January 26, 2015 - SBSE Training program

14h00 - 17h15 :

Part 1: Introduction & Fundamentals
Part 2: Optimization of SBSE
Coffee Break
Part 3: Application Overview
Part 4: Extending SBSE to more polar solutes
Part 5: Newest developments & looking forward

Frank DAVID, RIC

"It is clear that errors made in sampling, sample preparation or sample introduction (injection) cannot be corrected by using the most advanced MS systems."

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Part 1: Introduction & Fundamentals

- Origin of SBSE
- From SPME to SBSE
- How to calculate a theoretical recovery?

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Why Sample Preparation ? (EXIT)

- Extraction: remove solutes from matrix
- Enrichment: concentrate solutes (enrichment factor X)
- Isolation: selective extraction / clean-up / purification
- Transformation:
  - Derivatization
  - Pyrolysis

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Why SBSE?

- **Extraction**: remove from matrix
- **Enrichment**: concentrate
- **Isolation**: selective extraction/purification
- Transformation:
  - **Combined with Derivatization (for extraction & analysis)**
  - Pyrolysis

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State-of-the-Art Sample Prep

- Automation
- Miniaturization: small sample size
- "Solventless" (avoid contamination)
- "On-line"
  - or On-site sampling or On-site Analysis ?

→ **SBSE**

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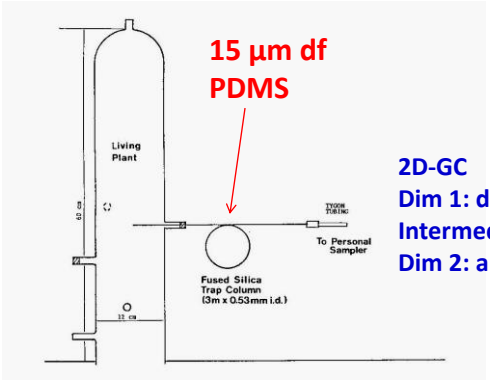
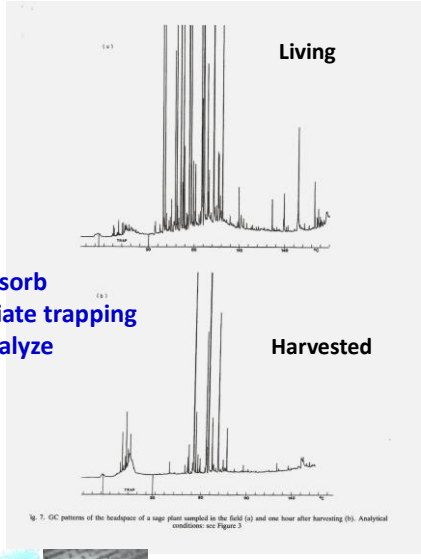
Open Tubular Trapping of Volatiles



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



Bicchi, D'Amato, David, Sandra
FFJ 1988

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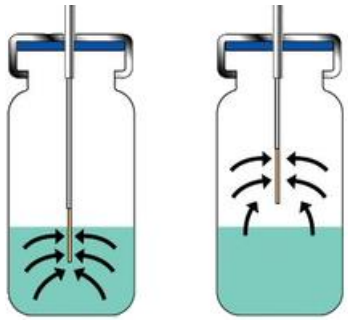
Solid Phase Micro-Extraction (SPME)
J. Pawliszyn, 1990



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

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

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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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Magnetic Stir Bar Coated with SPME-type Material (PDMS)

l = 10 mm, df = 0.5 mm ⟶ 24 µl
df = 1.0 mm ⟶ 63 µl
l = 20 mm, df = 0.5 mm ⟶ 47 µl
df = 1.0 mm ⟶ 126 µl

SPME : max. 0.5 µl

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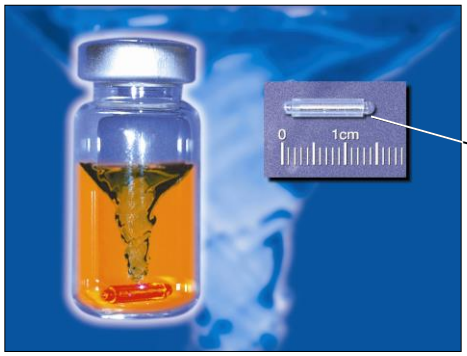
Stir Bar Sorptive Extraction (SBSE)



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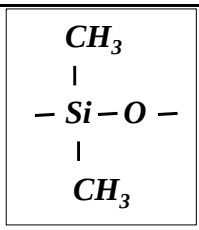
Best Sorptive Extraction Medium PDMS



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

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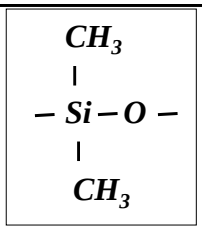
Alternatives for PDMS Check-list



- *Temperature range*
  - *Minimum (MiAOT) (see DSC – glass transition temp)*
  - *Maximum (MAOT) (see TGA: 1% loss is a lot!)*
- *Diffusion Coefficients*
- *Change of viscosity in function of temperature*
- *Sorption or Adsorption*

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SBSE (SPME) - Theory

Equilibrium

$$K_{PDMS/w} = \frac{C_{SBSE}}{C_w} = \frac{m_{SBSE}}{m_w} \times \frac{V_w}{V_{SBSE}} = \frac{m_{SBSE}}{m_w} \times \beta \approx K_{ow}$$

Recovery

$$\frac{m_{SBSE}}{m_0} = \frac{\left(\frac{Kow}{\beta}\right)}{1+\left(\frac{Kow}{\beta}\right)}$$

m_{SBSE}= amount on PDMS
m_0= initial amount
K_{ow} = octanol - water partitioning
β = phase ratio

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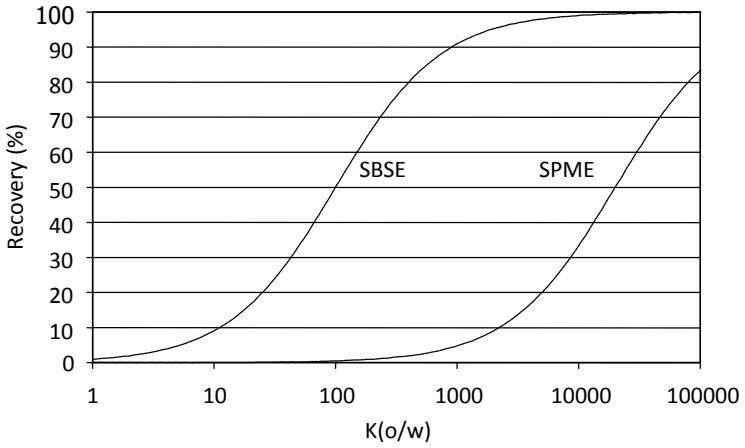
SBSE - Theory

Recovery of SBSE vs. SPME as a function of analyte polarity.



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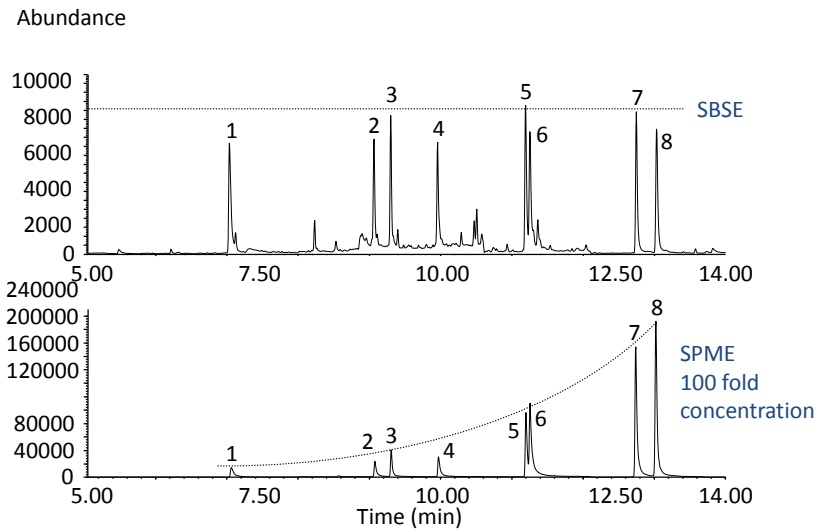
SBSE - Extraction of PAHs



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Recovery prediction

$$\text{Recovery}(\%) = \frac{m_{SBSE}}{m_0} x100 = \frac{\left(\frac{Kow}{\beta}\right)}{1+\left(\frac{Kow}{\beta}\right)} x100$$

EXCEL sheet 1

Gerstel Twister calculator

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Estimation of Recovery : Thiobencarb

Sample volume: 10 mL

Log $K_{o/w}$ 3.8971 → $K_{o/w}$ = $10^{3.8971}$ = 7890

SBSE

Twister : 24 µL PDMS

1/β : 0.0024

$$\frac{0.0024 \times 7890 \times 100}{0.0024 \times 7890 + 1}$$

95 %

SPME

Fiber : 0.5 µL PDMS

1/β : 0.00005

$$\frac{0.00005 \times 7890 \times 100}{0.00005 \times 7890 + 1}$$

28 %

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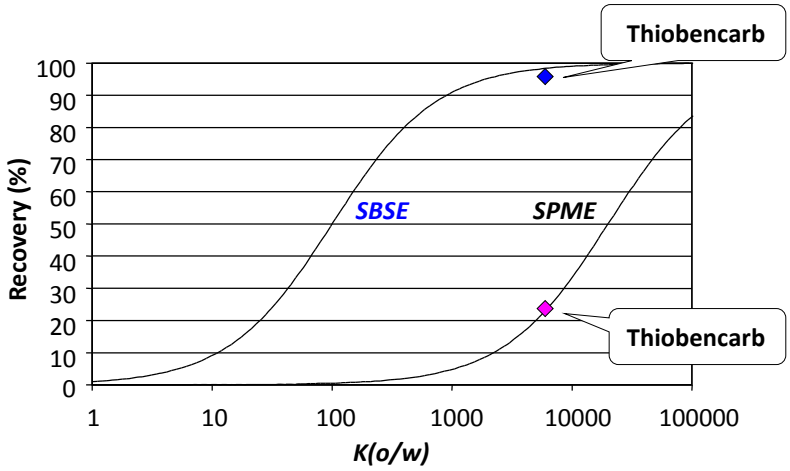
Comparison of recovery : SBSE *vs* SPME

Sample volume: 10 mL



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SBSE: advantages & limitations

- Extraction and concentration:
  - Extremely high enrichment factor possible
  - In TD-GC: "what is in coating can go to detector"
- Purification (Selectivity)
- Multi-residue analysis possible
  - Sample capacity depends on mass (not surface)
- Polar solutes?
  - No/little enrichment on PDMS – solutions ???

