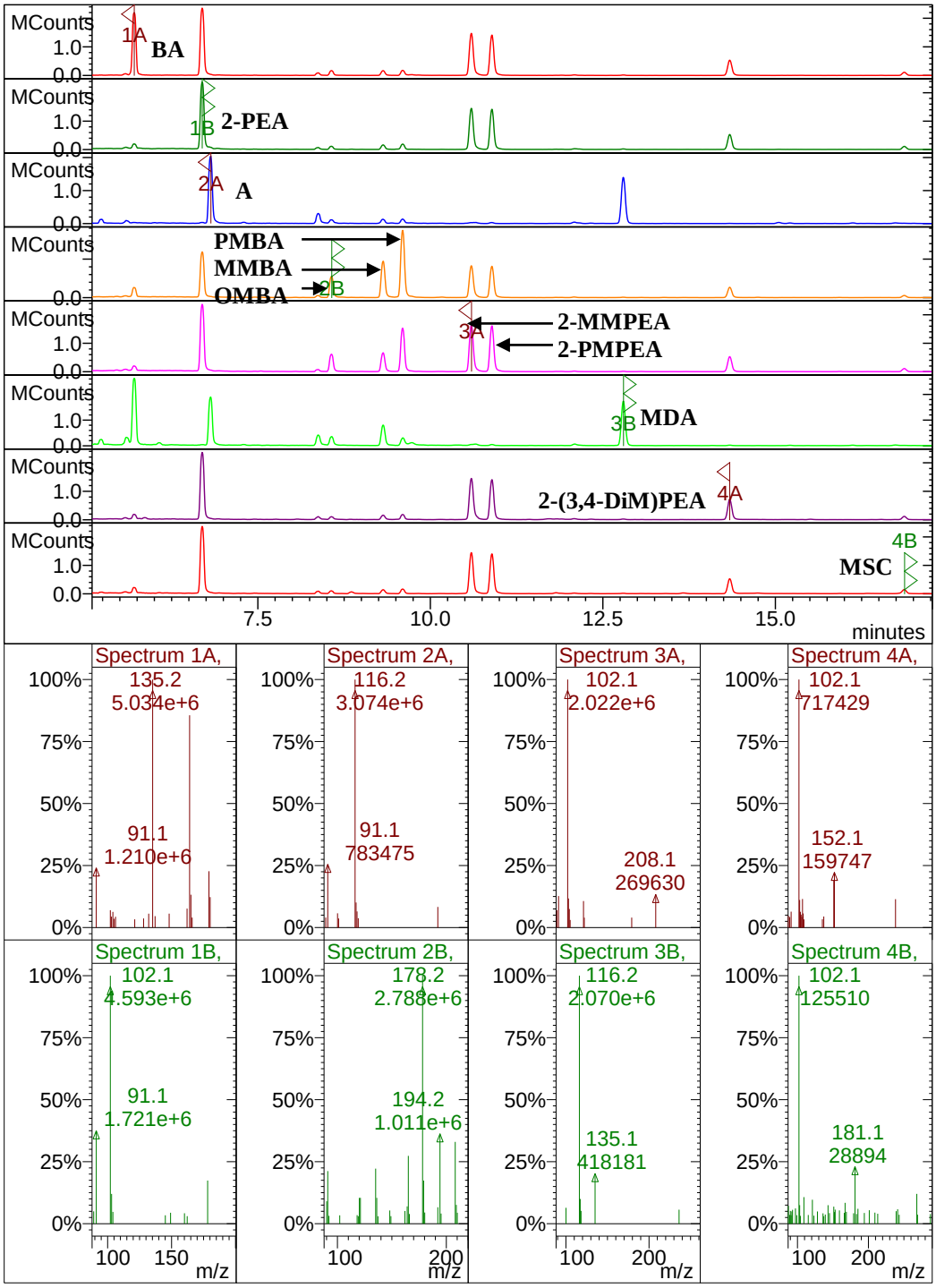


Figure S1.
Peak profiles and mass spectra of the monoTMS derivatives of PPAAs, including A and MDA

