Sense and Nonsense

in

Sample Preparation

pat.sandra@richrom.com

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This is NOT the way !

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Advances

in

Sample Preparation

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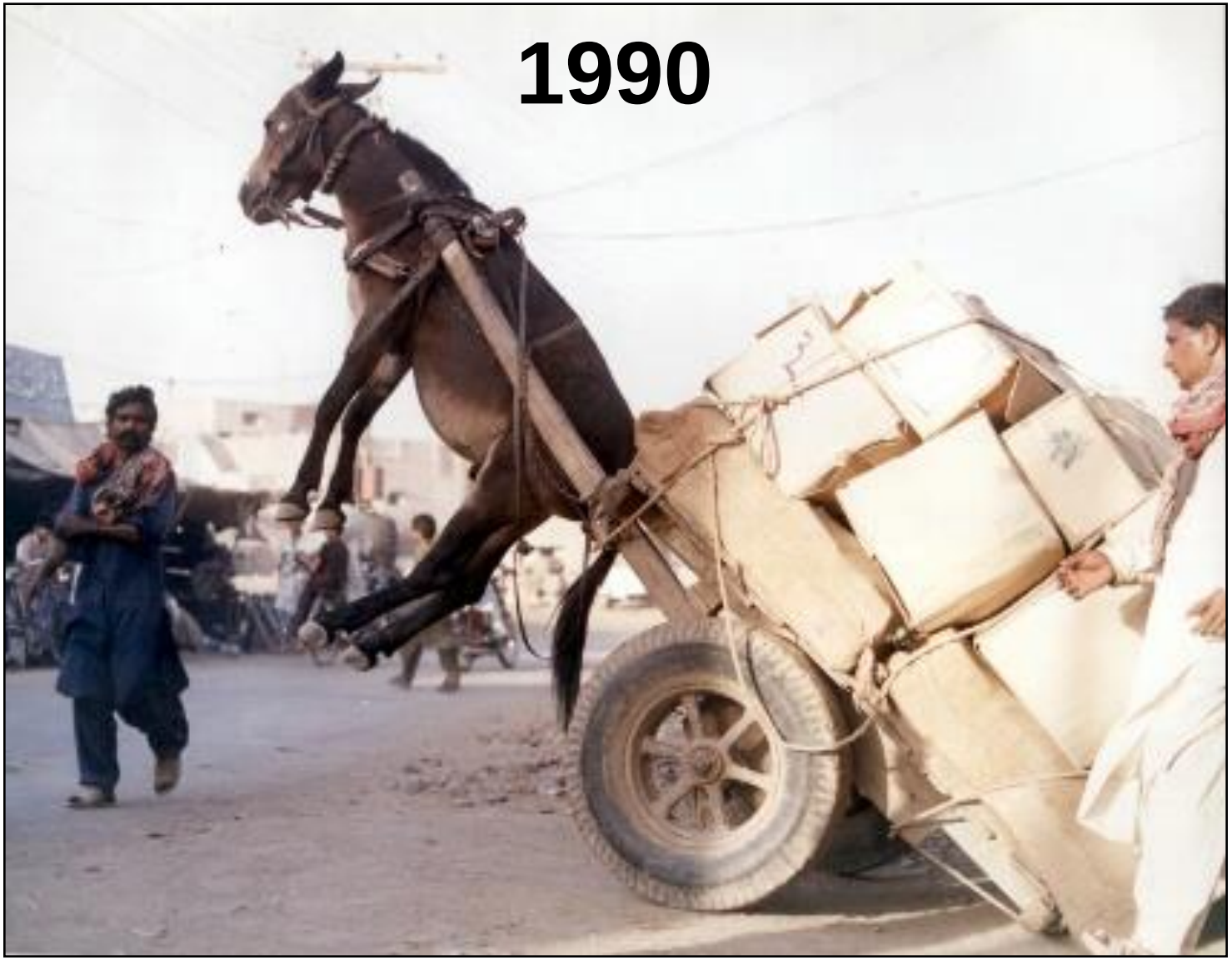
1990



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21st Century

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Scopus Search 2014 – Sample preparation

The facts

- Title, keywords, abstract — **7,292 (ca. 80.000 pages ≈ 320,000 A4 pages – 1,15)**
- QuEChERS — **284 (> 50% slightly modified!)**
- SBSE — **68 (12 Adsorption)**

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ANALYTICA CHIMICA ACTA
www.elsevier.com/locate/aca
Analytica Chimica Acta 436 (2001) 1–9

ELSEVIER

Application of stir bar sorptive extraction in combination with column liquid chromatography for the determination of polycyclic aromatic hydrocarbons in water samples

Peter Popp[a,*], Coretta Bauer[a], Luise Wennrich[b]
[a] UFZ-Centre for Environmental Research Leipzig-Halle, Department of Analytical Chemistry, Permoserstr. 15, D-04318 Leipzig, Germany
[b] Department of Urban Landscapes, Permoserstr. 15, D-04318 Leipzig, Germany
Received 18 December 2000; received in revised form 15 February 2001; accepted 16 February 2001

JOURNAL OF CHROMATOGRAPHY A
www.elsevier.com/locate/chroma
Journal of Chromatography A, 963 (2002) 225–230

ELSEVIER

Application of stir bar sorptive extraction to the determination of polycyclic aromatic hydrocarbons in aqueous samples

Bita Kolahgar*, Andreas Hoffmann, Arnd C. Heiden
Gerstel GmbH & Co. KG, Aktienstrasse 232–234, D-45473 Mülheim an der Ruhr, Germany

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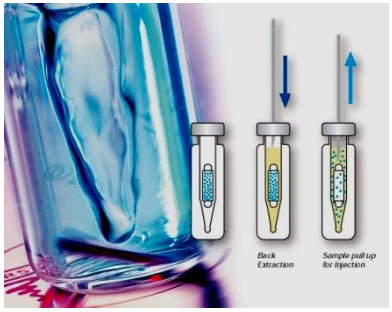
Calibration data obtained for SBSE of 30 mL spiked water

Prof. Dr. P. Popp et al. (ISC, London, 2000)
Anal. Chem. Acta 436, 2001, 1.



	R	LOD (ng/L)	Linear Range (ng/L)
Naphthalene	0.992	0.5	0.5 – 200
Acenaphthene	0.995	0.5	0.5 – 200
Fluorene	0.999	0.5	0.5 – 200
Phenanthrene	0.998	0.4	0.4 – 200
Anthracene	0.999	0.3	0.3 – 200
Fluoranthene	0.999	0.3	0.3 – 200
Pyrene	1.000	0.6	0.6 – 200
Benzo(a)anthracene	0.999	0.6	0.6 – 200
Chrysene	1.000	0.2	0.2 – 200
Benzo(b)fluoranthene	0.998	0.5	0.5 – 200
Benzo(k)fluoranthene	0.999	0.2	0.2 – 200
Benzo(a)pyrene	0.997	0.5	0.5 – 200
Dibenz(a,h)anthracene	0.997	0.8	0.8 – 200
Benzo(g,h,i)perylene	0.995	2.0	2.0 – 200
Indeno(1,2,3)pyrene	0.992	0.5	5.0 – 200

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Organigram

- **Sampling**
- **Sample preparation**
- **Chromatographic analysis**
  - **Capillary Gas Chromatography**
  - **Liquid Chromatography**
- **Detection**
  - **Selective detectors**
  - **Mass Spectrometers**
- **Data handling & Reporting**

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LC and GC - Mass Spectrometry

General

- Single quad MS:
  for identification of unknowns
  and quantitation of targets

- QQQ :
  for sensitive, precise and accurate
  target quantification

- QTOF:
  for sensitive identifications of unknows
  untargeted analysis

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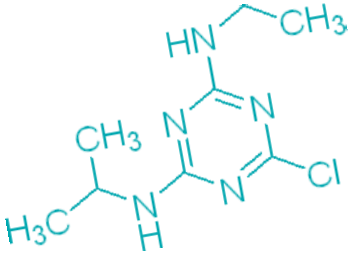
Generic Pesticides LC/MS-MS method

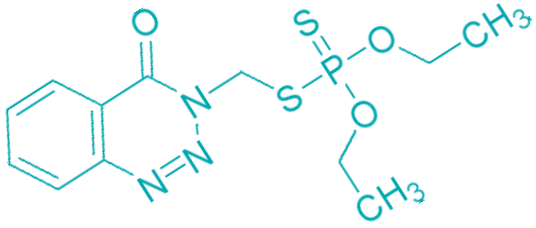


1200 LC parameters

Column	Eclipse Plus-C18, 2.1 x 100mm, 1.8 µm
Column temperature	35 ºC
Injection volume	5.0 µL
Autosampler temp	6 ºC
Needle wash	flushport (MeOH:H2O 75:25), 5 secs
Mobile phase	A = 0.01% formic acid in water
	B =5 mM ammonium formate 0.01% formic acid in 95:5 acetonitrile:water
Flow rate	0.3 mL/min
Gradient	0 min 6% B
	15 min 95% B
Stop time	20 min 6% B
Post time	1 min