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Part 2: SBSE optimization

- Extraction:
  - Sample volume
  - Stir bar volume
  - Extraction time
  - Sample adjustment: pH, salt, organic modifier
- Desorption: thermal or liquid?
- Conditioning and re-use of stir bars

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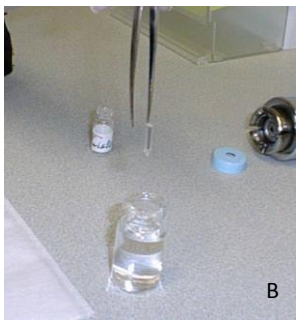
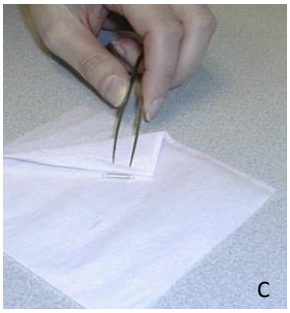
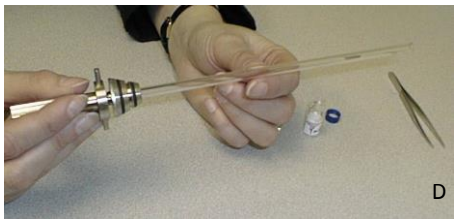
Extraction







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Optimization of Extraction (1)

- What is maximum recovery (%) under equilibrium conditions?
  - Sample Volume
  - Stir bar volume
  - Log P (Kow)

EXCEL sheet 1

- More volume = more extracted ?

EXCEL sheet 2

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Optimization of Extraction (2)

- Real recovery < (<<) maximum recovery (%) under equilibrium conditions.
- Kinetics: extraction time depends on
  - Sample Volume
  - Solutes (K)
  - stirring, vessel type,…

EXCEL sheet 3 & 4

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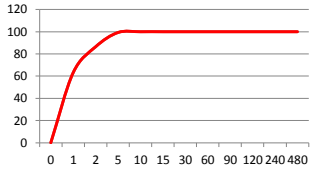
Extraction efficiency = fie (time)

$$C_{t,phase} = C_0.k.(1-e^{-t})$$



$$k = \frac{2.S.(M_s.M_F.K.V_F + M_s.M_F.V_w)}{M_s.V_F.V_w + 2M_F.K.V_w.V_F}$$

k: uptake/elimination constant; S: area; Vw: volume water; Vf: volume PDMS; K =Kow; Ms: mass transfer in water; Mf: mass transfer in PDMS

EXCEL sheet 3 & 4

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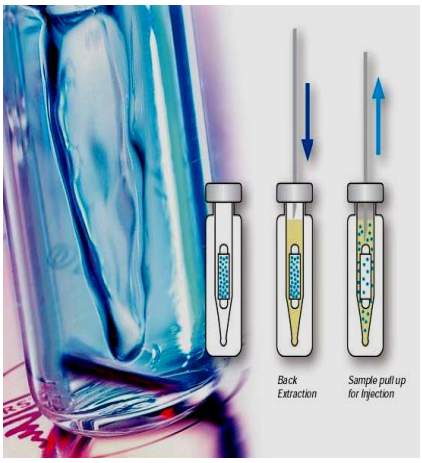
Desorption



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Optimization of Desorption

- Thermal desorption: best choice
  - Combined with GC
  - High enrichment = high sensitivity
  - Desorption = "gas chromatography on PDMS"
    $t_R = t_0 (1+k)$, $V_R = V_0 (1+K/\beta)$
- Liquid desorption: similar to liquid-liquid extraction and SPE
  - Enrichment factor?

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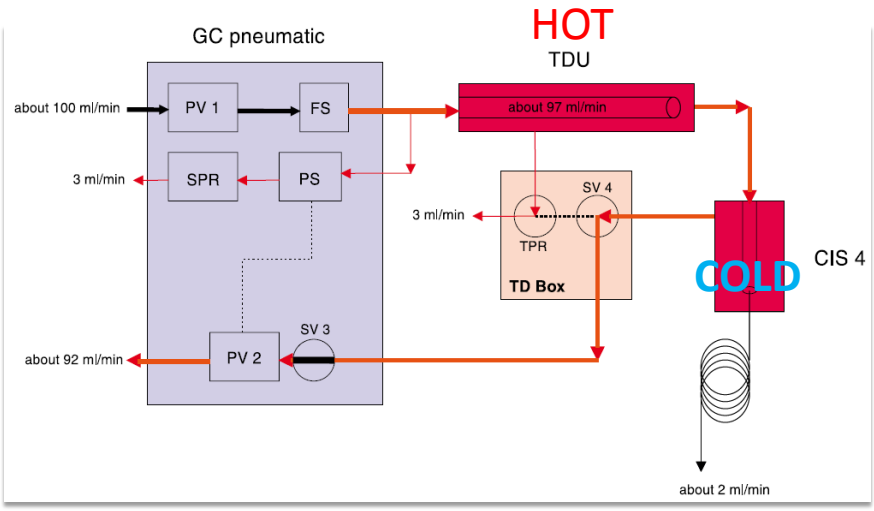
Pneumatics – TD splitless / CIS solvent vent



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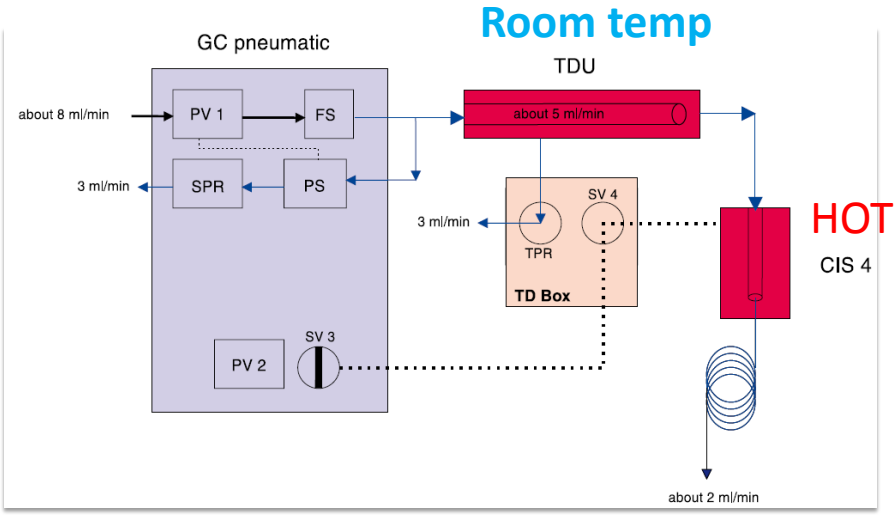
Pneumatics – CIS Splitless injection



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Optimization of SBSE

- Back-calculation:
  - Detection: IDL (instrument detection limit)?
  - Injection: split or splitless? (CIS PTV)
  - Extraction recovery (Kow)?
  - Sample volume/stir bar volume (dimensions)?
- Optimization of pH, salt addition, organic modifier
- Optimization of extraction time

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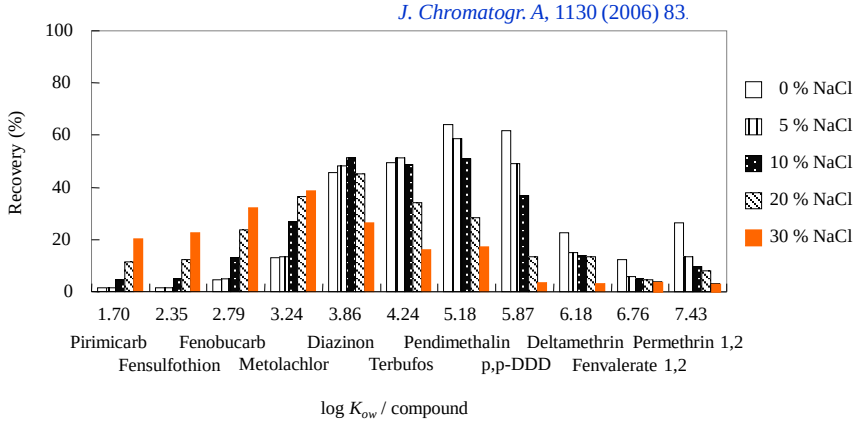
Influence of Salt Addition (NaCl)

N. Ochiai , K. Sasamoto, H. Kanda, S. Nakamura,
J. Chromatogr. A, 1130 (2006) 83.



Influence of salt addition (NaCl 0-30 %) on quantity extracted of representative pesticides with various octanol-water partitioning coefficients (K_{ow}) obtained for a spiked water at 5 ng mL^{-1} level

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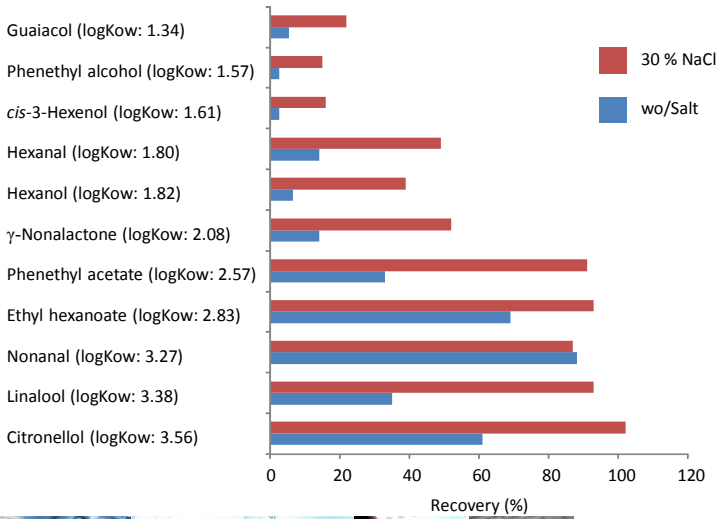
Recovery of Test Mix with or without Salt Addition (spiked water at 100 ng/mL)



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Influence of pH

- To obtain high extraction efficiency, the solutes should be in non-ionized form.
- This was clearly illustrated for the analysis of preservatives such as benzoic acid, sorbic acid and parabens in beverages.
- For benzoic acid (pKa=4.21), the sample was adjusted to low pH (pH=2).
- At pH > pKa, the ionic form results in very low recoveries (log $K_{o/w} < 0$ for benzoic acid in ionic form).
- At pH < pKa, the compounds are in acidic form, having higher K_{ow} (log $K_{o/w} = 1.87$ for benzoic acid in acidic form) and are extracted more efficiently.

