SUPELCO
Solutions within.

Application of Solid Phase Micro Extraction in Environmental Analysis

Frank Michel

sigma-aldrich.com/analytical

SIGMA-ALDRICH

SPME in Environmental Analysis

More than 900 references for Environmental Analysis on currently edition of SPME CD:

- Water
- Soil
- Air
- Pesticides

Plus literature, applications and videos

Official Methods in Environmental Analysis using SPME

ASTM D 6520, 2000

- Standard Practice for the SPME of Water and its Headspace for the Analysis of Volatile and Semi-Volatile Organic Compounds

ASTM D 6889, 2003

- Standard Practice for Fast Screening for Volatile Organic Compounds in Water Using Solid Phase Microextraction (SPME)

EPA Method 8272, 2007

- Parent and Alkyl PAHs in Sediment Pore Water by SPME-GC/MS

ISO 27108 (DIN 38407-34), 2013

- Determination of selected plant treatment agents and biocide products - Method using SPME followed by GC-MS

ISO 17943 (DIN 38407-41)

- Determination of VOCs in water - GC-MS after HS-SPME

ISO 27108 (DIN 38407-34)

Determination of selected plant treatment agents and biocide products in drinking water, ground water and surface water - Method using SPME followed by GC-MS

- Dichlobenil
- Desethylatrazin
- Desethylterbutylazin
- Simazin
- Atrazin
- Lindan
- Terbutylazin
- Metribuzin
- Parathion-methyl
- Heptachlor
- Terbutryn
- Aldrin
- Metolachlor
- Parathion-ethyl
- exo-Heptachlorepoxid
- Pendimethalin
- endo-Heptachlorepoxid
- Triclosan
- Dieldrin
- Carfentrazon-ethyl
- Diflufenican
- Mefenpyr-diethyl

- Method might be suitable for other compounds – need to be evaluated individually
- Operational range of method: above 0.05 µg/L (depending on matrix)
- IS: Atrazin-d5 or Lindan-d6

Conditions

SPME Conditions

- Fiber: Polyacrylate
- Conditioning: Fiber 20 min @ 300° C
- Extraction: pH 6-8, NaCl close to saturation (e.g. 2.4 g/8 mL sample)
  60 min @ 30° C, stirring 250 rpm
- Desorption: 10 min @ 280° C , splitless (6 min)

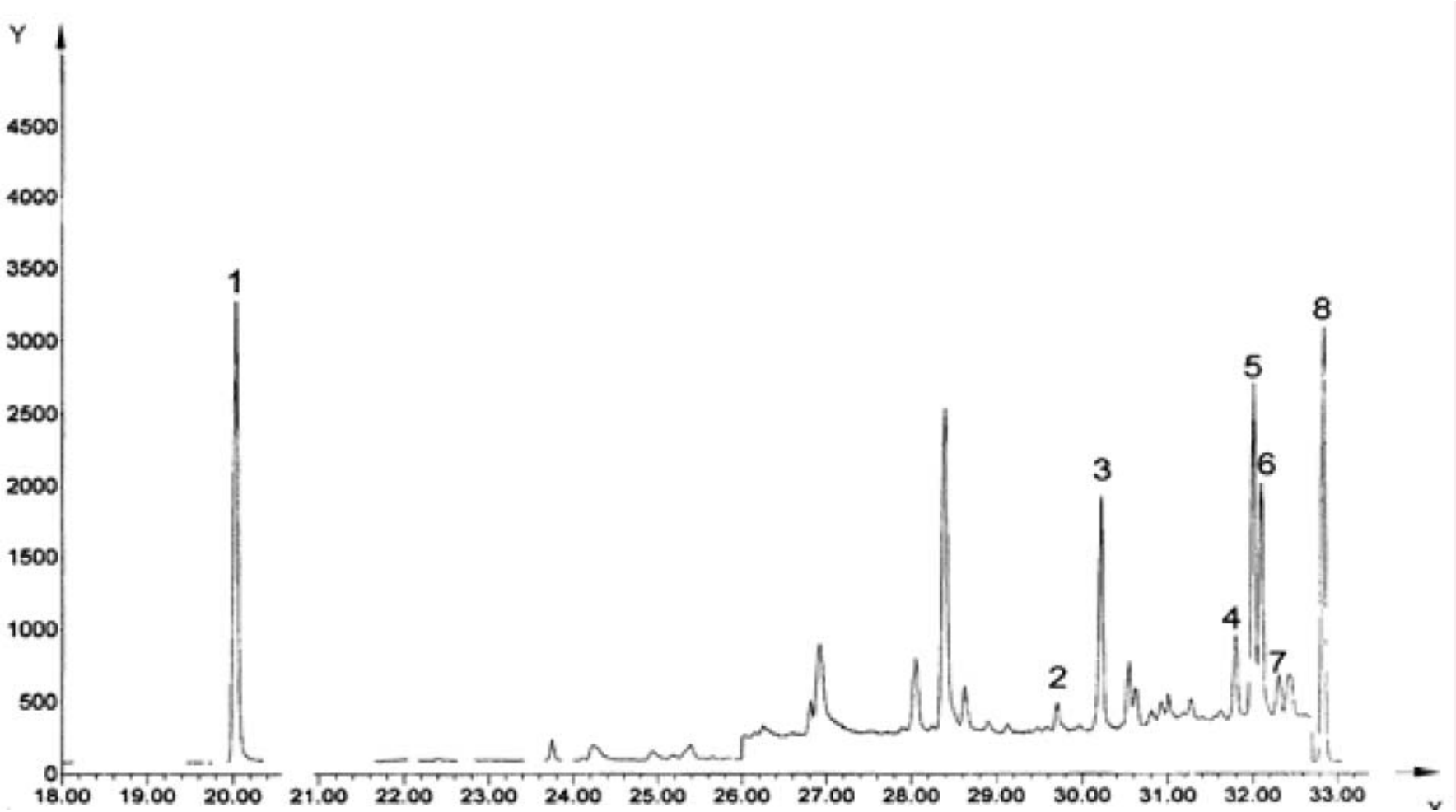
GC conditions (example)

- Injection: KAS/CIS 60° C; 10° C/s to 280° C; 10min; Splitless
- Column: 5% Phenyl, 30m x 0.25mm, 0.25µm
- Carrier gas: Helium (5.0), 0,9mL/min
- Oven: 60° C, 2 min; 4° C/min to 220° C; 10° C/min to 300° C
- Detector: MS, EI 70eV, SIM

