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Comparison of EG-Silicone-SBSE and Derivatization-PDMS-SBSE for the Analysis of Phenolic Compounds and Off-flavors in Water

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Abstract

16 phenolic compounds along with typical drinking water off-flavor compounds like geosmin, 2-methylisoborneol (MIB), and 2,4,6-trichloroanisole (TCA) were determined using two different approaches: 1) In-situ derivatization with acetic anhydride followed by SBSE using the PDMS Twister and Thermal Desorption TD-GCMS; 2) Direct SBSE without derivatization using the EG-Silicone Twister and subsequent TD-GCMS. In the case of the EG-Silicone twister, derivatization is not required due to its higher affinity for polar compounds. Both methods were evaluated for the extraction of 0.01 to 1 µg/L of phenols from water samples. Good linearity (> 0.996 for EG-Silicone Twister and > 0.993 for PDMS Twister with derivatization) and repeatability (0.7-11.8% RSD for EG-Silicone Twisters and 1.0-13.6% RSD for PDMS Twisters) were achieved for both methods. Limits of detection (LODs) were in the range 0.007-0.036 µg/L for the EG-Silicone Twister and 0.011-0.053 µg/L for the PDMS Twister respectively. The recoveries obtained with EG-Silicone Twisters were between 17% (2-methylphenol) and 127% (2,3,5-trichlorophenol). Both Twister types were successfully applied for the analysis of phenolic compounds in tap water samples.

Introduction

The presence of phenolic compounds in the aquatic environment is the result of their industrial application for plastics, dyes, drugs, pesticides, antioxidants, paper and in petrochemical products. Phenols are an important raw material and additive for many industrial purposes. Chlorophenols are present in drinking-water as a result of chlorination of phenols during disinfection, as by-products of the reaction of hypochlorite with phenolic acids, as biocides, or as degradation products of phenoxy herbicides [1]. Within the huge group of phenolic compounds, several compounds are important water pollutants due to their character as endocrine disrupters and possible carcinogens. At levels of only a few ppb, phenols can affect the taste and odor of water and fish. The United States Environmental Protection Agency (EPA) lists eleven common phenols including 2,4,6-trichlorophenol, 2-chlorophenol, 2,4-dichlorophenol, 2,4-dimethylphenol and Pentachlorophenol as priority pollutants [2]. In European, the European Union (EU) has classified several phenols as priority contaminants in water. The European Community's drinking water framework directive 80/778/EC regulates a maximum admissible total concentration of 0.5 µg/L and maximum individual concentration of 0.1 µg/L for phenols in drinking water. In the 2011 German Federal Law Gazette for surface and costal waters, maximum concentration limits for 11 phenols are also given [3].

To reach the quantification limits required for the determination of phenols in drinking water, a concentration step is necessary. Liquid/liquid extraction (LLE), solid phase extraction (SPE), solid phase microextraction (SPME) and stir bar sorptive extraction (SBSE) are commonly used extraction- and concentration techniques [4-9]. LLE is prescribed in standard official methods for determination of phenols in water. US EPA Method 604 stipulates that one to two liters of water must be extracted with an appropriate amount of methylene chloride. The methylene chloride extract is then concentrated by evaporation to a volume of 10 mL or less and the solvent exchanged with 2-propanol followed by derivatization and GC/MS determination. In comparison with LLE, SPE requires much less solvent when different sorbents are used

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for the extraction. Only a small amount of solvent is then used to elute the extracted analytes, but drying, (evaporative) concentration and derivatization must still be performed before GC/MS determination. SPME and SBSE, in contrast, are solvent free techniques. Compared with LLE and SPE, only a small water sample is needed for analysis. Depending on the sorbent materials used, the extraction can be performed with or without derivatization.