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Matrix Effects - Role of Organic modifier

- Observation: calibration of pesticides in white wine≠ red wine
- Samples containing high concentrations of ethanol, acids, polyphenols, etc. should be diluted before extraction. Based on our experience, a maximum of **10% ethanol** content is a good starting point. Whiskey samples, for instance, are diluted 1/4 - 1/5.
- Fatty samples (milk, yoghurt, emulsions) are also diluted to a **maximum of 3% fat**.
- For the extraction of **highly apolar solutes**, such as PAHs and PCBs from water samples, it is recommended to add an **organic modifier** (methanol, ethanol, acetonitrile) to minimize wall adsorption.

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Multiple Extraction – Single desorption

- **Increased sensitivity** (alternative to increased volume)
- **Broad polarity (log $K_{o/w}$) range** (multiresidue analysis of pesticides): **dual ("multi-shot") extractions**
- For apolar pesticides, a high content of organic modifier (acetonitrile, methanol) is recommended to reduce wall adsorption and matrix effects.
- For polar pesticides, high modifier content will lower recovery.
- From the extracts from fruit and vegetables:
  - two aliquots: 50% and 20% methanol.
  - parallel extraction – single (combined) desorption
- Water analysis:
  - 20 mL sample containing 30% NaCl (for log Ko/w < 3.5)
  - 20 mL sample without modifier (for log Ko/w > 3.5).

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Can Twisters be re-used?

- **Yes** (they are also too expensive for single use)
- How many times?
  - Depends on sample type
  - Importance of rinsing before desorption.
  - Water analysis: re-use > 50 times
- Recondition: solvent + thermal
  - Beware of swelling, PDMS + O_2 = death
- Keep track!!!
  - Complex (highy loaded) samples versus clean water samples

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Method Development summary (1)

- Verification of analyte log K_{ow}: Based on literature data or using a Kowin calculator, the log K_{ow} for the target solutes can be checked. If log K_{ow}>2, SBSE on PDMS can be used. For lower log K_{ow} values, in-situ derivatization, salt addition or another stir bar coating might be needed.
- The (maximum) extraction efficiency can be calculated. Sample volume and stir bar dimensions can be selected for optimal recovery and enrichment.

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Method Development summary (2)

- **Thermal desorption-GC-MS suitability test**: If TD-GC-MS is used, a tube can be spiked with the target solutes and thermal desorption, cryo-trapping, injection and analysis can be performed. In this way, the suitability of the analytical equipment is checked and thermal desorption, GC and MS parameters can be optimized. At this stage, it can also be checked if the solutes are thermostable (for thermal desorption and GC analysis), if they are well focused, etc.
- Measurement of **practical extraction efficiency in function of time**: A series of spiked samples are analysed with increasing extraction times and the response for the target solutes is measured.

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Method Development summary (3)

- Finally the method can be optimized and validated using different spiking levels. Linearity, limit of detection and repeatability can be measured.
- Recently some papers described the use of **experimental design** in SBSE method development

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Experimental design

- A. Prieto, O. Zuloaga, A. Usobiaga, N. Etxebarria, L.A. Fernández,
Use of experimental design in the optimisation of stir bar sorptive extraction followed by thermal desorption for the determination of brominated flame retardants in water samples
Analytical and Bioanalytical Chemistry, 390 (2) (2008) pp. 739-748.

- K. MacNamara, R. Leardi, F. McGuigan,
Comprehensive investigation and optimisation of the main experimental variables in stir-bar sorptive extraction (SBSE)-thermal desorption-capillary gas chromatography (TD-CGC)
Analytica Chimica Acta, 636 (2) (2009) pp. 190-197.

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Part 3: Applications

- Environmental: semi-volatiles (GC amenable)
  - Water > air > soil/sediment
- Food: flavor & fragrance, wine, off-odours, contaminants,…
- Consumer products: allergens, leachables,…
- Life Science: biological fluids, target & non-target (metabolomics) mode

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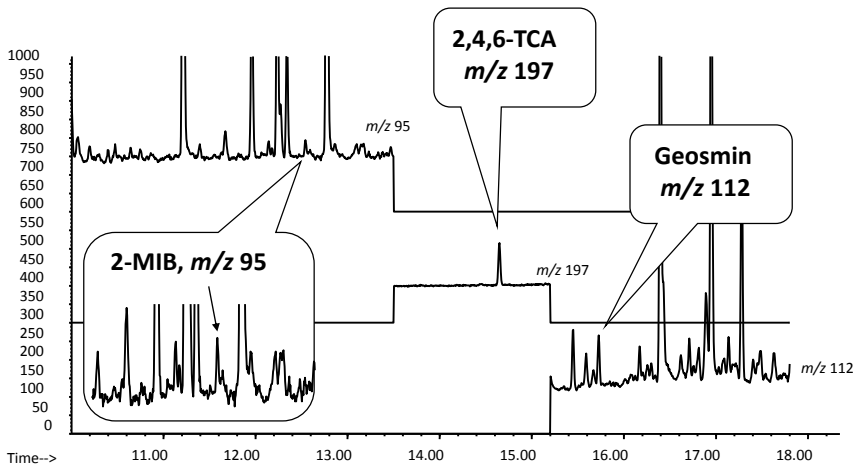
Musty odour in Drinking Water (each 100 ppq : 6 pg/60 mL, 240 min stirring)



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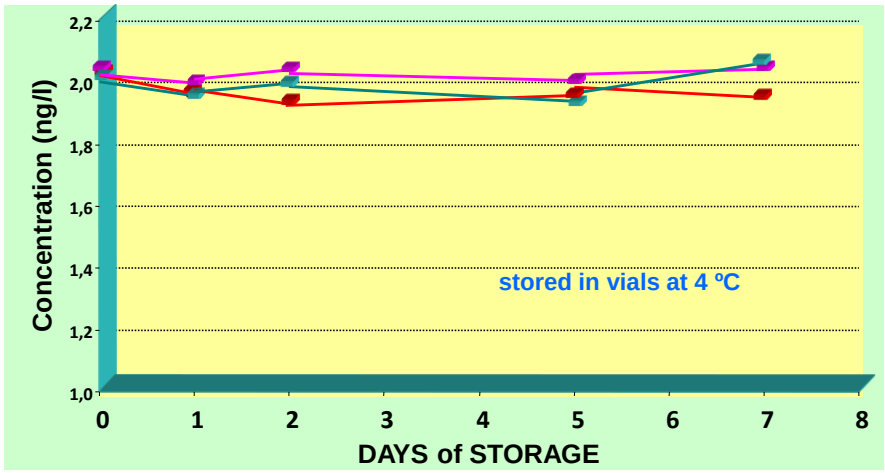
TCA in Water

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



On-site SBSE !

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

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

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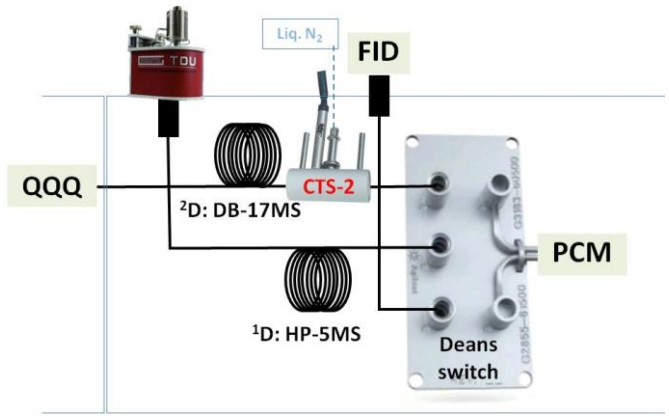
Determination of Tributyltin in Water Samples at the Quantification Level Set by the European Union (0.2 ng/L)

SBSE
TDU
2DGC
QQQ



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

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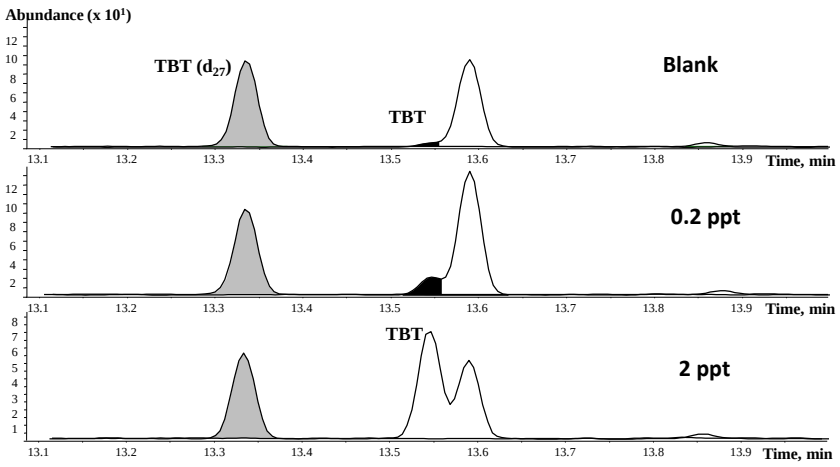
GC-MS/MS: Interference Detected @ TBT



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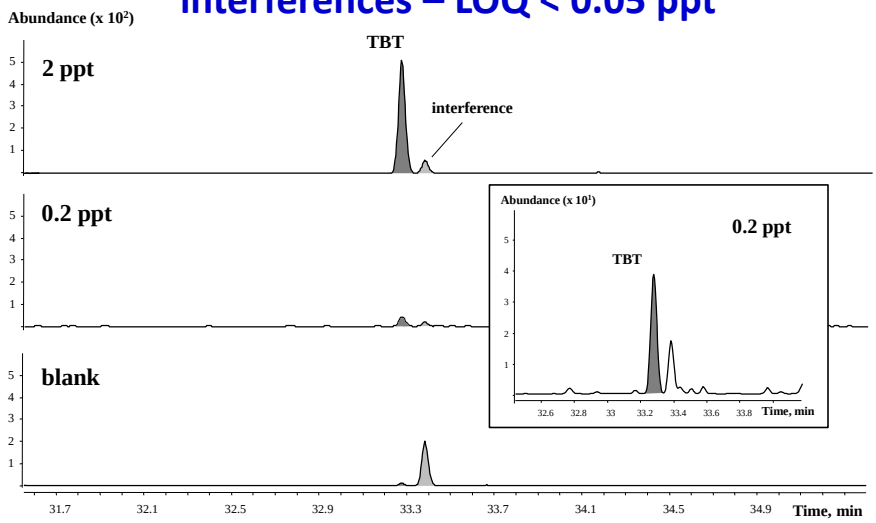
GC-GC-MS/MS: TBT resolved from interferences – LOQ < 0.05 ppt