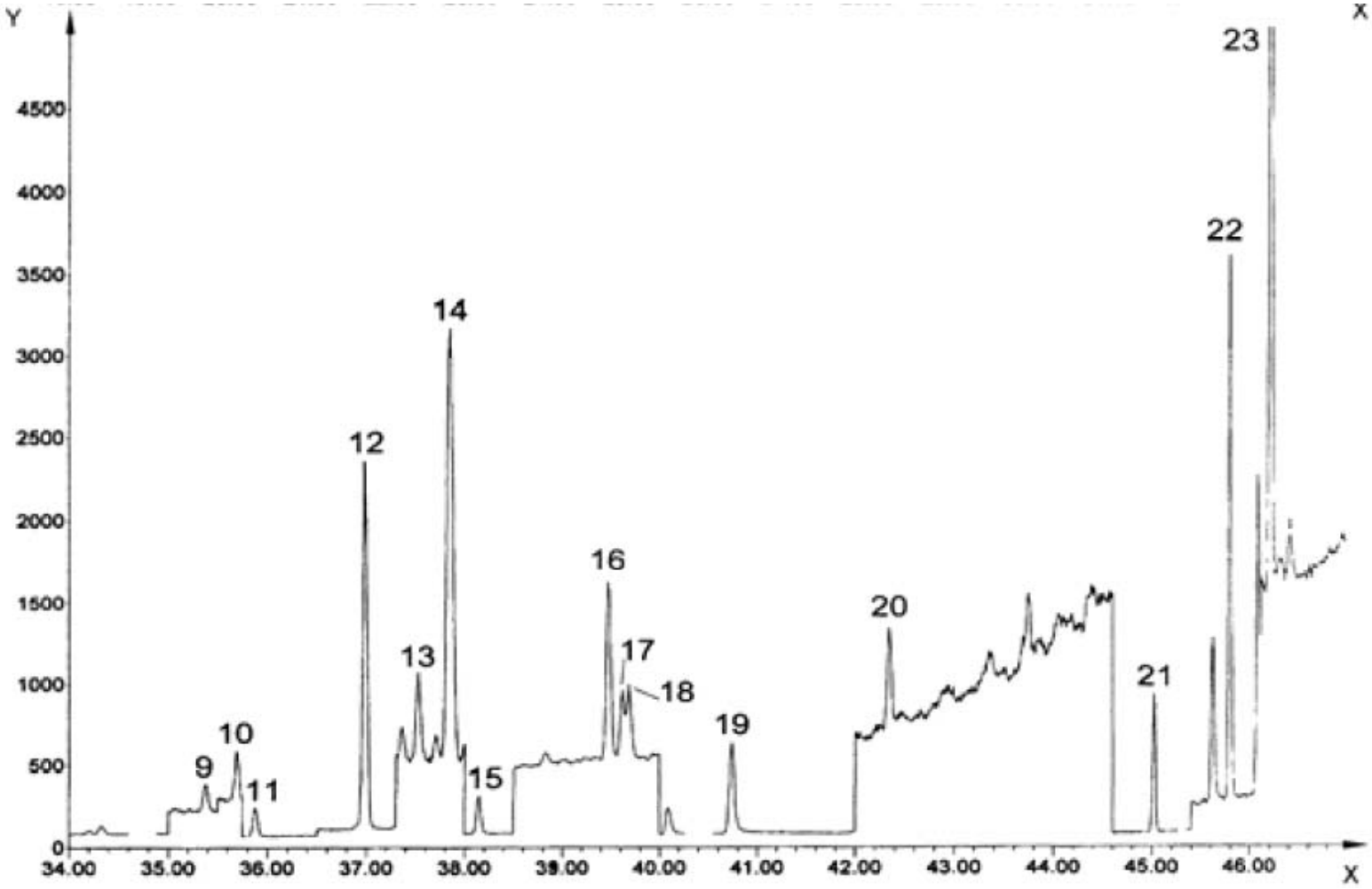
Selected Ions for Identification and Quantification

Analytes	Selected Ions for Identification and Quantification (m/z)
Dichlobenil	100, 136, 171, 173
Desethylatrazin	145, 172, 174, 187
Desethylterbutylazin	186, 188, 201
Simazin	173, 186, 201
Atrazin	173, 200, 215
Lindan	109, 181, 183, 219
Terbutylazin	173, 214, 229
Metribuzin	103, 144, 198, 214
Parathion-methyl	109, 125, 263
Heptachlor	237, 272, 274, 337
Terbutryn	170, 185, 226, 241
Aldrin	261, 263, 265, 293
Metolachlor	162, 238, 240
Parathion-ethyl	109, 155, 263, 291
exo-Heptachlorepoxid	353, 355, 357
Pendimethalin	162, 191, 252, 281
endo-Heptachlorepoxid	183, 253 289
Triclosan	218, 288, 290
Dieldrin	79, 263, 277, 279
Carfentrazon-ethyl	290, 312, 340, 411
Diflufenican	246, 266, 394
Mefenpyr-diethyl	227, 253, 255, 299

Example Chromatogram



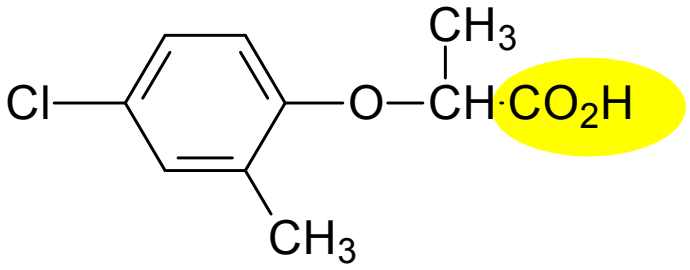
Example Chromatogram



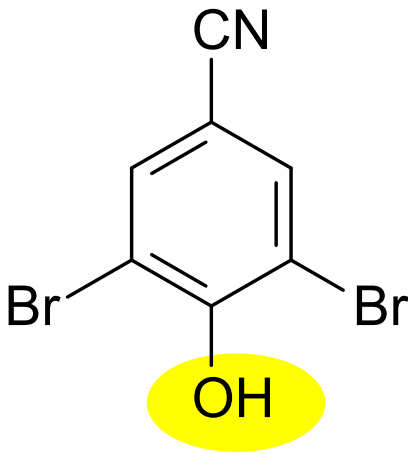
Peak Identification in Example Chromatogram

1 Dichlobenil
2 Desethylatrazin
3 Desethylterbutylazin
4 Simazin
5 Atrazin-d5
6 Atrazin
7 Lindan
8 Terbutylazin
9 Metribuzin
10 Parathion-methyl
11 Heptachlor
12 Terbutryn
13 Aldrin
14 Metolachlor
15 Parathion-ethyl
16 exo-Heptachlorepoxid
17 Pendimethalin
18 endo-Heptachlorepoxid
19 Triclosan
20 Dieldrin
21 Carfentrazon-ethyl
22 Diflufenican
23 Mefenpyr-diethyl