Experimental

Standards and Water Samples

EPA 8040 phenol calibration mix (500 µg/mL each in isopropanol), 2-isopropyl-3-methoxypyrazine (100 µg/mL in methanol), 2-isobutyl-3-methoxypyrazine (100 µg/mL in methanol), 2,4,6-tribromophenol (1 g), 2,4-dibromophenol (1 g), 2,4,6-trichloroanisole (1 g), geosmin and 2-methylisoborneol (100 µg/mL in methanol) were purchased from Sigma-Aldrich. All standards were diluted to a stock concentration of 100 µg/L in methanol and used to spike 10 mL water samples to the required calibration levels. Methanol of analysis grade and HPLC water were obtained from Merck. Acetic acid anhydride, potassium carbonate and hydrochloric acid of analysis grade were obtained from Sigma-Aldrich. The stock solution and standard solutions were all stored in a refrigerator at 4 °C.

Calibration solutions were prepared with HPLC water with 5% (v/v) methanol added to prevent a possible glass wall adsorption effect of the analytes. For EG-Silicone Twister extraction, the pH value was adjusted to pH=4 with hydrochloric acid to ensure that phenolic compounds were present in their non-dissociated form. Tap water samples were obtained from Wakefield, England and Mülheim an der Ruhr, Germany.

Sample Preparation - Extraction with PDMS Twisters

Before extraction with PDMS Twisters, the phenols were acetylated by adding acetic anhydride and potassium carbonate to the samples [9]. Derivatization was necessary in order to increase SBSE analyte recovery with the PDMS Twister and to provide better peak shapes on non-polar GC columns.

To prepare the calibration solutions, a mixture of LC grade water with 5% methanol was spiked with standard solutions to the required concentrations ranging from 0.01 to 1.0 µg/L. The water samples were also modified with 5% (v/v) methanol to prevent analyte adsorption on the sample vial walls. One gram of potassium carbonate was placed into each 20 mL vial and conditioned at 110 °C for 15 minutes. Then a 10 mL aliquot of the water sample was pipetted into a 20 mL vial and 0.5 mL acetic acid anhydride

(Sigma-Aldrich) was added. A vial screw cap was loosely placed onto the vial to contain sample spray resulting from the CO_2 formation while still enabling the release of excess pressure. The vials were shaken for 10 minutes. The PDMS Twister was then placed into the sample and the vial was cap was firmly closed.

For each of the seven calibration levels, five replicate extractions were performed using 10 mm GERSTEL Twisters (24 µL PDMS phase volume). SBSE was performed at room temperature for two hours, stirring at 1200 rpm on a multiple position magnetic stirplate. Following the extraction step, the Twisters were removed from the samples using a magnetic rod and then dried with a lint-free tissue and placed in individually sealed glass liners in the autosampler tray for analysis.

Sample Preparation - Extraction with EG-Silicone Twisters

Due to the ethylene glycol composition of the EG-Silicone phase, no derivatization is needed when it is used for extraction of phenolic compounds. 10 mL aliquots of sample were pipetted into 10 mL vials. Before extraction, the pH value was adjusted to pH=4 in order to prevent dissociation of the phenols. EG-Silicone Twisters were then placed in the samples and the vials sealed with screw caps. The extraction conditions were similar to those used with PDMS Twisters: 2 hours at room temperature while stirring at 800 rpm. For each of the seven calibration levels, five replicate extractions were performed.

Instrumentation

The TD-GC/MS analysis was performed using the GERSTEL LabWorks Platform on an Agilent 7890A gas chromatograph with an Agilent 5975 mass selective detector (MSD). The entire analysis system was operated under GERSTEL MAESTRO software control integrated with ChemStation software (Agilent Technologies) using one integrated method and one integrated sequence table.

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Analysis Conditions LabWorks Platform (PDMS Twister)
TDU
Temperature	40 °C (0.2 min); 720 °C/min to 270 °C (5min)
Pneumatics	40 mL/min solvent vent (0.5 min)
	splitless

CIS 4
Temperature	-100 °C (0.2 min); 12 °C/s to 250 °C (8 min)
Pneumatics	solvent vent, splitless (2 min)
Liner	glass wool deactivated, d_i = 2 mm

Analysis Conditions Agilent 7890 GC (PDMS Twister)
Oven	50 °C (2 min); 5 °C/min to
	115 °C (5 min); 25 °C/min to 320 °C (4 min)
Column	30 m Rxi-5ms (Restek)
	d_i = 0.25 mm d_f = 0.25 µm
Pneumatics	He, constant flow = 1 mL/min