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Wine Analysis using SBSE-GC-MS

Multi-residue methods

Prof De Revel, Céline Franc
Univ Bordeaux

- 2007 : **Off-flavours**

IBMP, EP, EG, TCA, TeCA, PCA, TBA, Géosmine

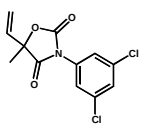




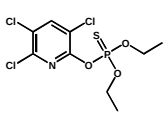

- 2010 : **Markers of wine aroma (fruity)**

C13-norisoprenoides and lactones

- 2010 : **Pesticide residues**



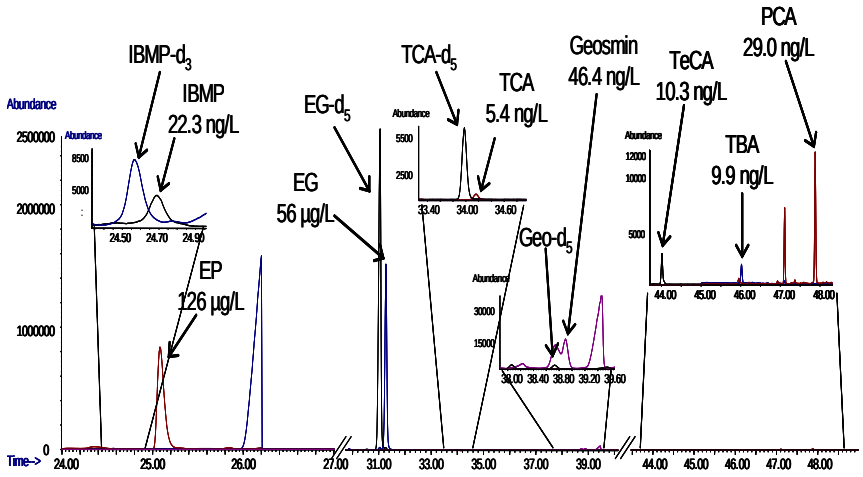
Vinclozoline



Chlorpyriphos

Multiresidue Analysis of Wine Defects

Céline Franc, Frank David, Gilles de Revel , JCA 2009



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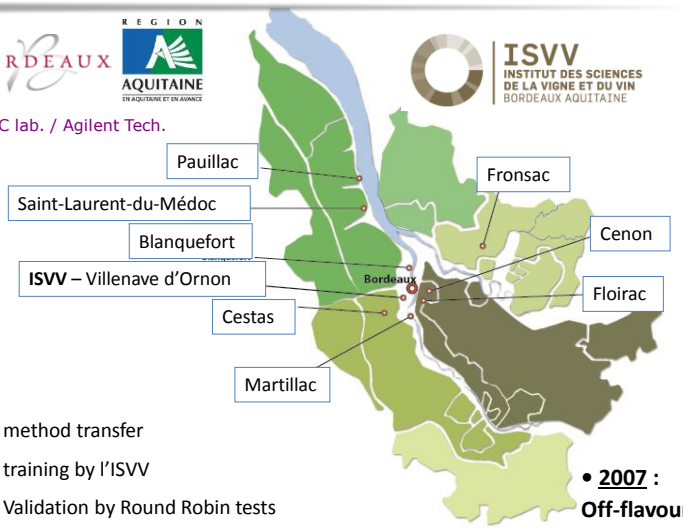
Transfer of SBSE-GC-MS methods into 8 laboratories

BORDEAUX REGION AQUITAINE

ISVV INSTITUT DES SCIENCES DE LA VIGNE ET DU VIN BORDEAUX AQUITAINE

RIC lab. / Agilent Tech.



- method transfer
- training by l'ISVV
- Validation by Round Robin tests

- **2007 : Off-flavours**
- **2010 : Pesticides**

Application : Round-Robin test SBSE-GC-MS « off-flavors"

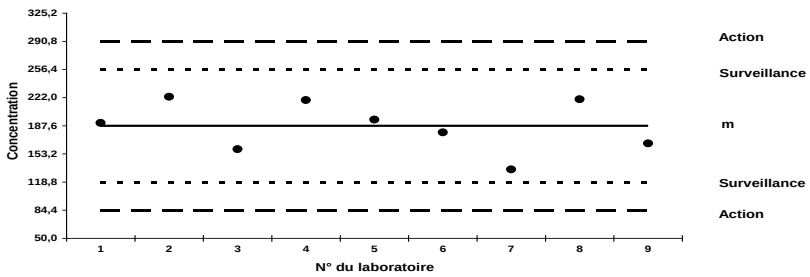
2009 : inter-laboratory test, 8 compounds – 9 laboratoires

↳ **CONFIDENCE in RESULTS**

Volatile phenols

nombre de laboratoires retenus :	9		
valeur assignée m :	187,6		
écart-type s* :	34,4		
limites de surveillance :	118,8	;	256,4
limites d'action :	84,4	,	290,8

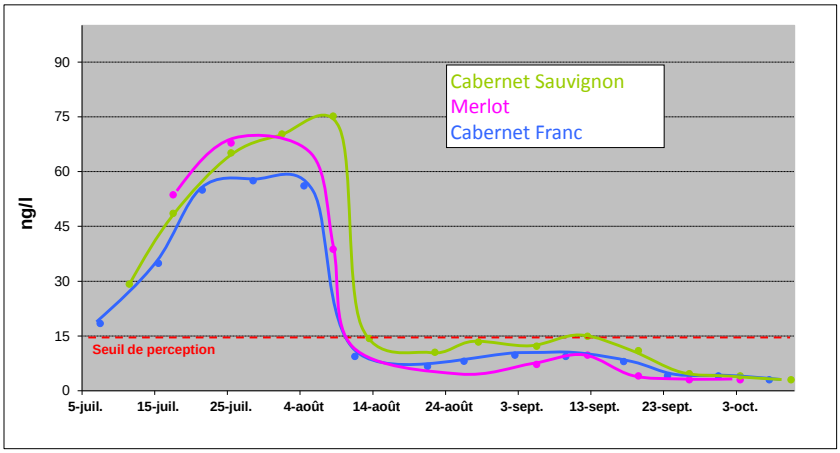
Répartition des résultats des laboratoires



Château Léoville Las Cases

2d Cru Classé - Saint Julien

Application: IBMP in grapes (2008)



- Augmentation de l'IBMP entre la fermeture de grappe (début juillet) et la véraison (début août).
- Ensuite, dégradation plus ou moins rapide lors de la maturation du raisin en fonction des conditions climatiques du millésime.

QC on solid material

2 extraction methods

1- « Passive Extraction » :

10 corks – leaching during 24h

in 500ml wine simulant (10 % Ethanol)

Leaching of Haloanisoles

SBSE extraction for leachable haloanisoles:

- 100ml « extract (10 % Ethanol) »
- IS: TCA-d5 (10ng/l),
- 2 h extraction with 20 mm x 0.5 mm stir bar

QC on solid material

2 extraction methods

2- « Active Extraction » by ASE (Dionex) :
Cork + wood (for barrels)

Solvent extraction (Acetone/Methanol)
at high pressure (100 bars) and
tempearture (max 180°C)

Total haloanisoles and halophenols

SBSE for Total haloanisoles & halophenols:
- ASE extract (Acetone/Methanol)
- IS : TCA-d5 (10ng/l) forhaloanisoles,
  TCP-d2 (200 ng/l) for halophenols.
- In-situ derivatization with acetic anhydride
- 2 h extraction with 20 mm x 0.5 mm stir bar

SBSE procedure for vegetables and fruit

15 g sample + 15 mL ACN

Ultra-Turrax + ultrason (15 min)

(=QuEChERS)

1 mL extract

+ 10 mL water

SBSE: 60 min

TD-RTL-CGC-MS

P. Sandra, B. Tienpont and F. David
J. Chromatogr., 1000 (2003) 299-309

Modified ratio water/organic Multi-Twister extraction
N. Ochiai, K. Sasamoto, H. Kanda, T. Yamagami, F. David, B. Tienpont and P. Sandra
J. Sep. Sci 28 (2005) 1083-1092

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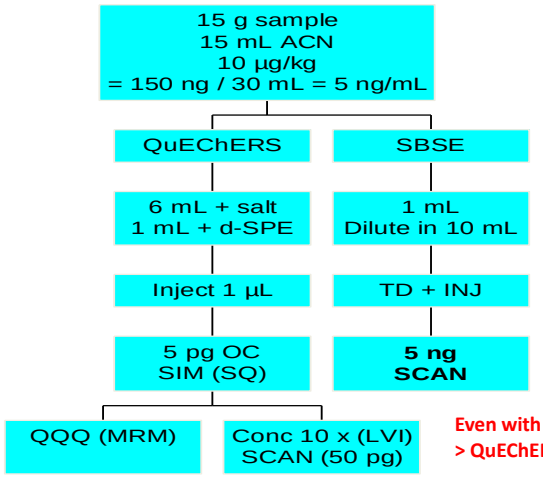
Comparison of Sensitivity of QuEChERS – SBSE



Even with 10% recovery, sensitivity SBSE > QuEChERS

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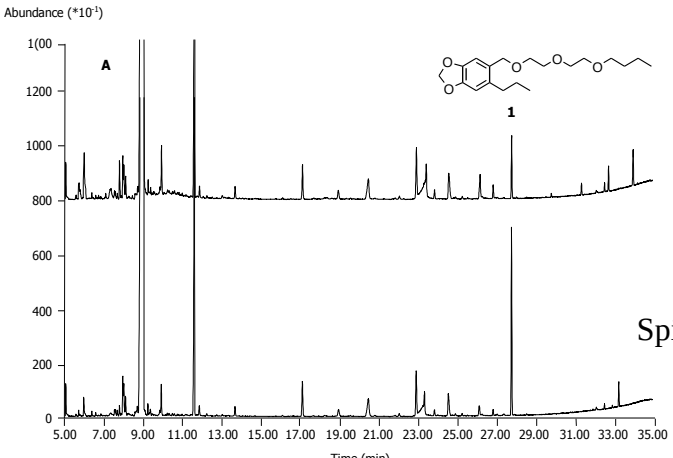
Analysis of Baby Food by SBSE-TD-GC-MSD (mixed vegetables, rice, chicken). Detection of piperonylbutoxide



Non-spiked

Spiked - 2 ppb

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SBSE for solid samples?