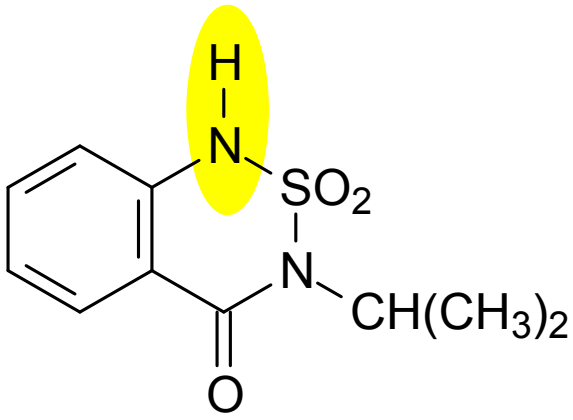
Challenge: highly polar Pesticides



Mecoprop (MCPP)



Bromoxynil



Bentazon

Challenge: highly polar Pesticides

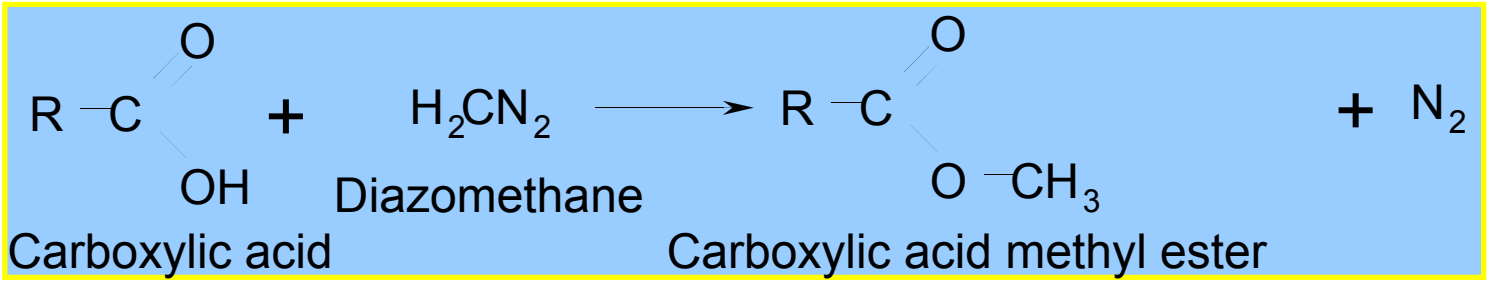
Solution: Combination of SPME and Derivatization

- Derivatization of analytes in water sample *before the extraction*
- Derivatization of analytes after extraction
  - On fiber
  - In injector

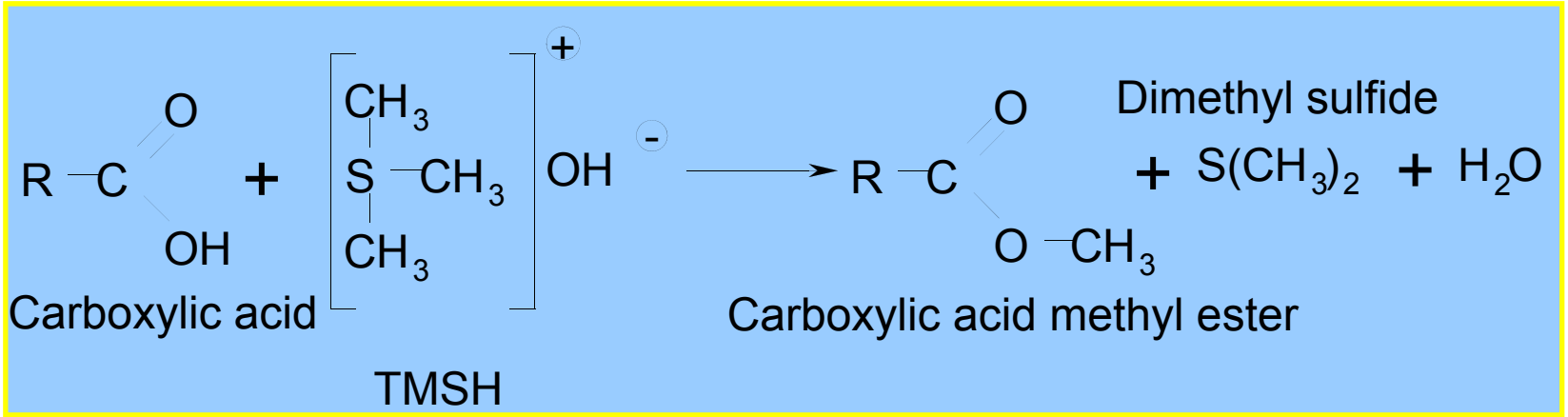
From presentation: Dr. Friedrich Werres,
„Pesticides in water – efficient determination by SPME-GC/MS“ (2005)