Analysis Conditions LabWorks Platform (EG-Silicone Twister)
TDU
Temperature	40 °C (0.2 min); 720 °C/min to 220 °C (5min)
Pneumatics	40 mL/min solvent vent (0.5 min)
	splitless

CIS 4
Temperature	-100 °C (0.2 min); 12 °C/s to 250 °C (8 min)
Pneumatics	solvent vent, splitless (2 min)
Liner	glass wool deactivated, d_i = 2 mm

Analysis Conditions Agilent 7890 GC (EG-Silicone Twister)
Oven	40 °C (2 min); 20 °C/min to
	100 °C; 3 °C/min to
	238 °C; 15 °C/min to 250 °C (3 min)
Column	30 m Stabilwax-DA (Restek)
	d_i = 0.25 mm d_f = 0.25 µm
Pneumatics	He, constant flow = 1 mL/min

Analysis Conditions Agilent 5975 MS (both Twister)
MSD	SIM mode

Results and Discussion
PDMS Twister

The low polarity of the acetylated phenols enabled separation on an Rxi-5ms (Restek) column. Figure 1 shows an overlay of SIM traces at 7 calibration levels (0.01-1 µg/L).
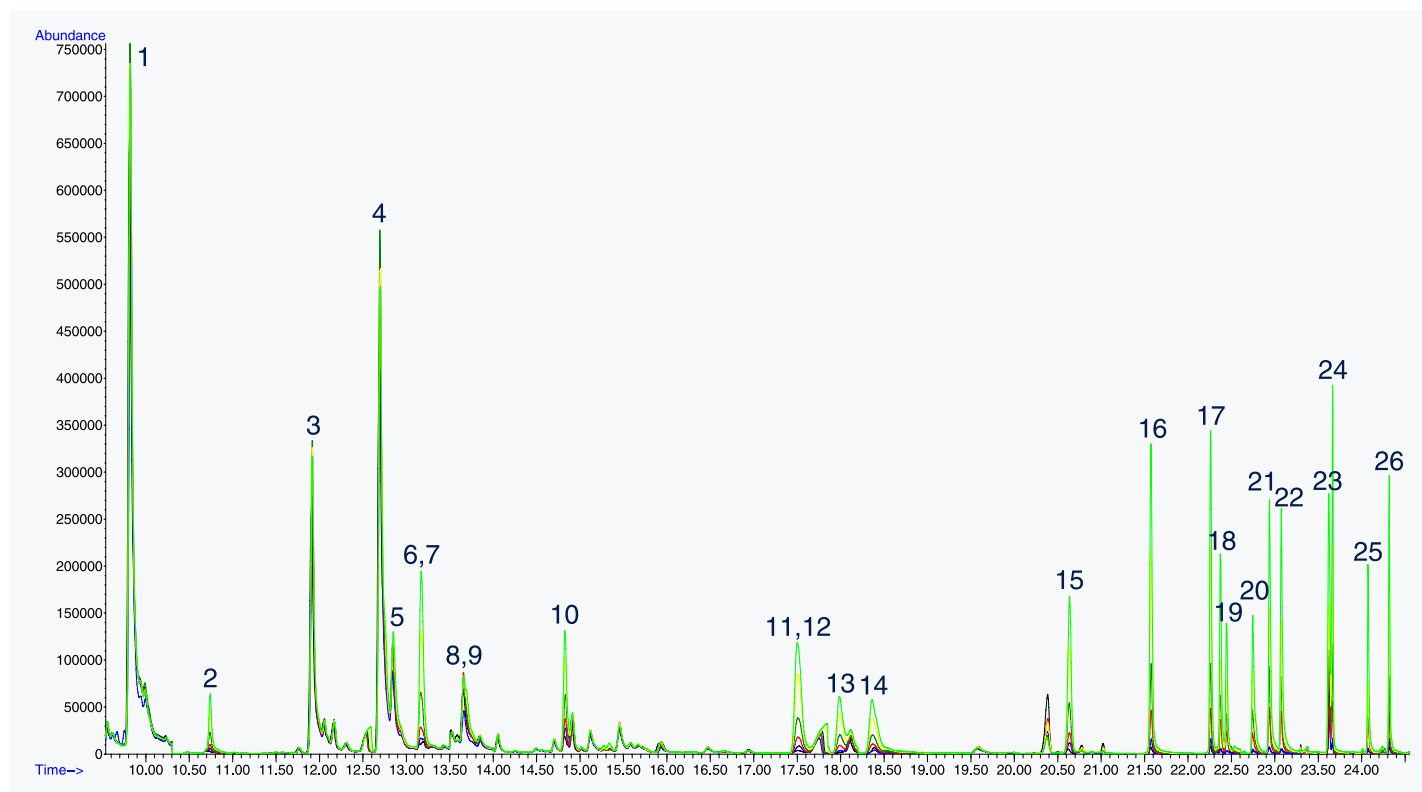
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Figure 1: Selected ion monitoring (SIM) chromatograms obtained from 7 calibration levels after extraction with PDMS Twisters. Column: Rxi-5ms (30 m x 0.25 µm x 0.25 mm), splitless.

