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SPME for the determination of volatile organic compounds in water: Results from global interlaboratory trial for validation of new ISO 17943

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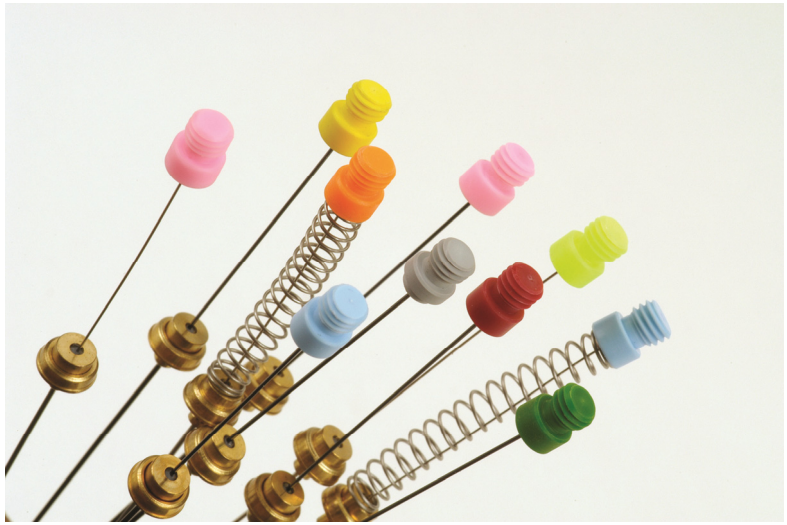

VOCs in Water

Use of Volatile Organic Compounds (VOCs):

- Petroleum products
- Adhesives
- Pharmaceuticals
- Paints
- Refrigerants
- Additives
- Solvents

VOCs in Water

VOC contamination of water resources is a human-health concern because many substances are toxic and are known or suspected human carcinogens.

Control of VOCs in water is highly regulated [1-4].

[1] Council Directive 98/83/EC. Official Journal of the European Communities, L330, 32-54
[2] Directive 2000/60/EC. Official Journal of the European Communities, 22/12/2000, L327, 1-73
[3] Decision No 2455/2001/EC. Official Journal of the European Communities, 15/12/2001, L331, 1-5
[4] US Safe Drinking Water Act 55 (SDWA)

VOCs in Water

Water Frame Directive requires application of ISO and CEN standards

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

VOCs in Water by SPME

Headpace-SPME is reliable and advantageous for determination of VOCs in water [4-15]

[5] Alonso, A., Fernández-Torroba, M. A., Tena, M. T., Pons ,B., Chromatographia, 57 (2003) 369-378.
[6] Nakamura, S., Daishima, S., Anal. Chim. Acta, 548 (2005) 79-85.
[7] Antoniou, V., Koukouraki, EE., Diamadopoulos, E., J. Chromatogr., 1132 (2006) 310-314.
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[14] Antelo, A., Lasa, M., Millán, E., Chromatographia, 66, (2007) 555-563.
[15] Prikryl, P., et al., Chromatographia, 64 (2006) 65-70.

Official Methods using SPME

2000: ASTM D 6520 (Volatiles and Semivolatiles from water)

2001: ASTM E 2154 (Ignitable Liquid Residues from Fire Debris)

2003: ASTM D 6889 (VOCs in Water)

2004: OENORM A 1117 (Volatiles in cellulose-based materials)

2005: ASTM D 6438 (Organics in Paint and Coatings)

2007: EPA Method 8272 (PAHs in Sediment Water)

2013: ISO 27108 (Pesticides in Water)

DIN 38407-41 (2011)

German standard methods for the examination of water, waste water and sludge – Jointly determinable substances (group F) – Part 41: Determination of selected easily volatile organic compounds in water – Method using gas chromatography (GC-MS) after headspace solid-phase micro extraction (HS SPME) (F41)

- 25 VOCs
- Drinking water, ground water and surface water
- Headspace-SPME and GC/MS
- LODs mostly less than 0,01 µg/L, linearity 0,02 µg/l - 2,6 µg/l
- Interlaboratory trial with 35 participants (21 labs suitable for evaluation)