Jet stream conditions

Drying gas temperature	275 ºC
Drying gas flow (nitrogen)	6 L/min
Nebulizer gas pressure (nitrogen)	35 psig
Capillary voltage	4000 V
Sheath gas temperature	325 ºC
Sheath gas flow	12 L/min
Nozzle voltage	Off



6460A QQQ settings

MS1 and MS2 resolution	Unit
Time Filtering	peak width = 0.03 min
Dynamic MRM transitions	up to 4000
Constant cycle time	373 ms
Delta EMV	400 V

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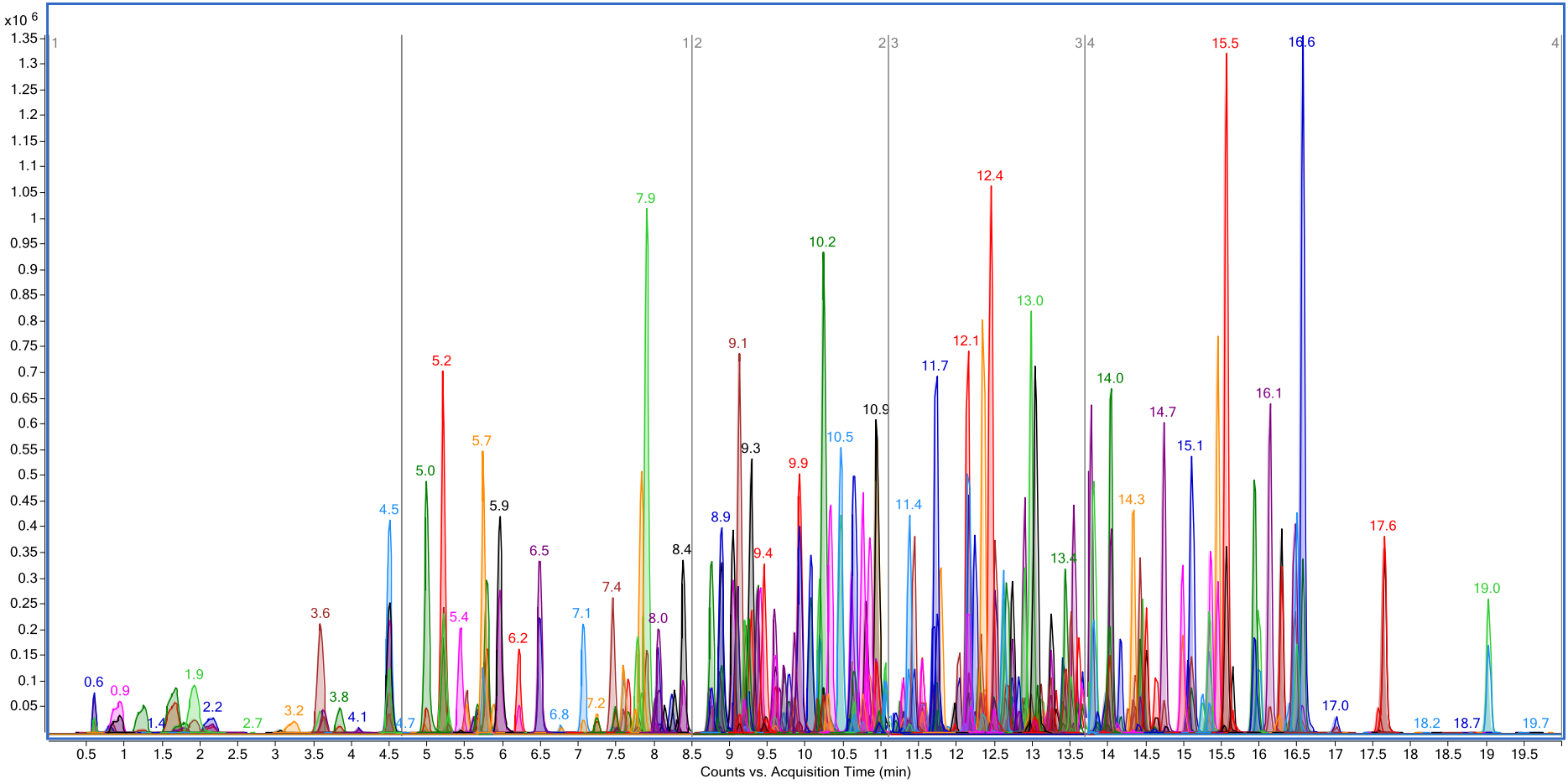
Dynamic MRM of 300 Pesticides
2 Transitions Each



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

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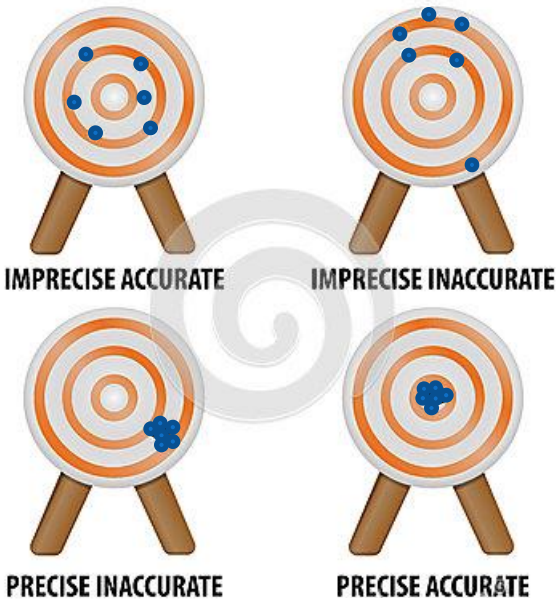

Sampling

and

Sample Preparation:

" the Keys "

to Meaningful Analytical Data

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Sense-Nonsense in Sample Preparation

- **Miniturization versus representative sample**

  for a MRL of 10 µg/kg and considering the sensitivity of contemporary MS (10 pg) – 1 mg sample is required – TD?

- **EU SANCO directives (96/23/EC)**

  Performance of analytical methods and the interpretation of results

- **Robustness (repeatability and reproducibility)**

- **Conflicting interests of academia – suppliers – industry**

✓ **Is commercialization of the procedure – device realistic?**

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Sense-Nonsense in Sample Preparation

- ✓ **Sensitivity versus toxicological relevance ?**
  OrganoSn at 60 ppq ? Dreaming versus reality!

- ✓ **Selectivity versus Generic (Multiresidue)**
  Misuse of MIPs

- ✓ **L'art pour l'art versus conclusive productivity**
  1999 Belgian Dioxin Crisis
  - Separation of all PCBs congeners (GCxGC) ?
  - Separation of PCB 28/31 ?
  - QuEChERS for meat ?

- ✓ **Automation, throughput, on-line, off-line**

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Journal of Chromatography A, 1261 (2012) 151–157

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Journal of Chromatography A

journal homepage: www.elsevier.com/locate/chroma

A new validated analytical method for the determination of tributyltin in water samples at the quantification level set by the European Union

Christophe Devos, Frank David, Pat Sandra*

Research Institute for Chromatography (RIC), Kennedypark 26, B-8500 Kortrijk, Belgium

ARTICLE INFO

Article history:
Available online 31 July 2012

Keywords:
Capillary gas chromatography–triple quadrupole mass spectrometry
Two-dimensional GC
Ultra-trace analysis
Tributyltin
Stir bar sorptive extraction

ABSTRACT

According to recent directives of the European Union (EU), limits of quantification (LOQ) for the determination of tributyltin (TBT) in surface waters should be ca. 60 pg/L (ppq). This put very stringent requirements on analytical methodologies; definitely when they have to be applied in a routine environment. Stir bar sorptive extraction (SBSE), followed by thermal desorption (TD) and capillary gas chromatography–triple quadrupole mass spectrometry (GC–MS/MS) can provide accurate and precise data at the 2 ng/L level (ppt). For lower concentrations, matrix and reagent interferences together with contamination may provide too high TBT values. A two-dimensional heart-cut GC method was developed to fractionate TBT from interferences. The GC–GC–MS/MS method shows excellent linearity in the range 50 pg/L–4 ng/L, good repeatability (RSD < 20% at 200 pg/L), and a limit of detection of 11 pg/L. The method performance is demonstrated with representative samples i.e. harbor water and waste water samples.

