ENVIRONMENTAL

Improved Determination of Volatile Organic Compounds in Water by SPME and GC/MS: ISO Standard 17943

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The analysis of water for volatile organic compounds is important due to their toxicity. The current methods for this determination lack sensitivity, selectivity or capability for automation. This paper presents the new ISO 17943 Standard using Solid Phase Microextraction (SPME) and GC/MS. The sample preparation by SPME enables lower limits of detection and easy automation of the entire method. GC/MS provides the required sensitivity and selectivity. This ISO standard was validated by an interlaboratory trial, whose results confirm the outstanding performance of this method.

Introduction

Volatile Organic Compounds (VOCs) can occur from natural sources such as plant scents. However, a large amount of VOCs do have an anthropogenic origin, because they are released from products in daily use or emitted during the manufacturing of such products, as well as from polymers, adhesives, paints, petroleum products or pharmaceuticals. Typical applications for VOCs are use as additives for gasoline or as solvents and hydraulic fluids or for dry-cleaning. As many VOCs are toxic or are known or suspected human carcinogens, contamination of water resources is a serious human health concern worldwide.

Because of this, many international regulations have been established to limit and control the amount of VOCs in drinking water, groundwater or surface water. Examples of such regulations are the Safe Drinking Water Act (SDWA)[1] in the USA, and a corresponding law in Canada that established national standards for drinking water including VOC listings that are based on health considerations. Another example is the European Council Directive 98/83/EC on the quality of water intended for human consumption that regulates the values for individual volatile organic substances[2]. In the EU Water Framework Directive (WFD) in article 16 of the Directive 200/60/EC[3] a "strategy against pollution of water" is described.

Figure 1. SPME Manual Holder

According to Directive 2008/105/EC (EQS Directive)[4] Environmental Quality Standards (EQS) values for single VOCs should be in the range of 0.4 to 20 µg/L. In annex V of WFD (standards for monitoring of quality elements) the use of ISO and CEN standards for the analysis of water is required, if available.

The existing ISO and CEN standards for the determination of VOCs in water are not state-of-the-art methods anymore. ISO 10301[5] uses Liquid/Liquid Extraction (LLE) in combination with Gas Chromatography (GC) and detection using Flame Ionization Detection (FID) or Electron Capture Detection (ECD). ISO 11423[6] employs headspace (HS) sampling in combination with GC/FID or GC/ECD. For certain relevant VOCs, the required limits of detection cannot be achieved using these ISO standards because the detectors are not sensitive or selective enough. ISO 15680[7] exhibits an alternative by using purge-and-trap enrichment and Gas Chromatography-Mass Spectrometry (GC-MS) analysis leading to better selectivity and limits of detection. The downside of purge-and-trap is the susceptibility of the trap to become contaminated and that automation is rather challenging to achieve[8].

Improved Method for Determination of VOCs in Water by HS-SPME and GC/MS: ISO Standard 17943

Solid Phase Microextraction (SPME) in combination with GC-MS is an attractive alternative for the determination of VOCs in water. SPME was developed by Janusz Pawliszyn in 1990[9] (**Figure 1**). Since then SPME has gained broader acceptance in environmental, pharmaceutical and food analysis as demonstrated by the growing number of publications on SPME developments and applications. The prevalence of this technique was additionally increased by the automation of SPME using regular GC autosamplers beginning in 1993. The use of SPME for the extraction of VOCs from water is described in several publications[10-12]. In these publications, headspace SPME (HS-SPME) was proven to be a reliable and beneficial alternative to classical methods for VOC determination in water. Furthermore, SPME has been successfully used in many other official methods[13-15].

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Due to this, the new ISO standard 17943 was developed for VOCs in water. The scope of the standard is the determination of more than 60 VOCs from very different classes such as halogenated hydrocarbons, gasoline additives (like BTEX, MTBE and ETBE), volatile aromatic compounds and highly odorous substances like geosmin and 2-methylisoborneol in drinking water, groundwater, surface water and treated wastewater by HS-SPME and GC-MS. Of course the limit of detection depends on the matrix, on the specific compound and on the applied mass spectrometer, but for most compounds in ISO 17943, it is equal to or better than 0.01 µg/L. Additional validation data derived from standardization work show applicability of the method within a concentration range from 0.01 µg/L to 100 µg/L for individual substances.