Methylation for highly polar Pesticides

Derivatization with Diazomethane

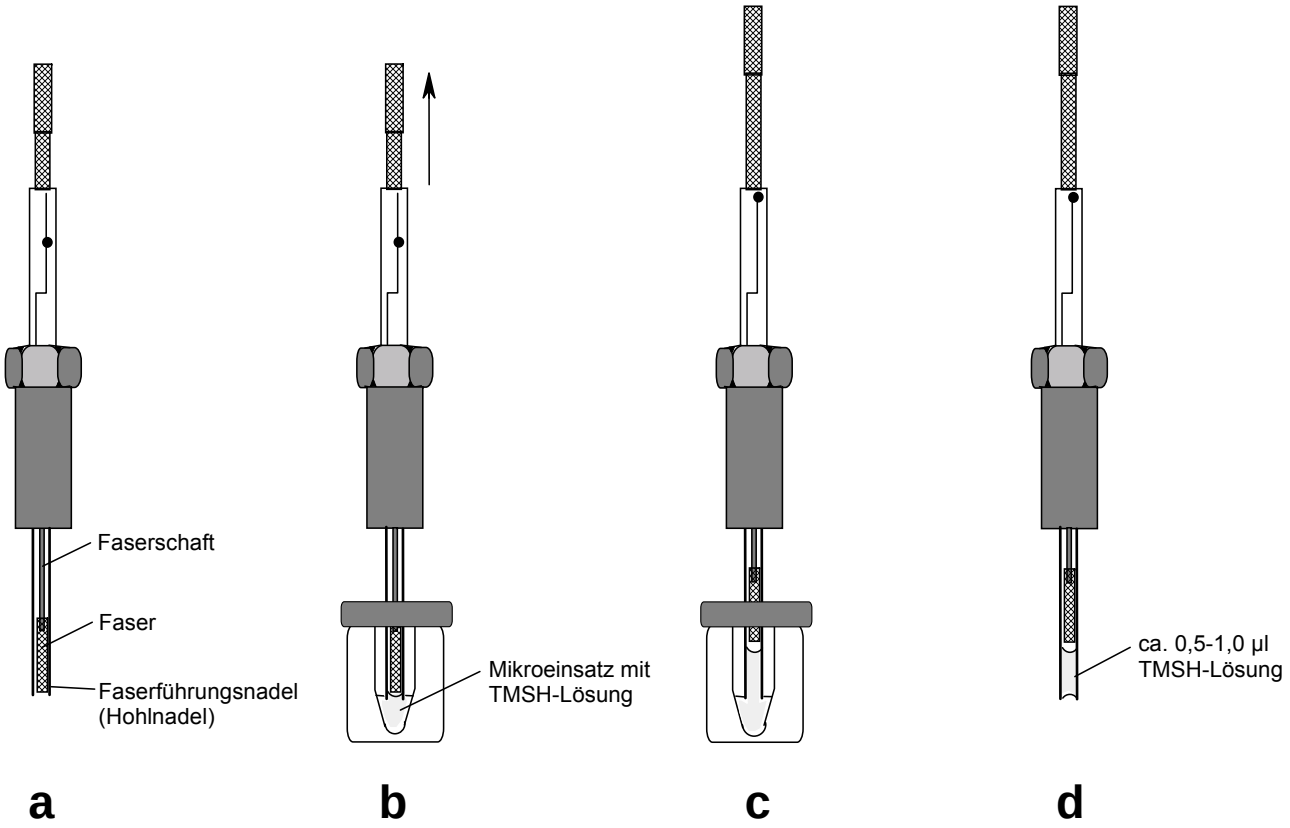


Derivatization with TMSH



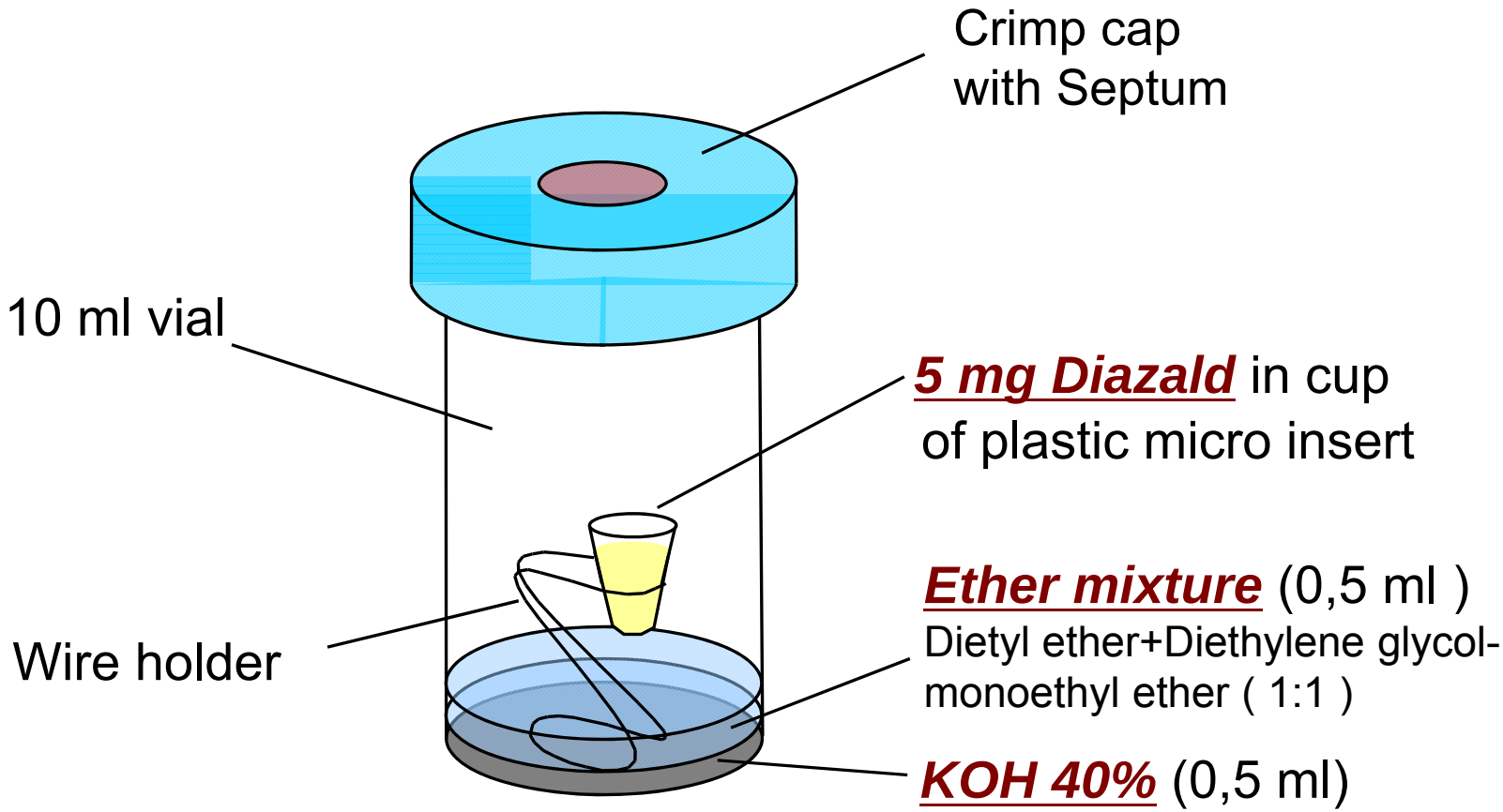
From presentation: Dr. Friedrich Werres,
„Pesticides in water – efficient determination by SPME-GC/MS“ (2005)

Methylation for highly polar Pesticides - TMSH



From presentation: Dr. Friedrich Werres,
„Pesticides in water – efficient determination by SPME-GC/MS“ (2005)

Methylation for highly polar Pesticides - Diazomethane



From presentation: Dr. Friedrich Werres,
„Pesticides in water – efficient determination by SPME-GC/MS“ (2005)

Nitrosamines in water

SPME used in a direct immersion extraction of nitrosamines from water. These are often difficult analytes to extract especially dimethylnitrosoamine.