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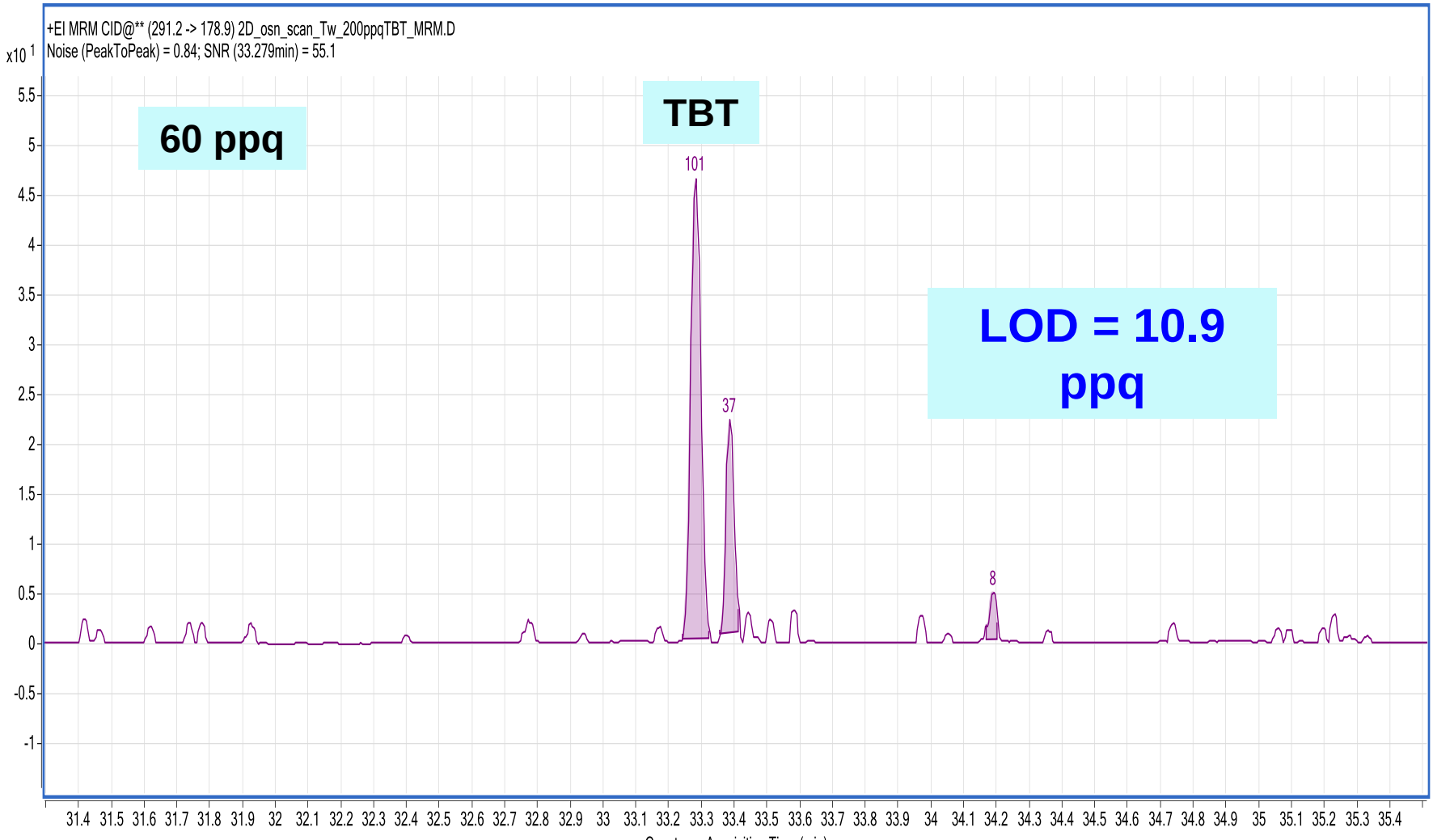
TBT with SBSE - TDU – GC-GC – QQQ (MRM)



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Sense-Nonsense in Sample Preparation

- ✓ Sensitivity versus toxicological relevance ?
  - OrganoSn at 60 ppq ? Dreaming versus reality!
- ✓ **Selectivity versus Generic (Multiresidue)**
  - **Misuse of MIPs**
- ✓ L'art pour l'art versus conclusive productivity
  - **1999 Belgian Dioxin Crisis**
  - **- Separation of all PCBs congeners (GCxGC) ?**
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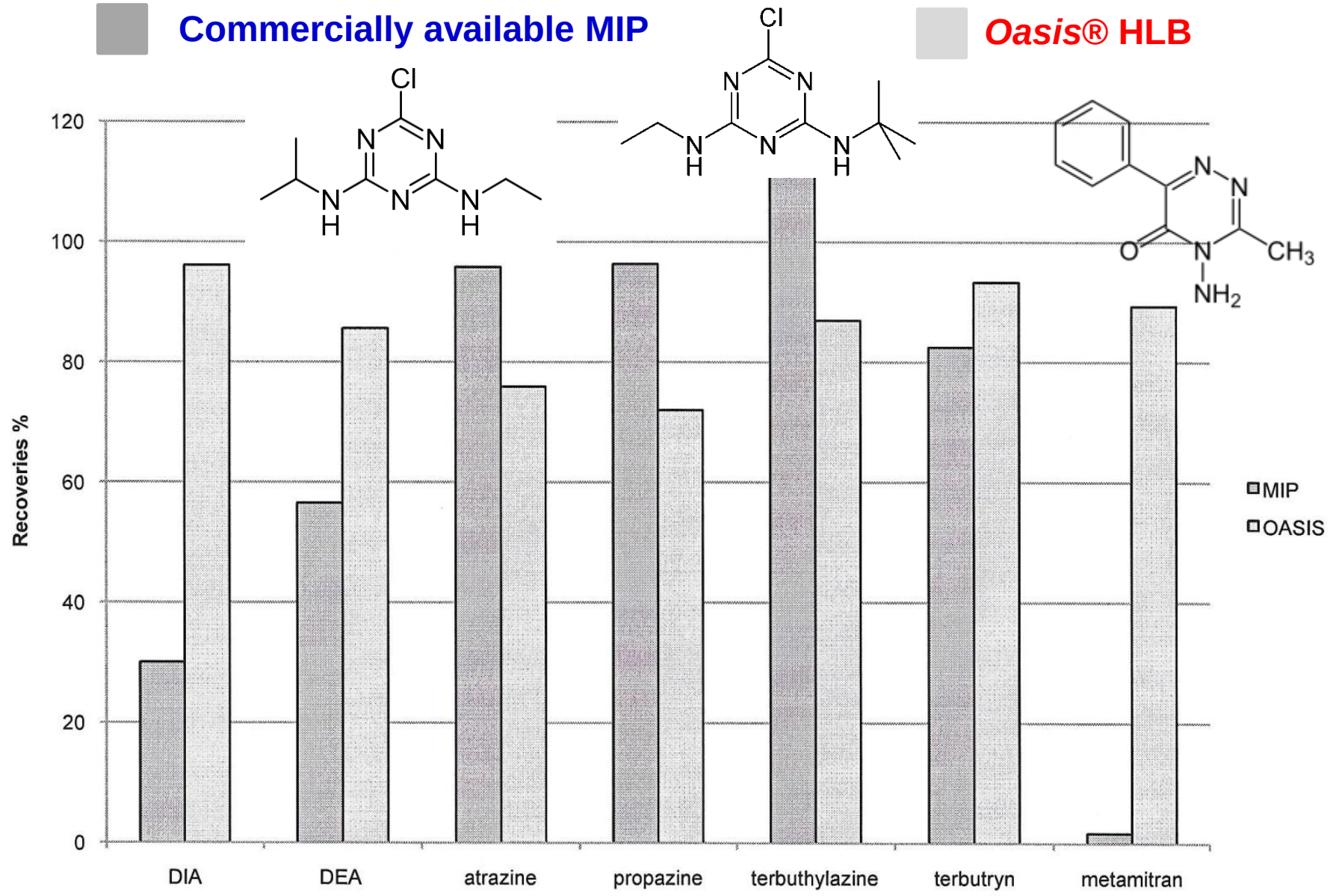

