5TH SBSE INTERNATIONAL MEETING
23 & 24 SEPTEMBRE 2019 - NOVOTEL PARIS-SUD
SBSE Technical Meeting

Two decades of Stir Bar Sorptive Extraction

Frank David and Pat Sandra

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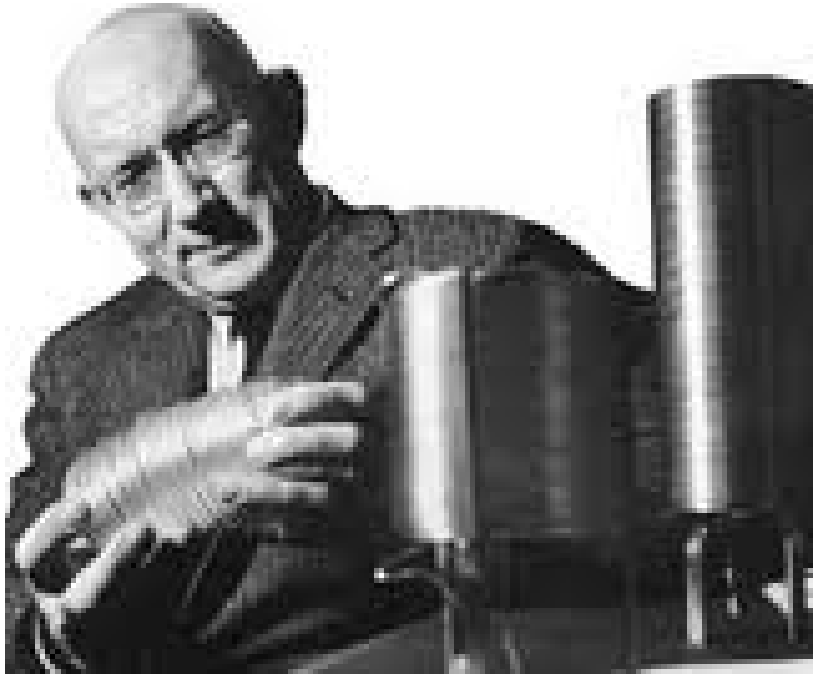
30 YEARS OF EXCELLENCE

Capillary GC Milestones



M. Golay, 1959

Static coating:
J. Bouche, M. Verzele (U Gent),
J. Gas Chromatogr, 6 (1968) 501

Fused Silica: 1979
(R. Dandenau, HP)

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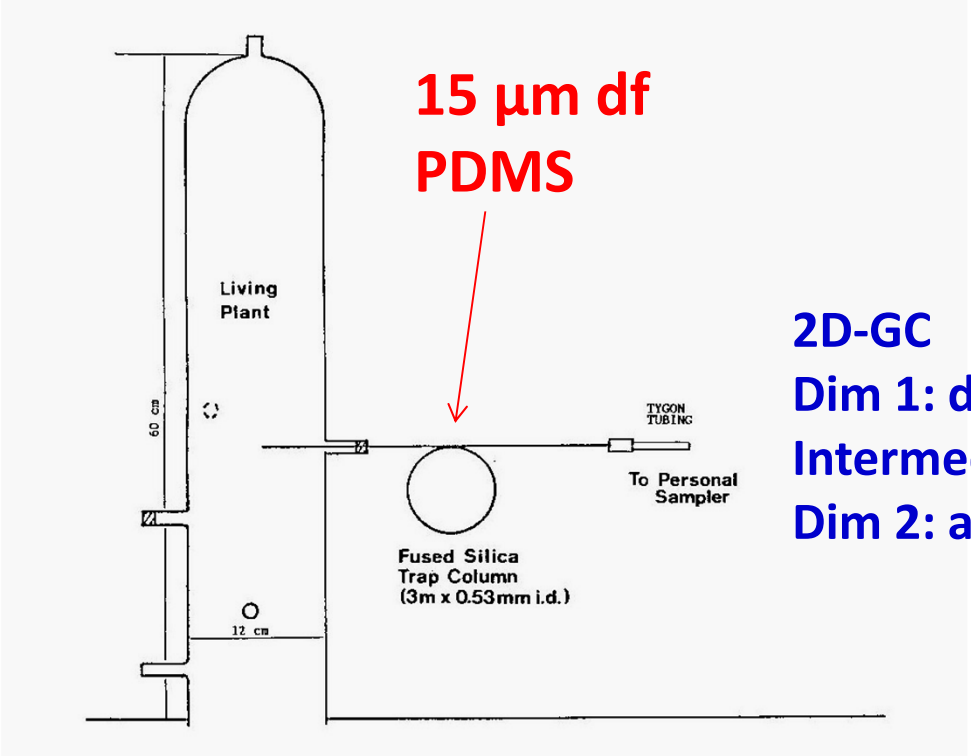
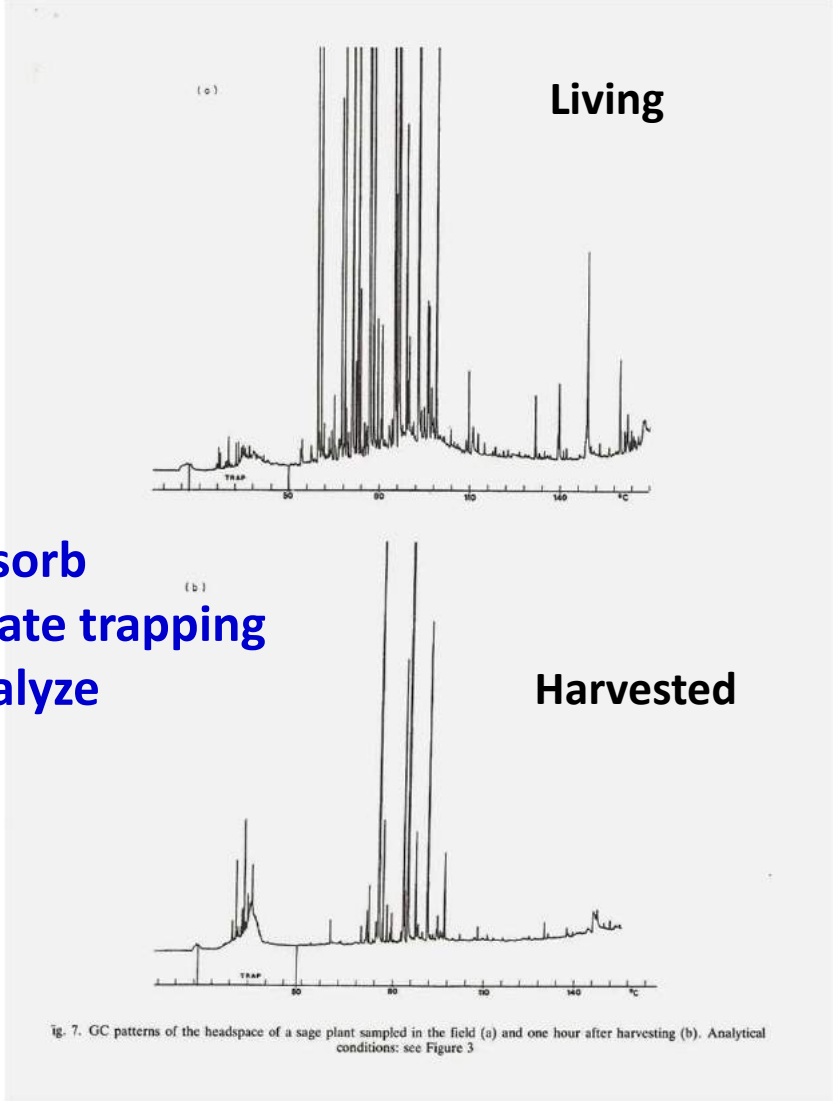
Open Tubular Trapping of Volatiles



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



ig. 7. GC patterns of the headspace of a sage plant sampled in the field (a) and one hour after harvesting (b). Analytical conditions: see Figure 3

Bicchi, D'Amato, David, Sandra
FFJ 1988

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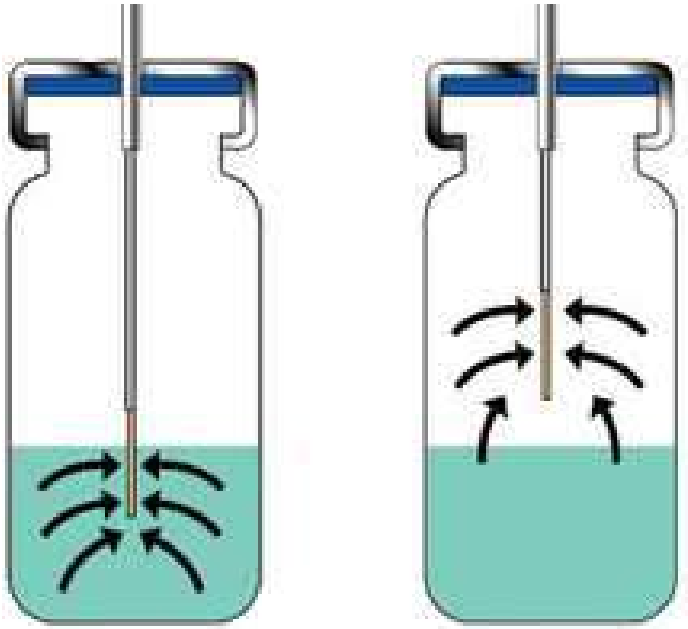
Solid Phase Micro-Extraction (SPME)
J. Pawliszyn, 1990



$$n = \frac{K_{fs} V_f C_0 V_s}{K_{fs} V_f + V_s}$$

$(K_{fs} = K_{fa} * K_{as})$

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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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Why SBSE?

