



On the Intriguing Properties of

Polysiloxanes

to Develop Sample Preparation Methods
for Gaseous, Liquid and Solid Matrices

Pat Sandra



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In Combination with ...

State-of-the-Art

Chromatographic &
Mass Spectrometric
Instrumentation

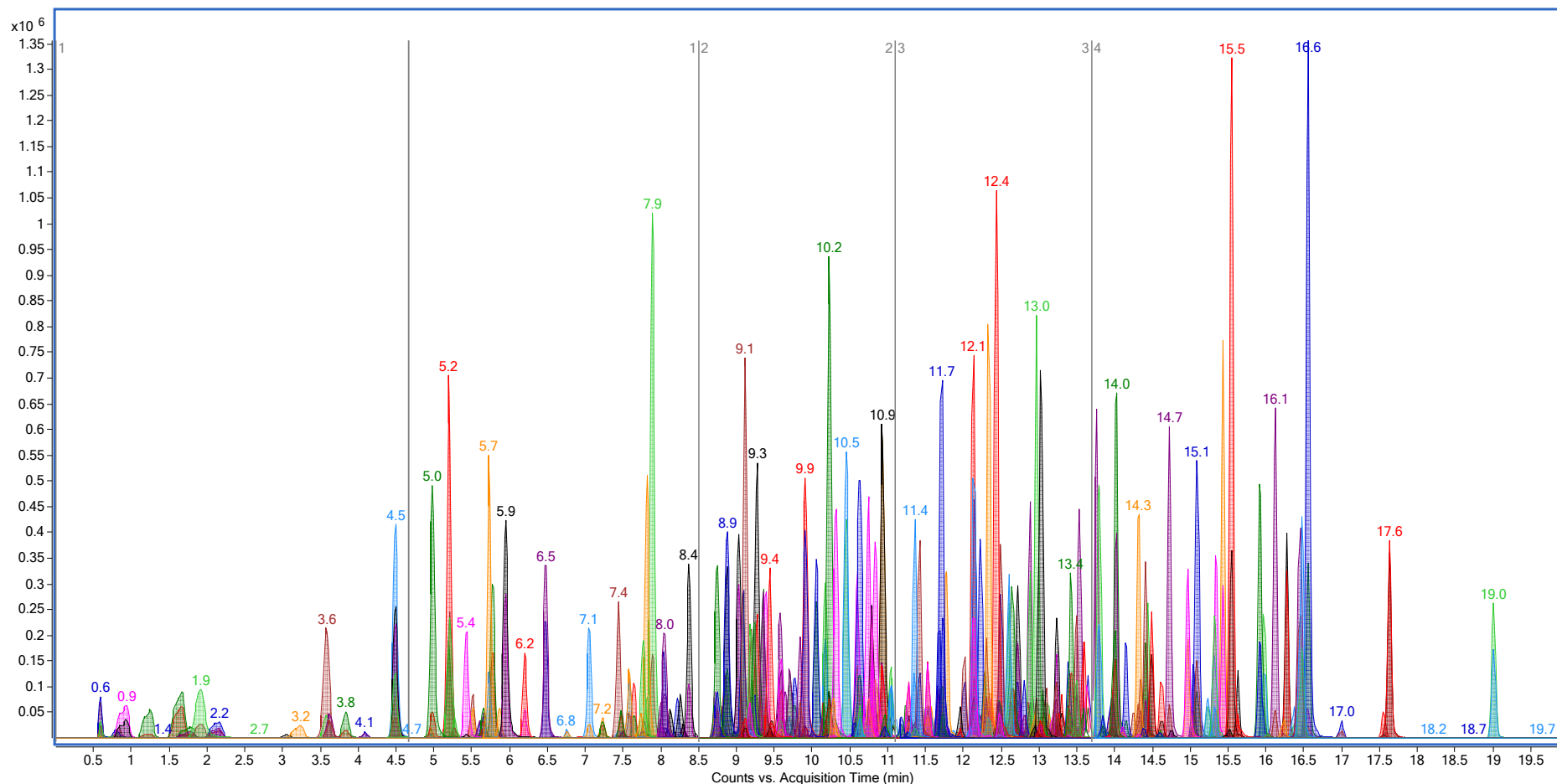


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QqQ - Dynamic MRM of 300 Pesticides

2 Transitions Each



Run with 1200-SL LC 2.1 x 100 C18 Eclipse PLUS 1.8 μ m



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Content

- Polysiloxanes
- Polysiloxanes and sorptive extraction
- Sorptive extraction formats
- Applications for gaseous samples
- Applications for liquid samples
- Applications for solid samples
- Conclusion



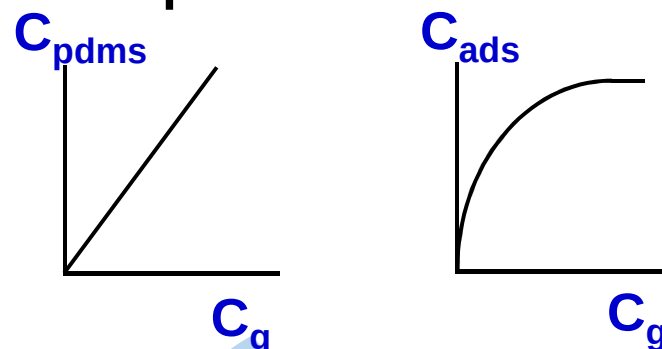
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-

Sorptive extraction on PDMS

- Compounds partition from the sample into the bulk of the phase
- Bulk retention instead of surface adsorption
- Advantages of sorption
 - Well known chromatographic process
 - High inertness
 - Absence of catalytic degradation reactions
 - Superior performance for reactive compounds
 - Linear sorption isotherms



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Sorptive extraction on PDMS

- Decomposition products very specific and not related with solutes of interest
- Retention indices available for a wide number of compounds
- PDMS/water distribution ~ octanol/water distribution, $K_{o/w}$ values can be applied
(if not available log P can be calculated using KOWWIN)

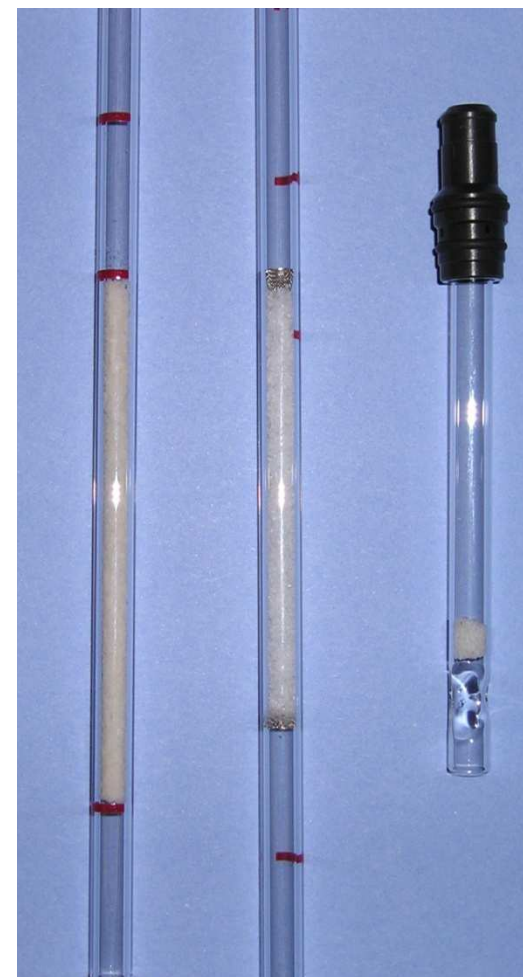


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PDMS formats for sorptive extraction

- PDMS bulk material (for coating)
- PDMS tubes (thin and thick walls)
- PDMS sheets (from 0.1 to 2 mm)
- PDMS particles from 50 to 500 μm
- PDMS foam

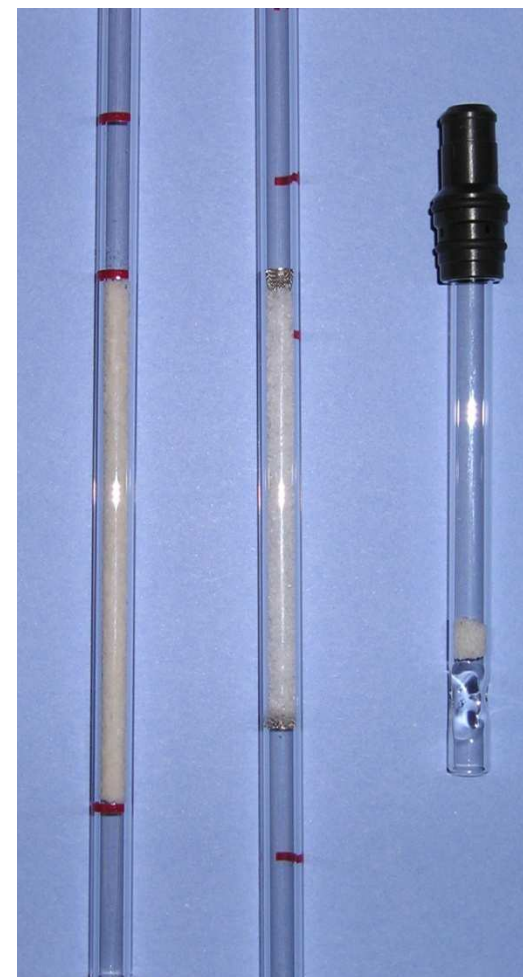


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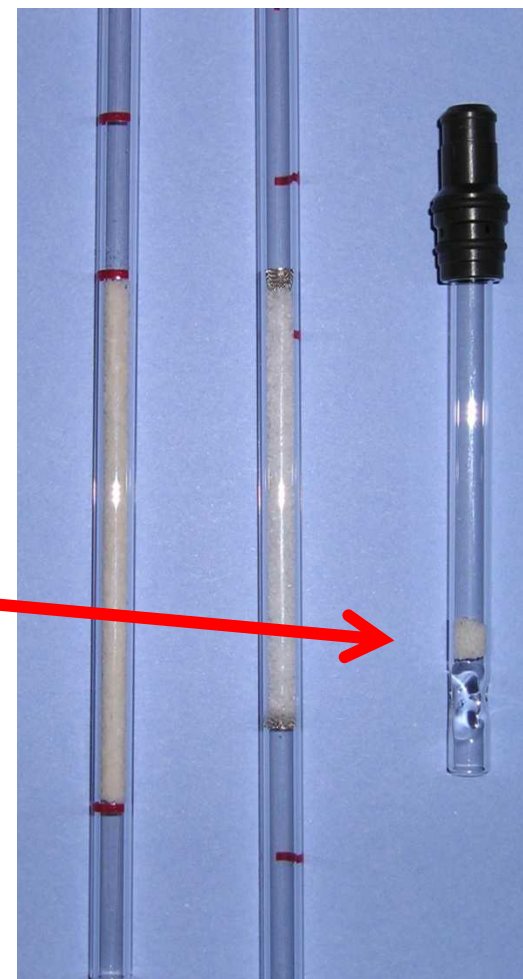


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PDMS formats for sorptive extraction

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Sorptive extraction formats

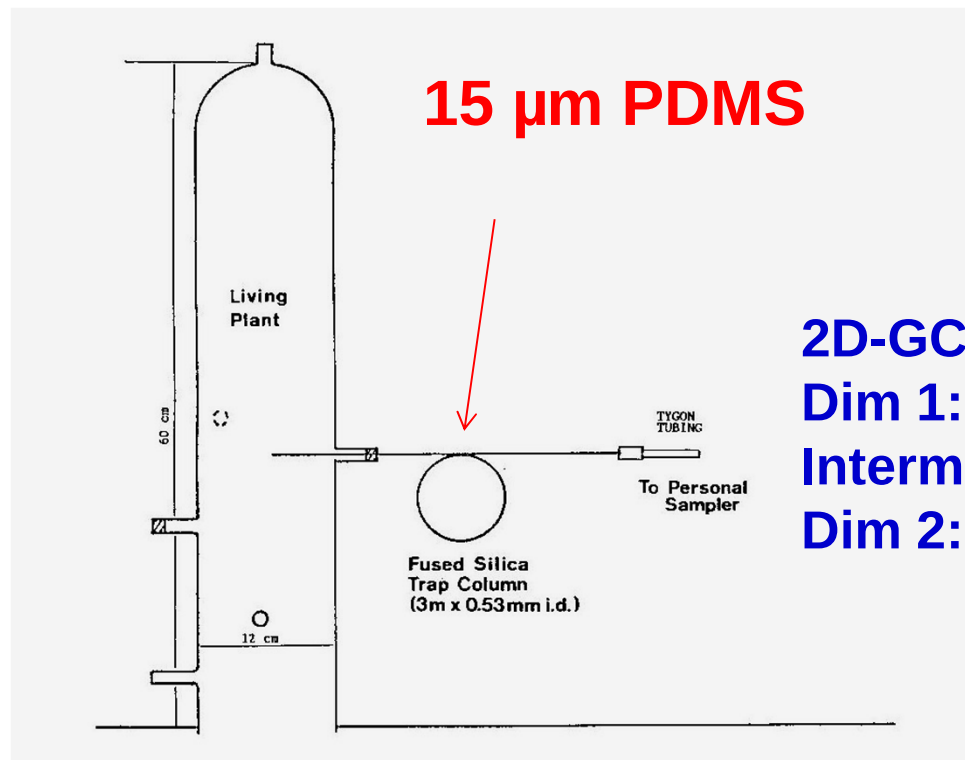
- Open Tubular Traps
- Solid Phase Microextraction (SPME)
- Gum Phase (PDMS) Extraction (GFE) – (SPE)
- Stir Bar Sorptive Extraction (SBSE)
- Head Space Sorptive Extraction (HSSE)
- Sorptive Tape Extraction (STE)
- Silicone Membrane Sorptive Extraction (SMSE)
- Automated Liner Exchange (ALEX)