Global Interlaboratory Trial for Validation of New ISO Standard 17943

As part of the development of this new ISO standard, an international interlaboratory trial was conducted to validate the new method[16]. Each of the labs had to determine the concentration of 61 compounds in the two water samples (one surface water, one wastewater). The surface water sample was taken from an urban and industrialized area (the Ruhr River in Muelheim, Germany). The municipal wastewater sample was taken from a plant effluent. Both samples had been pre-treated to stabilize them and had been spiked with concentrations unknown to the participating labs in the range of 0.02 – 0.80 µg/L (~ 50 % < 0.10 g/L) for the surface water and 0.05 – 3.0 µg/L (~ 50 % < 0.50 g/L) for the wastewater. The labs in the interlaboratory trial had to conduct four independent replicate analyses from each of the two samples, strictly following the procedure as prescribed in the draft standard method. All laboratories were provided with a set of calibration solutions placed in three ampoules each containing certified reference substances of the 61 VOCs dissolved in methanol. These stock solutions contained the individual substances in concentrations of 100 µg/mL each and were intended to be used for preparation of the corresponding aqueous multi-component reference solutions used for calibrating the total procedure. The results had to be delivered within 30 days after receipt of the samples.

The Supelco® Application Lab was one participant in the interlaboratory trial. The two water samples were analyzed according to the drafted ISO Standard 17943 (**Table 1 & 2**, **Figure 2**) using toluene-d_8, benzene-d_6 and fluorobenzene as internal standards. For the GC analysis a VOCOL capillary GC column was used, which is an intermediate polarity column that is designed for analysis of VOCs and provides great retention and resolution of highly volatile compounds. For HS-SPME a DVB/CAR/PDMS fiber was used which was also used by the majority of the interlaboratory trial participants. A smaller share of the labs used a CAR/PDMS fiber. According to ISO Standard 17943 both the Carboxen/PDMS (85 µm) and the DVB/Carboxen/PDMS (50/30 µm) fiber can be used.

Table 1. Conditions for HS-SPME Extraction

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 CombiPAL™ (agitated by circular motion of the vial, velocity: 250 rpm)

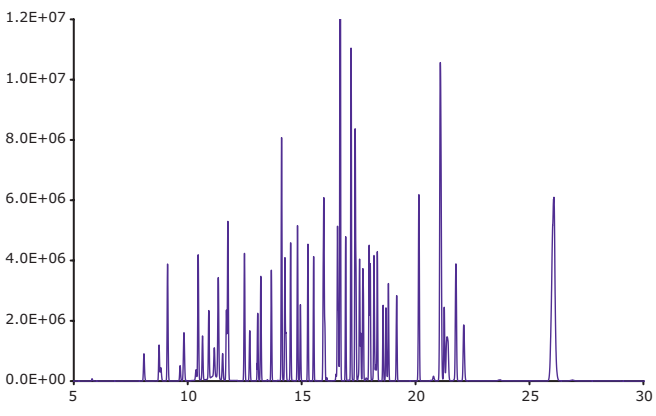
Table 2. Conditions for GC/MS Analysis

GC:	Agilent® GC/MS
Column:	VOCOL®, 60 m x 0,25 mm I.D., 1.5 µm
Carrier gas:	He, 1 mL/min
Injection/Liner:	Splitless, SPME liner w/ 0,75 mm ID
Desorption/ Injector:	10 min @ 270 °C
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

Figure 2. Chromatogram of 61 VOCs in water after HS-SPME using a VOCOL® GC column on an Agilent® GC/MS