Conversion of DIN 38407-41 to ISO 17943

Expanding the scope of the standard

- 63 instead of 25 compounds (requests from different countries)
- Validation of additional compounds
- Including waste water (beside drinking, ground and surface water)
- Implementations of corrections, explanations, improvements

New global interlaboratory trial with spiked surface water and waste water

ISO 17943 – Compounds covered

vinyl chloride
1,1-dichloroethene
dichloromethane
methyl tert-butyl ether (MTBE)
trans-1,2-dichloroethene
1,1-dichloroethane
ethyl tert-butyl ether (ETBE)
2,2-dichloropropane
cis-1,2-dichloroethene
trichloromethane (chloroform)
bromochloromethane
1,1,1-trichloroethane
tert-amyl methyl ether (TAME)
1,1-dichloropropene
tetrachloromethane
1,2-dichloroethane
benzene
trichloroethene
1,2-dichloropropane
bromodichloromethane
dibromomethane
cis -1,3-dichloropropene
toluene
trans -1,3-dichloropropene
2-ethyl-4-methyl-1,3-dioxolane
1,1,2-trichloroethane
1,3-dichloropropane
tetrachloroethene
dibromochloromethane
1,2-dibromoethane
ethylbenzene
chlorobenzene
1,1,1,2-tetrachloroethane
o-, m-, p-xylene
styrene
2-ethyl-5,5-dimethyl-1,3-dioxane
isopropylbenzene (cumene)
1,1,2,2-tetrachloroethane
tribromomethane (bromoform)
1,2,3-trichloropropane
n-propylbenzene
1,3,5-trimethylbenzene (mesitylene)
bromobenzene
2-chlorotoluene
4-chlorotoluene
n-butylbenzene
1,2,4-trimethylbenzene (pseudocumene
sec-butylbenzene
4-isopropyltoluene (p-cymene)
1,3-dichlorobenzene
1,4-dichlorobenzene
tert-butylbenzene
1,2-dichlorobenzene
1,2-dibromo-3-chloropropane (DBCP)
1,3,5-trichlorobenzene
2-methylisoborneol
1,2,4-trichlorobenzene
hexachlorobutadiene
naphthalene
1,2,3-trichlorobenzene
geosmin

ISO 17943 – Compounds covered

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1,3-dichloropropane
tetrachloroethene
dibromochloromethane
1,2-dibromoethane
ethylbenzene
chlorobenzene
1,1,1,2-tetrachloroethane
o-, **m-, p-xylene**
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1,2,4-trichlorobenzene
hexachlorobutadiene
naphthalene
1,2,3-trichlorobenzene
geosmin