- **Extraction**: remove from matrix
- **Enrichment**: concentrate
- **Purification**: selective extraction/isolation

Statement 1

SBSE

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PDMS

SBSE phases

- **Best known GC stationary phase (apolar)**
- **Decomposition products very specific and not related to solutes of interest**
- **PDMS/water distribution ≈ octanol/water distribution, $K_{o/w}$ values can be applied**
- **WARNING: not all "silicone" material can be used for SBSE**
  - **high quality required, low bleed, cross-linker type**
- What about other phases for SBSE?
  - Thermal desorption or liquid desorption ?
  - Immersion or Headspace sampling ?
  - More material = bleeding more critical
  - Attempts: polyacrylate, polyurethane, carbon, sol-gel, monoliths, MIPs, RAM,…
  - But: bleeding, liquid desorption only, no significant improvement

Statement 2

More extraction phase

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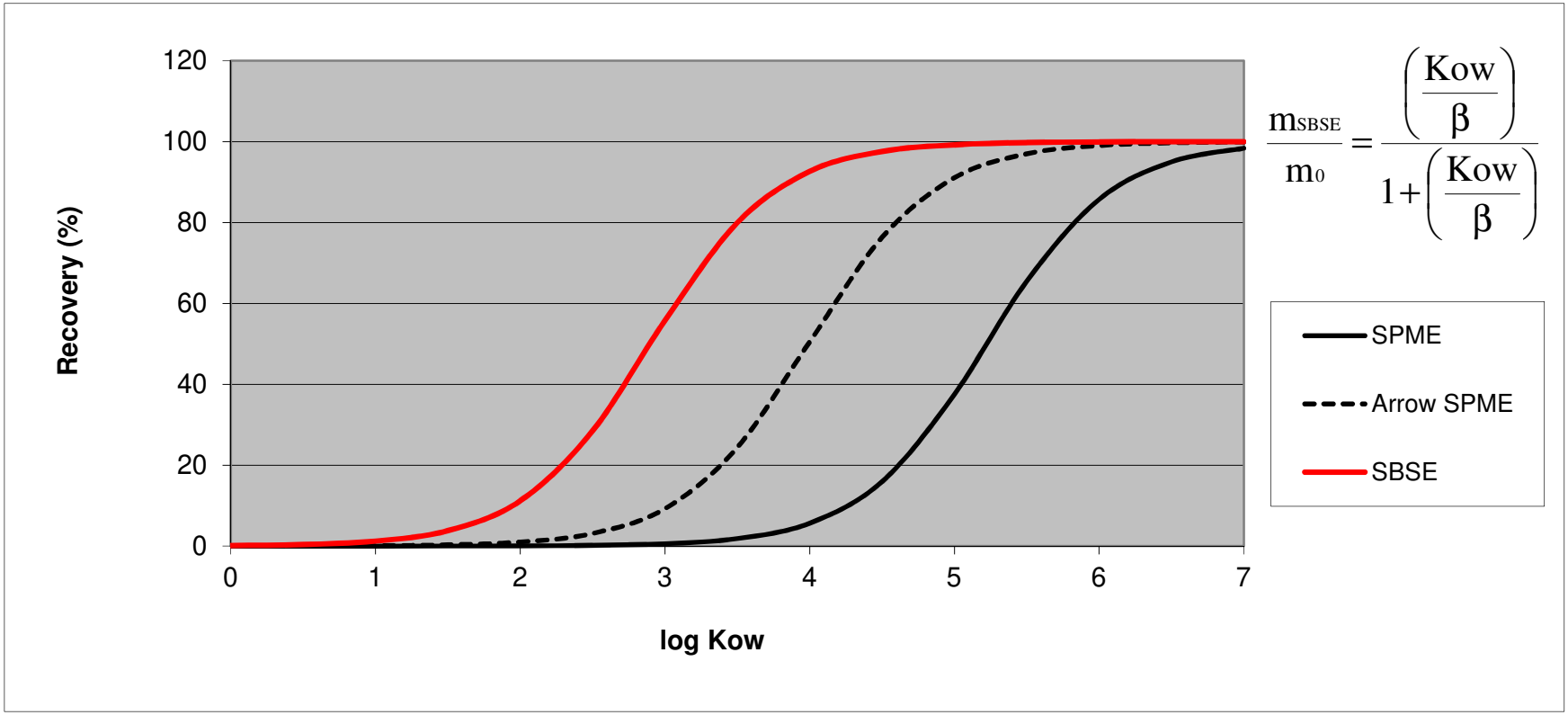
More compounds extracted

(<u>at equilibrium</u>)



		Recovery (%)		
Solute	Log Kow	SPME	Arrow SPME	SBSE
dichlorvos	1,47	0,02	0,30	3,59
atrazine	2,61	0,24	3,99	33,92
naphthalene	3,30	1,18	16,91	71,54
2,4,6-trichloroanisole	4,11	7,17	56,79	94,20
benzo(a)pyrene	5,99	85,43	99,01	99,92

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Statement 3

More extraction phase

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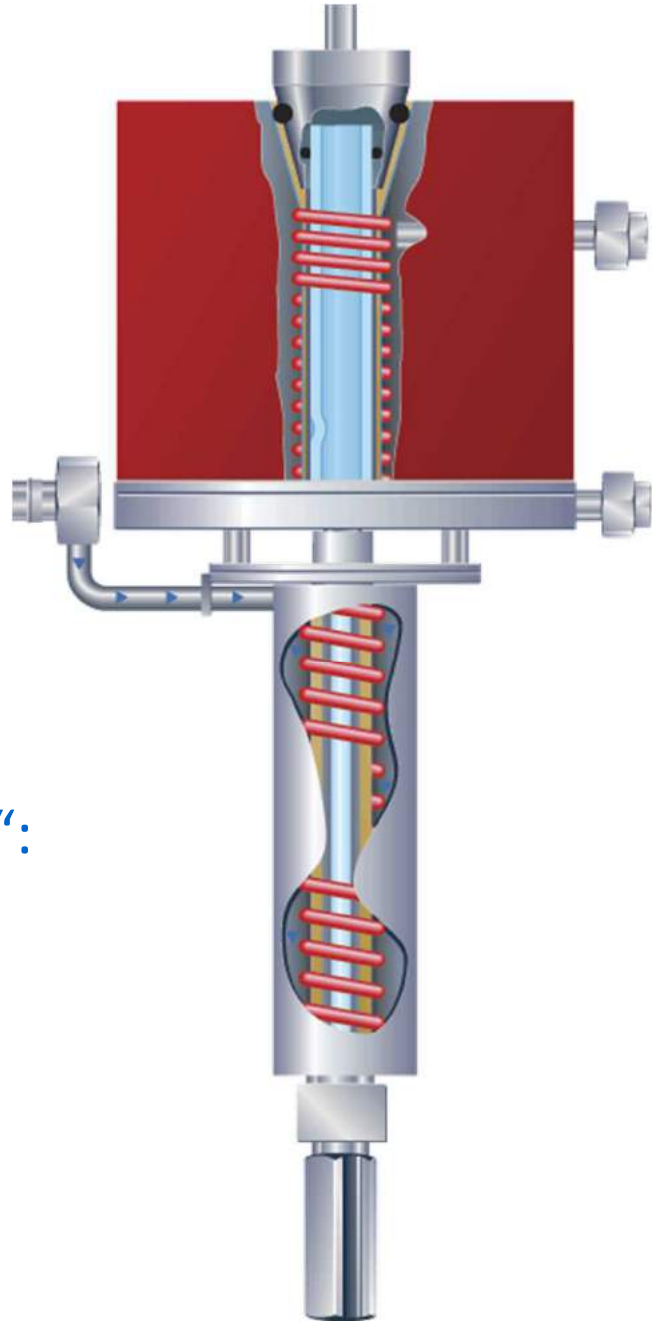
More difficult desorption & higher bleed

Thermal Desorber:

TDU



„Cryotrap“:

PTV

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Statement 4

SBSE

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Green Chemistry

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Comments on classical sample preparation methods for water analysis