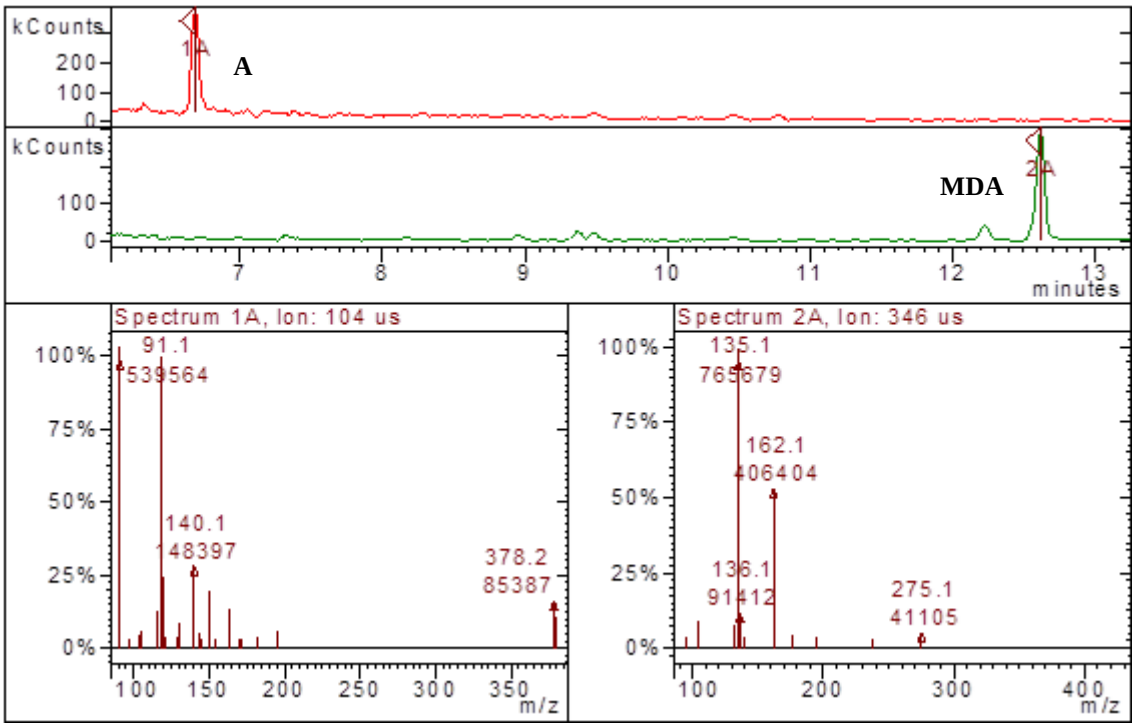


Figure S2.
Peak profile and mass spectra of acylated A and MDA derivatives obtained with the HMDS &TFA couple.[S3]

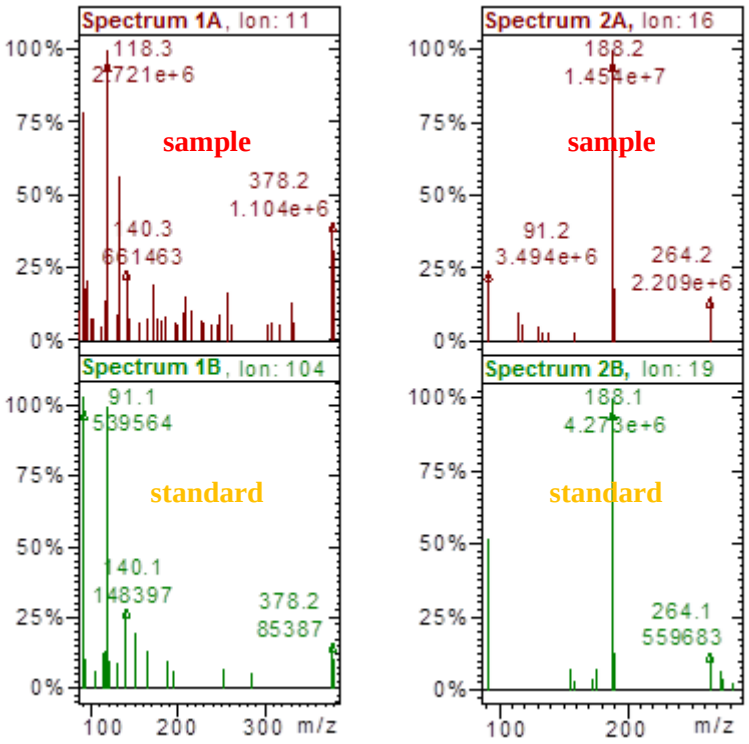


Figure S3.
Mass spectra of acylated (1A, 1B) and ditrimethylsilylated (2A, 2B) A, obtained from urine (1A, 2A) or standard (1B, 2B) samples

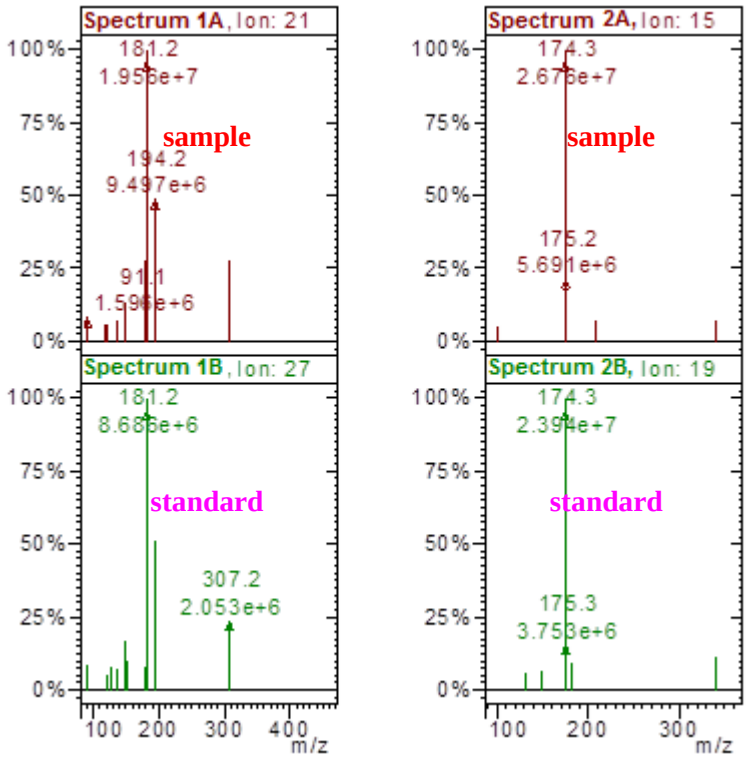


Figure S4.
Mass spectra of acylated (1A, 1B) and ditrimethylsilylated (2A, 2B) MSC, obtained from cactus (1A, 2A) or standard (1B, 2B) samples

References

[S1] Rösner, P. *Mass Spectra of Designer Drugs* [CD-ROM]; Wiley-VCH: Weinheim, 2015.
[S2] Rösner, P. University of Kiel, Kiel, Germany. Personal communication, 2015.
[S3] Molnár, B.; Csámpai, A.; Molnár-Perl, I. Anal. Chem. **2015**, 87, 848-852.