Table 1: List of target compounds identified in the SIM chromatograms resulting from PDMS Twister extractions.

No.	Compound	No.	Compound	No.	Compound
1	Phenol	10	2,4-Dimethylphenol	19	2,3,5-Trichlorophenol
2	2-Isopropyl-3-methoxypyrazine	11	2,6-Dichlorophenol	20	2,4-Dibromophenol
3	2-Methylphenol	12	2,4,6-Trichloroanisole (TCA)	21	2,3,6-Trichlorophenol
4	3-Methylphenol	13	4-Chloro-3-methylphenol	22	3,4,5-Trichlorophenol
5	4-Methylphenol	14	2,4-Dichlorophenol	23	2,3,5,6-Tetrachlorophenol
6	2-Methylisoborneol (MIB)	15	Geosmin	24	2,3,4,6-Tetrachlorophenol
7	2-Isobutyl-3-methoxypyrazine	16	2,4,6-Trichlorophenol	25	2,3,4,5-Tetrachlorophenol
8	2-Chlorophenol-3,4,5,6-d4 (ISTD)	17	2,3,4-Trichlorophenol	26	2,4,6-Tribromophenol
9	2-Chlorophenol	18	2,4,5-Trichlorophenol		

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The instrument blank chromatogram (figure 2) and the Twister blank chromatogram show no peaks that interfere with the peaks of interest. However, the reagent blank chromatogram (including blank sample, potassium carbonate, acetic anhydride and the PDMS Twister) shows signals for phenol and methylphenols. Due to this reagent background, the calibration curves for these compounds (highlighted in table 1) were not satisfactory in terms of the linearity achieved and they were not determined in this study.