Compound Name	RT (min)
Vinyl chloride	5.8
1,1-Dichloroethene	8.077
Methylenechloride	8.743
MTBE	8.819
trans-1,2-Dichloroethylene	9.113
1,1-Dichloroethane	9.667
ETBE	9.834
2,2-Dichloropropane	10.365
cis-1,2-Dichloroethylene	10.46
Trichloromethane	10.649
Bromochloromethane	10.927
1,1,1-Trichloroethane	11.166
TAME	11.339
1,1-Dichloro-1-propene	11.344
Carbon tetrachloride	11.533
1,2-Dichloroethane	11.7
Benzene	11.761
Trichloroethylene	12.491
1,2-Dichloropropane	12.722
Bromodichloromethane	13.073
Dibromomethane	13.21
cis-1,3-Dichloro-1-propene	13.671
Toluene	14.119
trans-1,3-Dichloro-1-propene	14.267
2-Ethyl-4-methyl-1,3-dioxolane	14.311
1,1,2-Trichloroethane	14.52
1,3-Dichloropropane	14.817
Tetrachloroethylene	14.946
Dibromochloromethane	15.277
1,2-Dibromoethane	15.527
Ethylbenzene	15.945

Compound Name	RT (min)
Chlorobenzene	15.975
1,1,1-2-tetrachloroethane	15.983
p-Xylene	16.573
o-Xylene	16.573
Styrene	16.619
2-Ethyl-5,5-dimethyl-1,3-dioxane	16.695
Cumene	16.933
Bromoform	17.162
1,1,2,2,-Tetrachloroethane	17.175
1,2,3-Trichloropropane	17.346
Propylbenzene	17.386
Pseudocumene	17.544
Bromobenzene	17.596
2-Chlorotoluene	17.688
4-Chlorotoluene	17.688
tert-Butylbenzene	17.966
Mesitylene	18.015
sec-Butylbenzene	18.173
p-Cymene	18.32
1,3-Dichlorobenzene	18.577
1,4-Dichlorobenzene	18.698
Butylbenzene	18.807
1,2-Dichlorobenzene	19.17
DBCP	20.145
2-Methylisoborneol	21.087
1,2,4-Trichlorobenzene	21.257
Hexachlorobutadiene	21.386
Naphthalene	21.773
1,3,5-Trichlorobenzene	22.113
Geosmin	26.074



Evaluation of the Interlaboratory Trial

More than 40 labs from all over the world registered for this interlaboratory trial. Out of these a total of 27 labs reported results to be included in the evaluation process according ISO 5725-2[17]. Nine laboratories did not submit any results. Six labs had to be excluded from the valuation due to significant deviation from the prescribed procedure. Some single results had to be excluded due to outliers.

All 61 parameters had been analyzed by ten labs and nearly all parameters had been analyzed by nine labs. Expressed in a different way, this resulted in the fact that nearly each of the 61 VOCs had been analyzed by more than 20 labs, which provides a valid base for statistical evaluation. The data was analyzed for the overall mean of results (without outliers), the recovery rate (from assigned value), the reproducibility (variation between different labs) and the repeatability (variation within a lab).

One example of such an evaluation is shown in **Figure 3** for 2-chlorotoluene. For this compound, results from 24 labs could be evaluated. The overall mean value (green line) is very close to the assigned value (purple line). The majority of the 24 labs, even those labs that were new to SPME, achieved results very close to the assigned value. The recovery rate for more than 90% of the compounds was between 84 and 116 % (surface water) and 81 and 118 % (wastewater). The reproducibility (variation between laboratories), for more than 90% of the compounds, was less than 31% (surface water) and less than 35% (wastewater), while the repeatability (variation within a lab) for more than 90% of the compounds was less than 10% (surface water) and less than 8% (wastewater).

Summary

The outstanding results in the interlaboratory trial underscore the high performance, reliability and reproducibility of HS-SPME in combination with GC/MS for the determination of VOCs in water. The new ISO 17943 is an improvement on existing official methods for this determination in terms of sensitivity and selectivity. In addition, the capability for full automation of SPME is beneficial for running this analysis 24/7.