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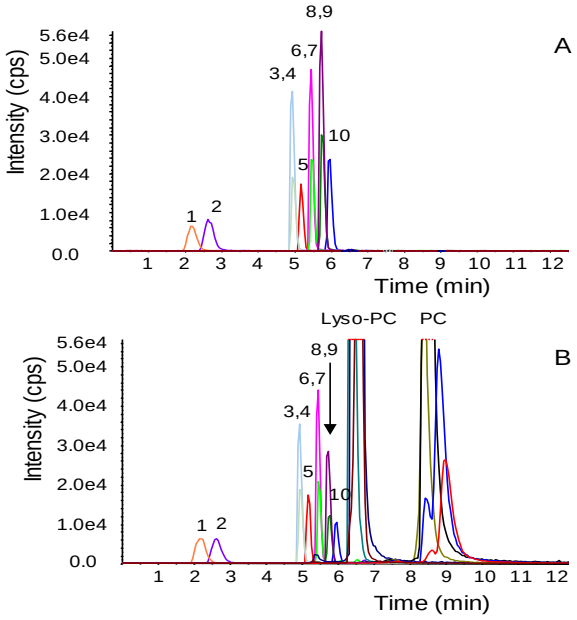
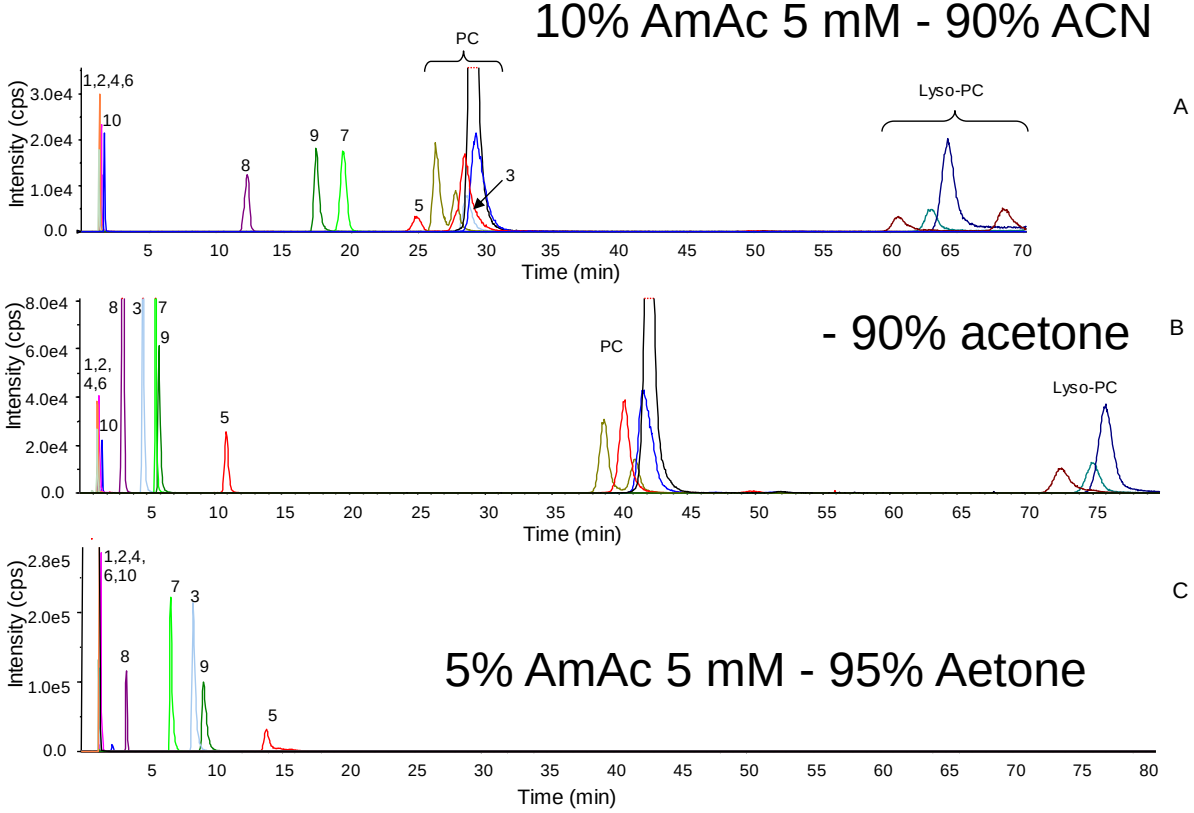
Developing SPE for biological fluids





SPE based on HILIC with acetone as eluent for eliminating matrix effects in the analysis of biological fluids by LC-MS

T. Van Damme, M. Lachová, F. Lynen, R. Szucs, P. Sandra

Anal Bioanal Chem 2014, 406, 401-407 - DOI 10.1007/s00216-013-7281-7

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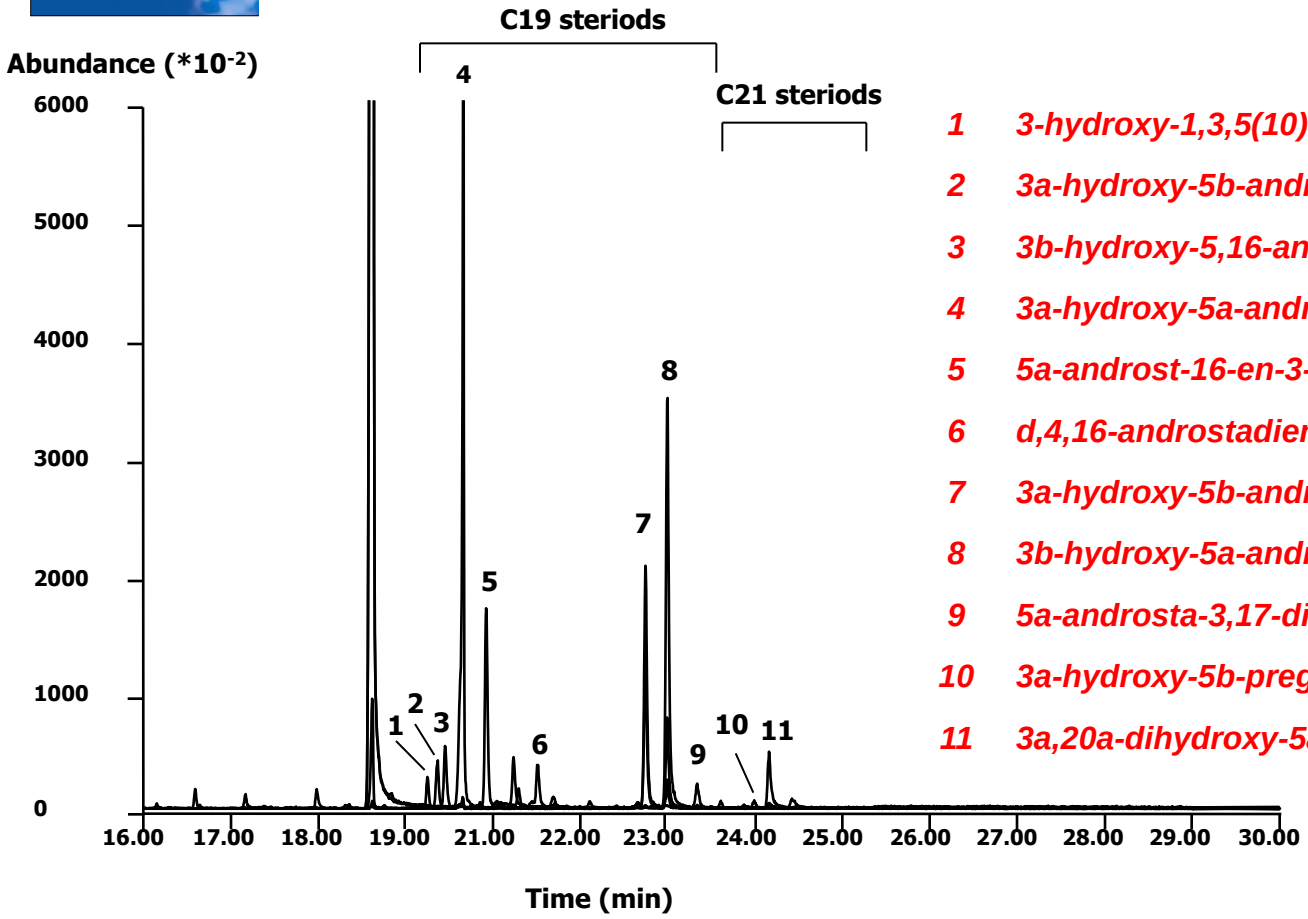
Free steroids in urine of a male adult