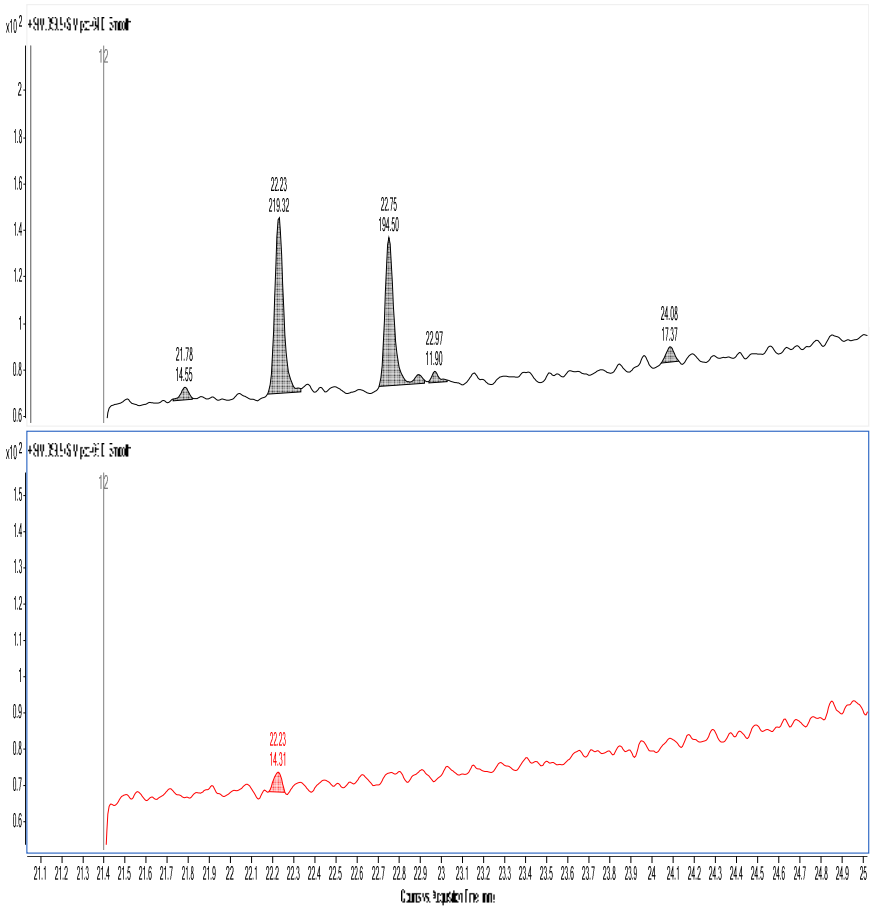
- In most official methods (ISO 6468, ISO 10695, EPA... with LLE or SPE):
  - (very) large sample amounts (250 mL...> 1L)
  - Whole sample bottle extracted (& rinsed) ≠ automation
  - **SPM < 50 mg/L**
  - Some LOQs > EQS levels (endosulfan, heptachlor)
- EU request: “generic” methods for up to 500mg/L SPM

SBSE in Water Analysis

- Well documented in literature
- Extremely sensitive (pg/L)
- Low external contamination (phthalates)
- Concern: SPM > low adaptation in regulatory & routine labs
- Recent research (Gerstel)
  - Dual SBSE extraction – single shot GC-MS/MS method
  - Validated for 100 priority pollutants according to WFD
  - Matrices spiked with 50-100-150 mg/L WEPAL SETOC 745 to simulate SPM

but... Sampling method should also be adapted!!!

Sampled in 20 mL vial → autosampler



Sampled in 1 L flask → aliquot to 20 mL vial → autosampler

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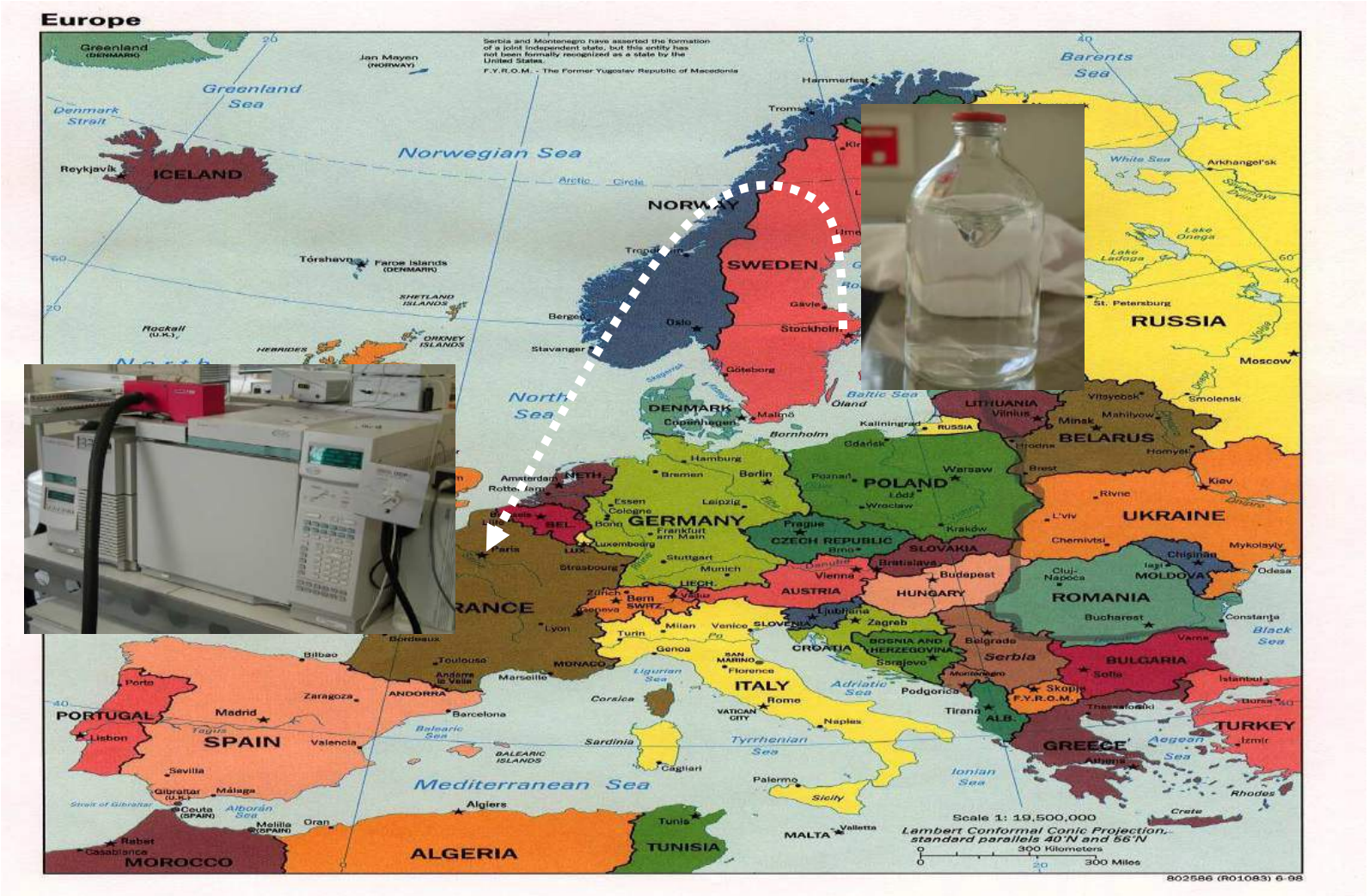
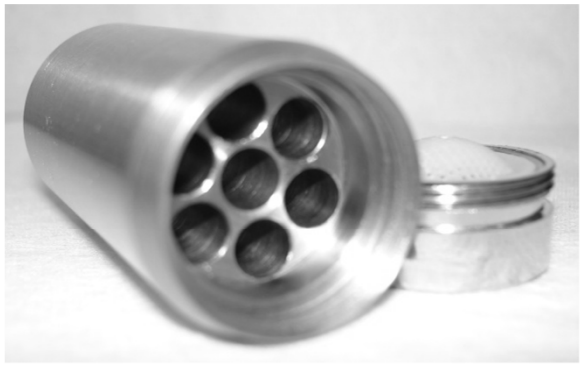
SBSE-TD-GC-MS - On-site SBSE

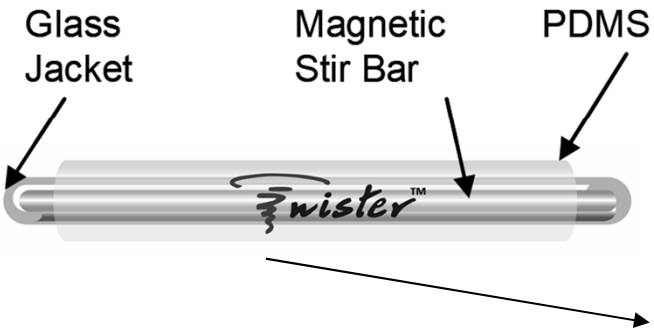
D. Benanou, presented at 27th ISCC, Riva del Garda, Italy, May 2004