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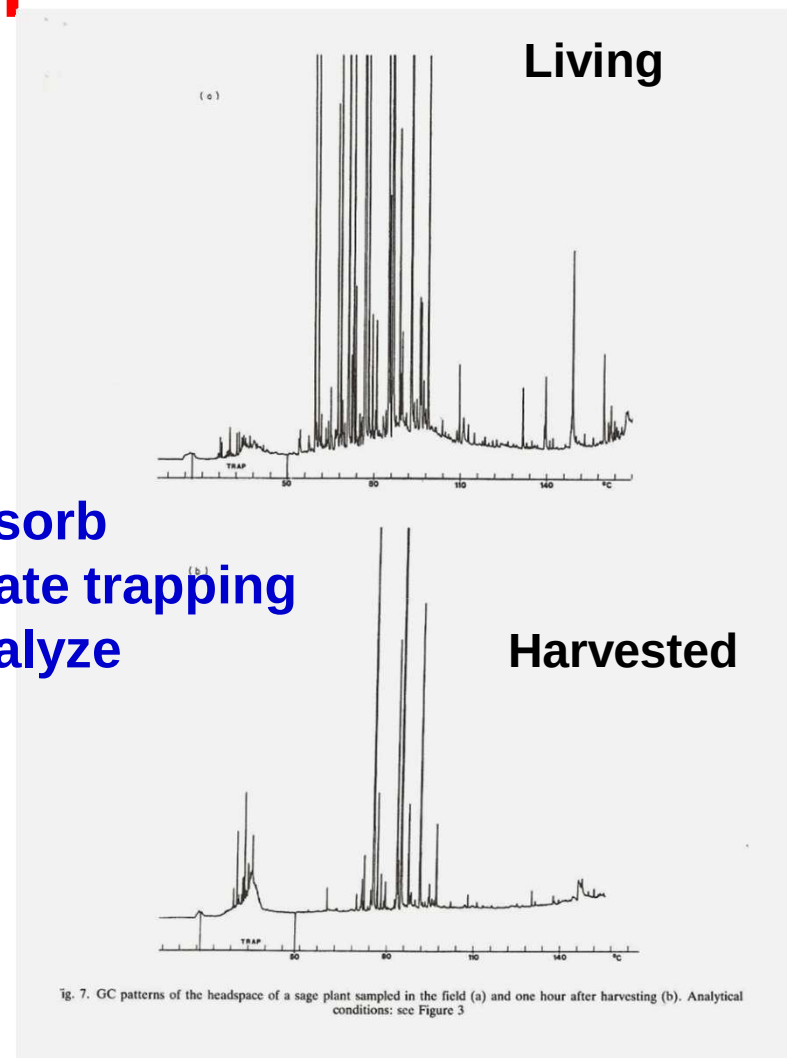
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Open Tubular Trapping of Volatiles in the Alps



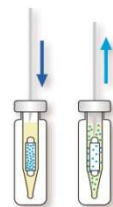
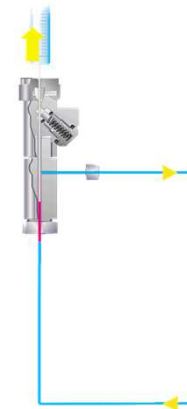
Bicchi, D'Amato, David, Sandra
FFJ 1988

2D-GC
Dim 1: desorb
Intermediate trapping
Dim 2: analyze



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AirPass: a Cutting-edge Sampling Technology for Organic Compounds in Air

IET January / February 2012
www.envirotech-online.com



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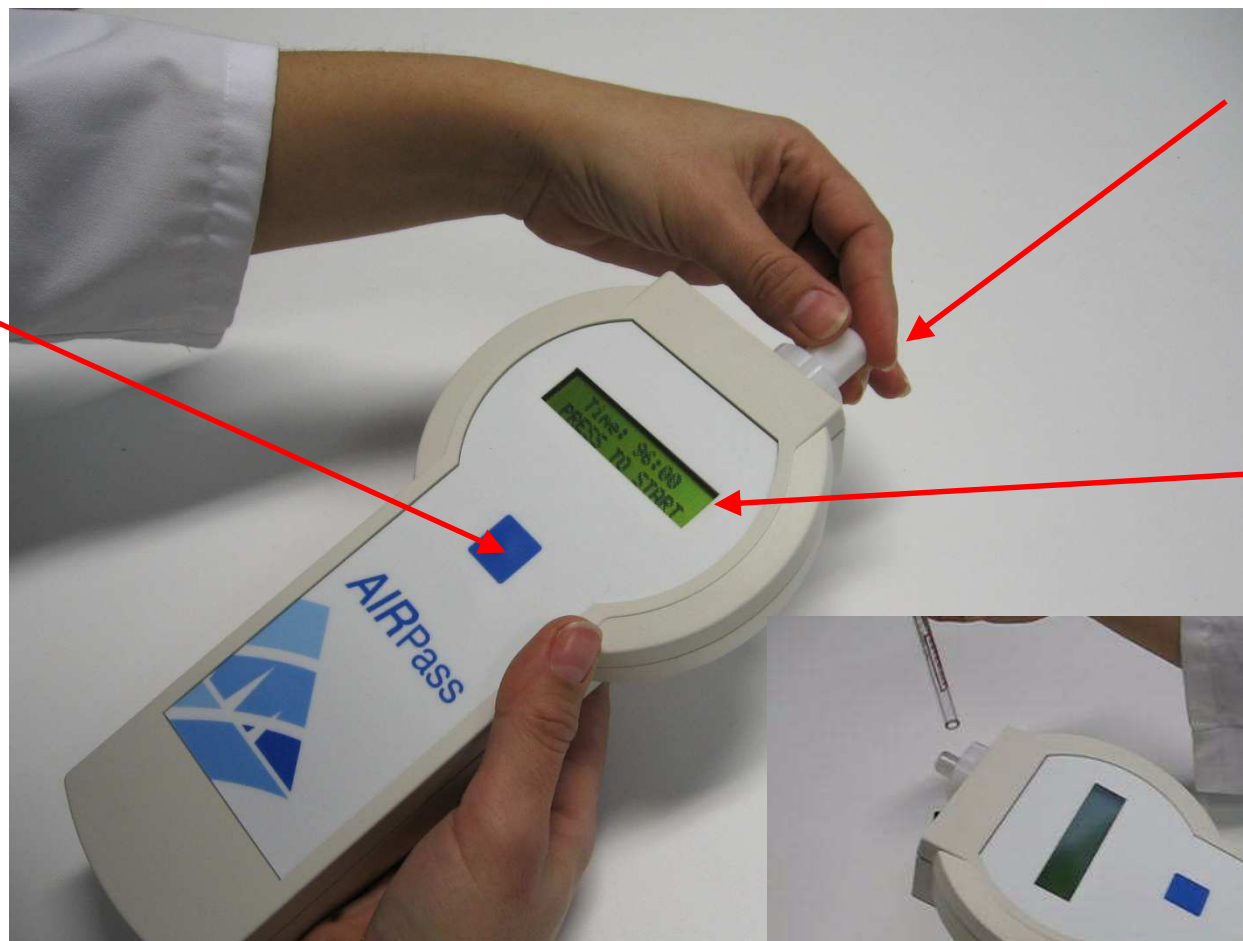
Do we have a “healthy” house ???
... endocrine disrupting chemicals ?
... allergens ?
... etc.



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**Only one
button !**



Tube insert:

- Universal
- diff. length
- diff. packing

Display:

- Flow

**Handheld device
Simple sampling set-up**

**Low and High s
volumes**



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AirPass → Features

- Handheld device (personal sampling)
- All-in-one universal air sampler
- Can be handled by inexperienced people
- Easy tube exchange
- Continuous flow measuring and regulating
- Suitable to take low and large air volumes
- Inert and contaminant free
- Use of a variety of (ad)sorbents



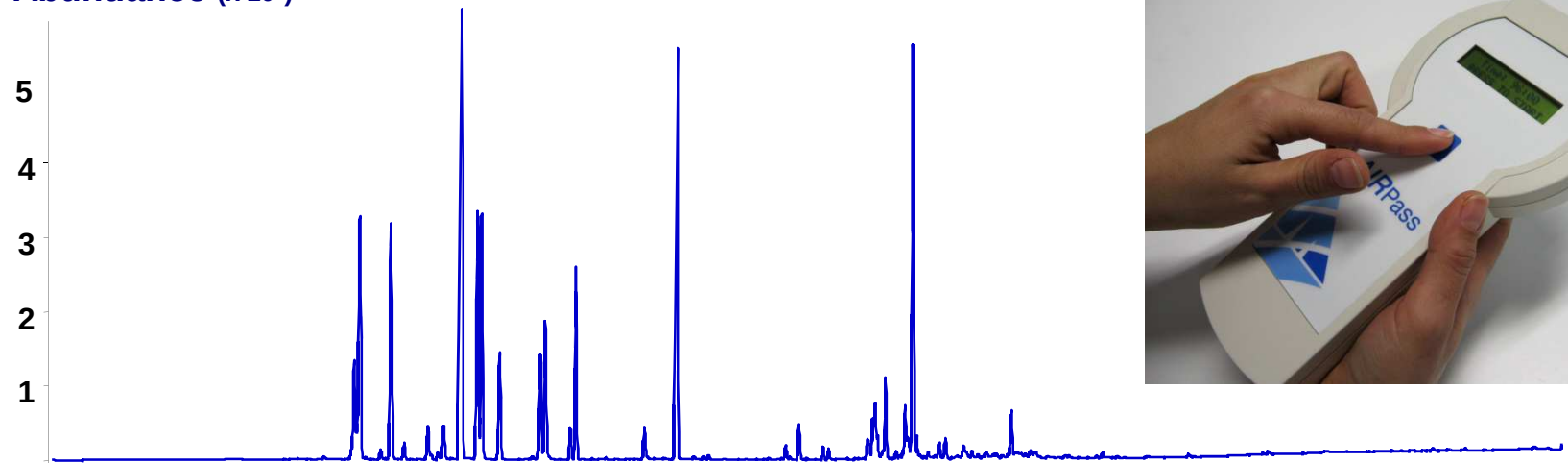
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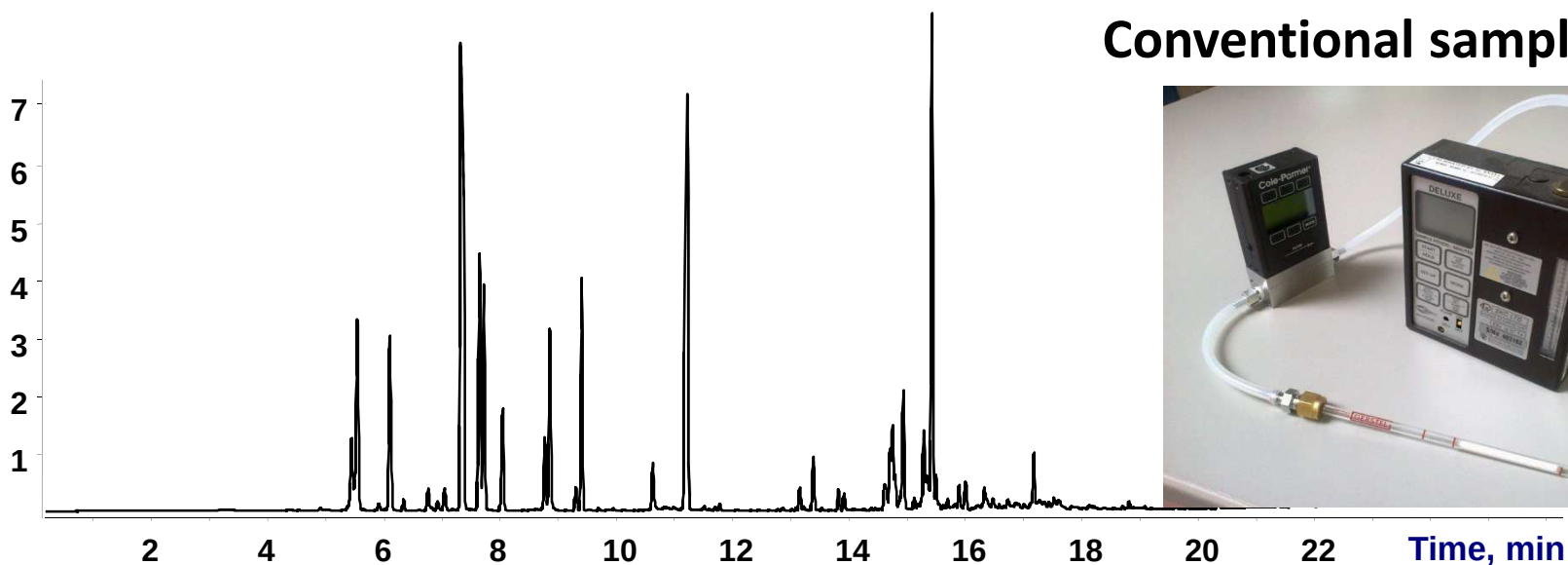
Sampling in a chemical storage room