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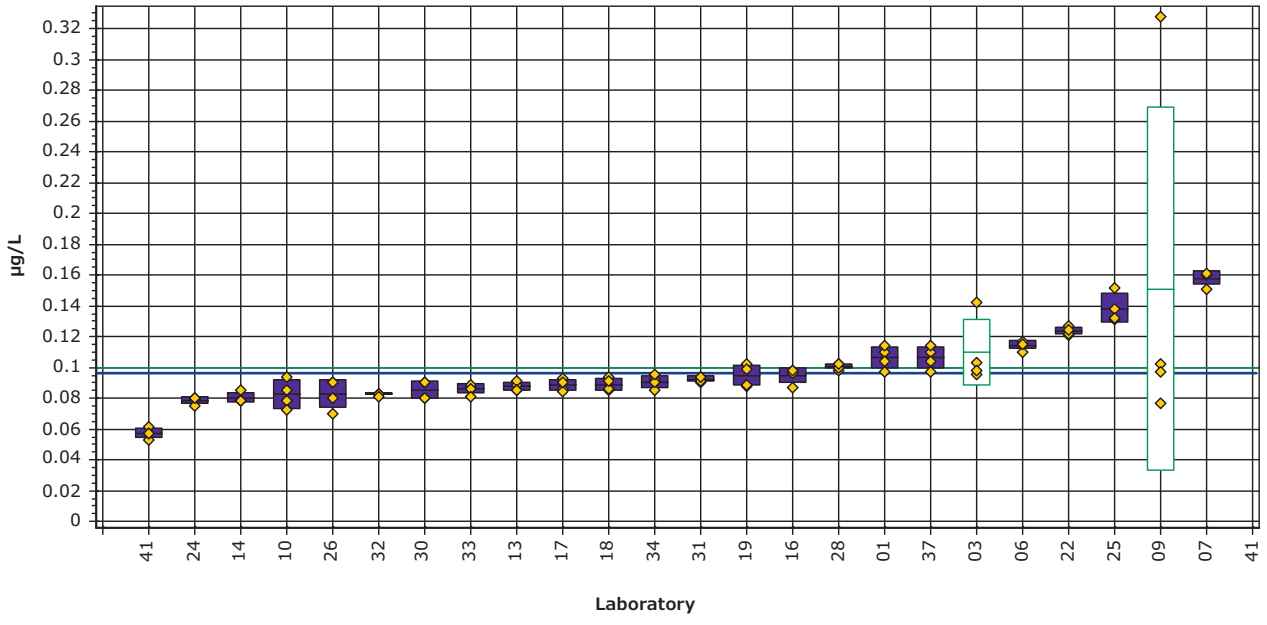
Figure 3. Graphical presentation of the example of 2-chlorotoluene which shows the results of the interlaboratory trial for the validation of ISO 17943. The purple horizontal line is the assigned value; the green horizontal line is overall mean.



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VOCOL® Capillary GC Column, 60 m × 0.25 mm, df 1.50 µm	1	**24154**

Description	Qty.	Cat.No.
Reference Standards		
ISO 17943 57 Component VOC Mix, 200 µg/mL each component in methanol, 1 mL, Certified Reference Material	1 mL	**44926-U**
SO 17943 Odor Compounds Mix, 200 µg/mL each component in methanol, 1 mL, Certified Reference Material	1 mL	**44923-U**
1,3,5-Trichlorobenzene Certified Reference Material, TraceCERT®	100 mg	**3824**
Vinyl chloride solution 200 µg/mL in methanol, analytical standard	1 mL	**48625**
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Magnetic Screw Cap for Headspace Vials, 18 mm thread PTFE/silicone septum, septum thickness 1.3 mm, Pk. 100	100	**SU860101**

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SPME fiber Divinylbenzene/Carboxen®/ Polydimethylsiloxane (DVB/CAR/PDMS), 23 ga, StableFlex™, for use with autosampler	3	**57298-U**
SPME fiber Carboxen®/Polydimethylsiloxane (CAR/PDMS) df 85 µm, needle size 23 ga, StableFlex™, for use with autosampler	3	**57295-U**

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