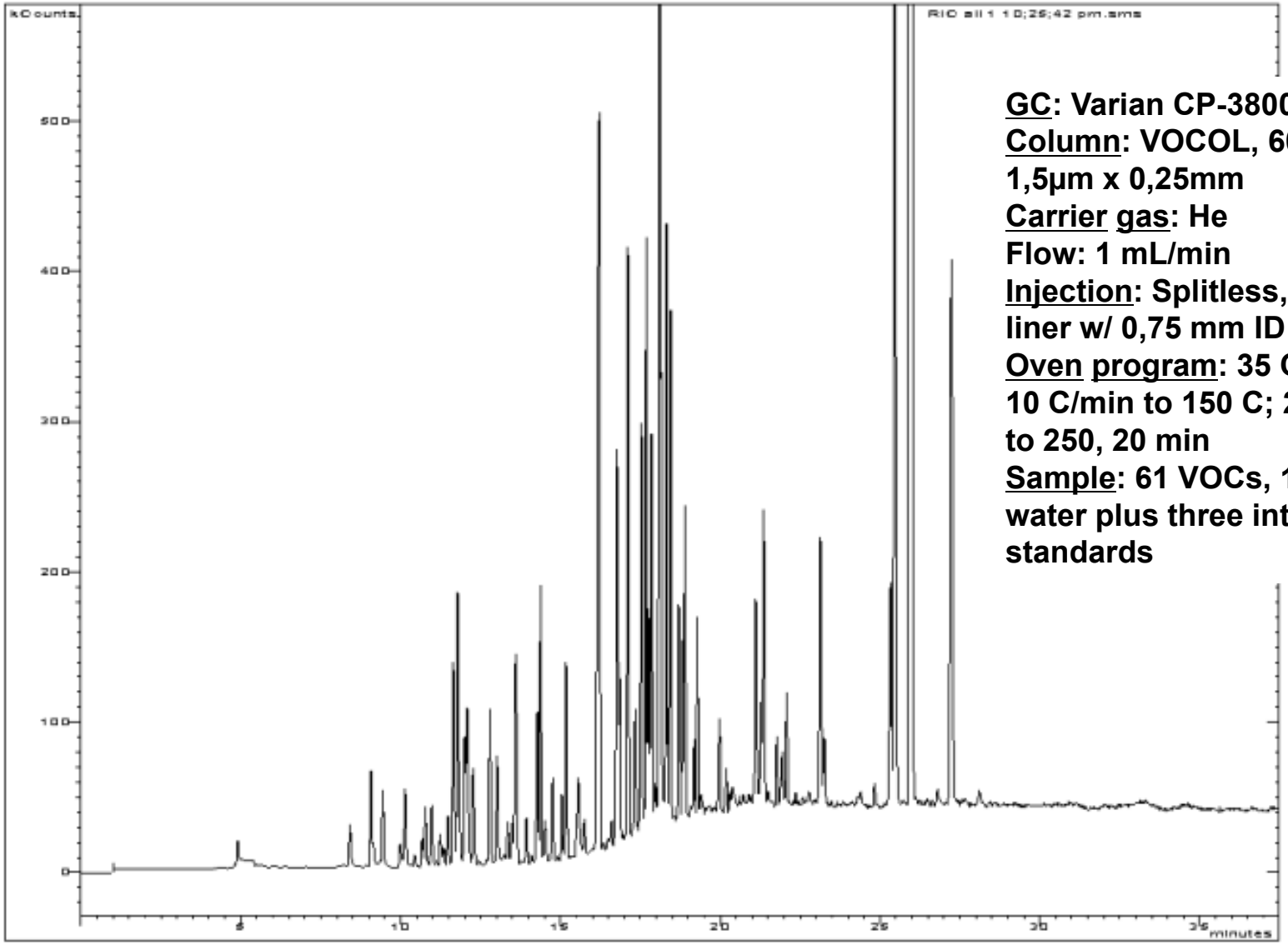
ISO 17943 – Content

- 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

Internal Standards

Supelco Applications Lab:

- Toluene-d8
- Benzene-d6
- Fluorobenzene

Other options:

- 1,2-dichlorobenzene-d4
- 1,2-dichloroethane-d4
- MTBE-d3
- Naphthalene-d8
- 4-bromofluorobenzene
- Chlorobenzene-d5
- Acenaphthene-d10, ethylbenzene-d10, trichloroethene-d1, trifluorotoluene, vinyl chloride-d3, o-xylene-d10 …

