Determination of volatile organic compounds in water by SPME and GC/MS: Validation of new ISO Standard 17943

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This work describes the details of the determination of more than 60 volatile organic compounds (VOCs) in different water matrices together with the required method optimizations. After extraction of the compounds in the headspace of the samples by SPME the analysis is conducted by GC-MS. Additionally the results from an interlaboratory trial for validation of this method as a new ISO standard will be presented. These demonstrate a very good performance of this method for the determination of VOCs in water.

Introduction

Volatile organic compounds (VOCs) are often used during the manufacturing of many different products such as petroleum products, adhesives, pharmaceuticals, paints or refrigerants. Additionally some are applied as additives, solvents or other agents. The contamination of water by VOCs is critical for health due to the fact that many of the VOCs are toxic.

Solid Phase Micro Extraction (SPME) was introduced in 1990 [1]. Since then SPME has gained broad acceptance in environmental, pharmaceutical and food analysis demonstrated by the still growing number of publications on SPME developments and applications. The prevalence of this technique was additionally increased by the automation of SPME using GC autosamplers since 1993. Another indication of the broad acceptance is the use of SPME in official methods and standards.

- ASTM D 6520 (Volatiles and semivolatiles from water)
- ASTM E 2154 (Ignitable liquid residues from fire debris)
- ASTM D 6889 (VOCs in water)
- OENORM A 1117 (Volatiles in cellulose-based materials)
- ASTM D 6438 (Organics in paint and coatings)
- EPA Method 8272 (PAHs in sediment water)
- ISO 27108 (Pesticides in water)

VOCs in water can be determined by different methods [2-4], but those were not sufficient in terms of LOD or automation.

Method

ISO 17943 covers the determination of 63 volatile compounds in different water matrices such as drinking, surface, ground and waste water. The SPME conditions can be found in Tab. 1.

Parameter	Setting (Supelco Lab, trial participant)
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:	10 min @ 270 °C

Tab. 1: Chromatographic conditions for SPME extraction

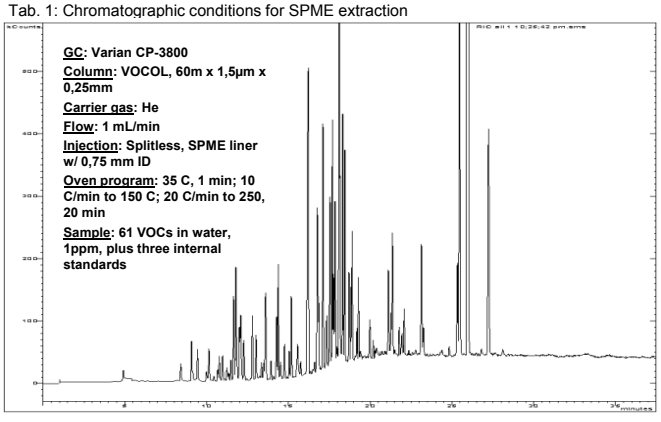

Fig. 1: Chromatogram and GC conditions (Supelco Lab, participating in interlaboratory trial) for analysis of the compounds by ISO Standard 17943

Results

Samples for the trial were surface water (river Ruhr in Muelheim, Germany) and municipal wastewater (plant effluent). The samples were filtered, sterilized and stabilized using sodium azide. After spiking (surface water: 0,02 – 0,80 µg/l; waste water: 0,05 – 3,00 µg/l) the samples were tested for homogeneity and stability.

At the interlaboratory trial 42 labs from 16 countries participated:

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

The results from the interlaboratory trial after exclusion of outliers were evaluated for recovery rate (from assigned value), reproducibility standard deviation and repeatability standard deviation (Fig. 2).

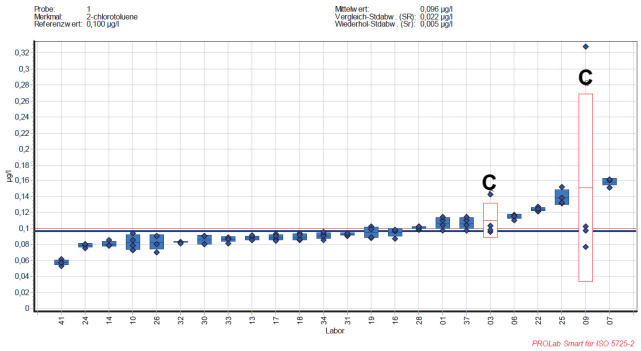

Fig. 2: Evaluation of the interlaboratory trial (example compound 2-chlorotoluene). For this compound results from 24 labs could be evaluated. The blue line is the assigned value, the red line is overall mean. Highlighted with the letter „C“ are two outliers due to too high within-laboratory variance.

The evaluation of the interlaboratory trial demonstrates a very good performance of ISO Standard 17943. For more than 90 % of the compounds:

- Recovery rate (from assigned value) is between 84 and 116% (surface water) and 81 and 118 % (waste water)
- Reproducibility standard deviation is less than 31 % (surface water) and less than 35 % (waste water)
- Repeatability standard deviation is 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

References:

[1] Arthur, C. L., Pawliszyn, J., Analytical Chemistry (1990), 62(19), 2145-8

[2] ISO 10301:1997, Water quality — Determination of highly volatile halogenated hydrocarbons – Gas chromatographic methods

[3] ISO 11423-1:1997 and ISO 11423-2:1997, Water quality — Determination of benzene and some derivatives — Part 1: Head-space gas chromatographic method & Part 2: Method using extraction and GC

[4] ISO 15680:2003, Water quality — GC determination of a number of monocyclic aromatic hydrocarbons, naphthalene and several chlorinated compounds using purge-and-trap and thermal desorption