Airpass

Abundance ($\times 10^7$)



Conventional sampling set-up

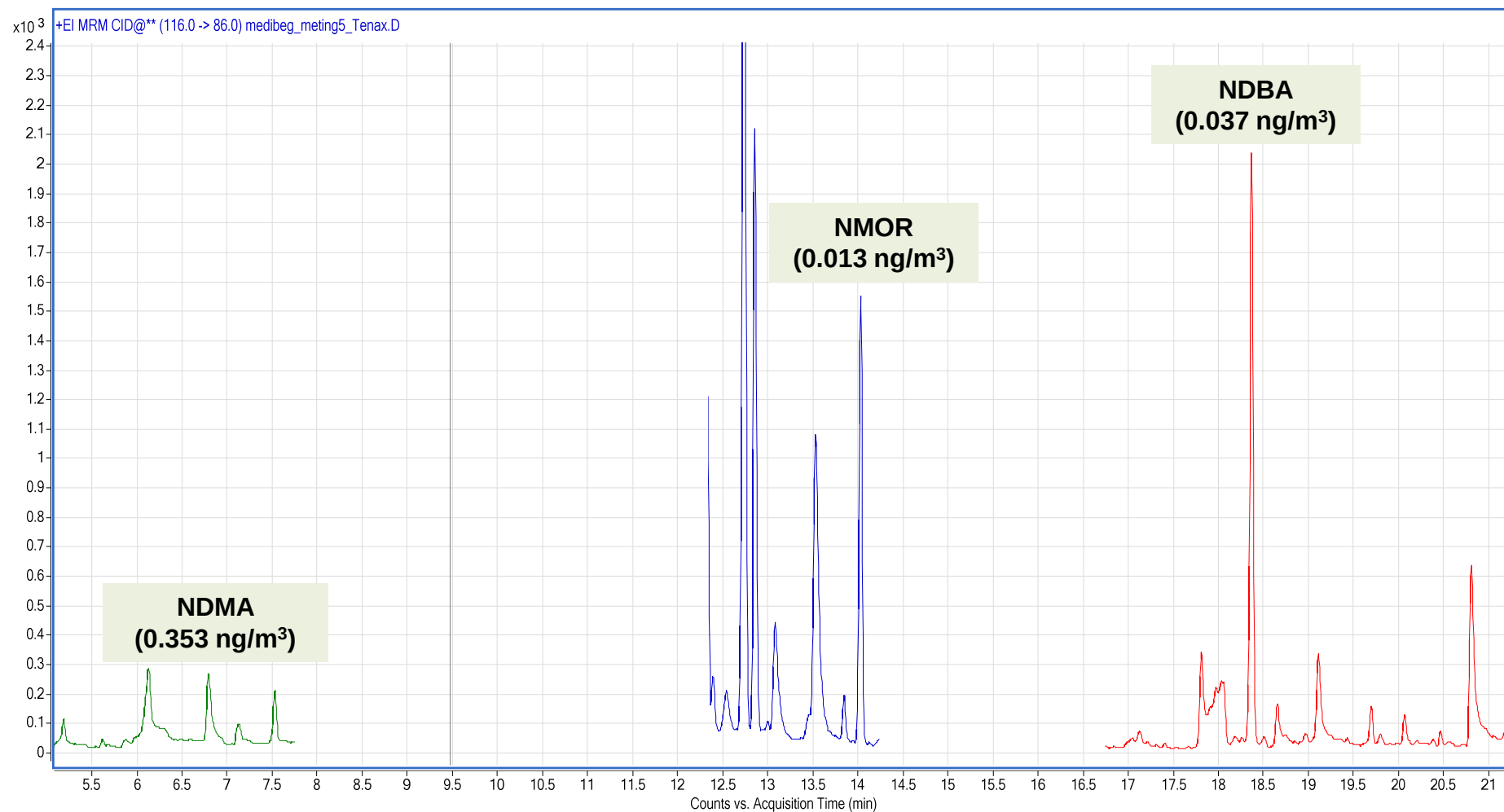


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Industrial air sampling (2 L) for nitrosamines

MRM sensitivity !!

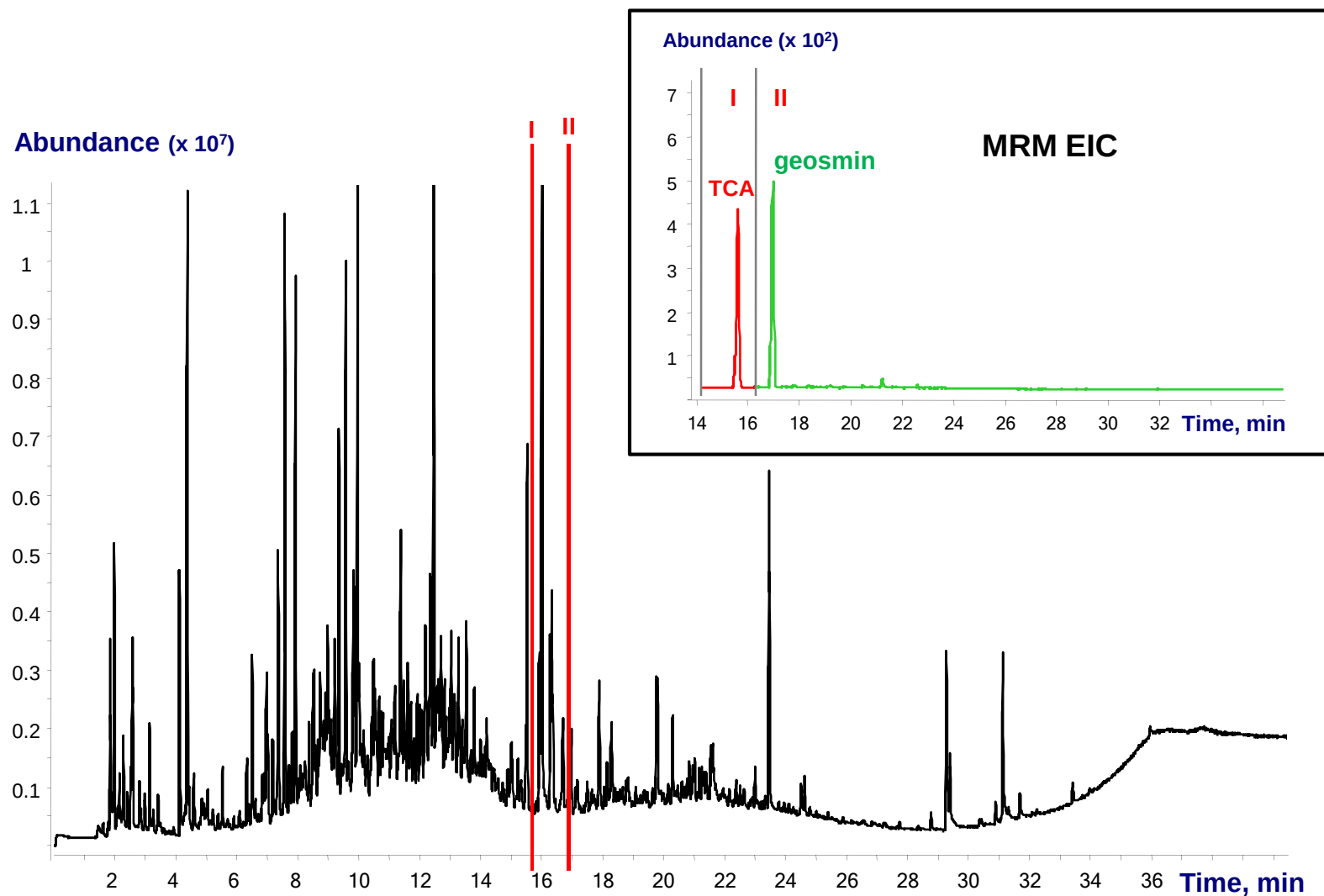


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Target analysis of odour compounds from a musty cellar

Detection of TCA and geosmin at trace levels (ng/m³)