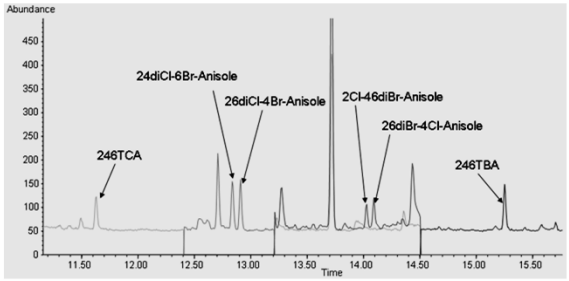


“On-TAP” sampling

Veolia Environnement, Paris, France







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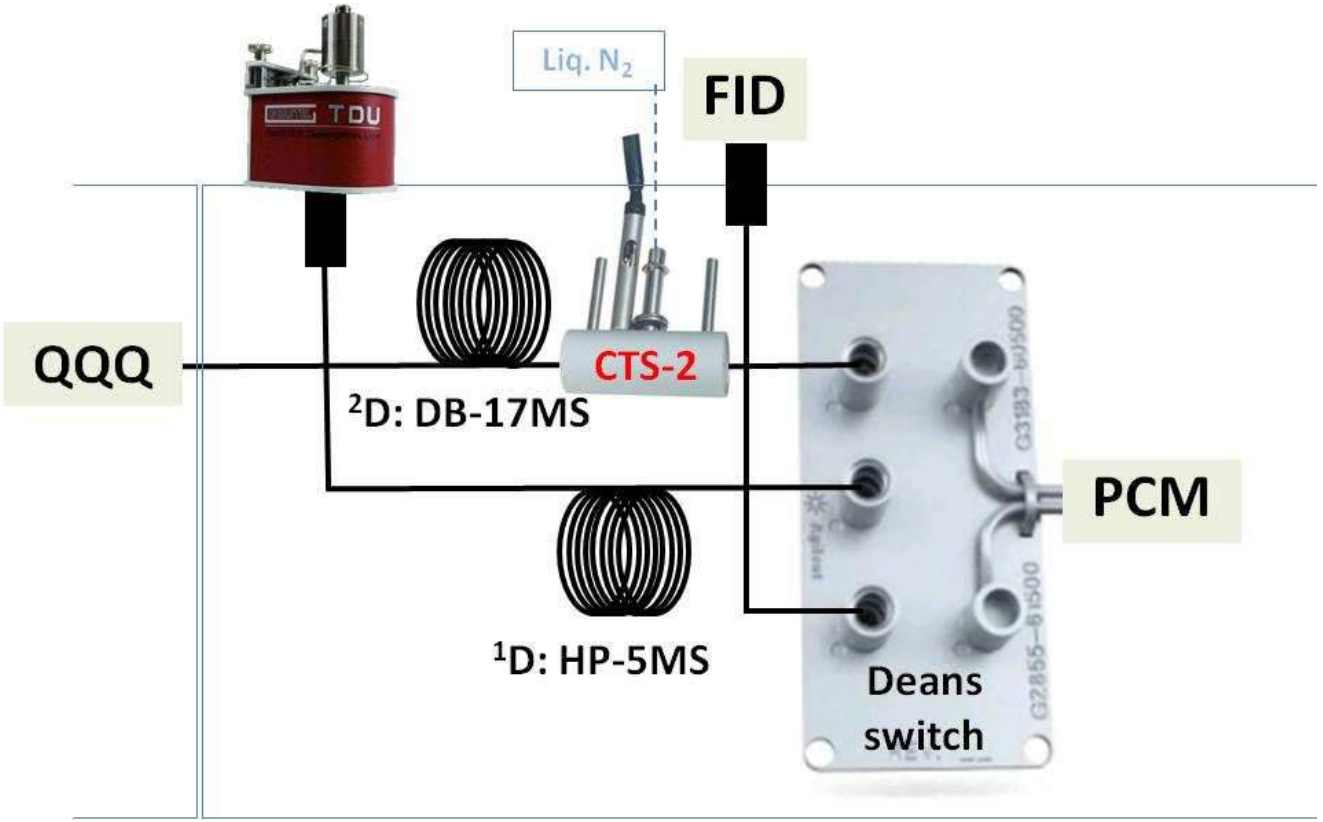
Determination of Tributyltin in Water Samples at the Quantification Level Set by the European Union (0.2 ng/L)

SBSE

TDU

2DGC

QQQ



C. Devos, F. David, P. Sandra, J. Chromatography A, 1261 (2012) 151–157

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Sampling procedure – SBSE parameters

→ Samples (50 mL) are spiked with deuterated Osn standards
→ 5 mL of buffer (NaOAc/HOAc buffer pH = 5.3) is added
→ 500 µl of 1 % $NaBEt_4$ is added for derivatization
→ 2 cm x 0.5 mm d_f Twisters
→ The Twister is stirred for 2 hours into 50 mL of water sample

Simple sample preparation – limited glassware and lab material needed

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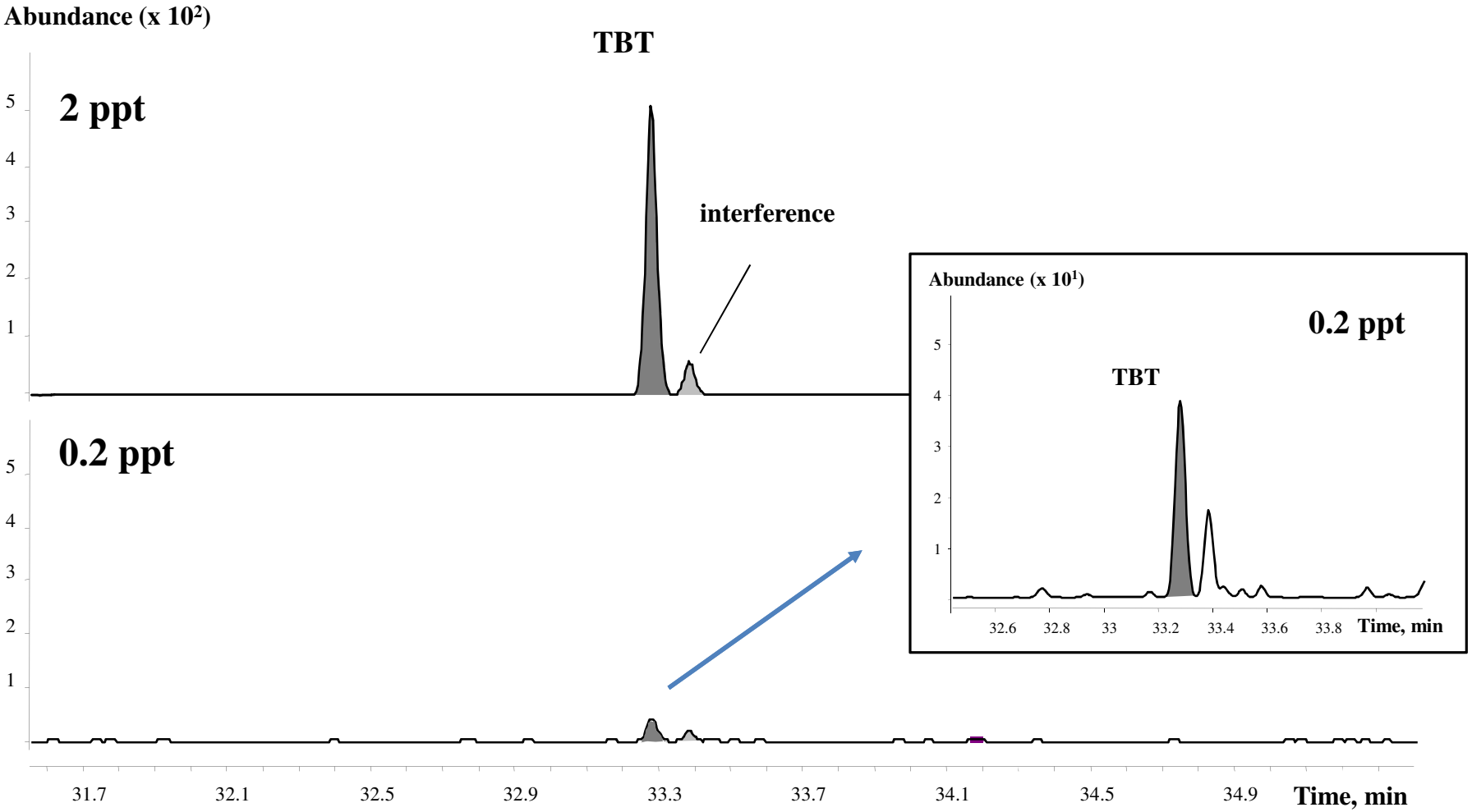
GC-GC-MS/MS: TBT resolved from interferences



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Towards modern methods for water analysis

- GC-MS/MS & LC-MS/MS are recommended methods
  - Remove “old” methods: GC-NPD, GC-ECD, LC-UV, LC-FLD
- Encourage (or at least allow) new sample preparation methods
  - → Green chemistry
- Define max SPM level: 50 mg/L > 500 mg/L???
  - 95% French water samples < 50 mg/L

