

IMPROVED DETERMINATION OF VOLATILE ORGANIC COMPOUNDS IN WATER BY SPME AND GC/MS: ISO STANDARD 17943

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 limits of detection and easy automation of the whole method. GC/MS provides the required sensitivity and selectivity. This ISO Standard was validated by an interlaboratory trial, with results confirming the outstanding performance for this method.

Introduction

Volatile organic compounds (VOCs) can occur from natural sources such as plant scents. However, a large amount of VOCs do have anthropogenic origin, because they are emitted from products of daily use or emitted during the manufacturing of such products as well as from polymers, adhesives, paints, petroleum products and pharmaceuticals. Typical applications for VOCs are additives for gasoline or use 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 world wide.

Due to this many international regulations have been set up to limit and control the amount of VOCs in drinking water, ground water or surface water. Examples for such regulations are the Safe Drinking Water Act (SDWA) [5] in the U.S and a corresponding law in Canada, that establish 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 [1]. In EU Water Framework Directive (WFD) in article 16 of the Directive 200/60/EC [2] a "Strategy against pollution of water" is described. One measure to ensure good quality of water is a "phasing out" of priority hazardous substances. The later published Annex X [3] lists many VOCs in the priority substance list. 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 any more. ISO 10301 [6] 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 [7] employs for the determination of VOCs in water 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. Furthermore, LLE is not considered to be of greater relevance for such analysis in today's world. ISO 15680 [8] 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 for contamination and that automation is rather challenging to achieve [9].

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 [10] (Fig. 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 regular GC autosamplers since 1993. The use of SPME for the extraction of VOCs out of water is described in several publications [11-19]. In these publications headspace SPME (HS-SPME) proved as a reliable and beneficial alternative to classical methods for VOC determination in water. Furthermore SPME is successfully used in many other official methods [20-24].

Due to this a 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 BTEX 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, ground water, surface water and treated waste water 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 at least 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.



Figure 1: SPME fiber holder with fiber immersed into aqueous sample

ISO standard 17943 was derived from DIN 38407-41 [25]. This German standard method covered 25 VOCs only and was limited to drinking water, ground water and surface water. With the creation of this ISO standard the scope was expanded to more than twice the number of VOCs and the matrixes have been extended to include treated waste water.

Global Interlaboratory Trial for Validation of new ISO Standard 17943

Within the development of this new ISO standard an international interlaboratory trial was conducted to validate the new method [26]. Each of the labs had to determine the concentration of 61 compounds (1,3,5-trichlorobenzene had to be excluded, because it is considered as a precursor for explosives compromising the shipment of the samples and m-xylene was excluded due to the high probability of co-elution with p-xylene) in the two water samples (one surface water, one waste water). The surface water sample was taken from an urban and industrialized area (river Ruhr in Muelheim, Germany) and did undergo a filtration using a glass fiber filter and stabilization with 50 mg/L sodium azide. The municipal waste water sample was taken from a plant effluent. This sample was pre-treated more comprehensively by sedimentation, by filtration through both 5 µm and 1 µm filters and irradiated by UV to avoid any degradation of the spiked analytes. Sterilization was conducted at 80 °C and final stabilization with 50 mg/L sodium azide. These sample have 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 waste water. Prior to delivery to the participants the samples were tested for homogeneity and stability. The labs in the interlaboratory trial had to conduct four independent replicate analyses from each of the 2 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 serve for preparation of the corresponding aqueous multi-component reference solutions used for calibrating of the total procedure. The results had to be delivered within 30 days after receipt of the samples.

The Supelco Application Lab was one participant at the interlaboratory trial. The two water samples have been analyzed according to the drafted ISO Standard 17943 (Tab. 1 and 2, Fig. 2) using toluene-d8, benzene-d6 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. This was used by the majority of the interlaboratory trial participants, too. A smaller share of the labs used the 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.

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 [27]. Nine laboratories did not submit any result. Six labs had to be excluded from the valuation due to significant deviation from the prescribed procedure in terms of calibrating without using internal standards (three laboratories) or other major deviations from the drafted ISO/CD 17943 (three laboratories). Some single results had to be excluded due to outliers.