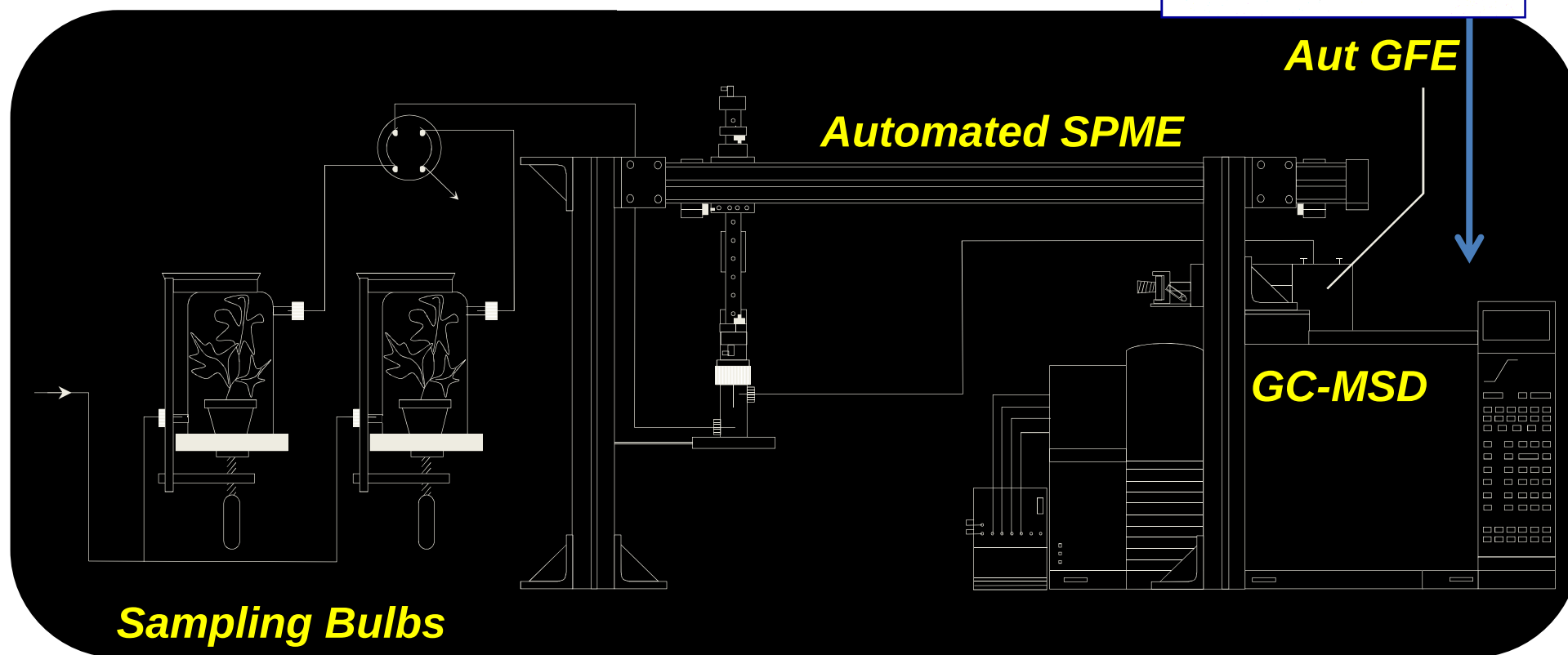


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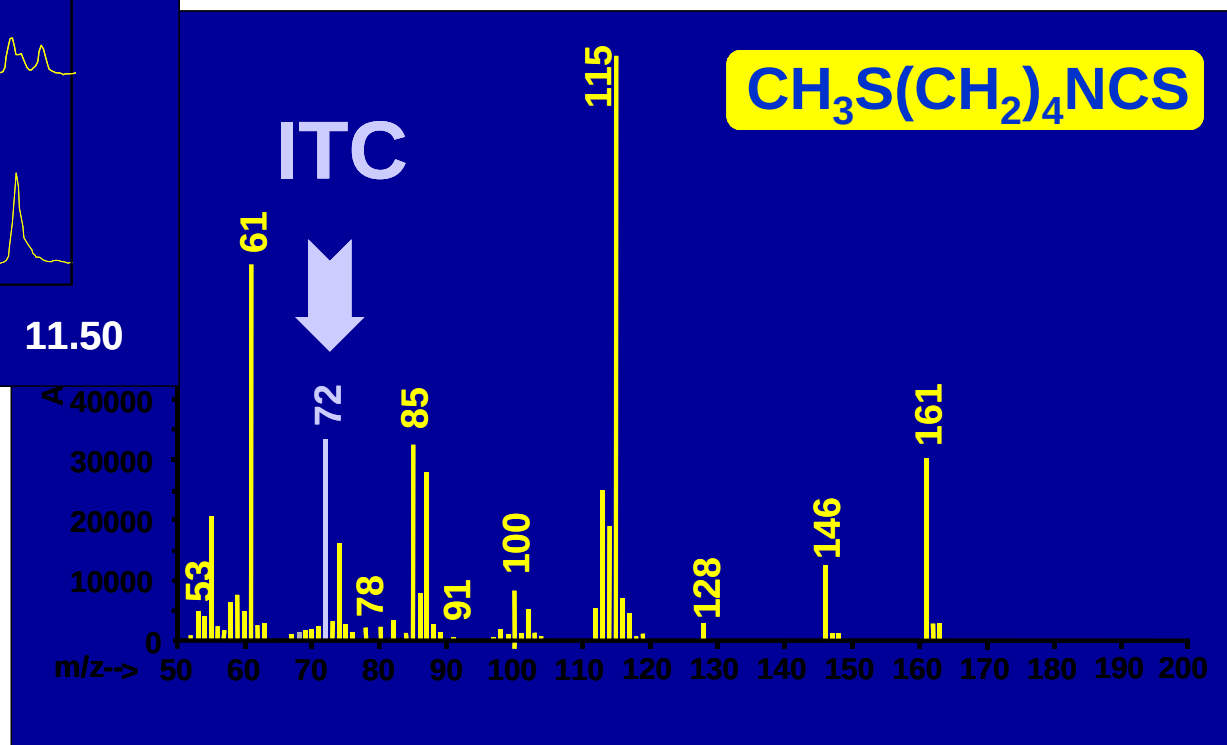
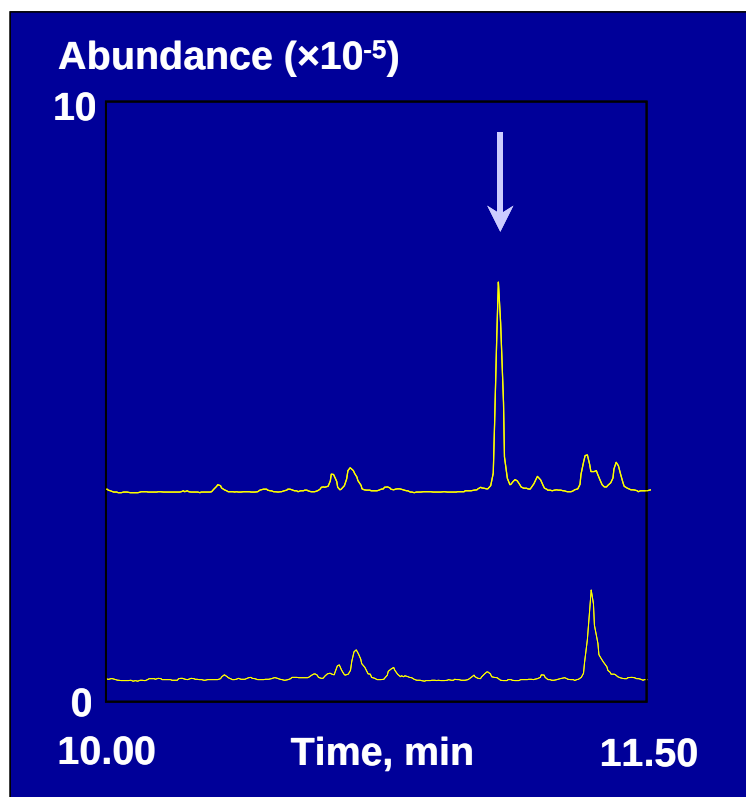


GPE



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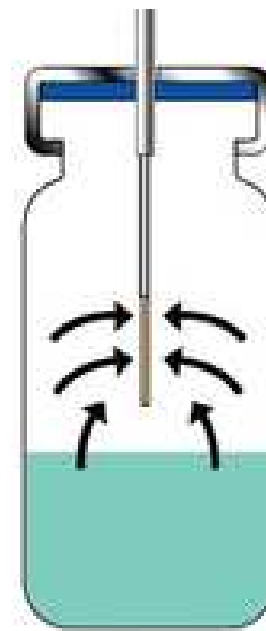
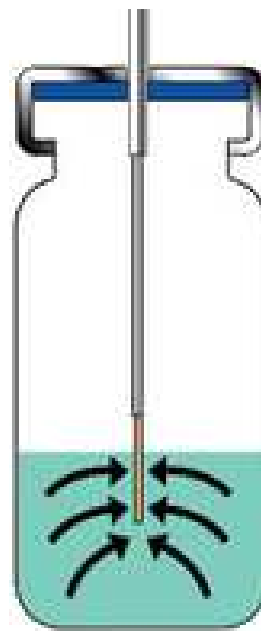


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Solid Phase Micro Extraction (SPME)

J. Pawliszyn, 1990



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Stir Bar Sorptive Extraction

Sandra, Baltussen and David [1999]

- **Origin: Publication on the SPME extraction of PCBs.**
 - Authors found very low recoveries for compounds with $K_{o/w}$ values of up to 10^{10}
 - Repeating the SPME experiments :
 - Similar SPME recoveries were obtained
 - However, more than 80 % of the spiked analytes were adsorbed on the (Teflon) stir bar
- **Idea: Extraction of aqueous samples with a PDMS coated stir bar**



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Stir Bar Sorptive Extraction (SBSE)



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Headspace Sorptive Extraction (HSSE)



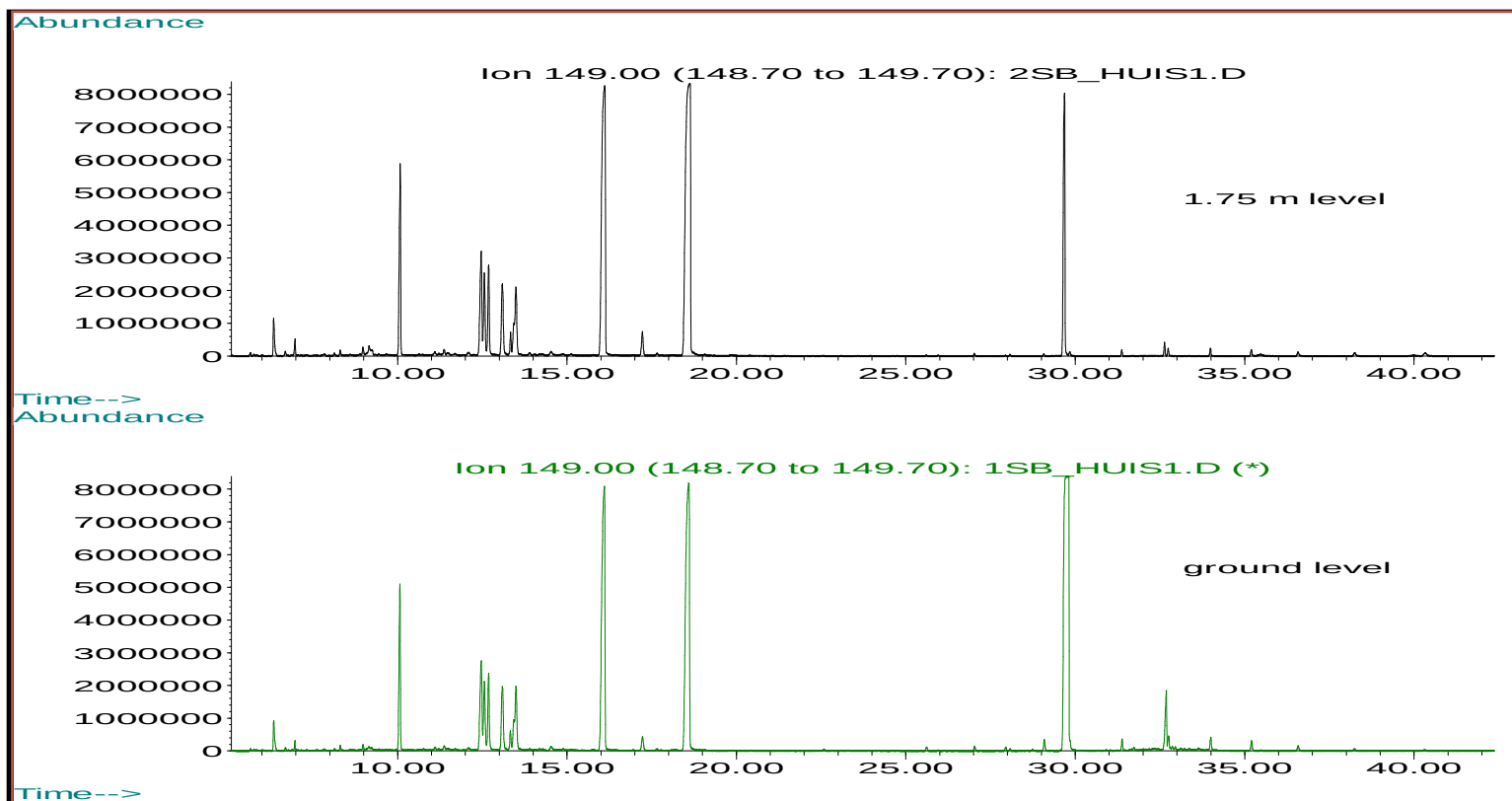
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Passive Sampling using HSSE. 24 h sampling - TD @ 300°C