Statement 5

SBSE

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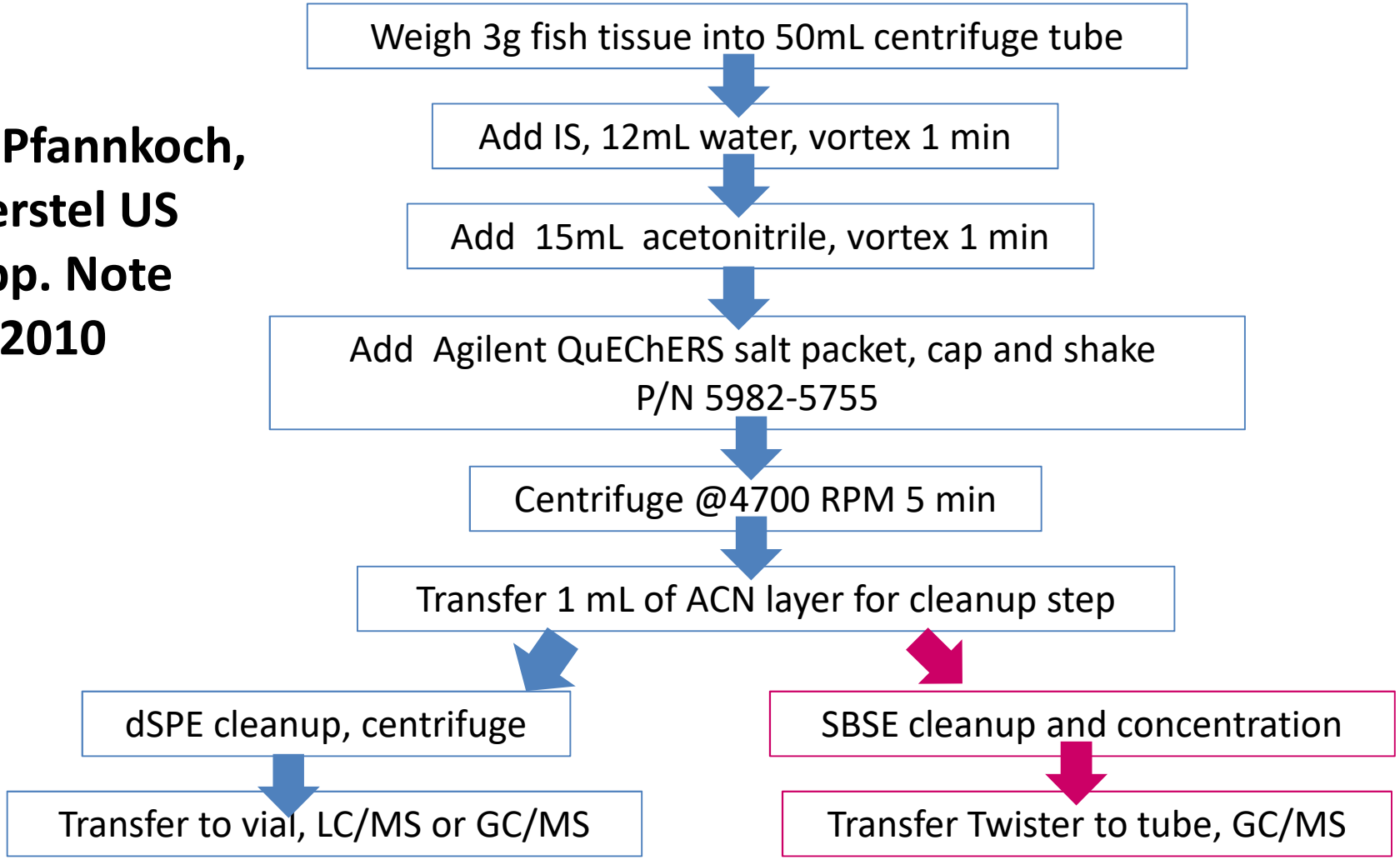
Only extraction of water samples

Determination of PAHs in Sea Food

E. Pfannkoch, Gerstel US App. Note 6/2010



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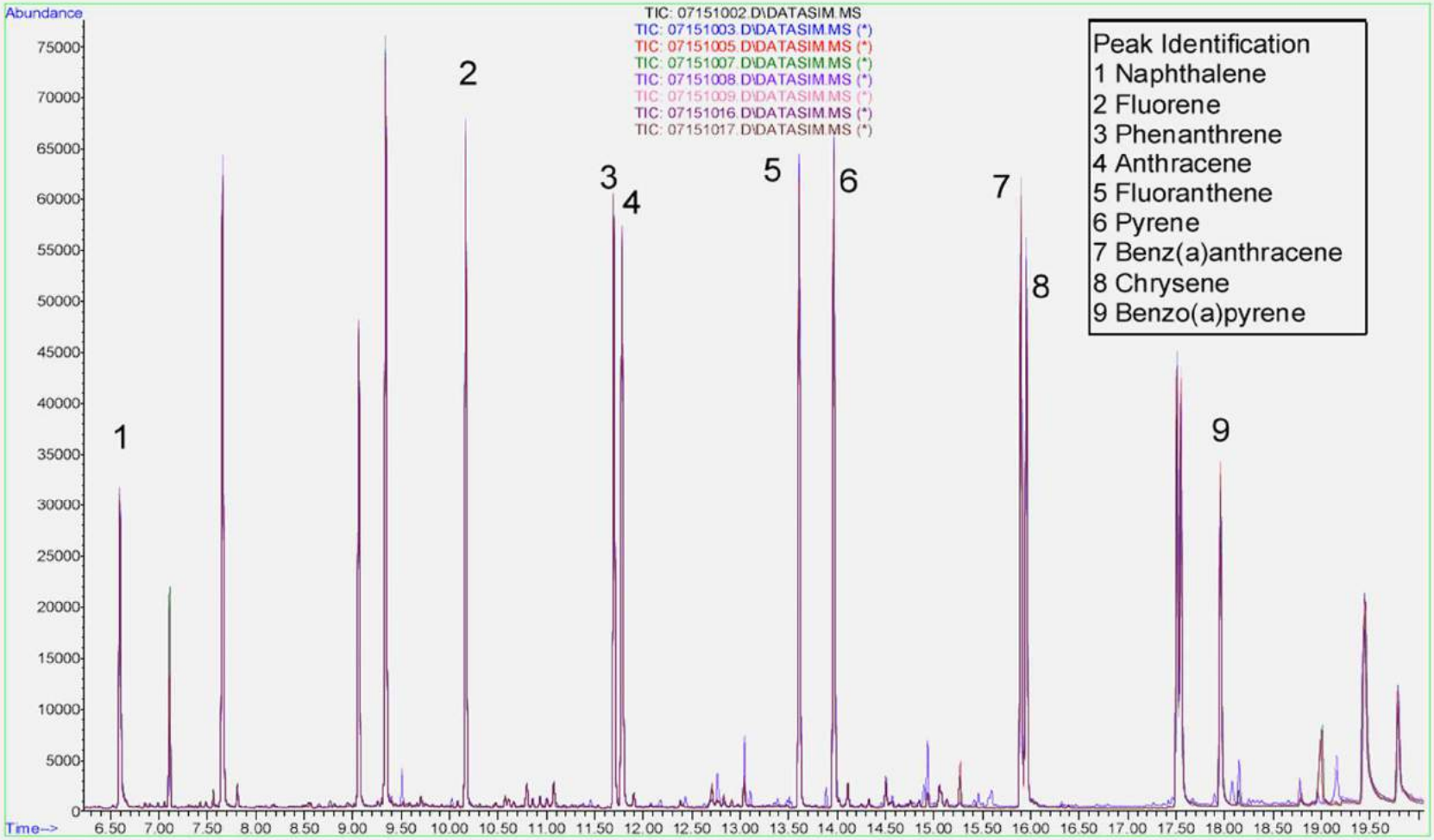
PAH Retention time stability
25ppb in tissue (croakers, oysters, red snapper)
18 runs overnight
8 chromatograms overlaid