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



1 *3-hydroxy-1,3,5(10)-estratrien-17-one (estrone)*

2 *3a-hydroxy-5b-androst-16-ene*

3 *3b-hydroxy-5,16-androstadiene*

4 *3a-hydroxy-5a-androst-16-ene*

5 *5a-androst-16-en-3-one*

6 *d,4,16-androstadien-3-one*

7 *3a-hydroxy-5b-androstan-17-one (etiocholanolone)*

8 *3b-hydroxy-5a-androstan-17-one (iso-androsterone)*

9 *5a-androsta-3,17-dione*

10 *3a-hydroxy-5b-pregnan-20-one*

11 *3a,20a-dihydroxy-5a-pregnane*

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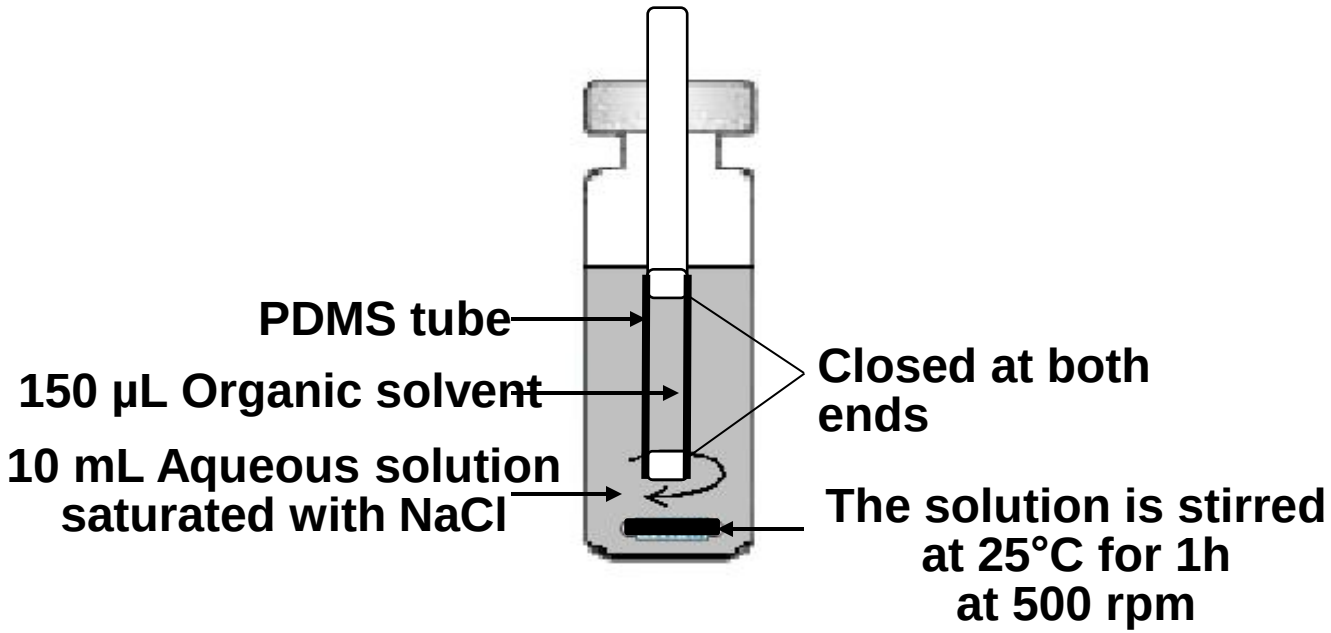
Silicone membrane sorptive extraction (SMSE)



- 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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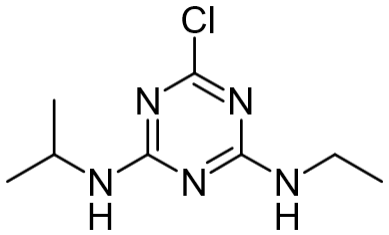
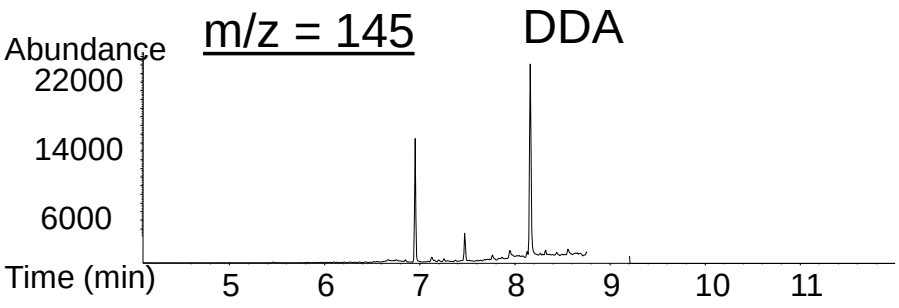
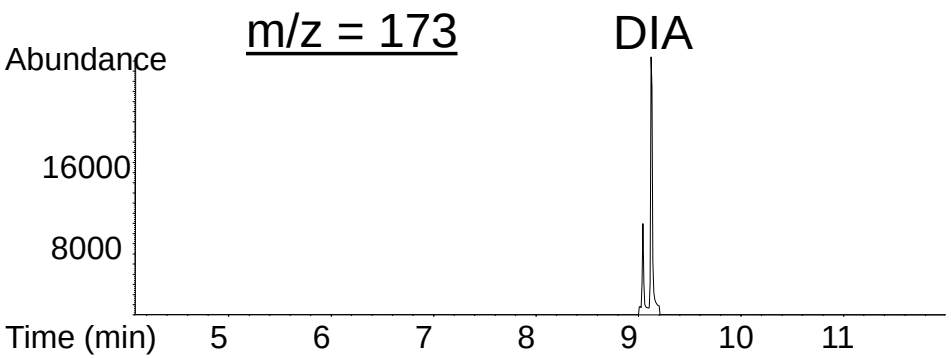
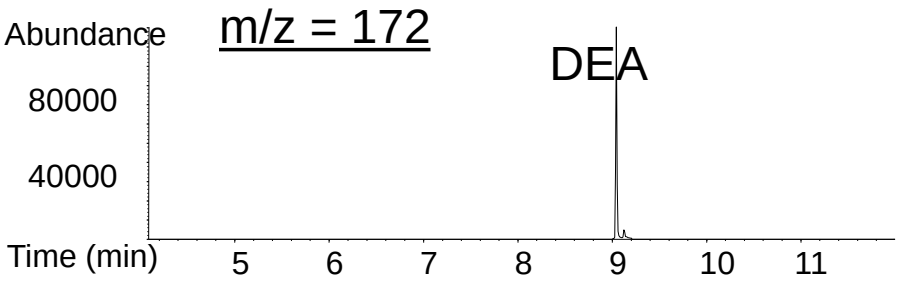
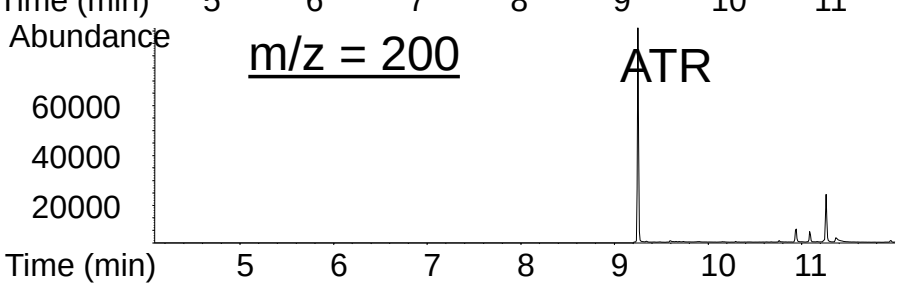
Metabolites of atrazine

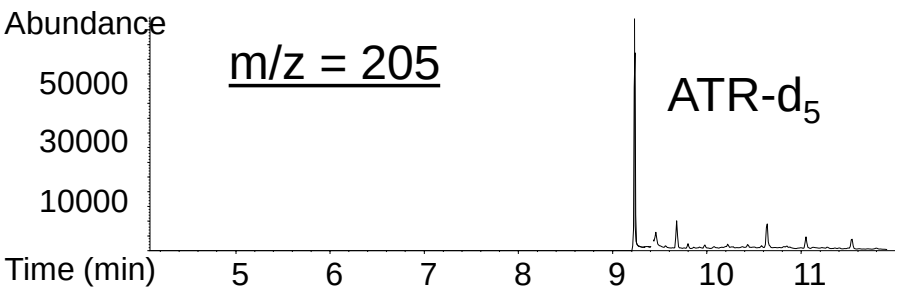












	LOD (ng/L)
ATR	0.47
DEA	1.98
DIA	1.25
DDA	6.07

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Sense-Nonsense in Sample Preparation

- ✓ Sensitivity versus toxicological relevance ?
  - OrganoSn at 60 ppq ? Dreaming versus reality!
- ✓ Selectivity versus Generic (Multiresidue)
  - Misuse of MIPs
- ✓ **L'art pour l'art versus conclusive productivity**
  - **1999 Belgian Dioxin Crisis**
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- ✓ Automation, throughput, on-line, off-line