Detection of phthalates

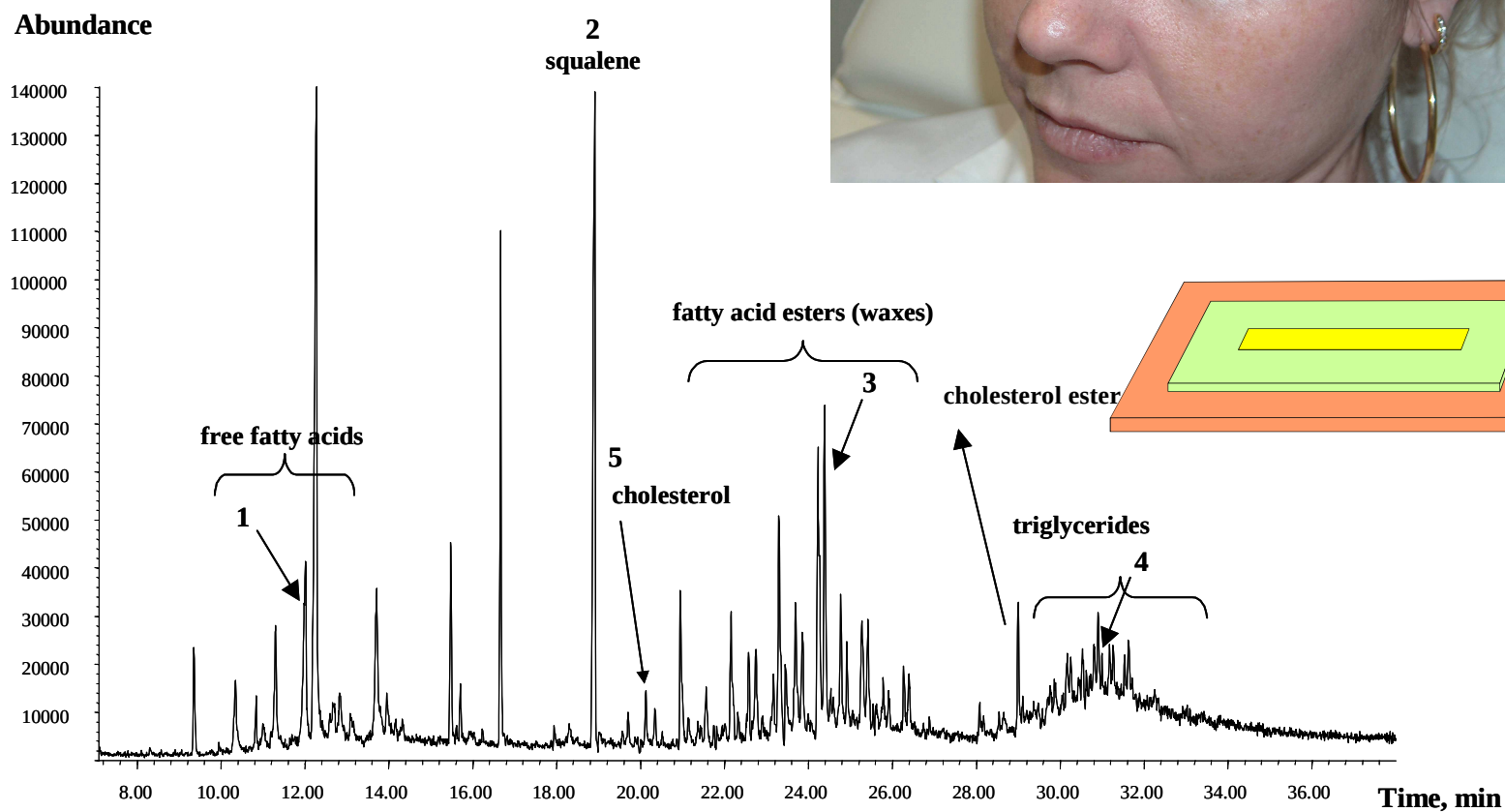


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Sorptive Tape Extraction

S. Sisalli, A. Adao, M. Lebel, I. Le Fur, P. Sandra
LC.GC Europe Jan 2006



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Profiling and Characterizing Skin Ceramides Using Reversed-Phase Liquid Chromatography–Quadrupole Time-of-Flight Mass Spectrometry

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[†]Metablys, President Kennedypark 26, 8500 Kortrijk, Belgium

[‡]Research Institute for Chromatography, President Kennedypark 26, 8500 Kortrijk, Belgium

[§]Chemistry Department, K.U. Leuven, Celestijnenlaan 200f, 3001 Heverlee, Belgium

Supporting Information

ABSTRACT: An LC-MS based method for the profiling and characterization of ceramide species in the upper layer of human skin is described. Ceramide samples, collected by tape stripping of human skin, were analyzed by reversed-phase liquid chromatography coupled to high-resolution quadrupole time-of-flight mass spectrometry operated in both positive and negative electrospray ionization mode. All known classes of ceramides could be measured in a repeatable manner. Furthermore, the data set showed several undiscovered ceramides, including a class with four hydroxyl functionalities in its sphingoid base. High-resolution MS/MS fragmentation spectra revealed that each identified ceramide species is composed of several skeletal isomers due to variation in carbon length of the respective sphingoid bases and fatty acyl building blocks. The resulting variety in skeletal isomers has not been previously demonstrated. It is estimated that over 1000 unique ceramide structures could be elucidated in human stratum corneum. Ceramide species with an even and odd number of carbon atoms in both chains were detected in all ceramide classes. Acid hydrolysis of the ceramides, followed by LC-MS analysis of the end-products, confirmed the observed distribution of both sphingoid bases and fatty acyl groups in skin ceramides. The study resulted in an accurate mass retention time library for targeted profiling of skin ceramides. It is furthermore demonstrated that targeted data processing results in an improved repeatability versus untargeted data processing (72.92% versus 62.12% of species display an RSD < 15%).

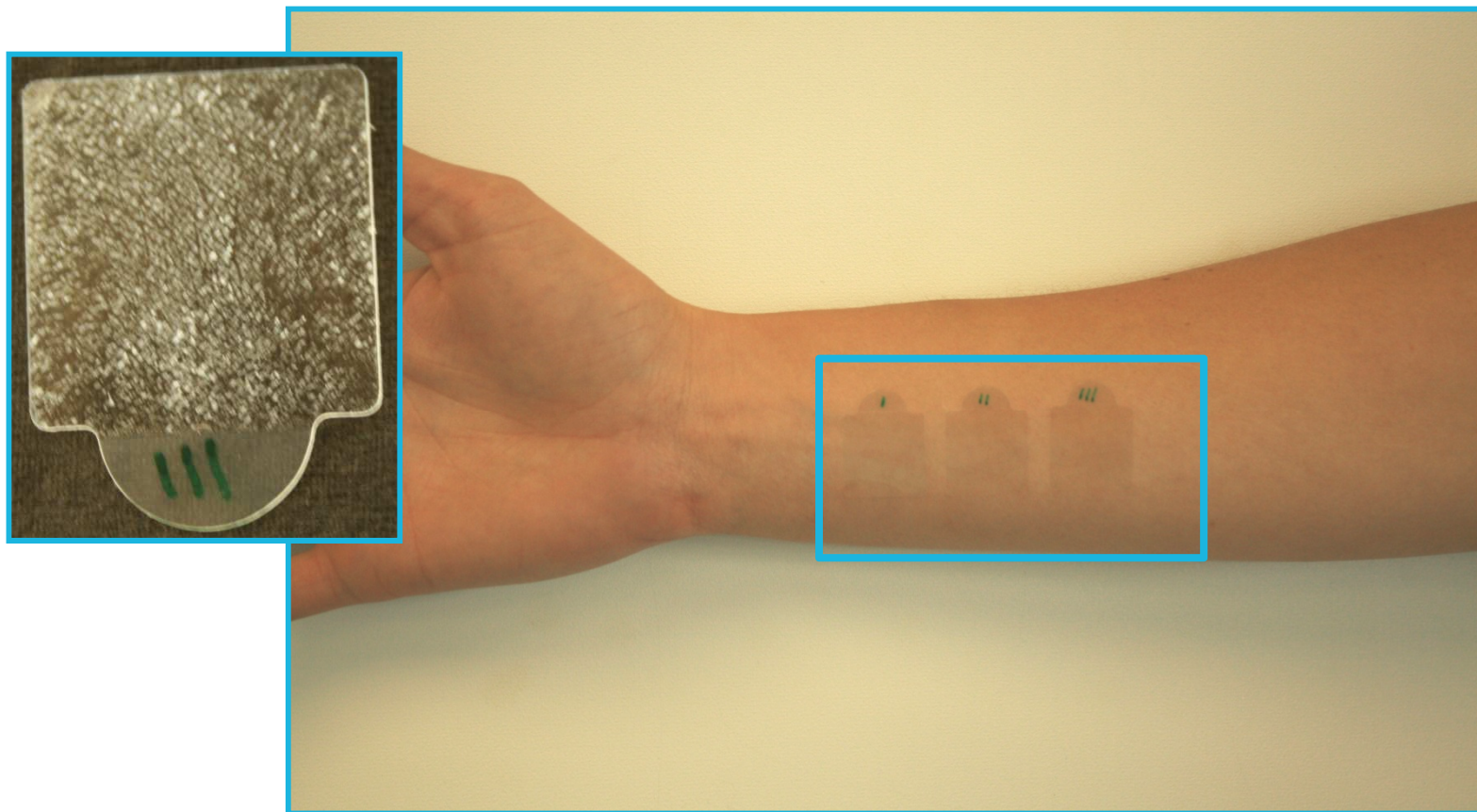


Insight into the skin ceramides

Profiling and Characterizing Skin Ceramides Using RPLC-QTOF-MS

R. t'Kindt, L. Jorge, E. Dumont, P. Couturon, F. David, P. Sandra, K. Sandra

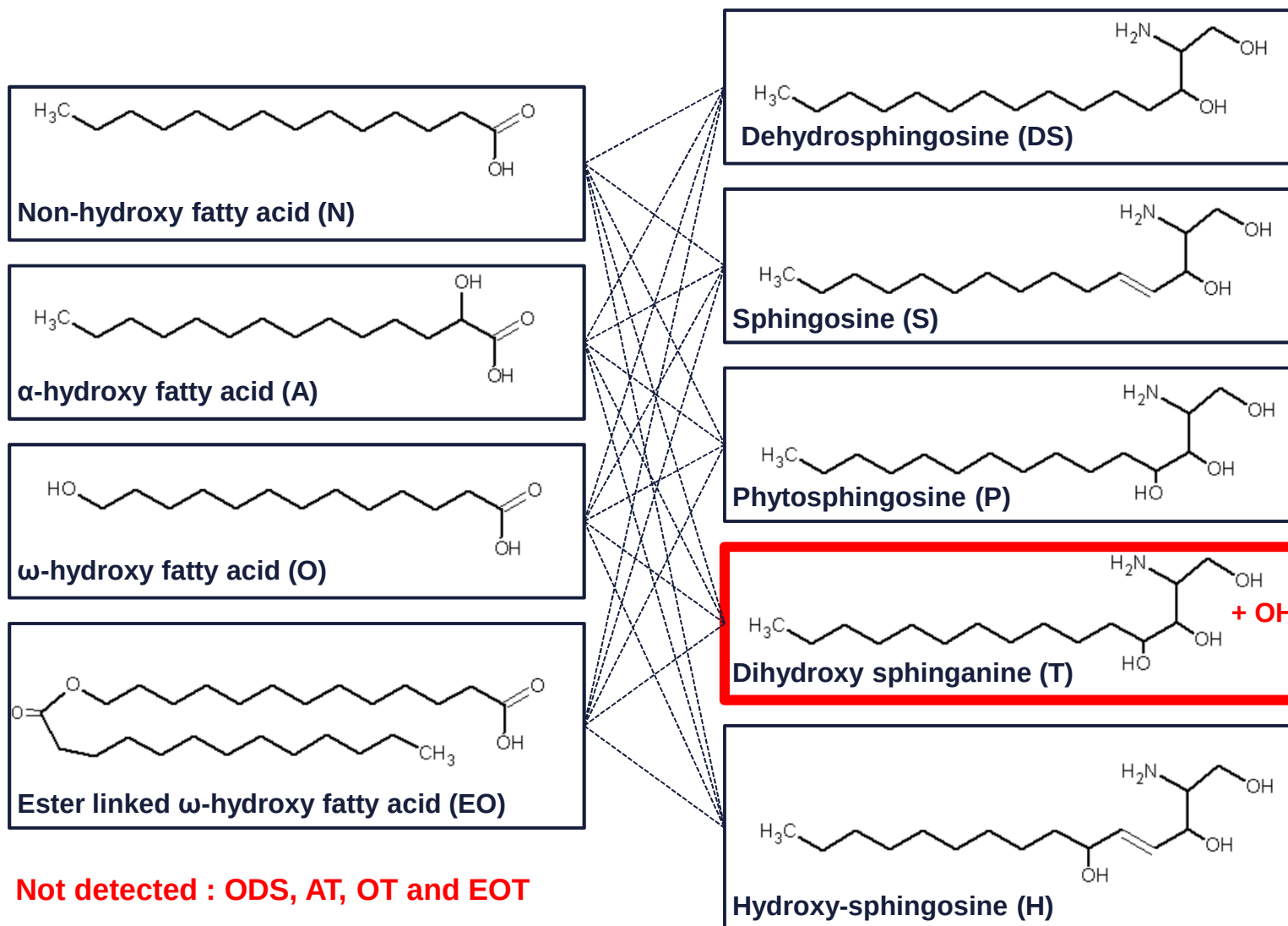
Anal. Chem. 84 (2012) 403



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Insight into the skin ceramides



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Tackling the lipidome by LC-MS

- **Chromatographic conditions:**
 - C18 (2.1 mm ID x 100 mm L x 1.7 μ m POROUS)
 - A: 20 mM NH_4 -formate pH 5 and B: MeOH
 - Flow rate: 0.5 mL/min
 - Column temperature: 80°C - Polaratherm
- **Mass spectrometric conditions:**
 - Q-TOF
 - Jetstream ESI source (pos/neg)
 - Extended dynamic range mode (10^5)
 - Resolution: 10,000 (m/z 1000)
 - Mass accuracy: < 2ppm