- Nitrosodimethylamine
- Nitrosodiethylamine
- Nitrosomethylethylamine
- Nitrosodipropylamine
- Nitrosopiperidine
- Nitrosodibutylamine
- Nitrosodiphenylamine

Environmental

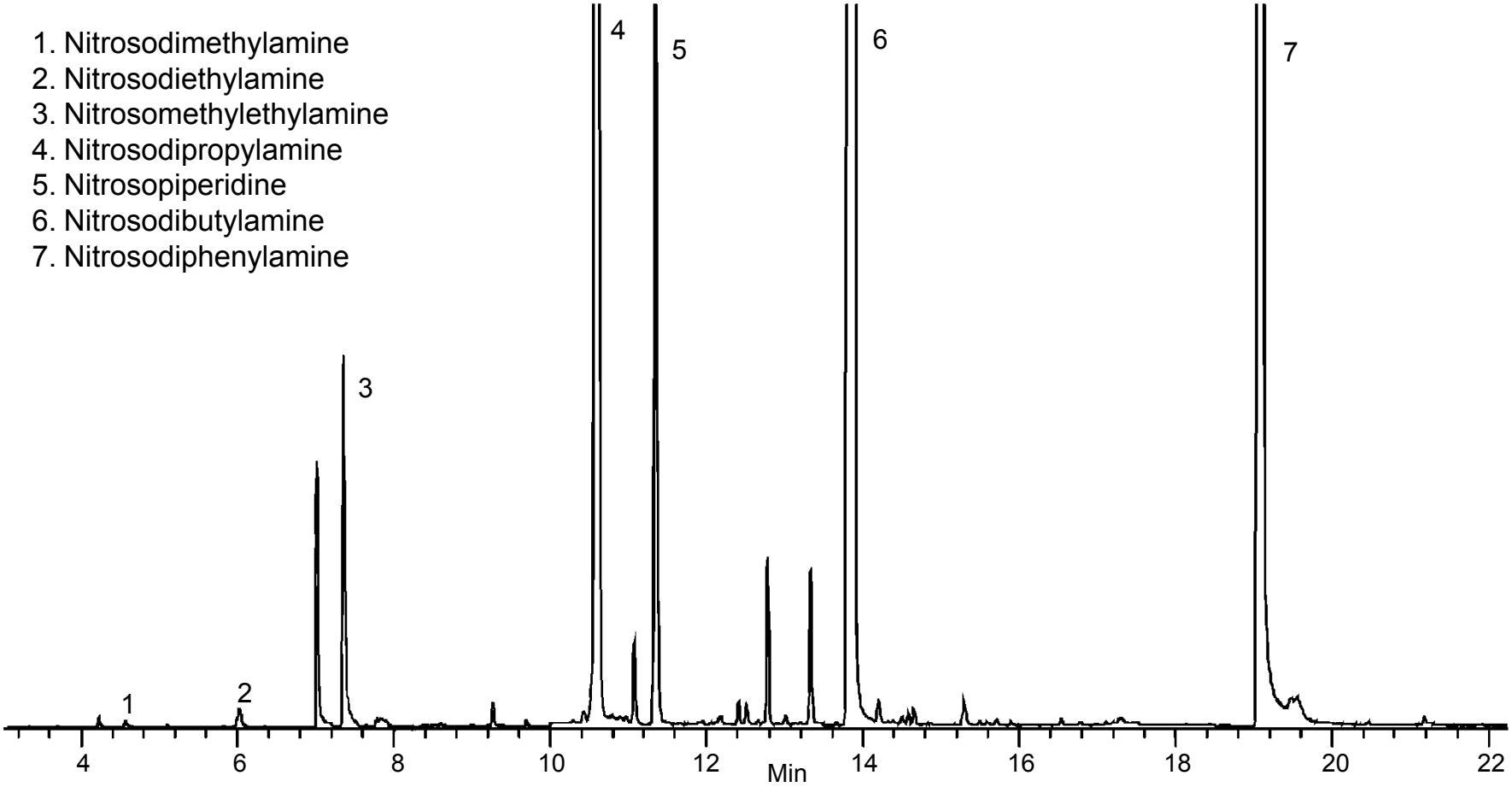
10ppb Nitrosamines in Water: SPME-GC/MS

Sample:	analytes in (water + 25% KCl, pH 10)
SPME Fiber:	65µm PDMS-DVB
Extraction:	immersion, 15 min (rapid stirring)
Desorption:	270° C, 1 min
Column:	PTA-5 (amine deactivated, 30m x 0.32mm, 0.5µm)
Oven:	50° C (1 min) to 250° C at 10° C/min, hold 2 min
Carrier:	helium, 30cm/sec
Det.:	GC/MS (quadrupole, SIM)
Inj.:	splitless, 250° C (0.75mm ID liner)

Environmental

10ppb Nitrosamines in Water: SPME-GC/MS

1. Nitrosodimethylamine
2. Nitrosodiethylamine
3. Nitrosomethylethylamine
4. Nitrosodipropylamine
5. Nitrosopiperidine
6. Nitrosodibutylamine
7. Nitrosodiphenylamine



Chromatogram courtesy of J. Clark, Liggett Group, Inc.

Standard Method 6040D: Odor compounds in water

This application demonstrates the use of headspace SPME and the SLB-5ms column for the low level extraction and detection of odor compounds in drinking water. Specifically, SPME is described for this analysis in Standard Method 6040D of these compounds at the part-per-trillion (ppt) level.