- **YES !!!**
- Preliminary extraction with water miscible solvent
- Dilute with water
- SBSE
  - Good recovery
  - Selective (extraction + clean-up)

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PAHs in sediment

- Wet sample: 15 g or Dry sample (lyophylized): 3 g + 12 g water
- Add 15 mL acetonitrile
- Add "Quechers Salt" ($MgSO_4$) + Shake/centrifuge
- Test 1: QuEChERS clean up + GC-QQQ
  - Clean-up on PSA (QuEChERS step 2)
  - Centrifuge
  - Inject **1 µL**
- Test 2: SBSE + TD-GC-QQQ
  - 100 µL + 900 µL acetone (dilute 1/10)
  - **10 µL** in 10 mL water (sama amount as liquid injection)
  - SBSE + TD-GC-MS

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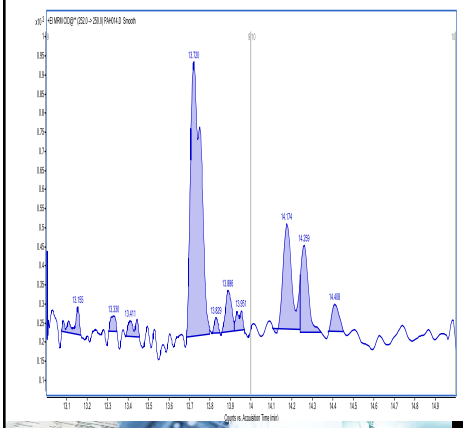
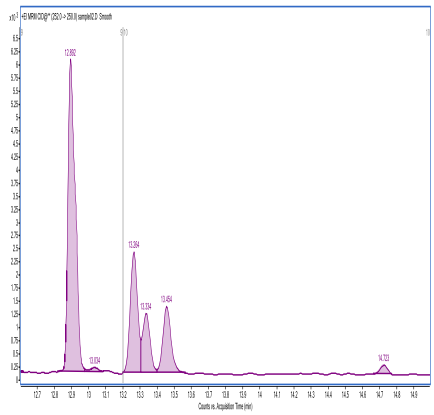
Sample 1 (wet) MRM 252-250 (benzofluoranthenes, benzo(a)pyrene)

liquid



SBSE



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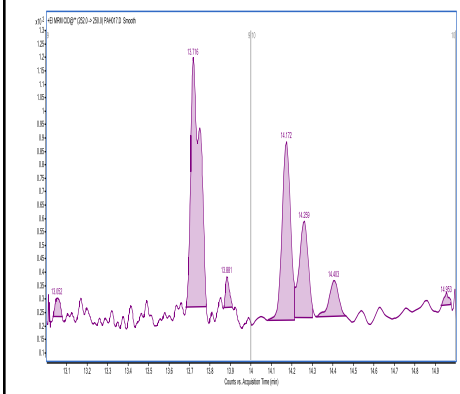
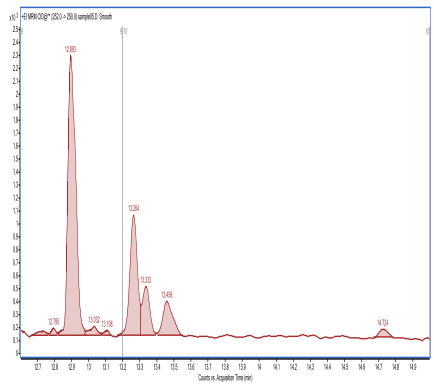
Sample 2 (dry) MRM 252-250 (benzofluoranthenes, benzo(a)pyrene)

liquid



SBSE



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Determination of PAHs in Sea Food

E. Pfannkoch, Gerstel US

Weigh 3g fish tissue into 50mL centrifuge tube

↓

Add IS, 12mL water, vortex 1 min

↓

Add 15mL acetonitrile, vortex 1 min

↓

Add Agilent QuEChERS salt packet, cap and shake
P/N 5982-5755

↓

Centrifuge @4700 RPM 5 min

↓

Transfer 1 mL of ACN layer for cleanup step

↓ dSPE cleanup, centrifuge

↓ Transfer to vial, GC/MS

↓ SBSE cleanup and concentration

↓ Transfer Twister to tube, GC/MS

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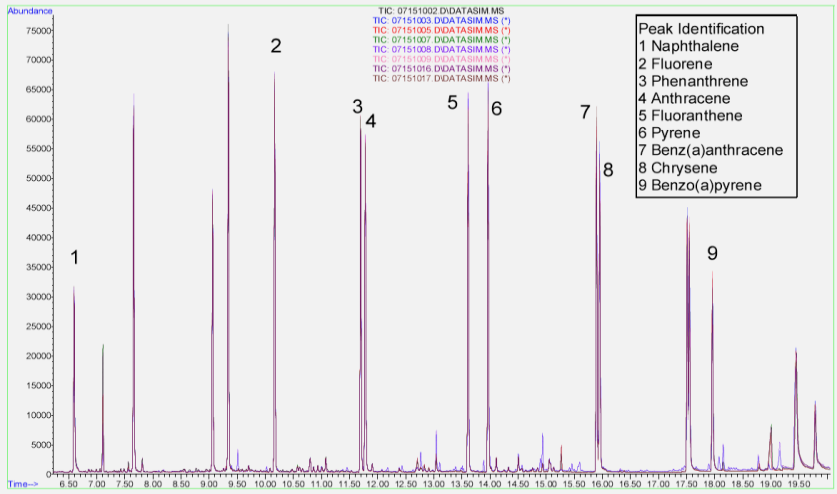
PAH Retention time stability
25ppb in tissue (croakers, oysters, red snapper)
18 runs overnight
8 chromatograms overlaid



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Part 4: Analysis of Polar Solutes

- Derivatization (increase extraction efficiency)
  - **In-situ (in aqueous matrix)**
  - *Post-extraction (during thermal desorption) (improve analysis & detection)*
- Sequential SBSE
  - Several extractions using different conditions/phases
  - Combined desorption
- New phases

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Derivatisation in Aqueous Media

- Acylation (acetic anhydride + K_2CO_3)
  - Phenols
- Oximation with pentafluorobenzylhydroxylamine (PFBHA)
  - Aldehydes and ketones
- Acylation with ethylchloroformate (ECF) (or hexylCF)
  - Alcohols (acylation), Amines (N-acetyl), Ccids (ethyl esters)
- Alkylation with $NaBEt_4$
  - Organotin (tetra-alkyl Sn)
- Derivatization of thiols with alkylpropiolate

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Analysis of chlorophenols

- 10 mL water sample
- 0.5 g K_2CO_3 and 0.5 mL acetic anhydride
- SBSE using a 10 mm x 0.5 mm d_f PDMS stir bar
- TD in splitless mode + GC-MS:
  - 30 m x 0.25 mm i.d. x 0.25 µm d_f HP-5MS
  - MS in selected ion monitoring (SIM) mode.
    - mono-chlorophenols (as acetates) (ion 128, 3 isomers),
    - dichlorophenols (ion 164, 6 isomers, 2 isomers not separated),
    - trichlorophenols (ion 196, 5 isomers),
    - tetrachlorophenol (ion 232, 1 isomer)
    - pentachlorophenol (ion 266).
- Same for: hydroxyl-PAHs, bisphenol A …

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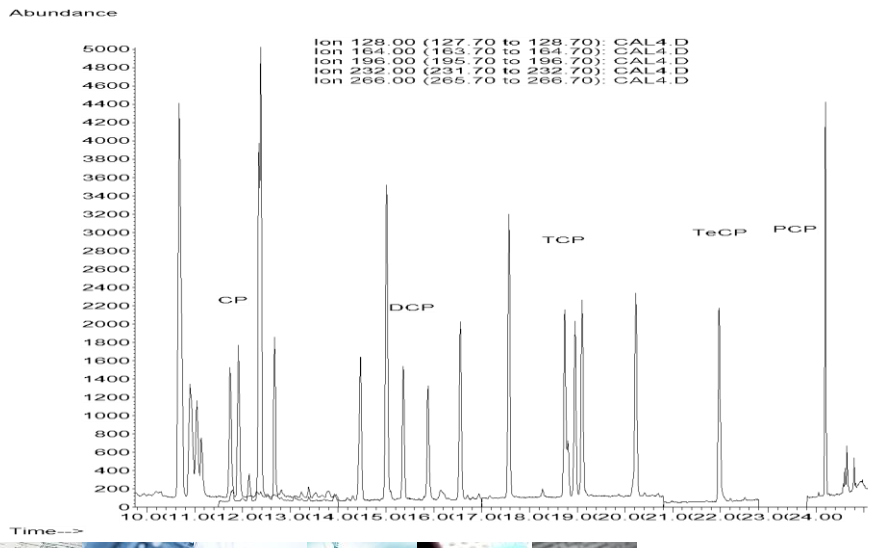
Analysis of chlorophenols (10 ppt in water)



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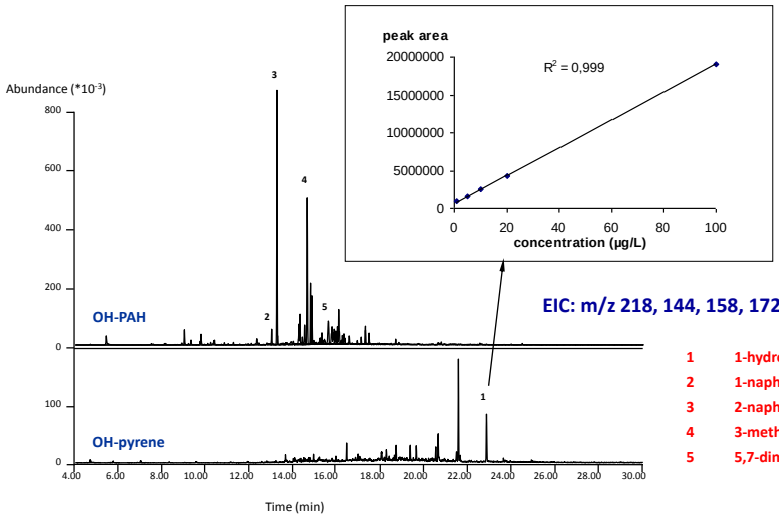
Acetylated OH-PAH in urine of a fireman



EIC: m/z 218, 144, 158, 172

1 1-hydroxypyrene
2 1-naphthol
3 2-naphthol
4 3-methylnaphthol
5 5,7-dimethyl-1-naphthol.