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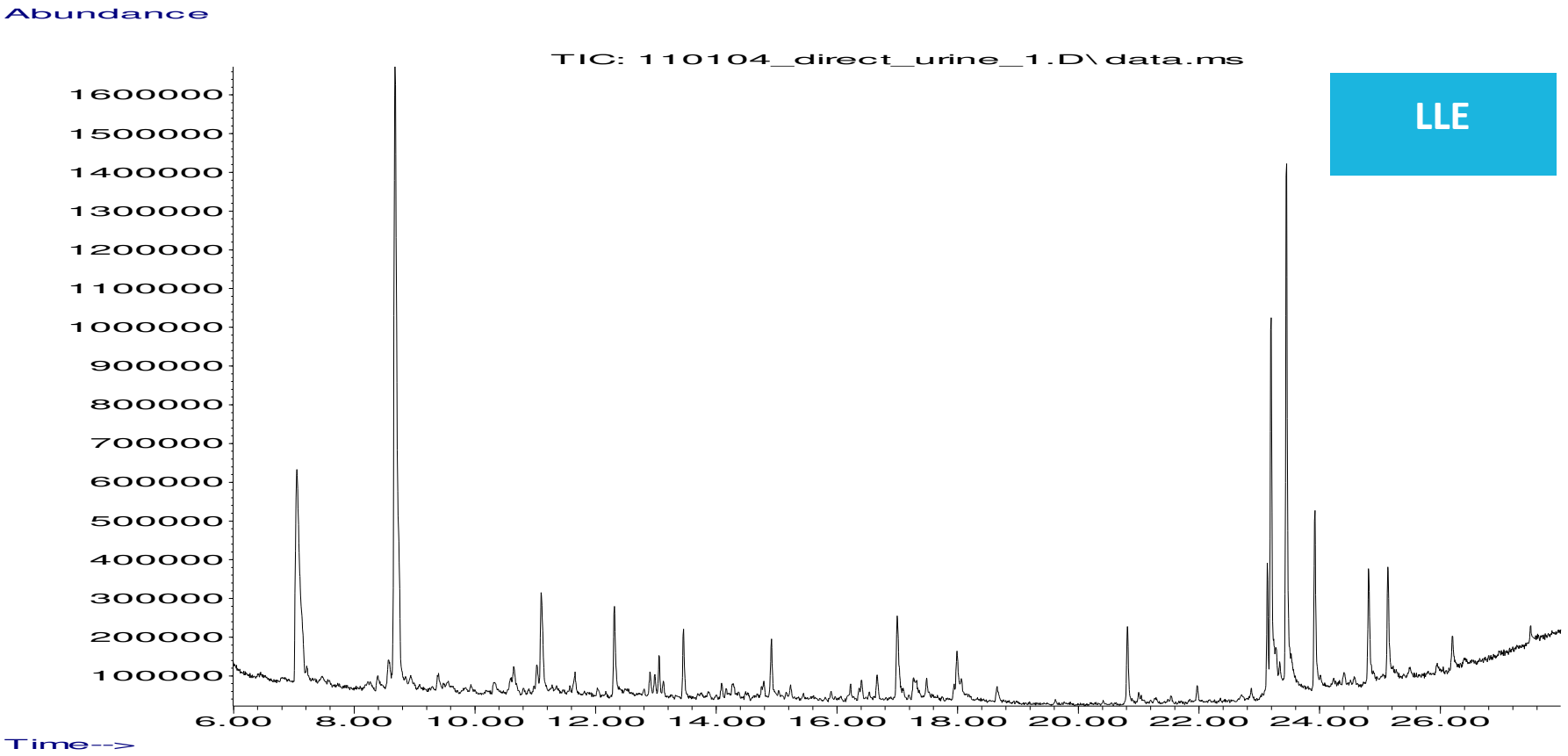
E. Pfannkoch, Gerstel US, App. Note 6/2010

Body fluid analysis (GC-QTOF)

- Analysis of 1 mL urine



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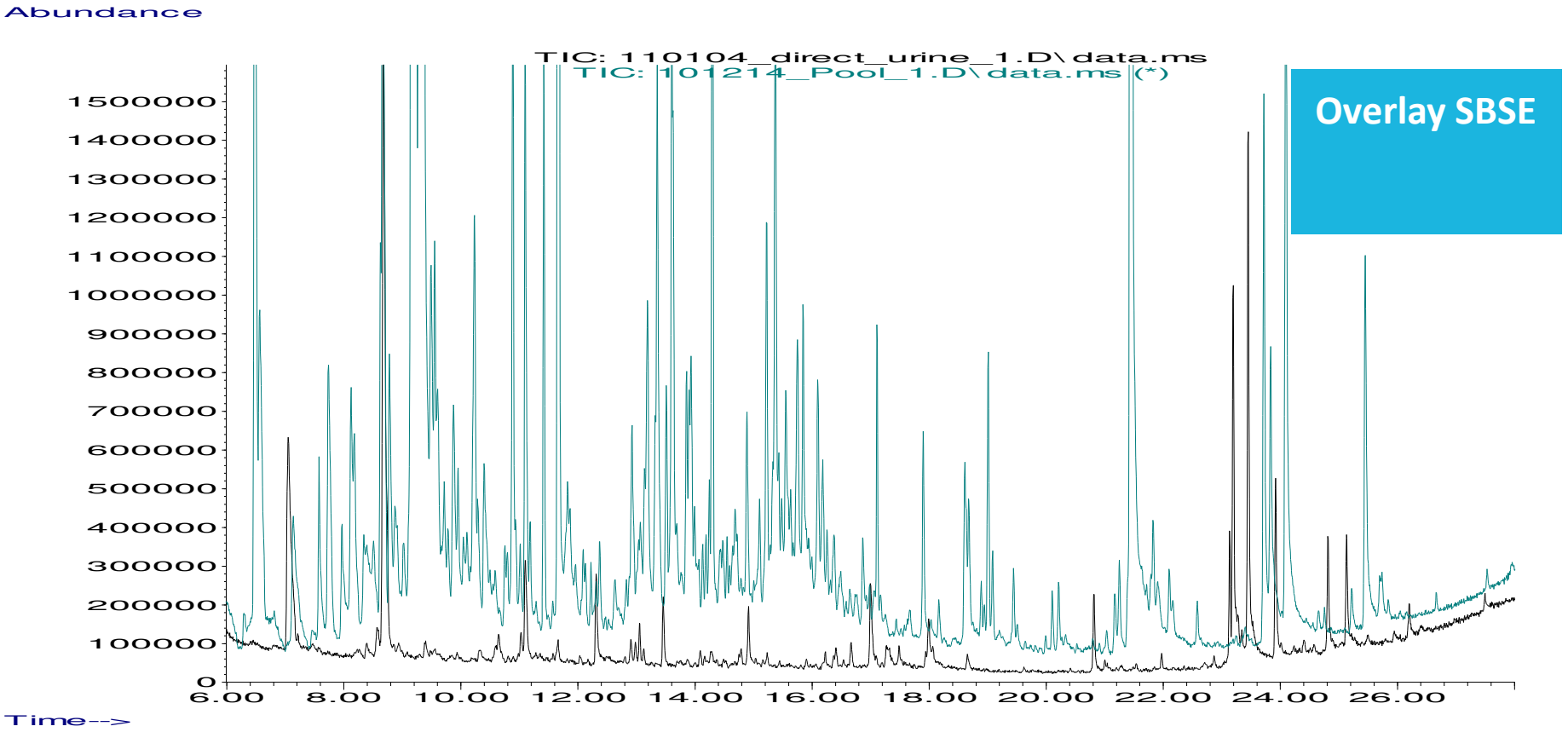
Comparison SBSE and LLE

- Analysis of 1 mL urine



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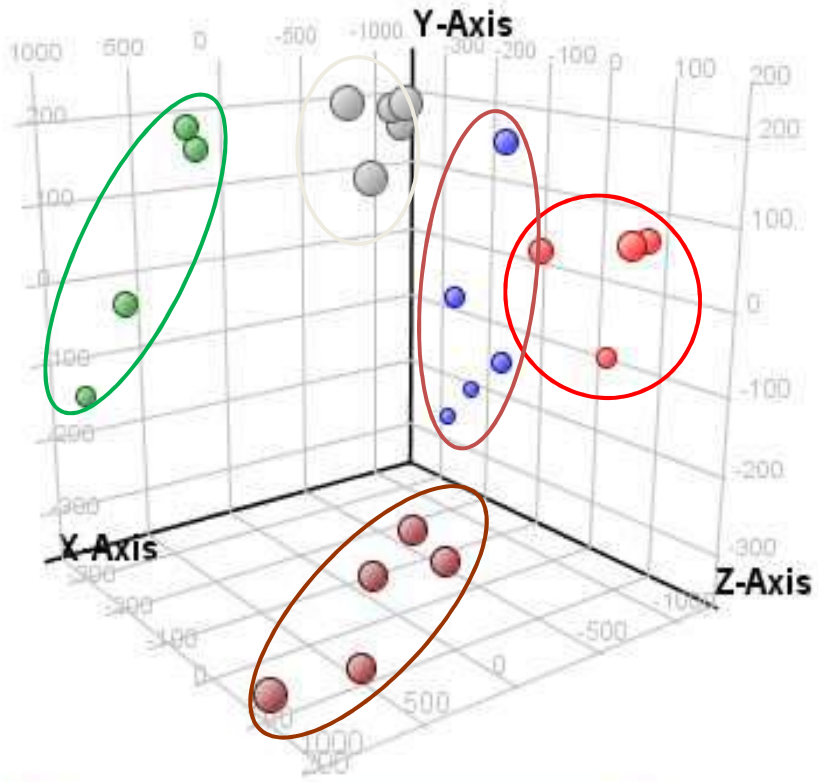
Urine analysis:
4 individuals x 5 samples + QC