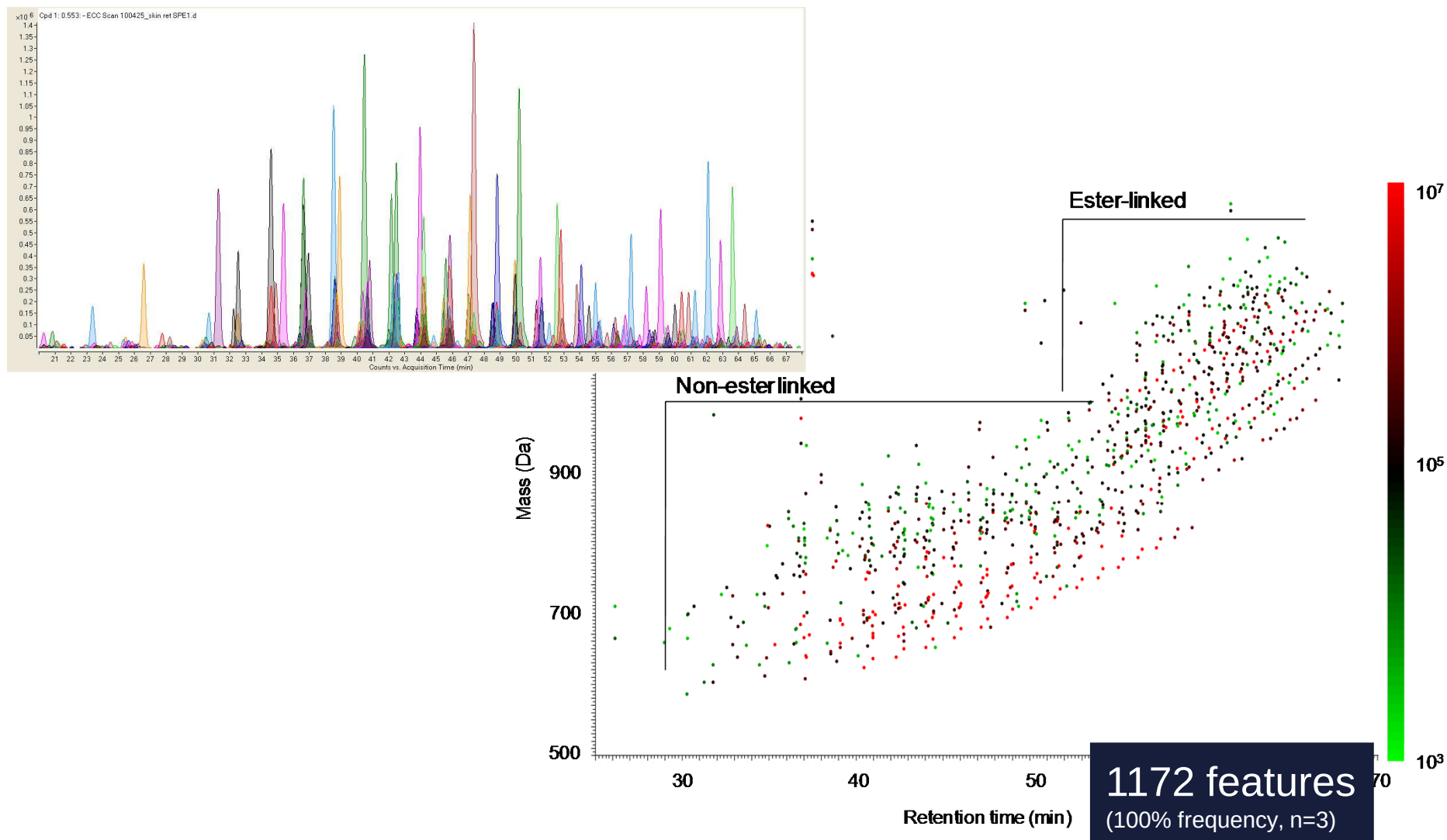


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Data handling

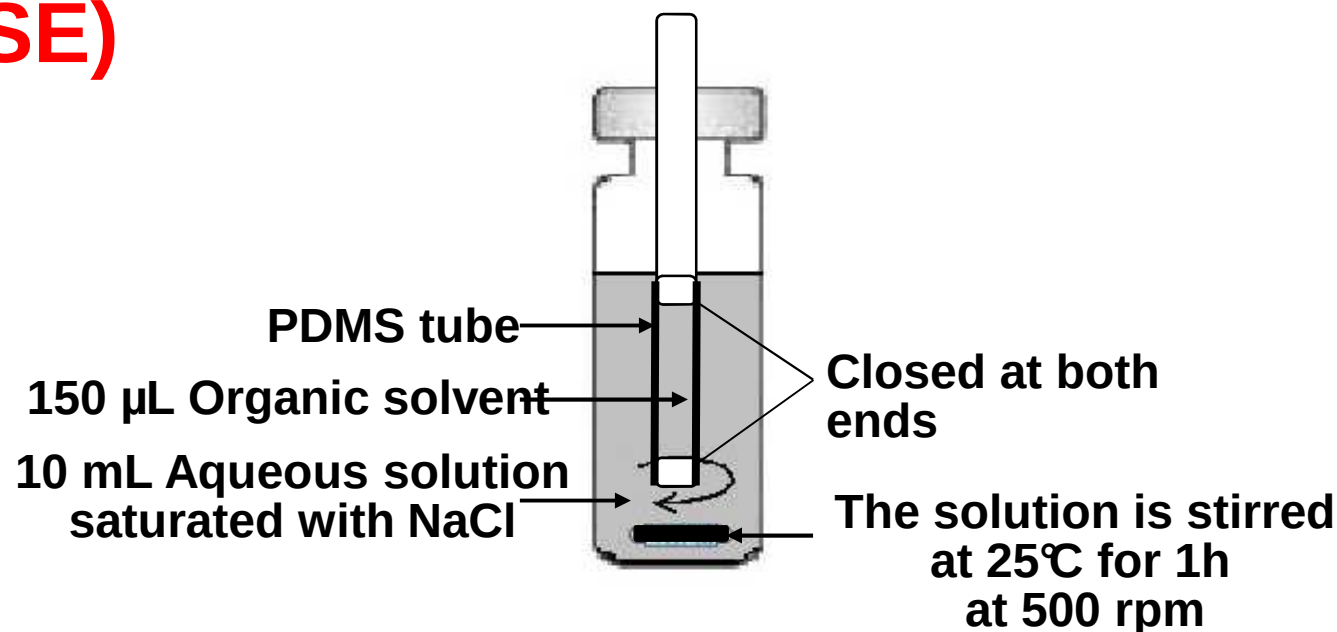
Construction of a skin ceramide map (feature plots)



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Silicone membrane sorptive extraction (SMSE)



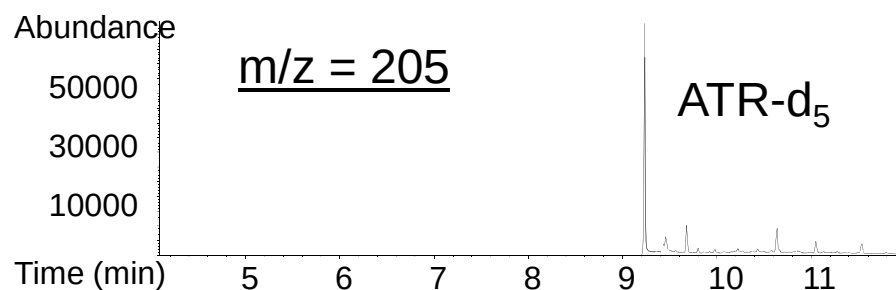
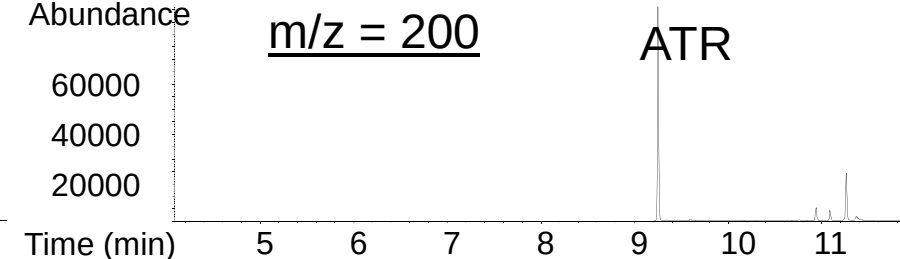
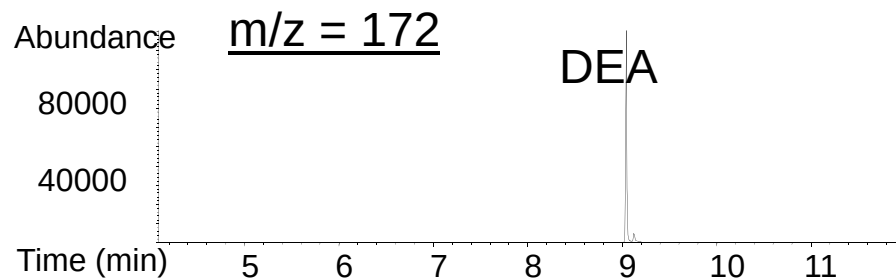
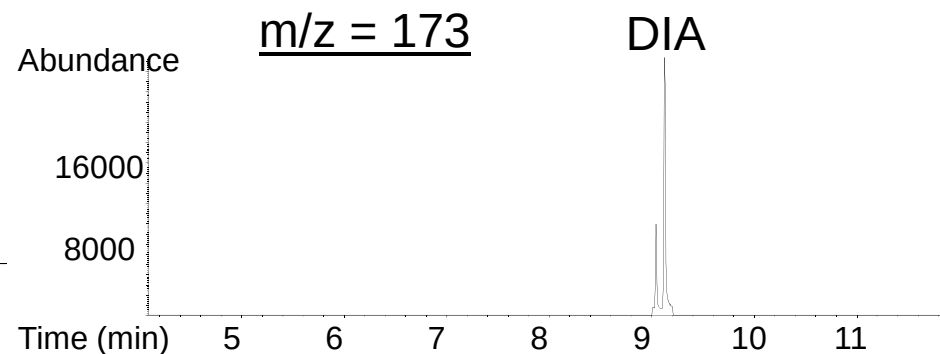
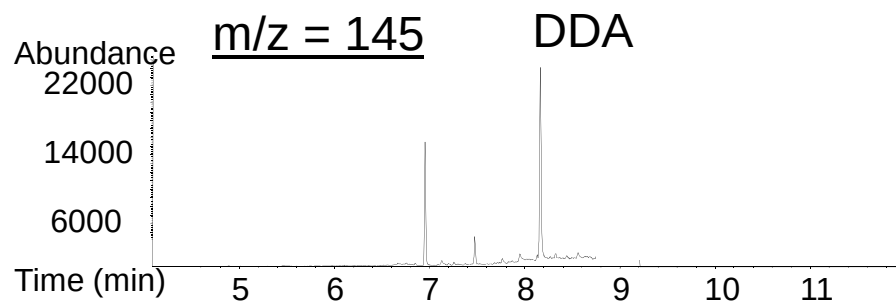
- First, the compounds are absorbed in the PDMS layer
- Very polar analytes move to the organic solvent
- Organic solvent is reduced in volume (time controlled)
- After extraction: Analysis of organic solvent by GC-MS or LC-MS



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Metabolites of atrazine



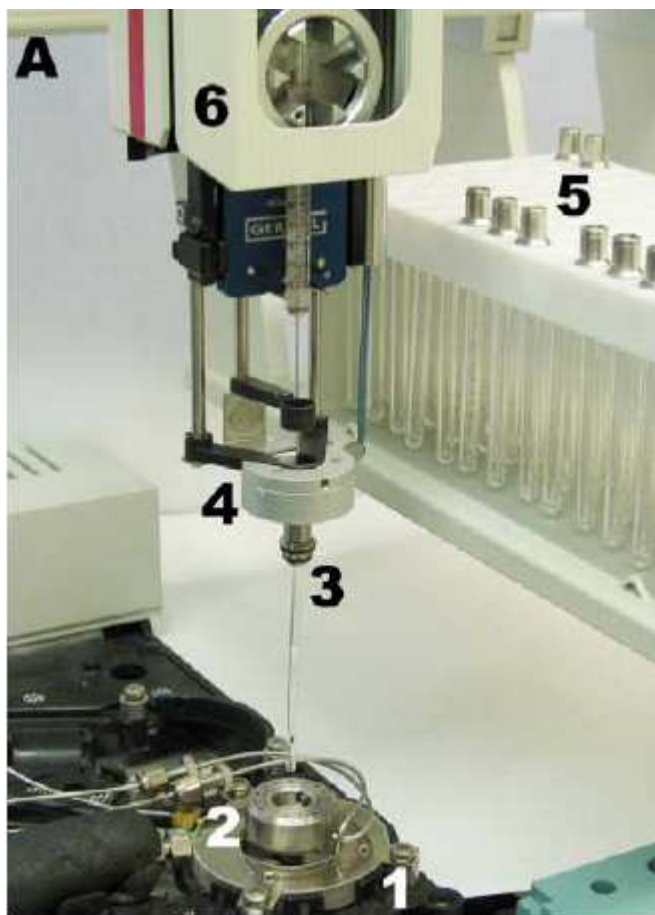
	LOD (ng/L)
ATR	0.47
DEA	1.98
DIA	1.25
DDA	6.07



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Automated Liner Exchange (ALEX)



Detailed view of ALEX system

1. PTV Injector, 2. ALEX support head,
3. Transport adaptor, 4. Electrical gripper,
5. Inlet liner tray, 6. Auto-sampler tower

QuEChERS extraction is not very selective – extracts are not clean !!