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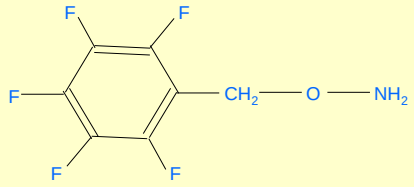
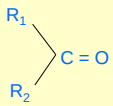
SBSE or HSSE of aldehydes/ketones

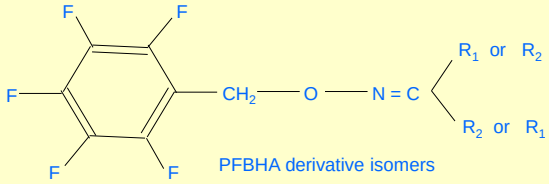


O-(2,3,4,5,6-pentafluorobenzyl) hydroxylamine (PFBHA)

+



Carbonyl compounds



PFBHA derivative isomers

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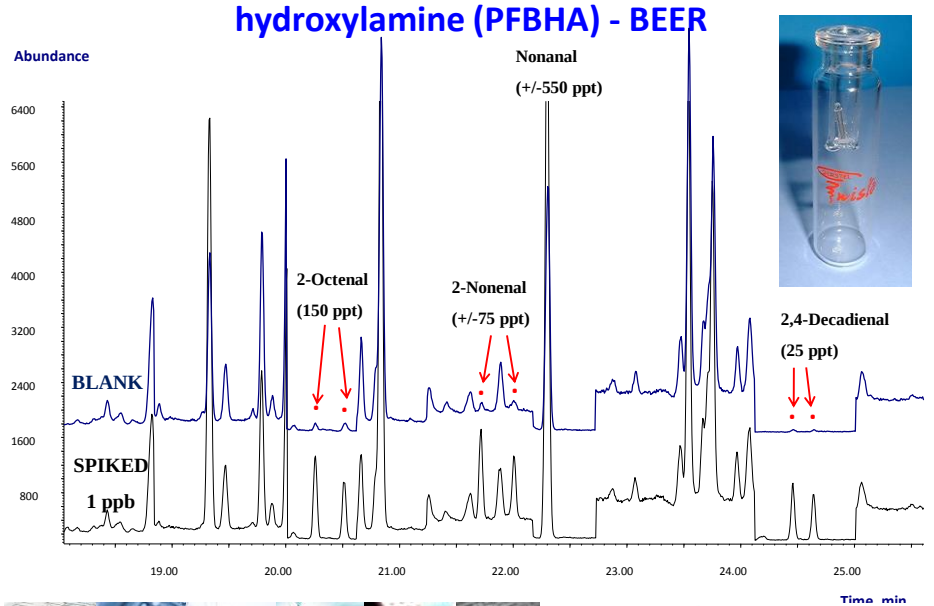
Derivatization in HSSE with pentafluorobenzyl hydroxylamine (PFBHA) - BEER



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SBSE procedures for biological samples

Urine 5 (1) mL

Blood/bile 1mL, 1g stomach content

1mL NH_4OAc + 10 µL β-glucuronidase, 90 min @ 37°C

Acetylation:
0.5 g K_2CO_3 + 0.5 mL AA

Ethylchloroformate:
2.5 mL EtOH/PYR (2:1) + 0.1 mL ECF

+ 10 mL water

+ 1 mL MeOH
+ 10 mL water

SBSE: 60 min

TD-CGC-MS

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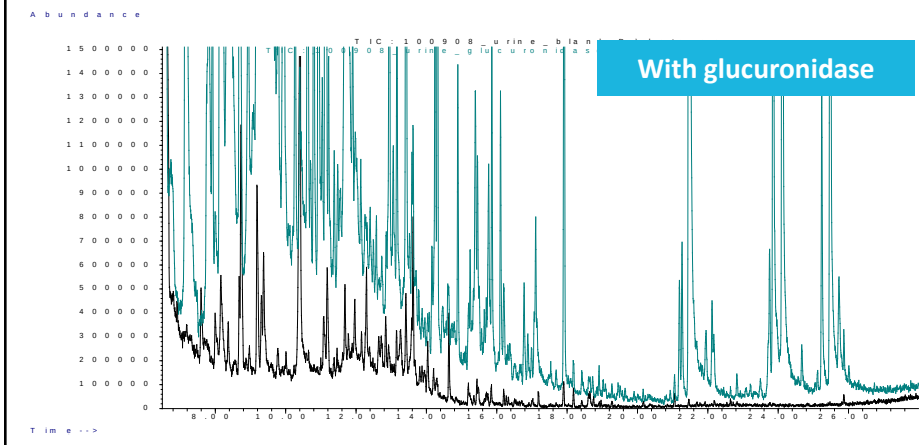
SBSE in metabolomics

- Analysis of 1 mL urine



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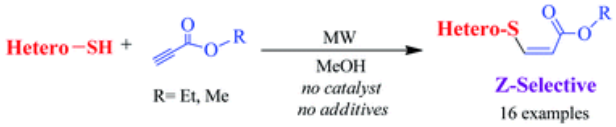
Analysis of Thiols (wine, beer,...)

- Polyfunctional thiols [3-mercaptohexan-1-ol (3MH), 3-mercaptohexyl acetate (3MHA) and 4-mercapto-4-methylpentan-2-one (4MMP)] are important aroma compounds. Current methods lack specificity and sensitivity.
- Derivatization with alkyl propiolate (ethyl propriolate) can be performed in-situ and, combined with SBSE, high sensitivity and good selectivity are obtained for the detection of the thioacrylates.



- See: N. Ochiai et al, in press

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Post-extraction derivatization

- Silylation: during desorption
- After liquid desorption : all derivatization methods
- HPLC derivatization methods

functional group	reagent
$-NH_2$	o-Phthalaldehyde
-NHR	9-Fluorenylmethylchloroformate (FMOC)
-COOH	p-Bromophenylacyl bromide 2-Naphthacyl bromide
-OH	Phenylisocyanate
-CHO, -CO	2,4-Dinitrophenylhydrazine

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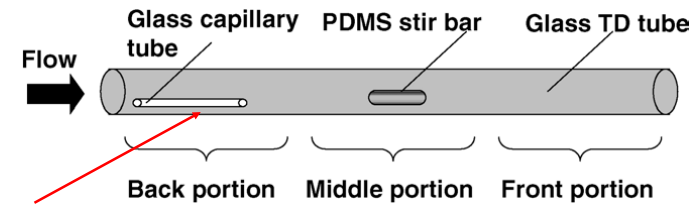
Desorption / derivatization



BSTFA (volatile)

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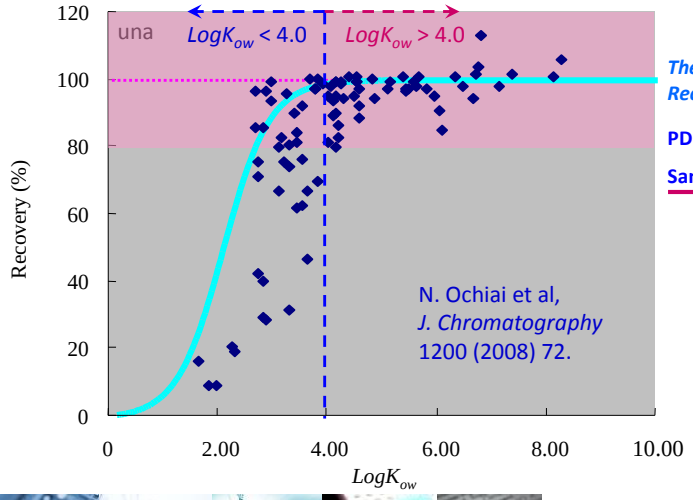
Sequential Stir Bar Sorptive Extraction

PDMS phase = Ko/w driven enrichment



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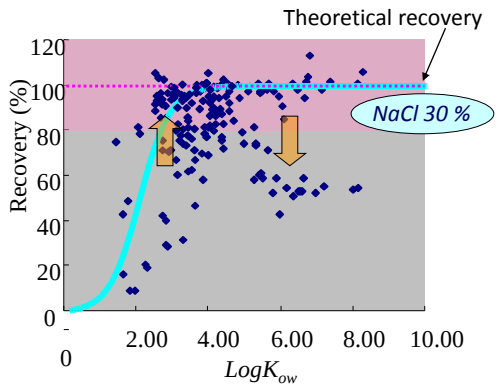
Sequential Stir Bar Sorptive Extraction

SBSE has a limitation for recovery of hydrophilic compounds because SBSE is based on distribution between PDMS and water.

Salt addition allows to improve recovery of hydrophilic compounds.

⇒ Negative effect for recovery of hydrophobic compounds …..

Sequential SBSE !



Recovery of 88 pesticides by SBSE

N. Ochiai et al, *J. Chromatography* 1200 (2008) 72.

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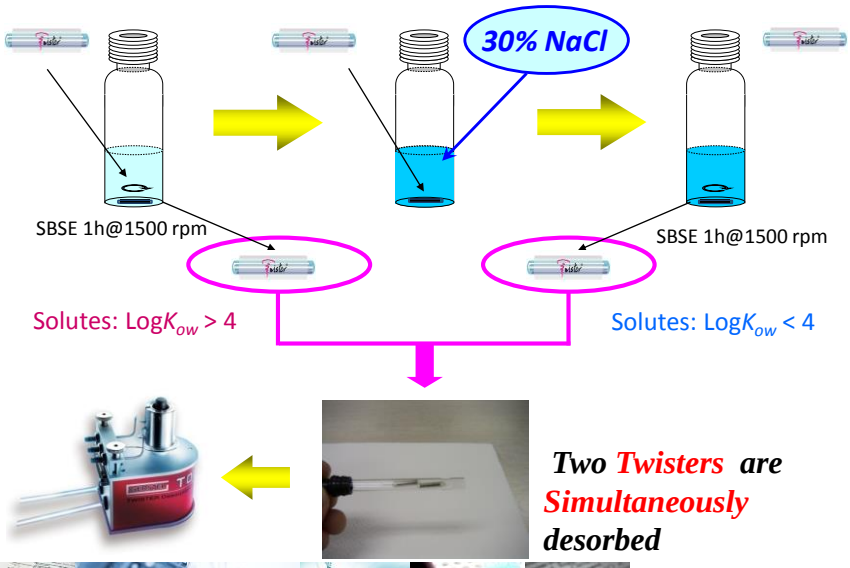
Sequential SBSE Procedure



Two Twisters are Simultaneously desorbed

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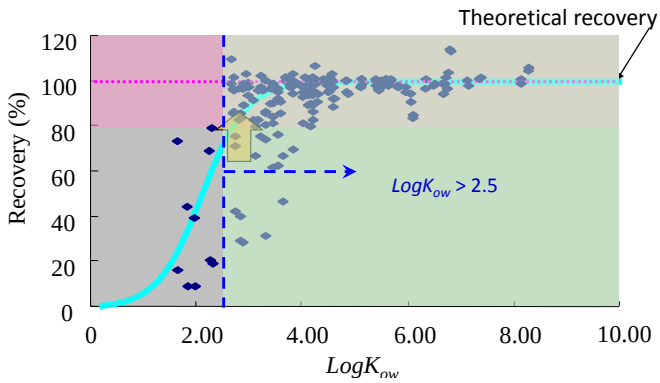
Sequential SBSE for Multi-residue pesticide analysis



Recovery of 88 pesticides by Sequential SBSE

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New phases for coating

- SPME: different fibers available
(PDMS, PDMS/carbon, DVB, CW, acrylate)

What about SBSE?