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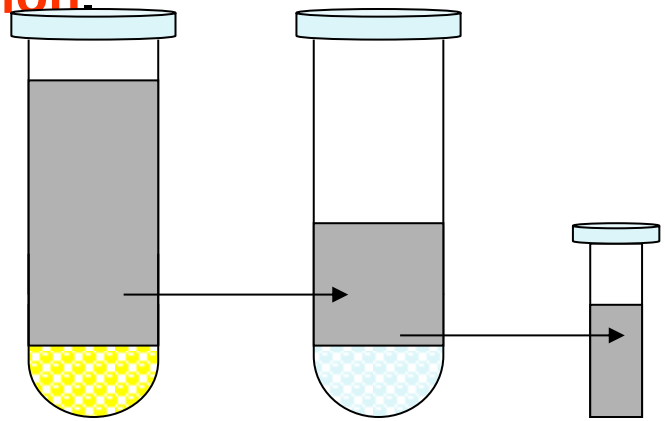
RIC Method - QuEChERS avant al lettre
Dioxine crisis 1999 - published 2000

- **1-3 g sample size = 200-400 mg fat.**
- **Add 10 mL cyclohexane (+ IS).**
- **Ultrasonic extraction (30 min).**
- **Transfer aliquot to test tube**
- **Clean-up by Matrix Solid Phase Dispersion.**

  Add 2 g modified silica.

  (44 g H_2SO_4 on 56 g activated silica)
- **Vortex and centrifuge.**
- **Analyse clear supernatant.**



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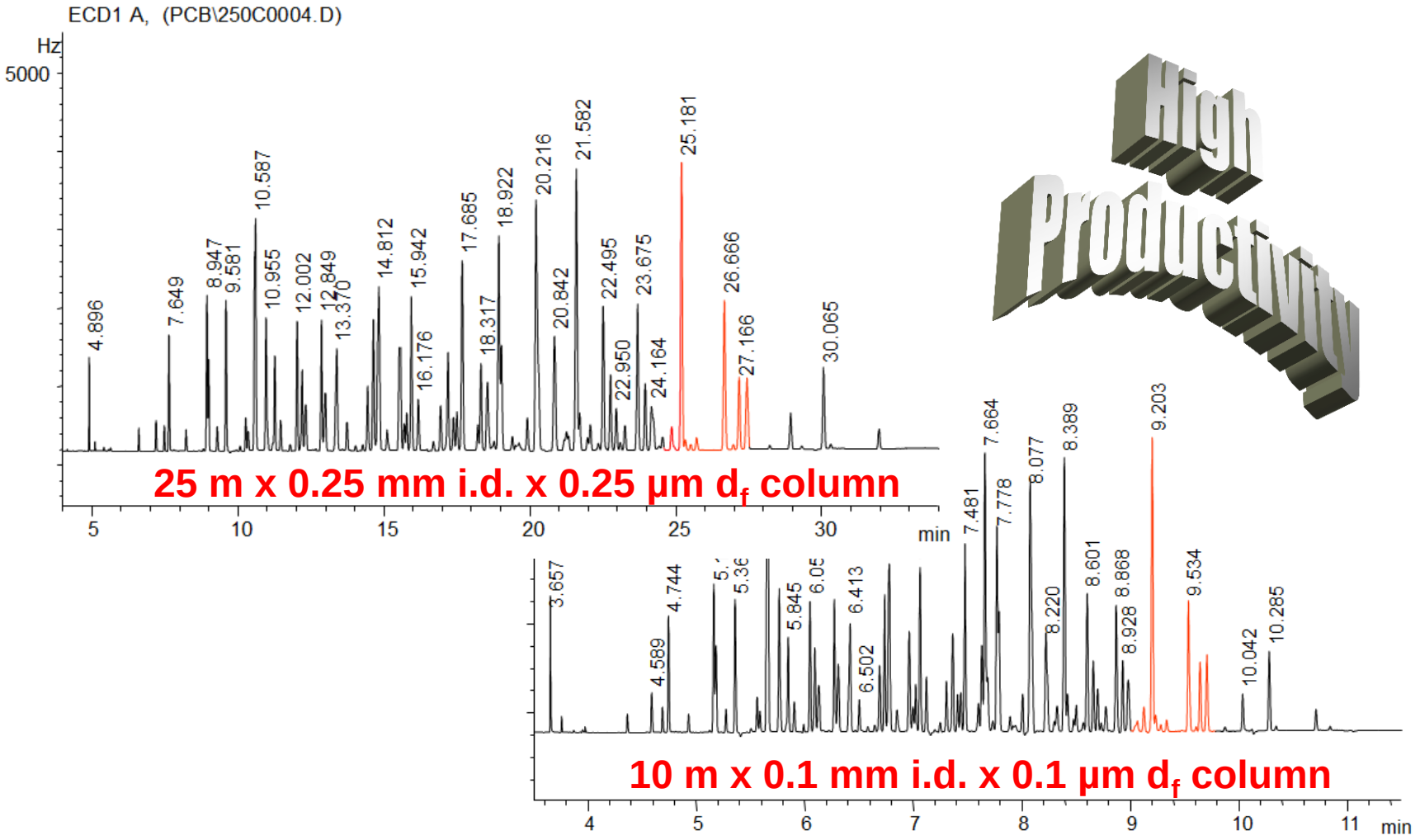
1999 Belgian dioxin crisis – EPC/MTS



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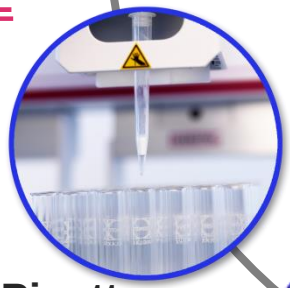
Dynamic Headspace DHS

TDU Thermal desorption and PYROlysis

Solid Phase Extraction SPE

ATEX Thermal Extraction in µVials

Disposable Pipette Extraction DPX



SPME & Multi-Fiber EXchange MFX

Static Headspace (HS)

ALEX Automated Liner EXchange

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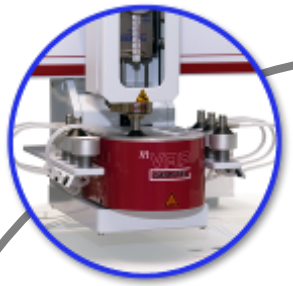
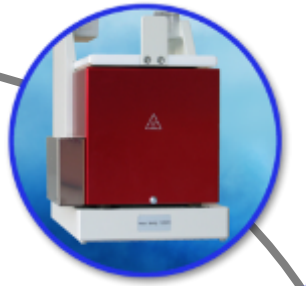
Evaporative Concentration mVAP