QuEChERS sample prep
5-10 μ L LVI
PTV solvent vent mode



**Automated Liner
Exchange System (ALEX)**



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Content

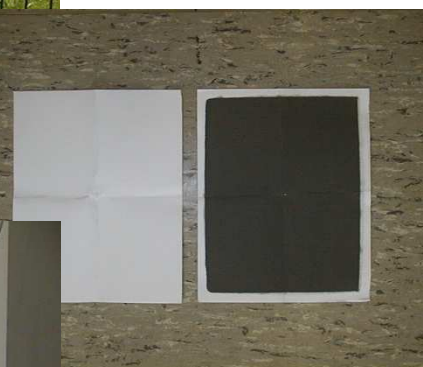
- Polysiloxanes
- Polysiloxanes and sorptive extraction
- Sorptive extraction formats
- **Applications for gaseous samples**
- **Applications for liquid samples**
- **Applications for solid samples**
- Conclusion



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Comparison ...



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Sorptive sampling

120 mg PDMS –
60 mg Tenax

Spike d-standards

24 h at 100 mL/min

Total: 144 L

Thermal desorption

High Volume sampling

Glass fibre filter + PUF

24 h at 0.9 m³/min

Total: 1.296 m³

Soxhlet Extraction

Spike d-standards



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Mean values 52 analyses - April 2005/March 2006

	Hvol (+PUF)	Mixed Bed	Ratio	TEF (*)	TEQ (*)	TEQ (*)
Component	ng/m ³	ng/m ³			Hvol (+PUF)	PDMS
Naphthalene	3.33	116.49	35.0	0.001	0.003	0.116
Acenaphtylene	3.08	6.11	2.0	0.001	0.003	0.006
Acenaphtene	0.31	7.14	23.0	0.001	0.000	0.007
Fluorene	5.38	7.92	1.5	0.001	0.005	0.008
Phenanthrene	11.74	13.85	1.2	0.001	0.012	0.014
Anthracene	0.72	0.92	1.3	0.01	0.007	0.009
Fluoranthene	3.43	4.50	1.3	0.001	0.003	0.005
Pyrene	1.98	2.90	1.5	0.001	0.002	0.003
Benzo(a)anthracene	0.36	1.01	2.8	0.1	0.036	0.101
Chrysene	0.81	1.96	2.4	0.01	0.008	0.020
Benzo(b)fluoranthene	0.57	1.78	3.1	0.1	0.057	0.178
Benzo(k)fluoranthene	0.29	0.52	1.8	0.1	0.029	0.052
Benzo(e)pyrene	NM	1.49				
Benzo(a)pyrene	0.48	1.11	2.3	1	0.480	1.110
Indeno(1,2,3-c,d)pyrene	0.30	0.43	1.4	0.1	0.030	0.043
Dibenzo(a,h)anthracene	0.65	1.07	1.6	1	0.650	1.070
Benzo(g,h,i)perylene	0.67	1.24	1.9	0.01	0.007	0.012
sum	34.10	170.44			1.333	2.754



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Twister applications

- **Environmental**
- **Food**
- **Biomedical**
- ...
- **Quality control**
- **Trace analysis**
- **Ultratrace analysis**



ppm

ppb

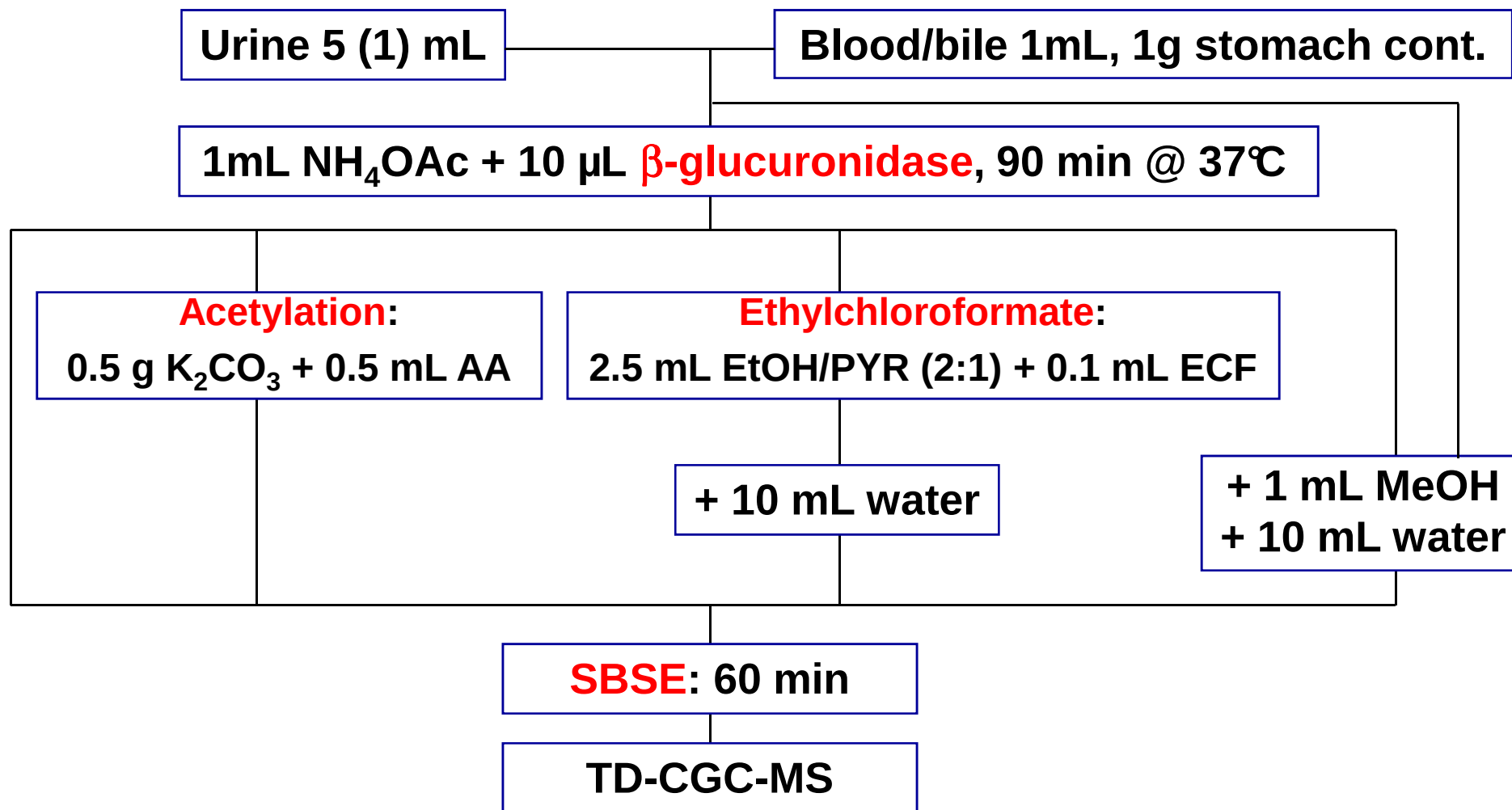
ppt - ppq



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SBSE procedures for biological samples

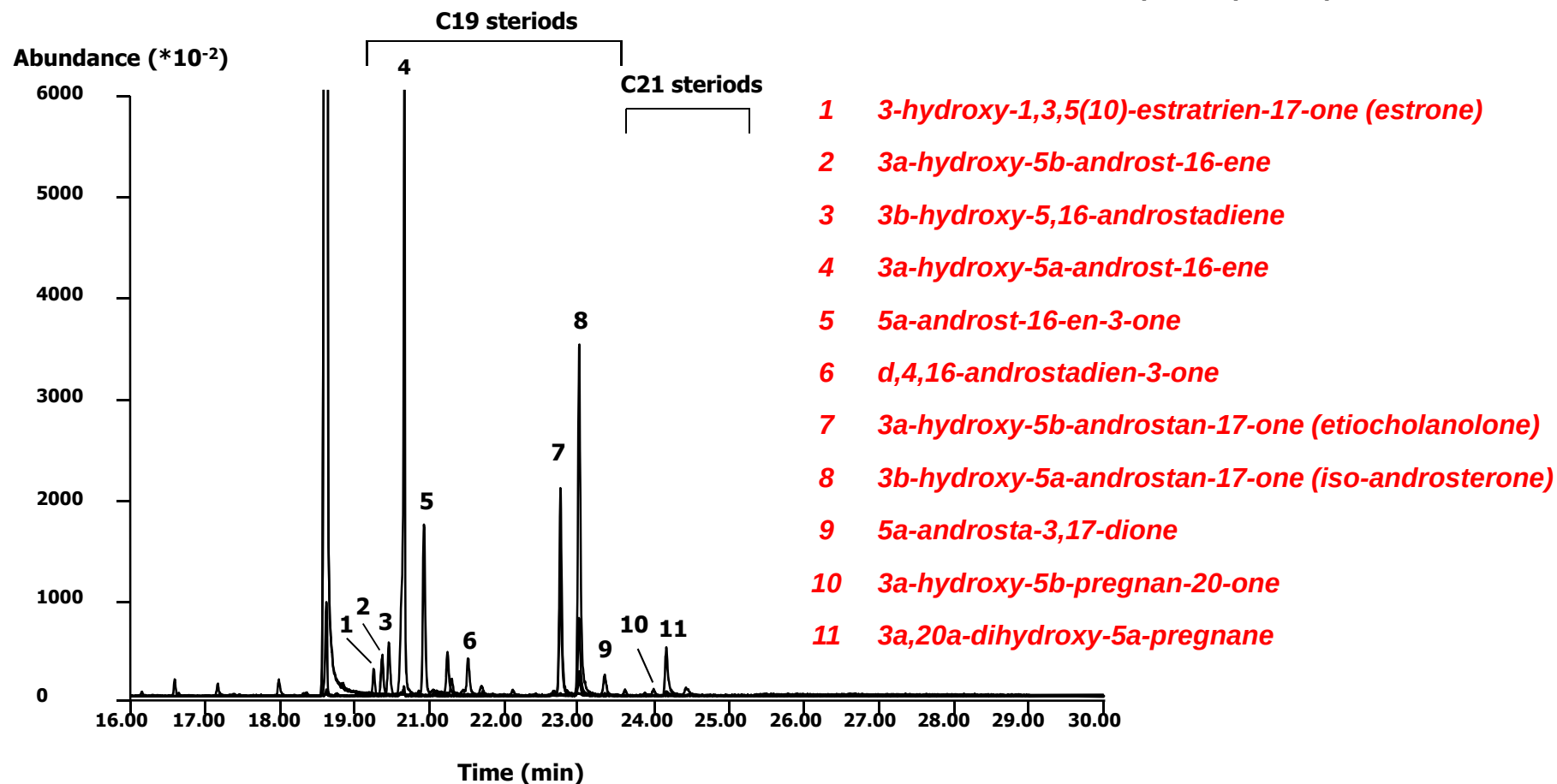


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Free steroids in urine of a male adult