Odor-causing compounds in water

SPME

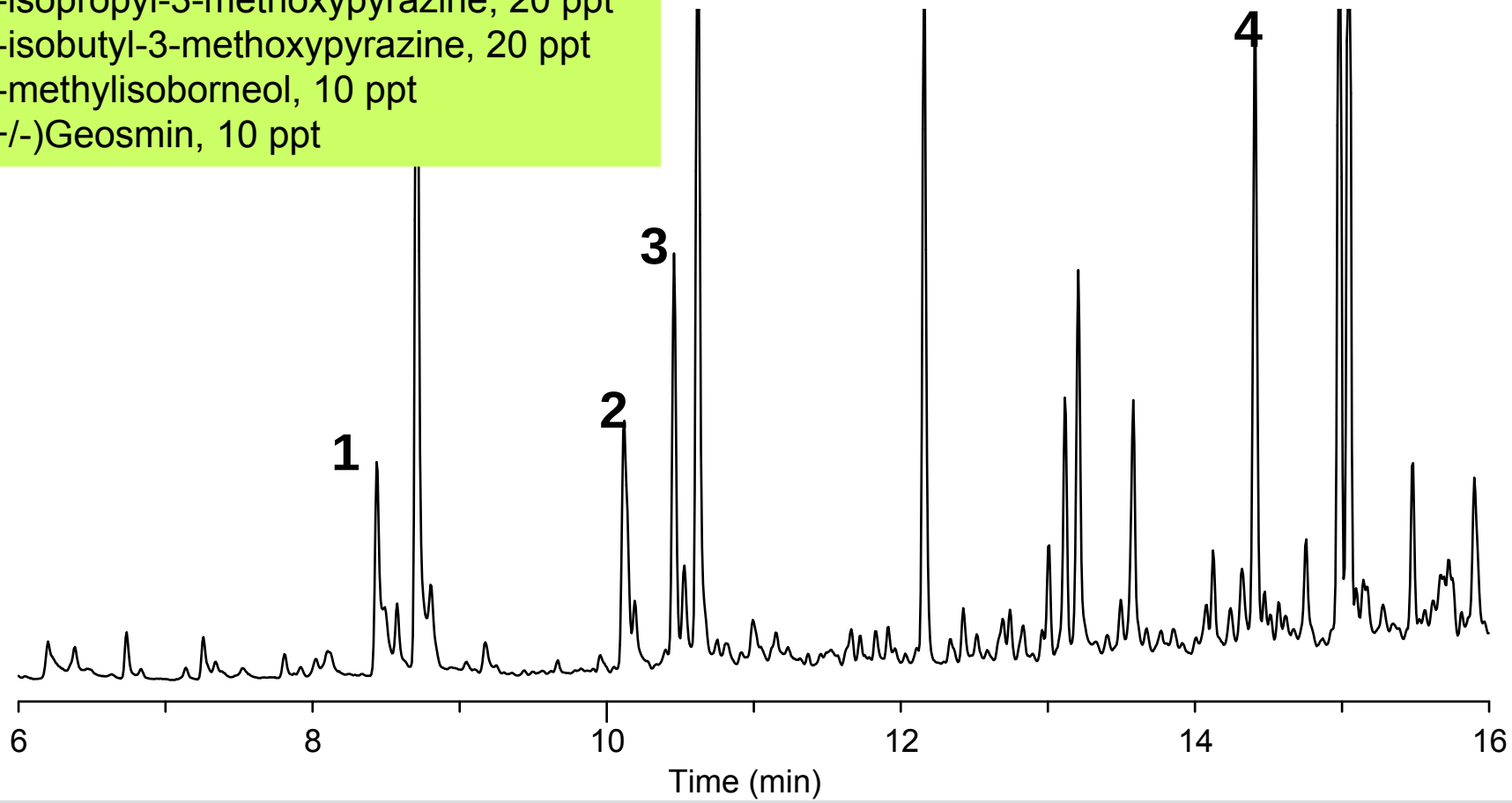
- SPME fiber: 2 cm Metal 50/30 µm DVB/CAR/PDMS
- Extraction: headspace, 65 ° C (30 min.)
- Desorption: 3 min. at 260 ° C

GC-MS

- Column: SLB-5ms, 30 m x 0.25 mm I.D., 0.25 µm
- Oven: 60 ° C (2 min.), 8 ° C/min. to 200 ° C
- MSD interf.: 300 ° C
- Scan range: SIM, m/z = 137, 124, 95, 112
- Carrier gas: helium, 1 mL/min. constant
- Liner: 0.75 mm I.D., SPME
- Sample: 20/10 ppt odor comps. in 25 mL water + 25 % NaCl

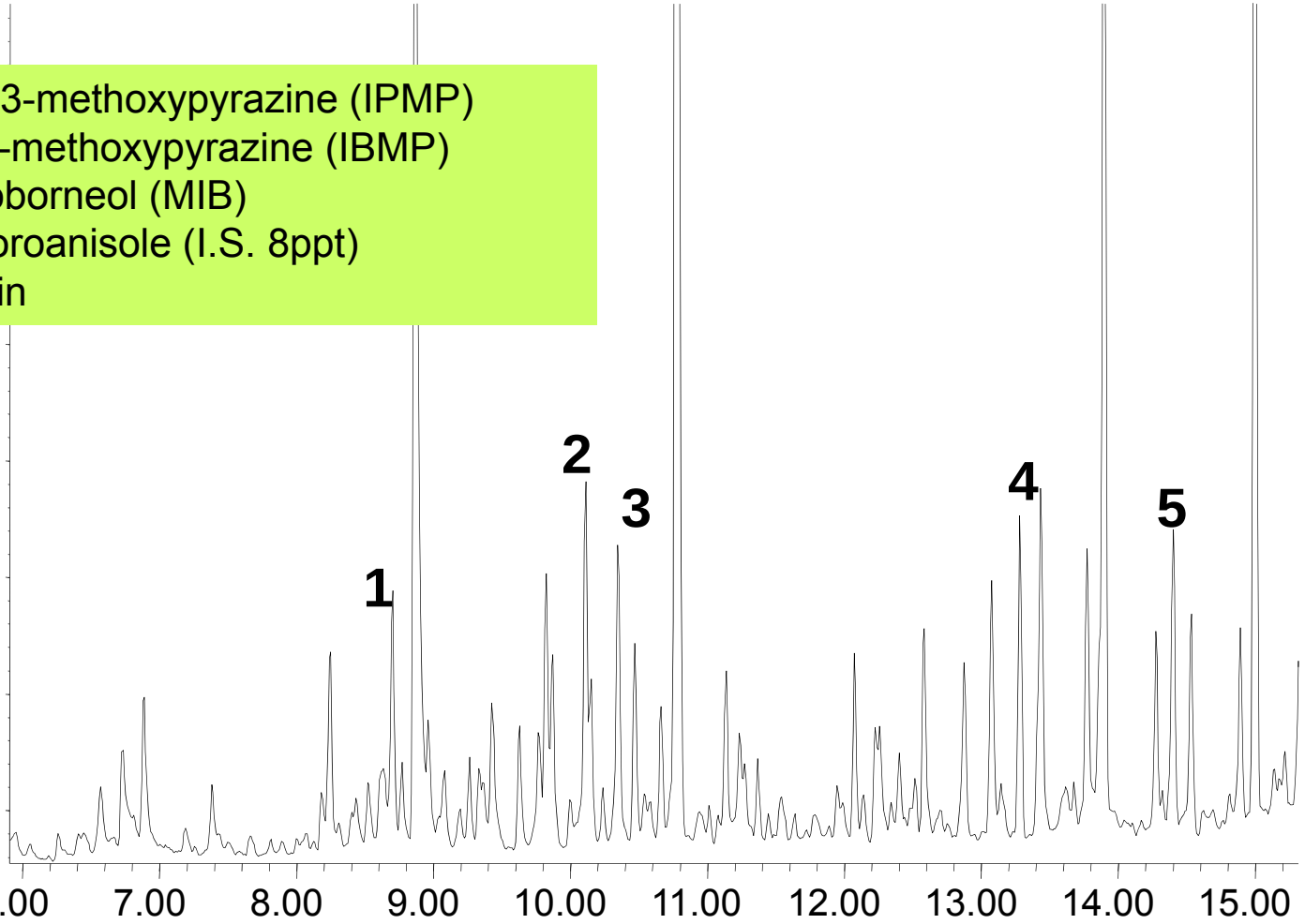
Odor-causing compounds in water

1. 2-isopropyl-3-methoxypyrazine, 20 ppt
2. 2-isobutyl-3-methoxypyrazine, 20 ppt
3. 2-methylisoborneol, 10 ppt
4. (+/-)Geosmin, 10 ppt