All 61 parameters have been analyzed by ten labs and nearly all parameters have 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 very 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 Fig. 3 for 2-chlorotoluene. For this compound results from 24 labs could be evaluated. The overall mean value (red line) is very close to the assigned value (blue line). The majority of the 24 labs, even those labs that have been new to SPME, achieved results very close to the assigned value. The recovery rate for more than 90% of the compounds is between 84 and 116 % (surface water) and 81 and 118 % (waste water). The reproducibility (variation between laboratories) is for more than 90% of the compounds less than 31 % (surface water) and less than 35 % (waste water) while the repeatability (variation within a lab) is for more than 90% of the compounds less than 10 % (surface water) and less than 8 % (waste water).

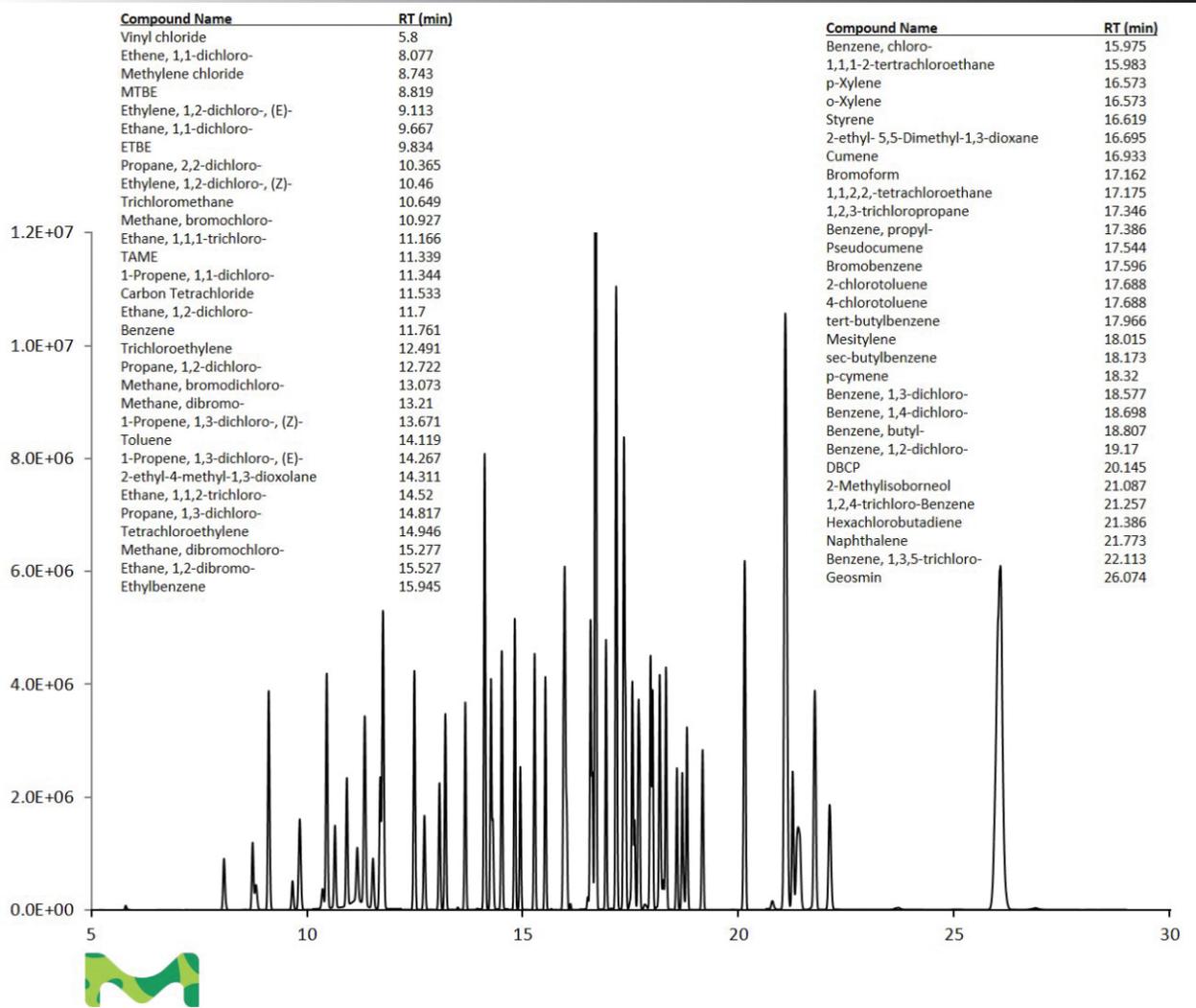


Figure 2: Chromatogram of 61 VOCs in water after HS-SPME using a VOCOL GC column on Agilent GC/MS

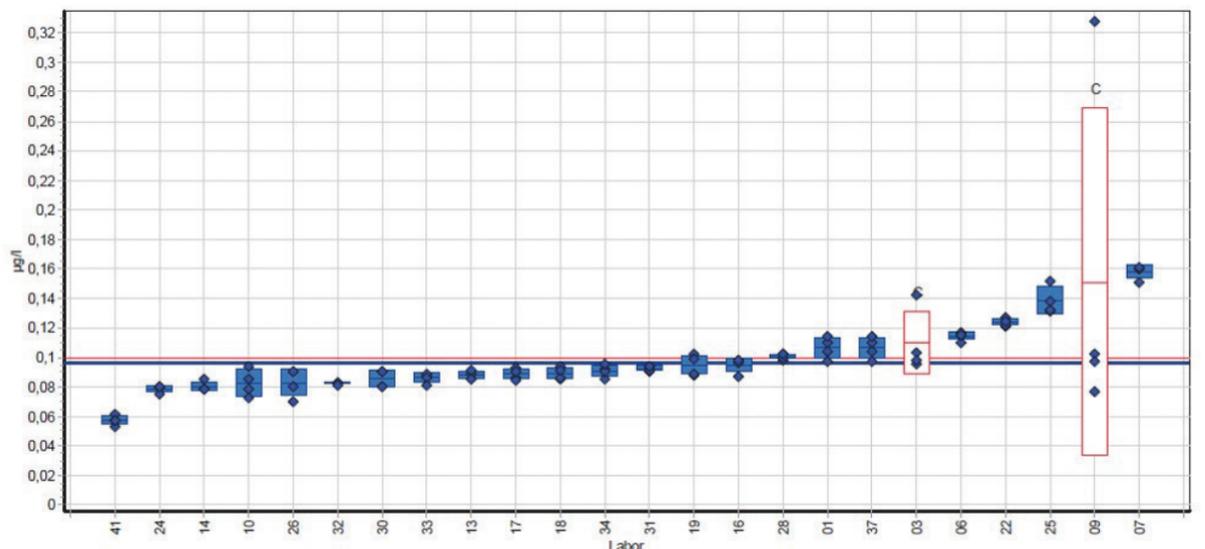


Figure 3: Graphical presentation of the results of participating labs at the interlaboratory trial for the validation of ISO 17943 at the example of 2-chlorotoluene. The blue horizontal line is the assigned value, the red horizontal line is overall mean. Data from Report "ISO 17943 – interlaboratory trial for validation on VOCs (ISO/TC 147/SC 2)", IWW Water Centre, Muelheim an der Ruhr, December 2013.

Tab. 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 Combi PAL (agitated by circular motion of the vial, velocity: 250 rpm)
Desorption/Injector:	10 min @ 270 °C

Tab. 2: Conditions for GC/MS analysis

GC:	Agilent GC/MS
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

Summary

The outstanding results in the interlaboratory trial underline 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 improves existing official methods for this determination in terms of sensitivity and selectivity. In addition, the capability for full automation of SPME is highly beneficial to run this analysis 24/7.

To find out more, go to sigmaaldrich.com/spme

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