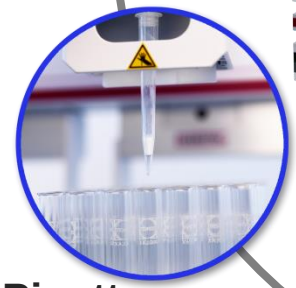


Extraction (LD-Twisters)
Derivatization
Addition of Standards



Solid Phase Extraction SPE & Filtration

Centrifuge



Disposable Pipette Extraction DPX

Cold storage of samples

Weighing Option

mVORX
Vortex

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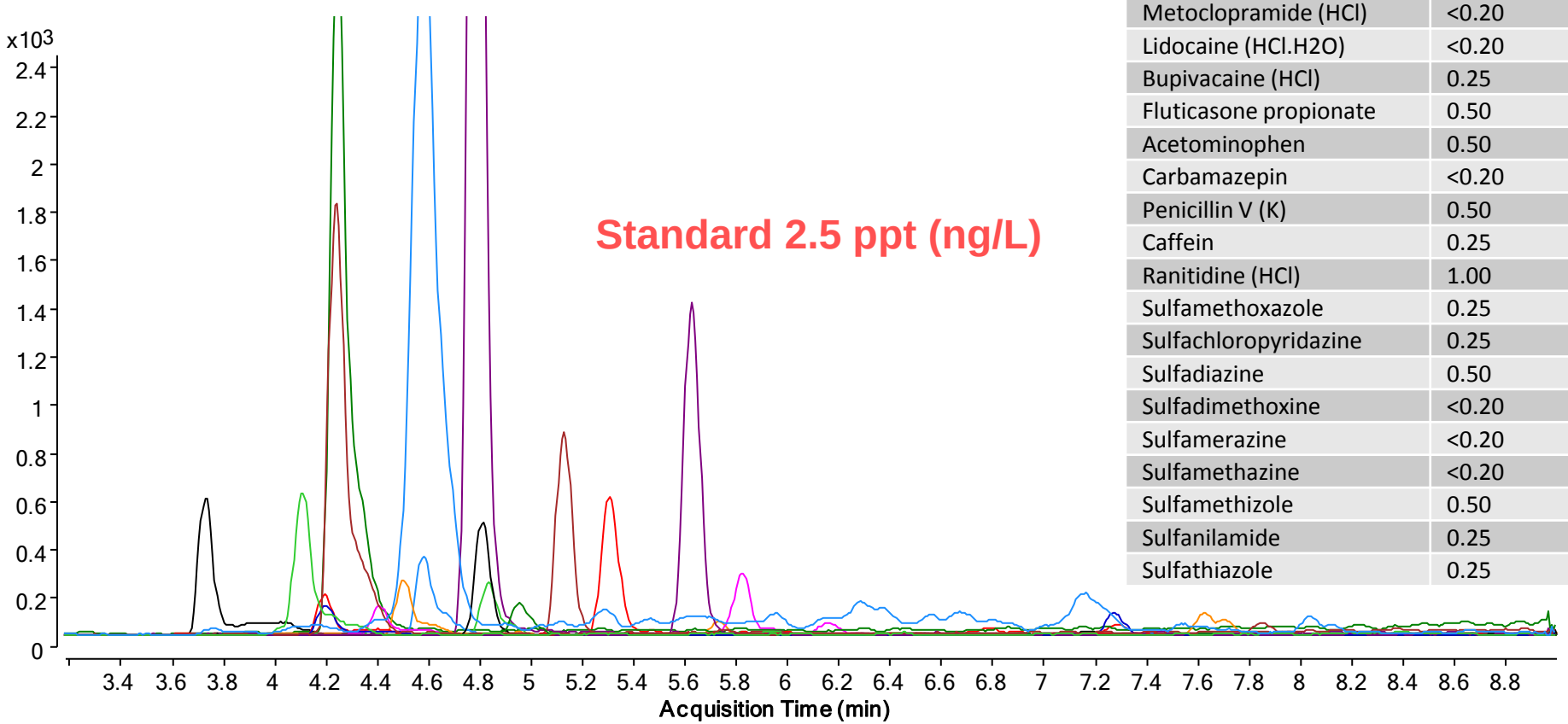
On-line PPCPs - Sensitivity

- 23 compounds, 46 transitions (Only Q is shown)
- 1.5 mL SPE

PPCP	LOD (ppt)
Diclofenac (Na)	0.25
Promethazin (HCl)	<0.20
Propranolol	<0.20
Clemastin (fumarate)	0.25
Metoclopramide (HCl)	<0.20
Lidocaine (HCl.H2O)	<0.20
Bupivacaine (HCl)	0.25
Fluticasone propionate	0.50
Acetominophen	0.50
Carbamazepin	<0.20
Penicillin V (K)	0.50
Caffein	0.25
Ranitidine (HCl)	1.00
Sulfamethoxazole	0.25
Sulfachloropyridazine	0.25
Sulfadiazine	0.50
Sulfadimethoxine	<0.20
Sulfamerazine	<0.20
Sulfamethazine	<0.20
Sulfamethizole	0.50
Sulfanilamide	0.25
Sulfathiazole	0.25



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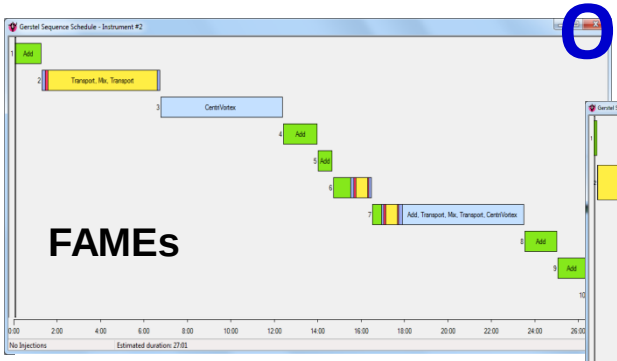
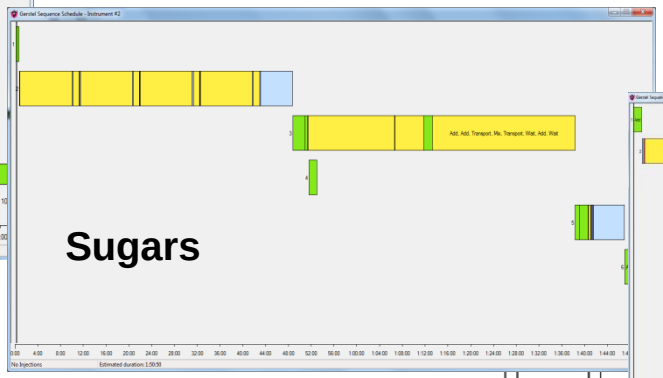
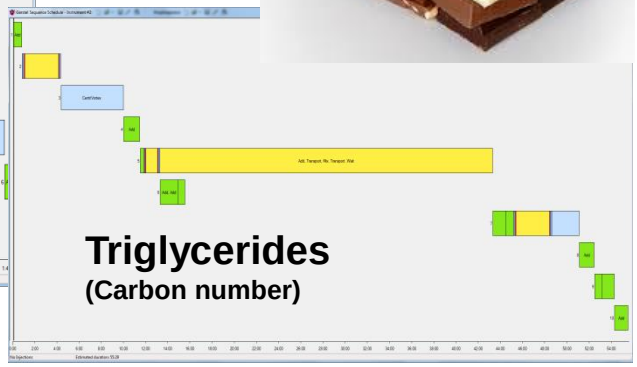
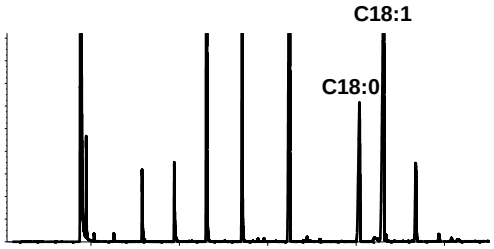
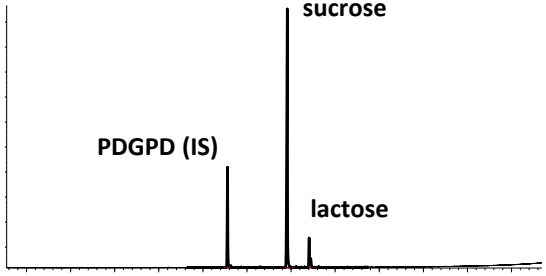
Off-Line Fully automated