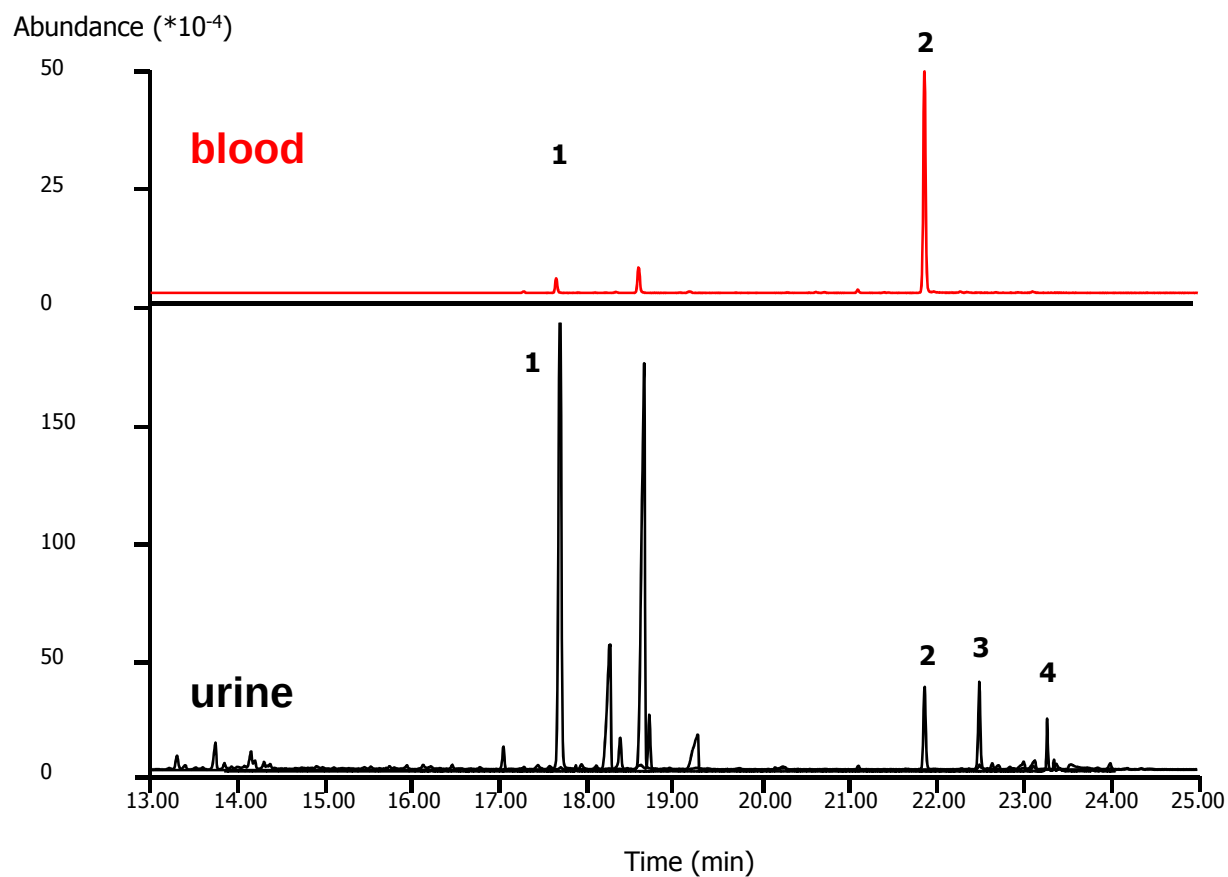
EIC: m/z 257, 270, 288, 299



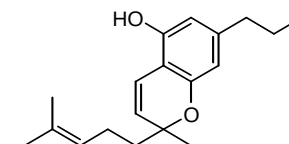
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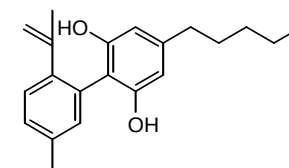
Cannabis metabolites in urine and blood of the same person



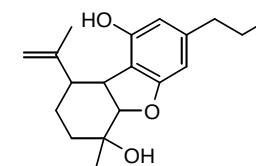
1 Cannabichromene



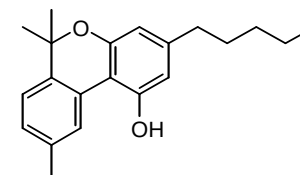
2 Cannabidiol



3 Cannabielsoin



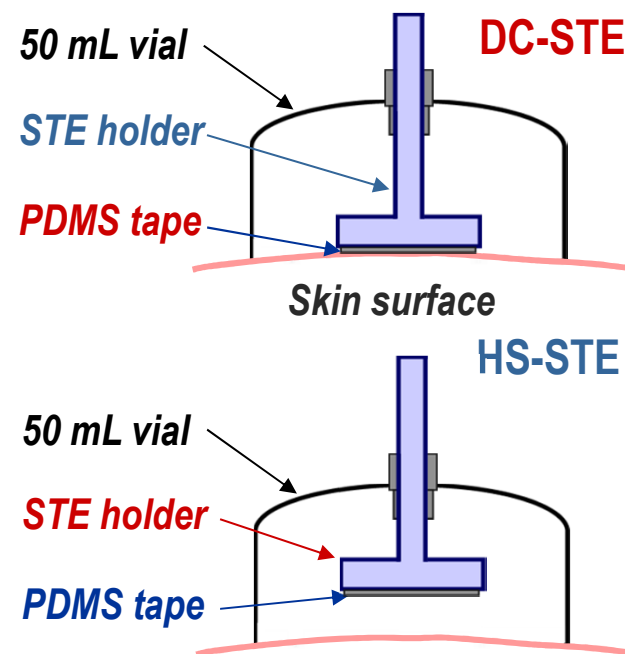
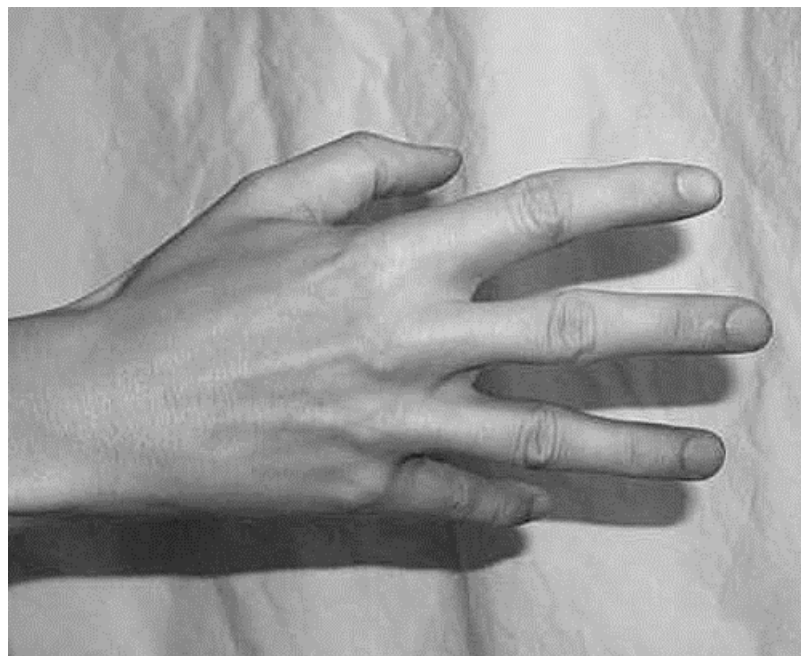
4 Cannabinol



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STE and the release of a perfume from skin



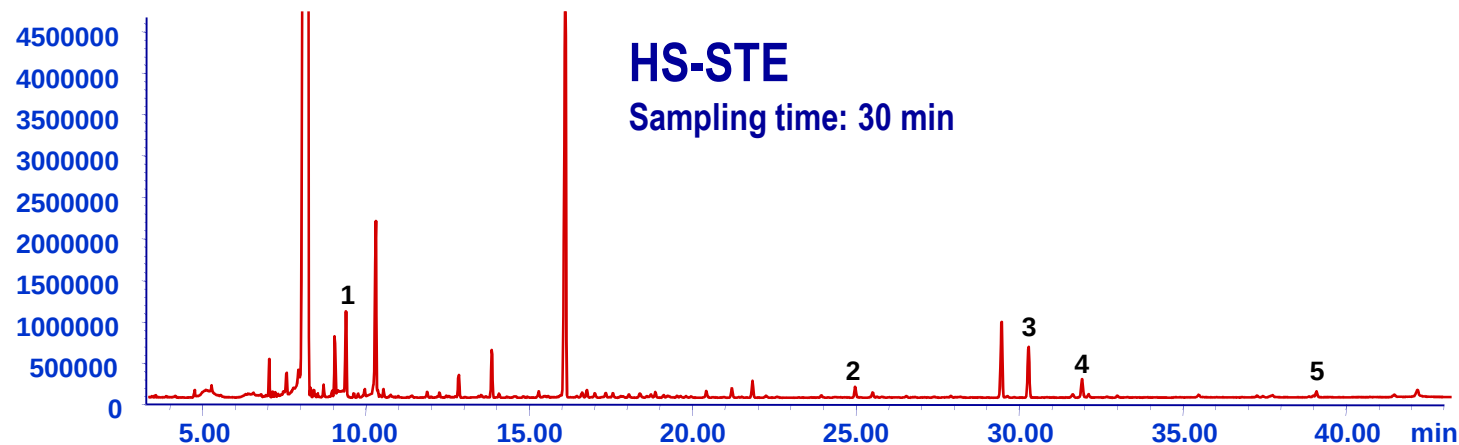
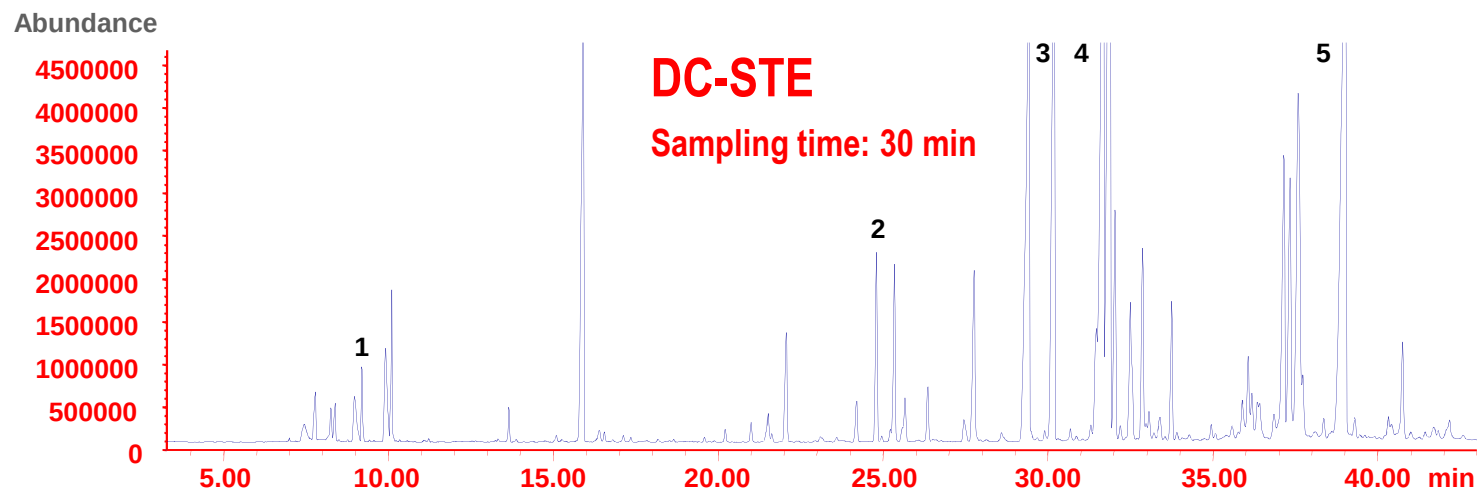
Sampling conditions: Sampling temperature: 25°C, time: 30 minutes; HS-STE: tape-hand dist.: 5 mm;
Thermal desorption: TDU (Gerstel): 30°C//60°C/min//250°C(5 min); CIS: -50°C//12°C/s//280°C (10 min);
Analysis conditions: GC 6890 Plus-MSD 5973 N (Agilent); Column: MEGA 5 (l: 30 m, I.d.: 0.25mm, df: 0.25 µm); Oven temp.: 0°C(1 min)//80°C/min//70°C//3°C/min//230°C(10 min);
Inj. mode: split (ratio: 1/50); Carrier: He (flow rate: 1 mL/min); Acquisition mode: full scan (m/z = 45-450)



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Persistence and release over time of a perfume on skin



Marker compounds 1: dihydromyrcenol, 2: α -i-methyl ionone, 3: MW 236, 4: dihydromethyl jasmonate, 5: benzyl salicylate



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Thank you

for your attention

Questions ?



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