Odor-causing compounds in water at 2 ppt (GC/MS)

1. 2-Isopropyl-3-methoxypyrazine (IPMP)
2. 2-Isobutyl-3-methoxypyrazine (IBMP)
3. 2- Methylisoborneol (MIB)
4. 2,4,6-Trichloroanisole (I.S. 8ppt)
5. (±) Geosmin



ISO Standard 17943

Water quality - Determination of VOCs in water - Method using HS-SPME followed by GC-MS

- Broad use of VOCs (Volatile Organic Compounds) in many products, more than 60 are covered in this method
  - Halogenated hydrocarbons
  - Trihalogen methanes
  - Gasoline additives (like BTEX, MTBE and ETBE)
  - Naphthalene
  - 2-Ethyl-4-methyl-1,3-dioxolane and highly odorous substances like geosmin and 2-methylisoborneol
- Concern for human health as many of them are toxic and known or suspected to be carcinogenic
- Application in drinking water, ground water and surface water

VOCs in Water

Water Framework Directive requires application of ISO or CEN standards (standard methods)

Current methods have not been state-of-the-art:

- ISO 10301 (1997, Liquid-Liquid extraction, GC/FID or GC/ECD)
- ISO 11423 (1997, Headspace-GC/FID or GC/ECD)
  - ☹ Sensitivity & Selectivity
- ISO 15680 (2003, Purge and Trap, GC/MS)
  - ☹ Susceptibility to contamination, automation is complex

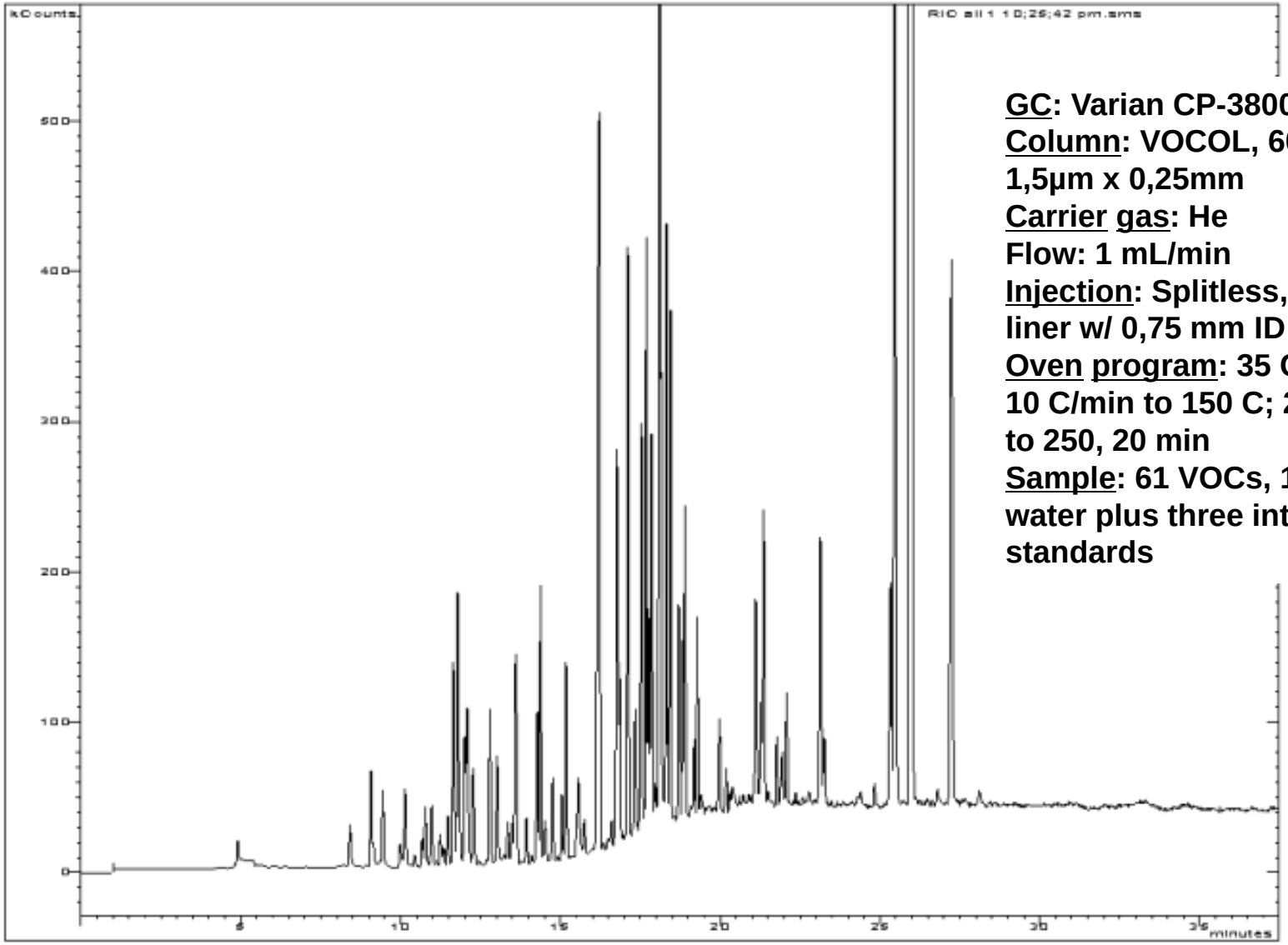
ISO 17943 – Content

- 45 pages
- Practical tips on using SPME and GC/MS
- Scope and principle
- Reagents, apparatus, sampling and sample pretreatment, procedure, calibration
- Calculation and expression of the results
- Examples of suitable SPME fibres, GC columns, internal standards, gas chromatographic conditions and example chromatograms

SPME Method (Supelco Applications Lab)

Sample volume:	10 mL
HS-Vial:	20 mL, addition of 3 g salt
SPME fiber:	DVB/CAR/PDMS, 24 gauge
Incubation time:	10 min @ 40 ° C
Extraction time:	10 min @ 40 ° C
Autosampler:	CTC Combi PAL (agitated by circular motion of the vial, velocity: 250 rpm)
Desorption/Injector:	10 min @ 270 ° C

GC Method (Supelco Applications Lab)