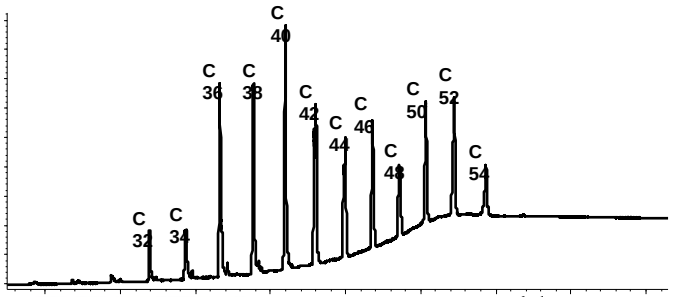


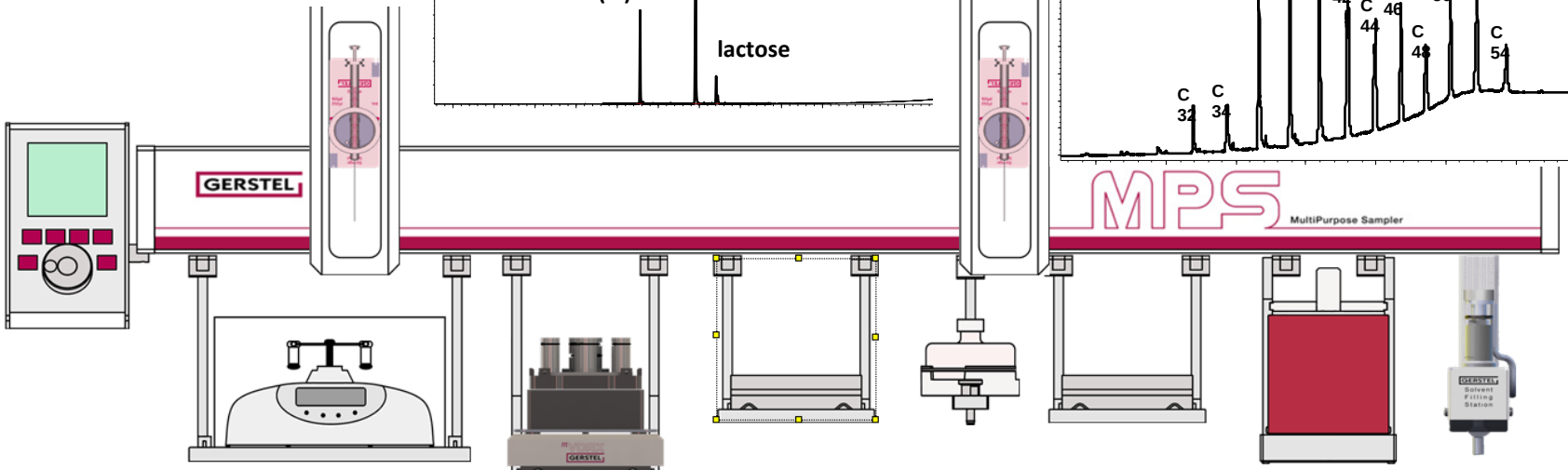












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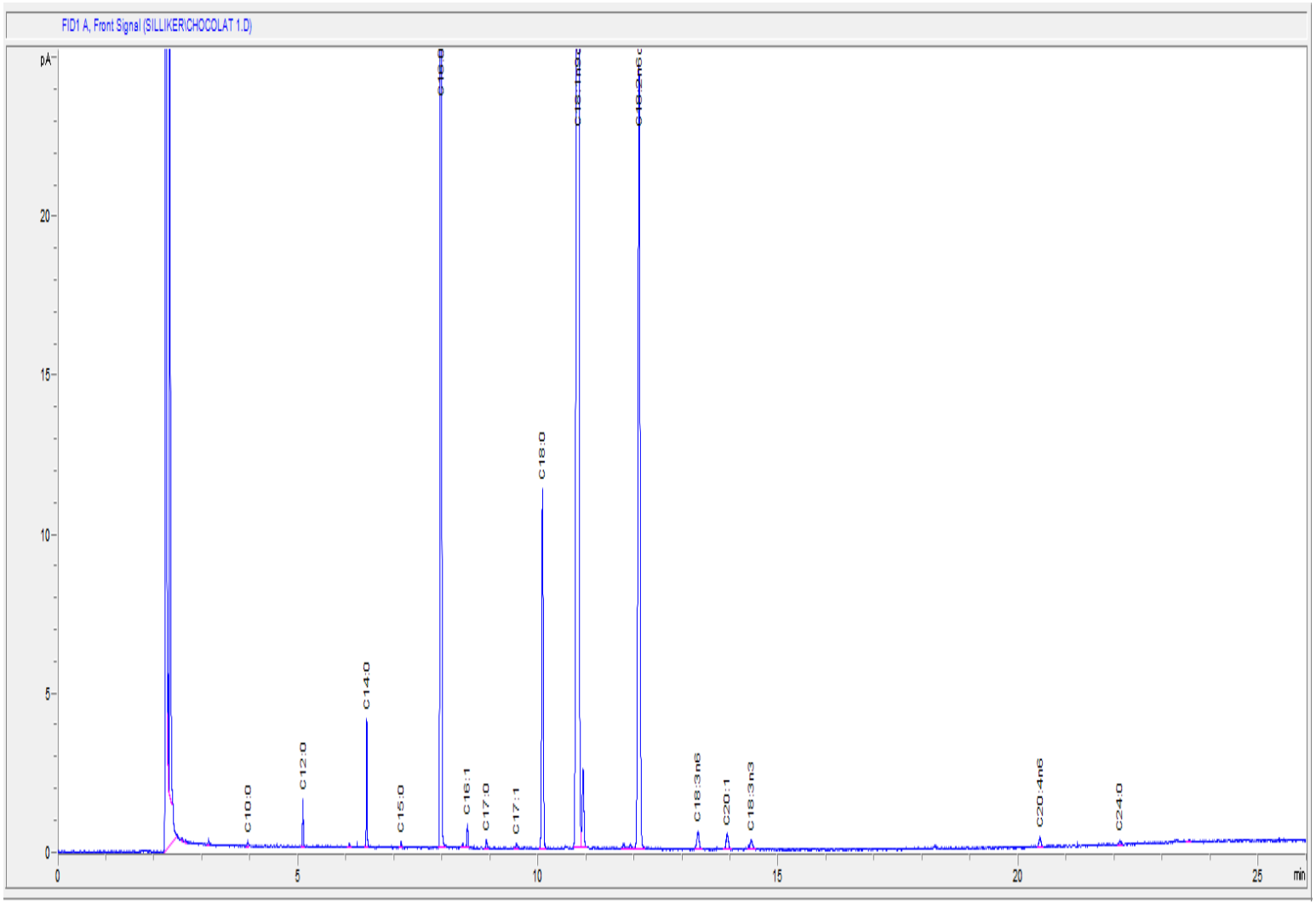
Fully automated method: Chocolate



Name	Area %
C10:0	0.03%
C12:0	0.29%
C14:0	0.80%
C15:0	0.04%
C16:0	28.00%
C16:1	0.22%
C17:0	0.08%
C17:1	0.05%
C18:0	4.18%
C18:1n9c	53.19%
C18:2n6c	12.15%
C18:3n6	0.31%
C20:1	0.26%
C18:3n3	0.18%
C20:4n6	0.15%
C24:0	0.06%

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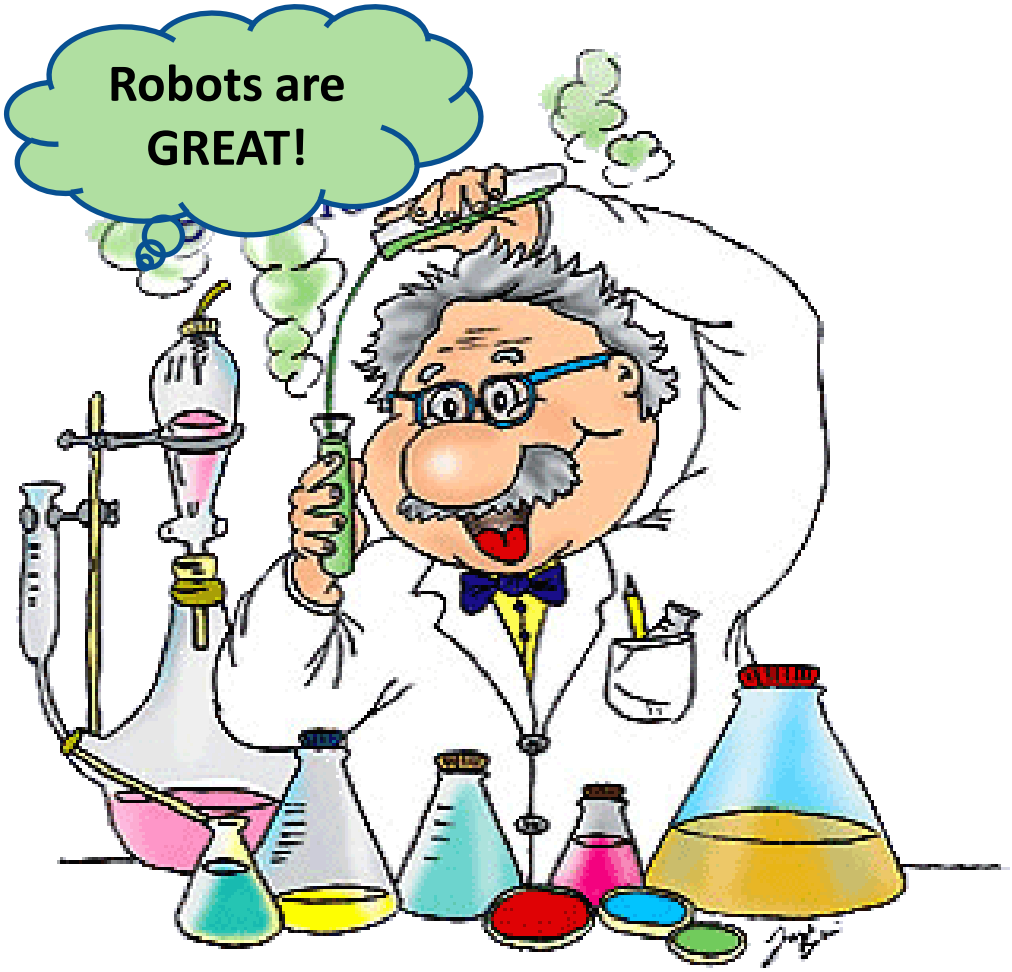
Thank you for your attention and ...



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