X-Axis Component 1 (60.72%) Y-Axis Component 2 (16.8%) Z-Axis Component 3 (13.2%)

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The Future of Stir bar Sorptive Extraction and Related Techniques

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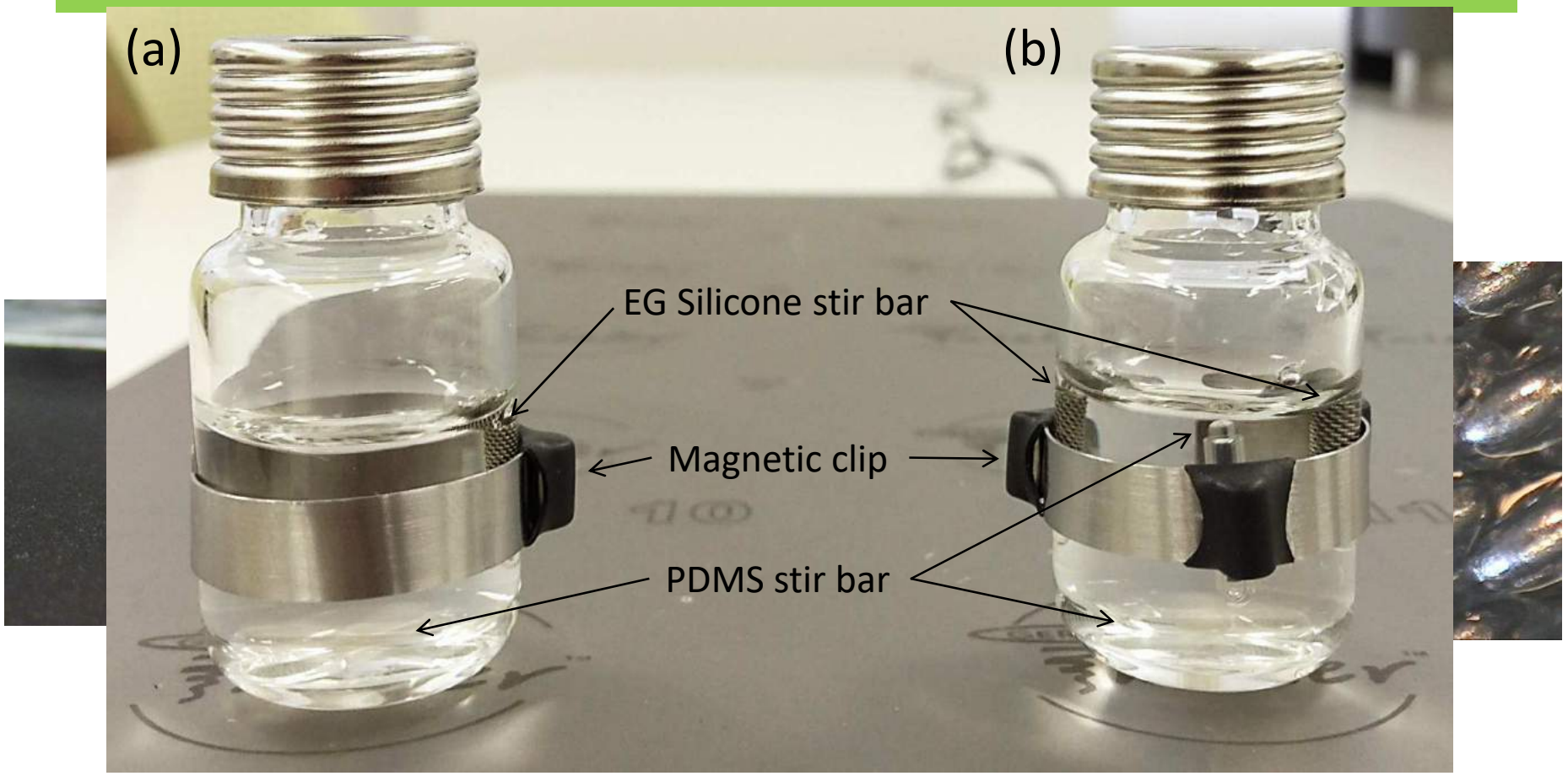
Development of Ethylene glycol modified silicone "EG Silicon Twister"



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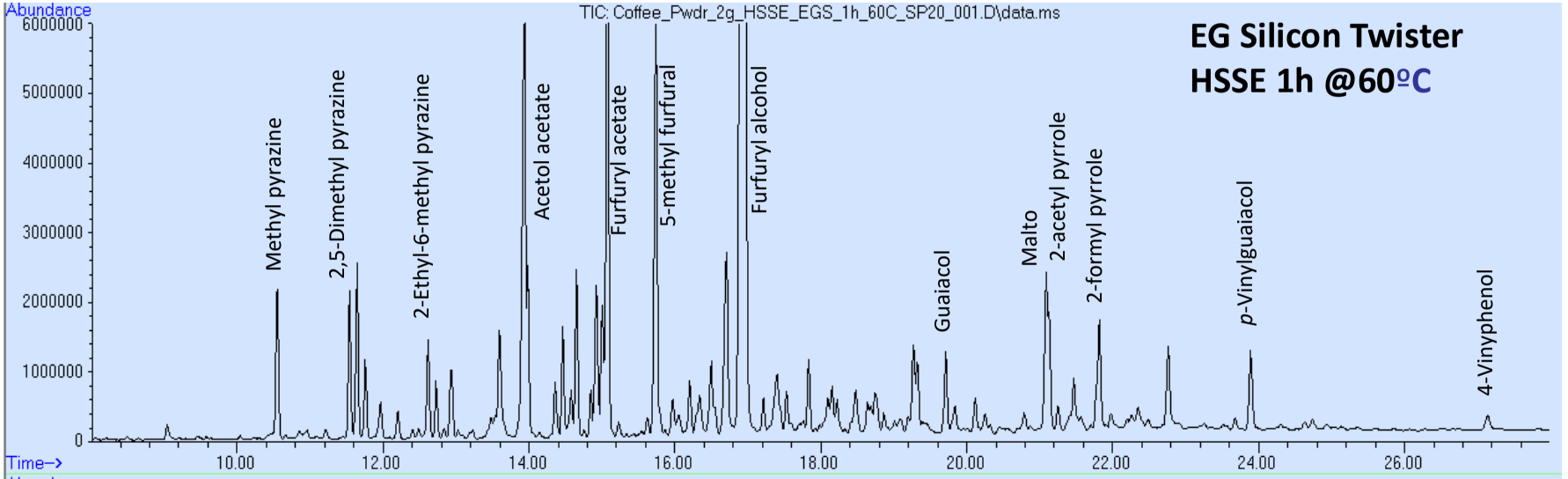
Comparison between EG Silicon Twister and PDMS Twister for HSSE of coffee powder



Journal of Chromatography A

Available online 26 May 2016

In Press, Accepted Manuscript — Note to users

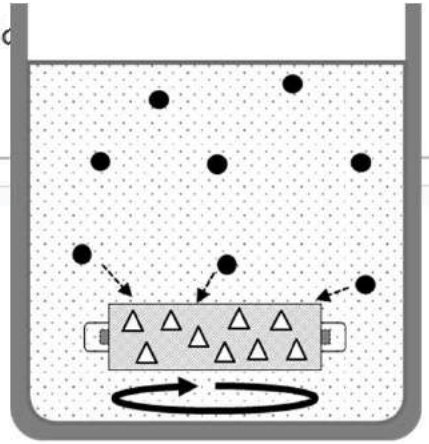
Solvent-assisted stir bar sorptive extraction by using swollen polydimethylsiloxane for enhanced recovery of polar solutes in aqueous samples: Application to aroma compounds in beer and pesticides in wine

Nobuo Ochiai[a], Kikuo Sasamoto[a], Frank David[b], Pat Sandra[b]

Show more

doi:10.1016/j.chroma.2016.05.085

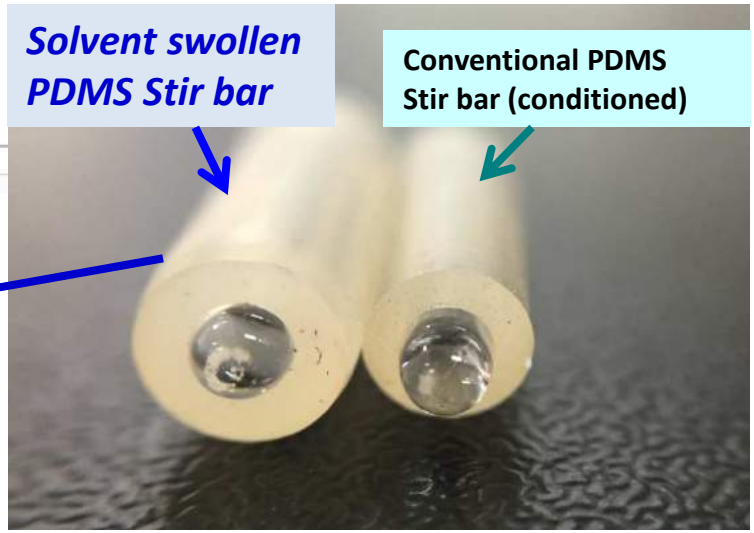
SBSE using a solvent swollen PDMS stir bar