- Thermal desorption or liquid desorption ?
- Immersion or Headspace sampling ?
- More material = bleeding more critical
- Attempts: polyacrylate, polyurethane, carbon, sol-gel, monoliths, MIPs, RAM,…

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New phases for coating - criteria

- Should be used with thermal desorption
  - Low bleed
  - Bleed does not interfere with solutes
- Liquid desorption = SPE
  - Compare enrichment factor!!!
- Should be significantly better than PDMS
(and compared to it)

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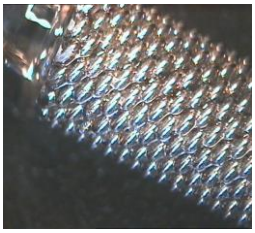
Development of New Phase Twister

Development of Ethylene glycol modified silicone "EG Silicon Twister"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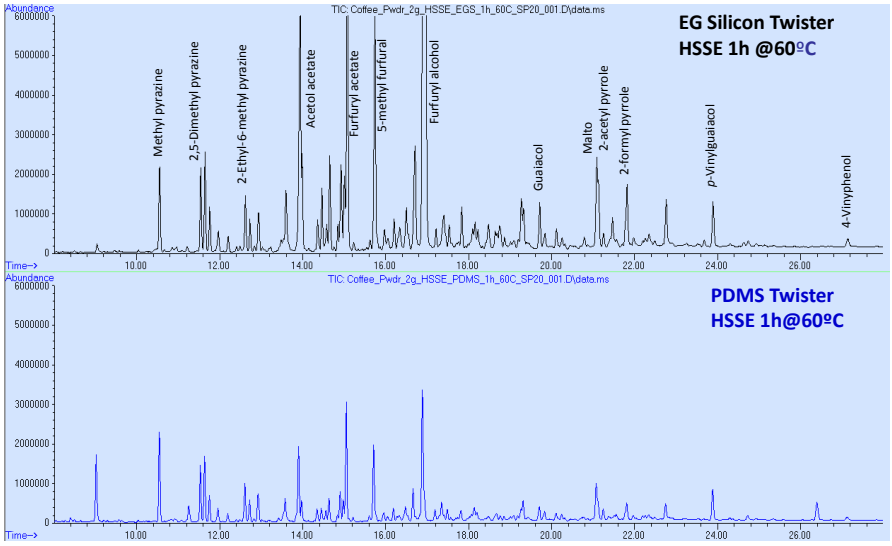
Comparison between EG Silicon Twister and PDMS Twister for HSSE of coffee powder



SBSE & polar compounds – New phases

- Extraction efficiency for selected compounds in whiskey

Compound	log Kow	Extracted (ng) PDMS	PDMS-EG	
Vanillin	1,05	14	400	(x 29)
Guaiacol	1,34	45	340	(x 8)
Phenethyl alcohol	1,57	380	3700	(x 10)
1-Hexanol	1,82	25	110	(x 4)
2-Methyl phenol	2,06	110	1500	(x14)
4-Ethyl guaiacol	2,38	210	550	(x 2,6)
Phenethyl acetate	2,57	1800	2200	(x1,2)
Ethyl hexanoate	2,83	640	640	(x1,0)
Ethyl octanoate	3,81	4600	4400	(x0,96)

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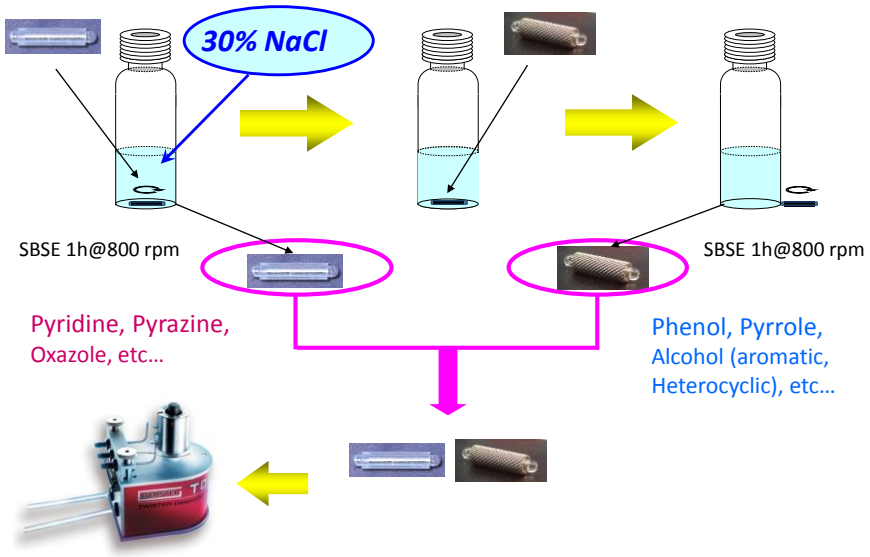
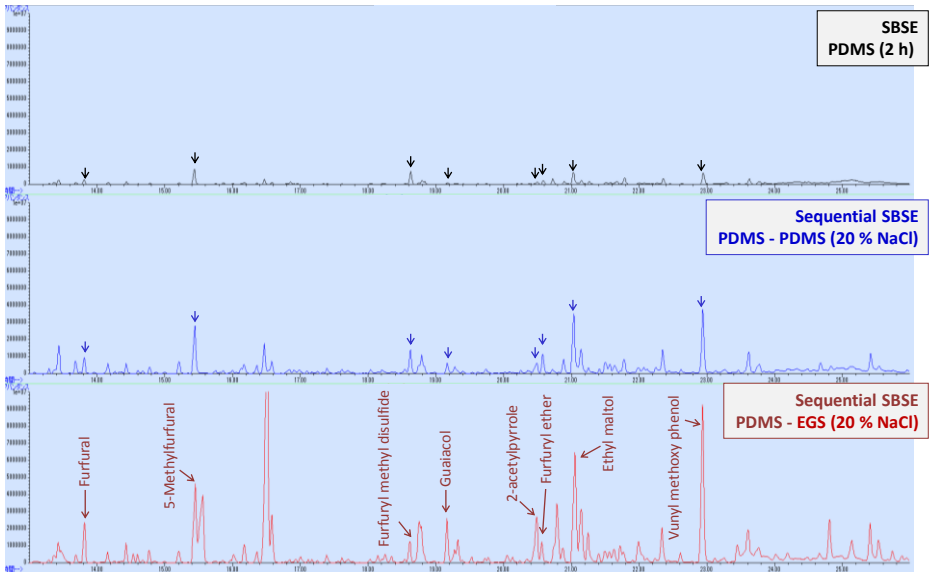
Sequential SBSE for odor analysis



N. Ochiai et al, J. Chromatography 1200 (2008) 72.

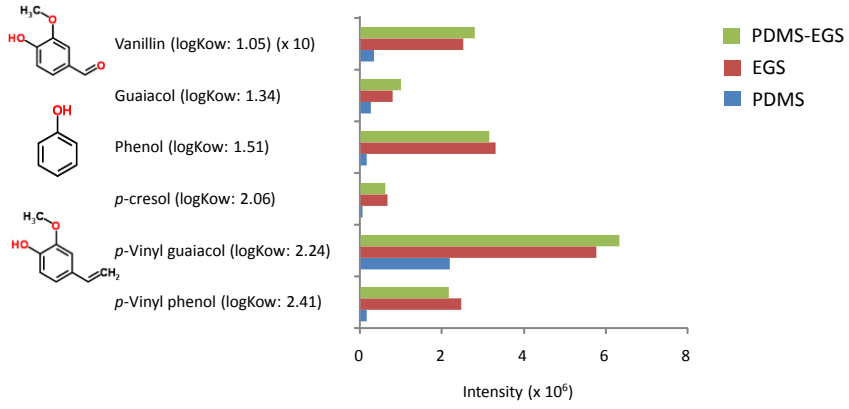
Comparison of TICs for coffee sample

SBSE *vs* Seq SBSE (PDMS-PDMS) *vs* Seq SBSE (PDMS-EGS)



From: N. Ochiai et al, Gerstel KK

Comparison of recovery of phenolic compounds between EG Silicon, PDMS and Seq-SBSE



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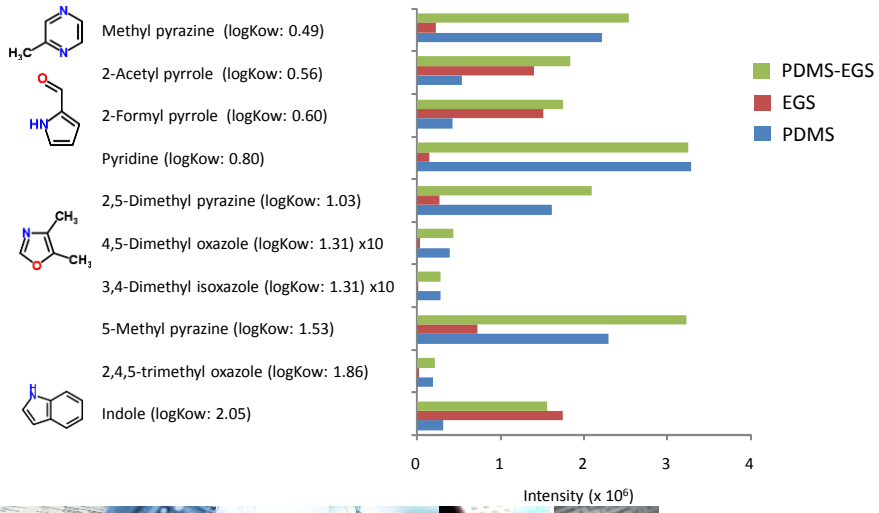
Comparison of recovery of nitrogen hetrocyclic compounds between EG Silicon, PDMS and Seq-SBSE