Participants at the Interlaboratory Trial

- 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

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

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

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

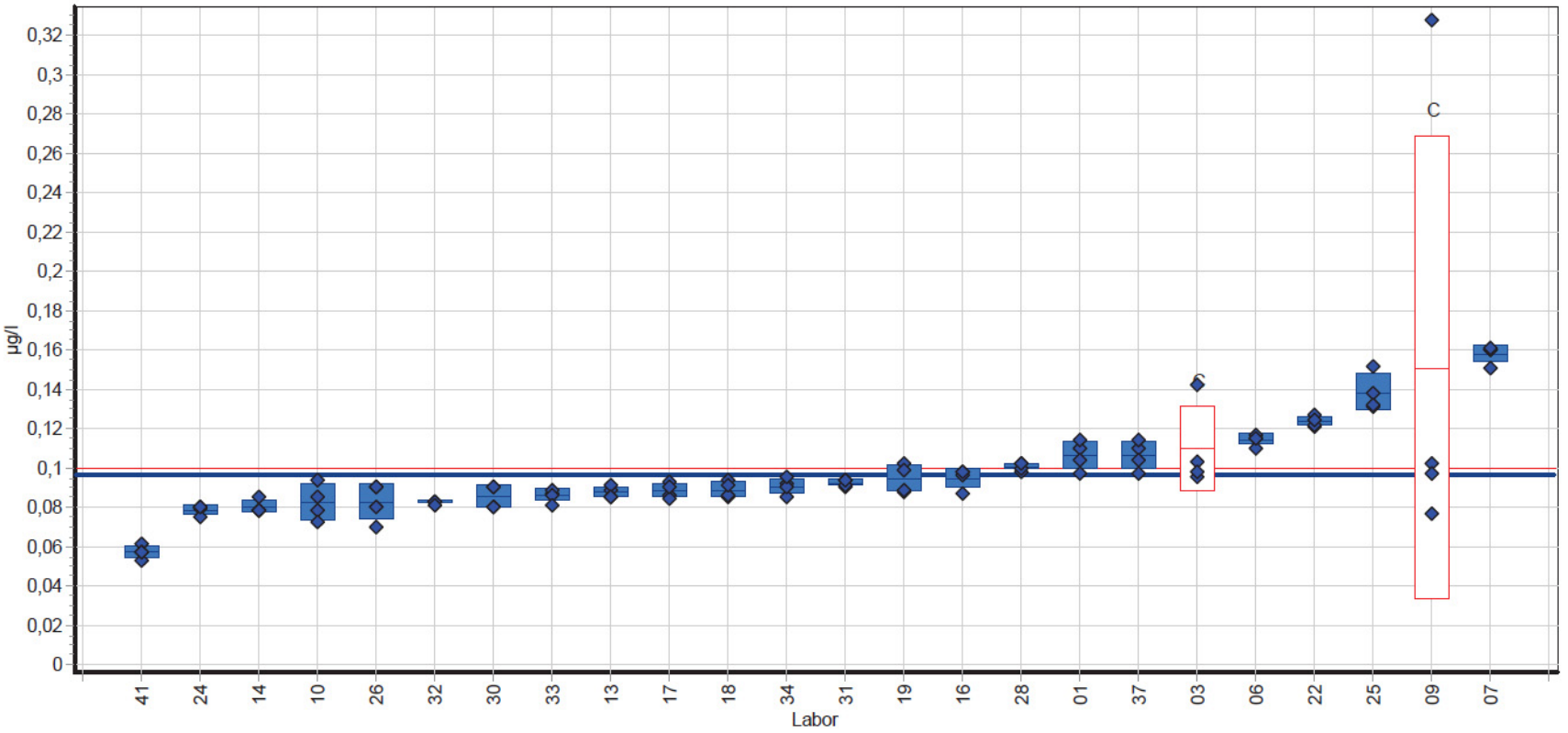
Analysis for

- Outliers
  - Type A: outlying single result of one laboratory
  - Type B: outlying laboratory mean
  - Type C: outlying within-laboratory variance
- Overall mean of results (without outliers)
- Recovery rate (from assigned value)
- Reproducibility standard deviation
- Repeatability standard deviation

Results from Interlaboratory Trial

Probe: 1
Merkmal: 2-chlorotoluene
Referenzwert: 0,100 µg/l

Mittelwert: 0,096 µg/l
Vergleich-Stdabw. (SR): 0,022 µg/l
Wiederhol-Stdabw. (Sr): 0,005 µg/l



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)

Summary

Reliable and reproducible method for VOCs in water was developed

Validation in ISO 17943 (and older DIN 38407-41)

Successful interlaboratory trial showing high performance

- Accuracy
- Precision

ISO 17943 will go live soon

Thank you!

Dr. Friedrich Werres, IWW Water Centre
All members of working group DIN NA 119-01-03-02-05 AK
All participants at the Interlaboratory Trial
Yong Chen, Bob Shirey

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