△ Solvent

● Solutes (log K_{ow} < 2.0)

SA-SBSE



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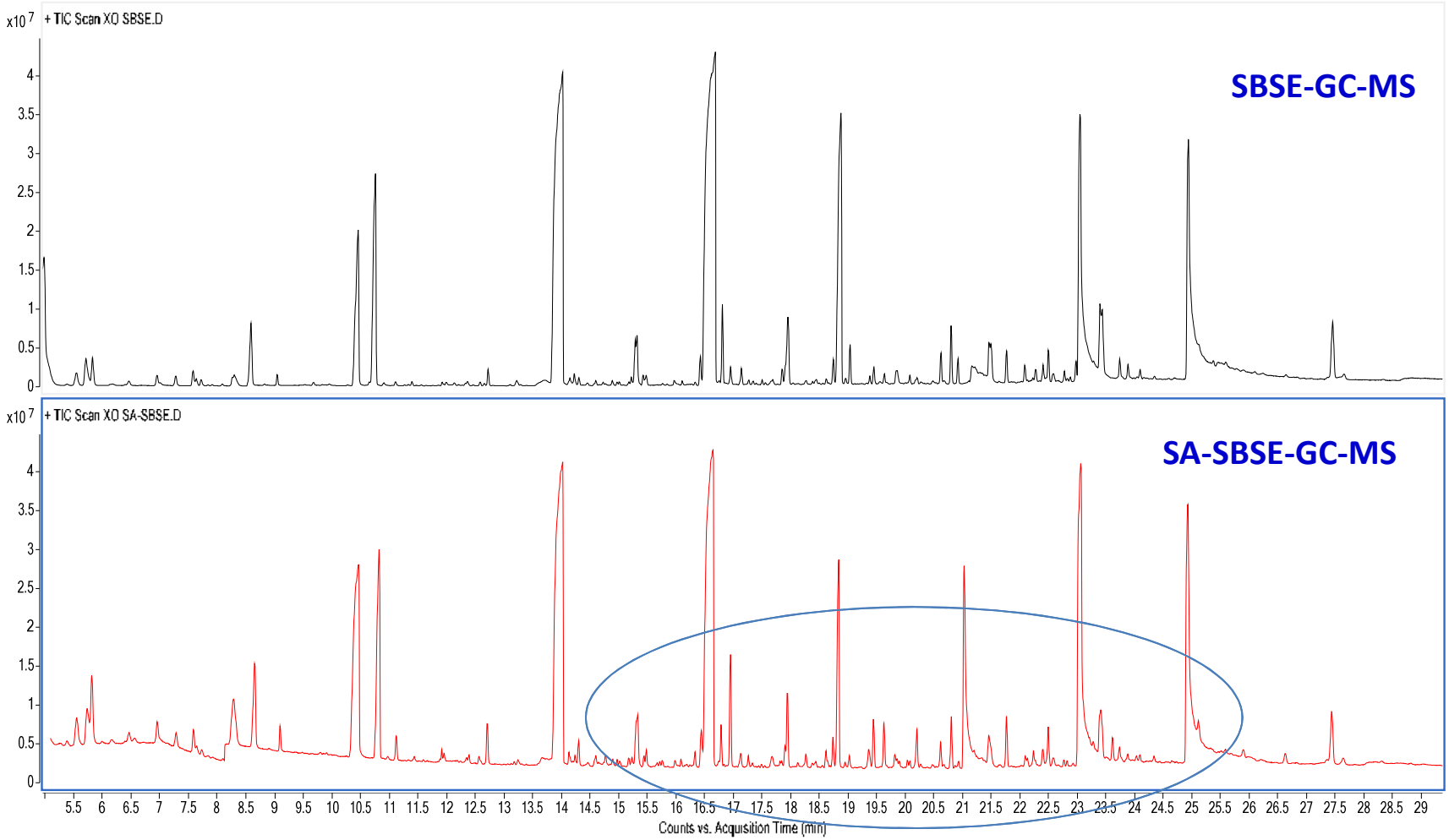
SA-SBSE versus classical SBSE – Cognac XO



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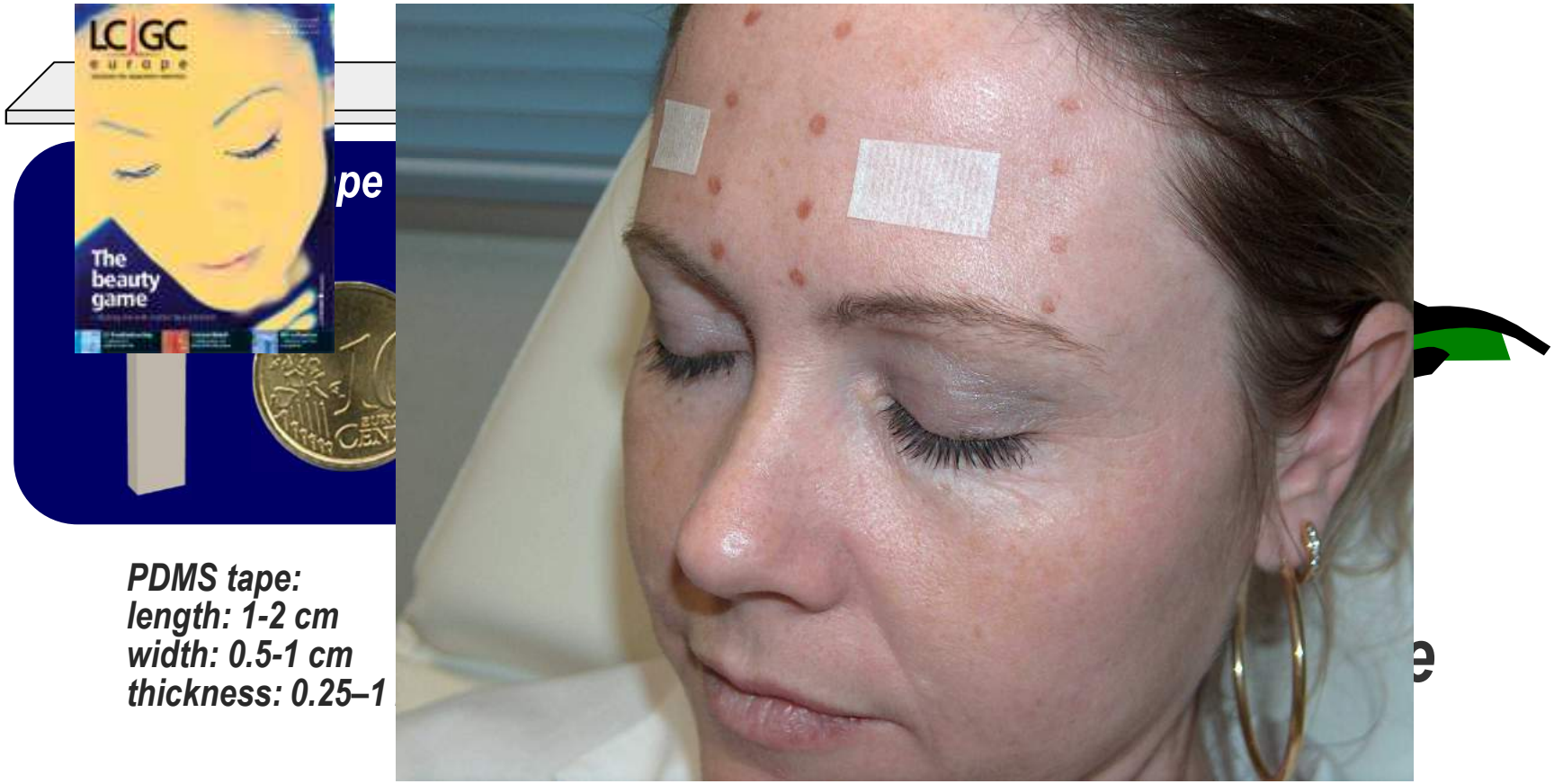
Conclusions

- **SBSE is a mature sample preparation technique: automated – miniaturized – solventless**
- **Very high enrichment factor**
- **Reduced risk of contamination**
- **On-site sampling/extraction**
- **Wide application area: QC – contaminants – metabolomics**

Other sorptive extraction methods

- Thin film SPME
- PDMS membrane (patch) sampling

Sorptive Extraction in Flavour and Fragrance Analysis
Carlo Bicchi, SBSE Technical meeting 2017



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* From: *P.Sandra, S. Sisalli, A. Adao, M. Lebel and I. Le Fur - LC-GC Europe, 19, (2006), 33-39*
C. Bicchi, C. Cordero, E. Liberto, P. Rubiolo, B. Sgorbini, P. Sandra, J. Chromatogr. A, 1148 (2007) 137

Thank you and enjoy the meeting

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