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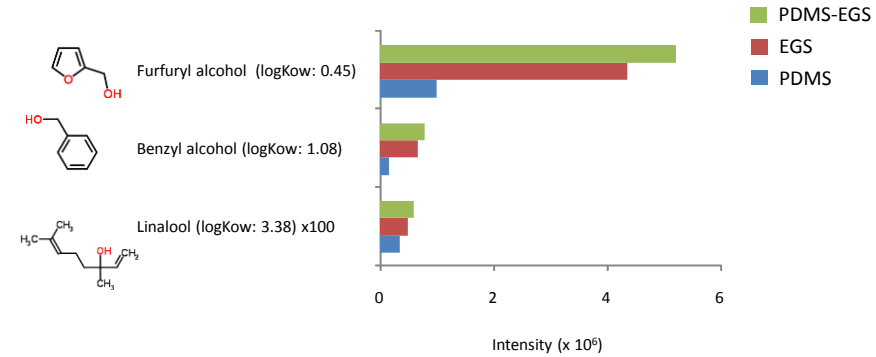
Comparison of recovery of alcohols between EG Silicon, PDMS and Seq-SBSE



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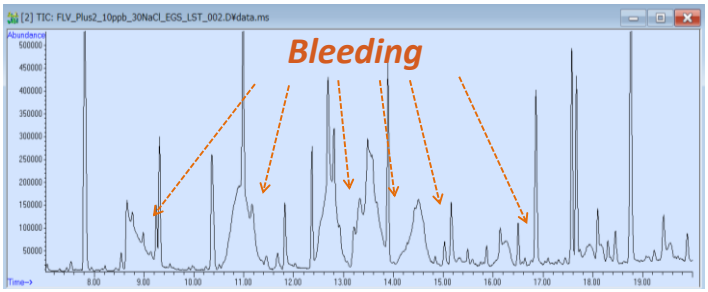
EG Silicone Twister in routine

Robustness:

Although the EG-Silicone stir bar showed good performance in SBSE, when re-used several times, increased bleeding from the decomposed phase and decreased repeatability were observed. For those EG-Silicone stir bars, ***numerous scratches were observed on the surface of the grid by using microscopy and tiny exposed metal surfaces appeared.***



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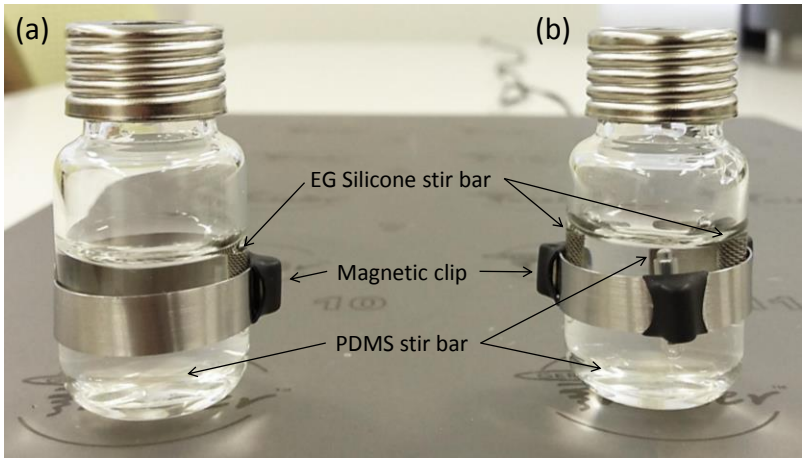
mSBSE using different coatings

N. Ochiai et al, HTSP, 2014



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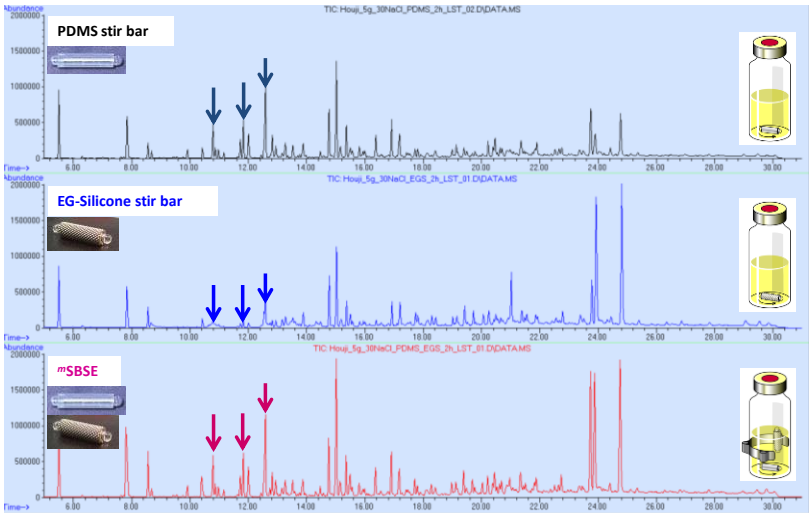
Comparison of TICs of the roasted green tea by single SBSE and *m*SBSE



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Other new materials ???

- Sol-Gel (PDMS, PVA): no stable coating at useful film thickness
- Monoliths (acrylate, vinylpyrrolidone): mostly similar to PDMS (no significant improvement for polar solutes)
- Polyurethane: liquid desorption
- Poly(phthalazine ether sulfone ketone) (PPESK): Guan et al, JCA 1177 (2008) 28
- Carbon materials???

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Newest Developments & looking forward

- Google: “SBSE”, from 2015: 35 articles!!!
- New phases
  (> 300 articles since 2011, mostly on new phases)
- New applications: SBSE-DART-MS
  - K. Brooks-Loftin, Univ Florida
  - Bridoux et al (CEA, Arpajon), Analysis of phosphoric acid esters by SBSE-DART-Orbitrap
- Passive sampling: SPMD, POCSIS

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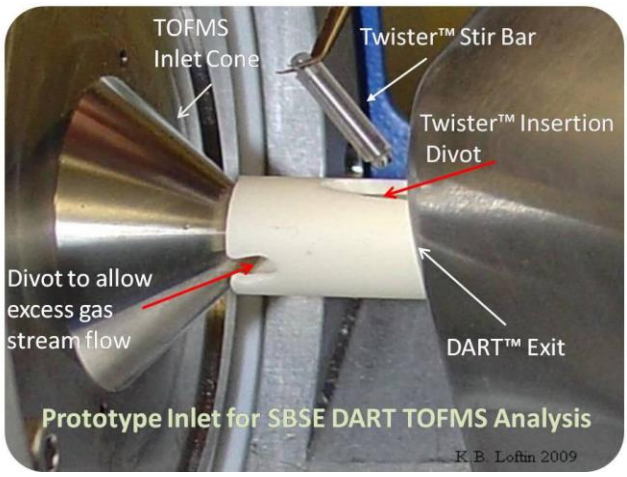
DEVELOPMENT OF NOVEL DART™ TOFMS ANALYTICAL TECHNIQUES FOR THE IDENTIFICATION OF ORGANIC CONTAMINATION ON SPACEFLIGHT-RELATED SUBSTRATES AND AQUEOUS MEDIA

KATHLEEN BROOKS LOFTIN, University of Central Florida, Orlando



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Conclusions (1)

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

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Conclusions (2)

- Complementary to SPME (immersion versus headspace)
- "My toolbox"
  - Static headspace (SHS)
  - HS-SPME (headspace)
  - Dynamic Headspace (DHS) – Full evaporation DHS (FEDHS) – Multi Volatile Method (MVM)
  - SBSE
  - SPE
- Still looking for new phases / new applications

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Reviews

- E. Baltussen, P. Sandra, F. David, C.A. Cramers,
  J. Microcol. Sep. 11 (1999) 737. (1009 citations on Jan 18, 2015)
- F. David, P. Sandra,
  Stir bar sorptive extraction for trace analysis
  Journal of Chromatography A, 1152 (1-2) (2007), pp. 54-69.
- F. Sánchez-Rojas, C. Bosch-Ojeda, J.M. Cano-Pavón,
  A review of stir bar sorptive extraction
  Chromatographia, 69 (SUPPL. 1), (2009) pp. S79-S94
- A. Prieto et al
  Stir-bar sorptive extraction: A view on method optimization, novel applications, limitations and potential solutions
  Journal of Chromatography A, 1217 (16),(2010) pp. 2642-2666.

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Reviews

- M. Kawagushi, R. Ito, H. Nakazawa, A.Takatsu,
  Applications of SBSE to food analysis,
  Trends in Analytical Chemistry 45 (2013) 280-293
- F.J. Camino-Sanchez et al
  Stir bar sorptive extraction: Recent applications, limitations and future trends,
  Talanta 130 (2014) 388-399
- N. Gilart, R.M. Marcé, F. Borrull, N. Fontanals,
  New coatings for stir-bar sorptive extraction of polar emerging organic contaminants,
  Trends in Analytical Chemistry 54 (2014) 11–23

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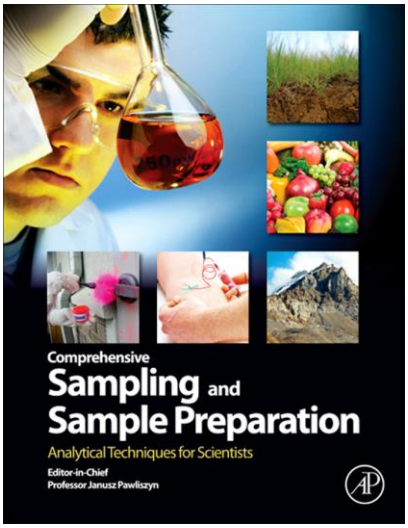
- From David, F.; In *Comprehensive Sampling and Sample Preparation,*
- Volume 4; Pawliszyn, J.; Mondello, L.; Dugo, P.; Eds; Elsevier, Academic Press: Oxford,
- UK, pp 473–493, 2012.
- ISBN: 9780123813732
-
- Academic Press



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Relevant Websites

- http://www.sbsetechnicalmeeting.com/ (website of technical meeting on SBSE, also includes presentations)
- http://logkow.cisti.nrc.ca/logkow/index.jsp (log Kow database)
- http://epa.gov/oppt/exposure/pubs/episuite.htm (to download log Kow calculator)
- http://www.gerstel.com/en/index_e.htm (commercial information on SBSE & equipment, also application notes)

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