GC: Varian CP-3800
Column: VOCOL, 60m x 1,5µm x 0,25mm
Carrier gas: He
Flow: 1 mL/min
Injection: Splitless, SPME liner w/ 0,75 mm ID
Oven program: 35 C, 1 min; 10 C/min to 150 C; 20 C/min to 250, 20 min
Sample: 61 VOCs, 1 ppm, in water plus three internal standards

Interlaboratory Trial for Validation: Participants

- Austria 1x
- Brazil 2x
- Canada 2x
- Croatia 1x
- France 2x
- Germany 12x
- Great Britain 1x
- Italy 5x
- Portugal 3x
- Romania 1x
- Serbia 1x
- South Africa 2x
- Spain 4x
- Sweden 1x
- Swizerland 1x
- United States 3x

42 Participants out of 16 countries

Interlaboratory Trial

Determination of the concentration of 61 compounds in the two samples

Four independent replicate analysis from each of the 2 samples

Strictly following the procedure as prescribed in the draft standard (ISO/CD 17943)

Results had to be delivered 30 days after receipt of the samples

Samples for Interlaboratory Trial

Sample 1: Surface water was taken from an urban and industrialized area (river Ruhr in Muelheim, Germany)

- Filtration using a glass fiber filter.
- Stabilization with 50 mg/L sodium azide.

Sample 2: Municipal wastewater was taken from a plant effluent.

- Sedimentation and pumping into a large fluid tank while being filtrated by both 5 µm and 1 µm and irradiated by UV
- Sterilisation (80 ° C), introduction of gas: (1) CO2, (2) N2
- Stabilization with 50 mg/L sodium azide.

Spiking of samples:

- Surface water: 0,02 – 0,80 µg/l (~ 50 % < 0,10 g/l)
- Waste water: 0,05 – 3,00 µg/l (~ 50 % < 0,50 g/l)

Samples were tested for homogeneity and stability

Results from Interlaboratory Trial

No submission of results: 9 labs

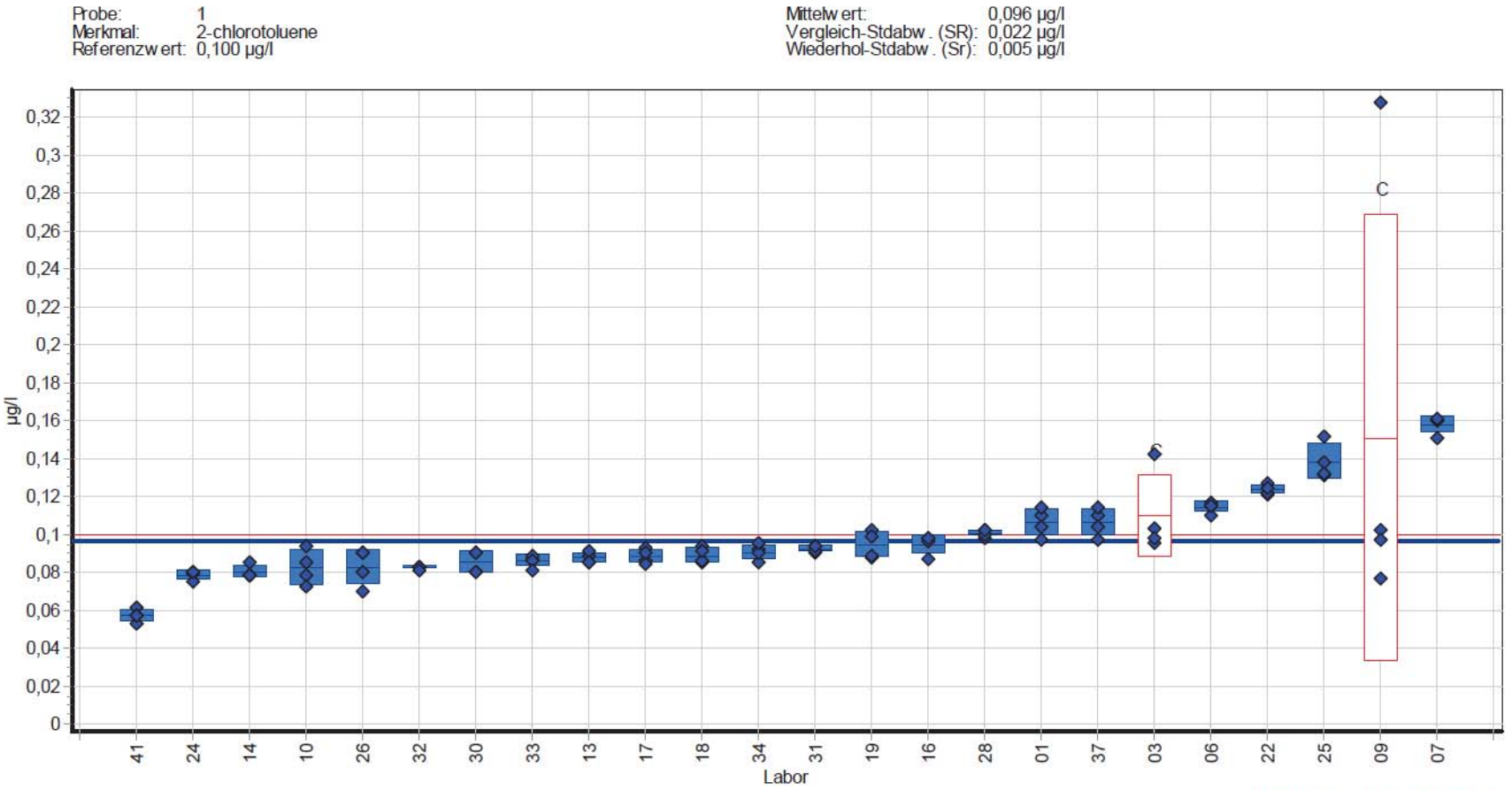
Significant deviation from the procedure prescribed: 6 labs

- calibration without internal standards (3x)
- other major deviations from draft ISO/CD 17943 (3x)

A total of 27 labs reported results to be included in the evaluation process according ISO 5725-2

- All parameters analysed: 10 labs
- Nearly all parameters analysed: 9 labs
- Nearly each parameter had been analysed by > 20 labs

Results from Interlaboratory Trial



PROLab Smart für ISO 5725-2

Results from Interlaboratory Trial

Analysis for

- Recovery rate (from assigned value)
  - For most of the compounds between 84 and 116 % (surface water) and 81 and 118 % (waste water)
- Reproducibility standard deviation
  - For most of the compounds less than 31 % (surface water) and less than 35 % (waste water)
- Repeatability standard deviation
  - For most of the compounds less than 10 % (surface water) and less than 8 % (waste water)

Thank you!

S ample
P rep
M ade
E asy