Unfortunately, the instrumentation was not available to continue and pursue clarification of the matter with a different reagent. The time required for the derivatization is approximately 30 minutes (baking out potassium carbonate, adding sample & reagent, shaking), but multiple samples can be handled simultaneously, enabling the preparation of a large number of samples in approximately the same amount of time.
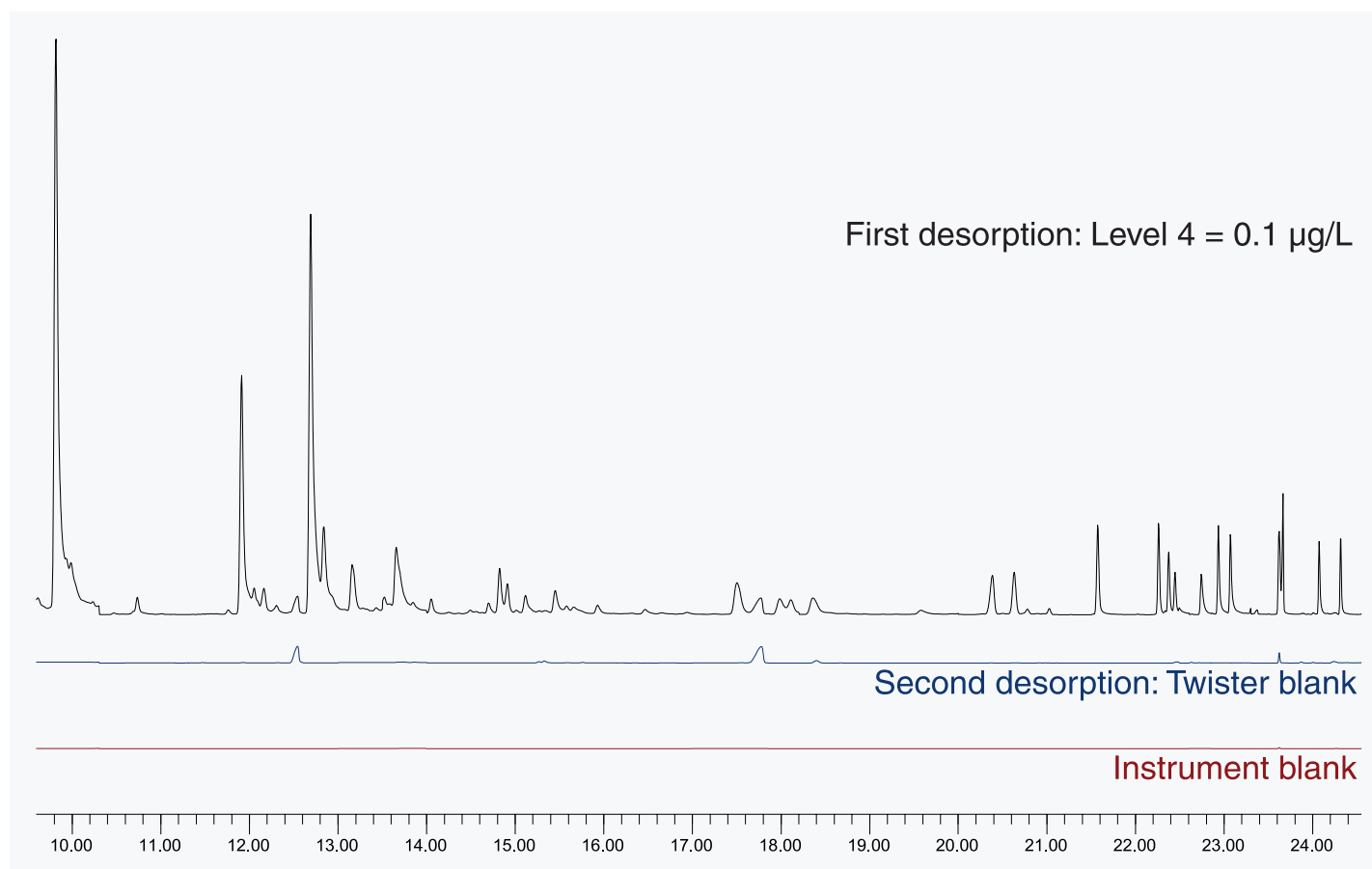

First desorption: Level 4 = 0.1 µg/L

Second desorption: Twister blank

Instrument blank

Figure 2: Selected ion monitoring (SIM) traces obtained from PDMS Twister extraction of derivatized phenols: First desorption after extraction of a 0.1 µg/L spiked water sample (blue trace); Second desorption of the same Twister showing the blank chromatogram (red trace); The instrument blank chromatogram without Twister (green trace). Column: Rxi-5ms (30 m x 0.25 µm x 0.25 mm), splitless analyte transfer.

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EG-Silicone Twister
In order to obtain good separation and good peak shape for underivatized phenols, a wax column (Stabilwax-DA, Restek) was used. The instrument parameters were the same as those used for the PDMS Twister apart from the GC oven program and the analyte ion masses monitored. The different TDU final desorption temperatures of 270 °C and 220 °C reflect the lower maximum desorption temperature of EG Silicone Twisters.

Figure 3 shows the SIM chromatograms obtained from seven calibration levels. The identified analytes are listed in table 2.
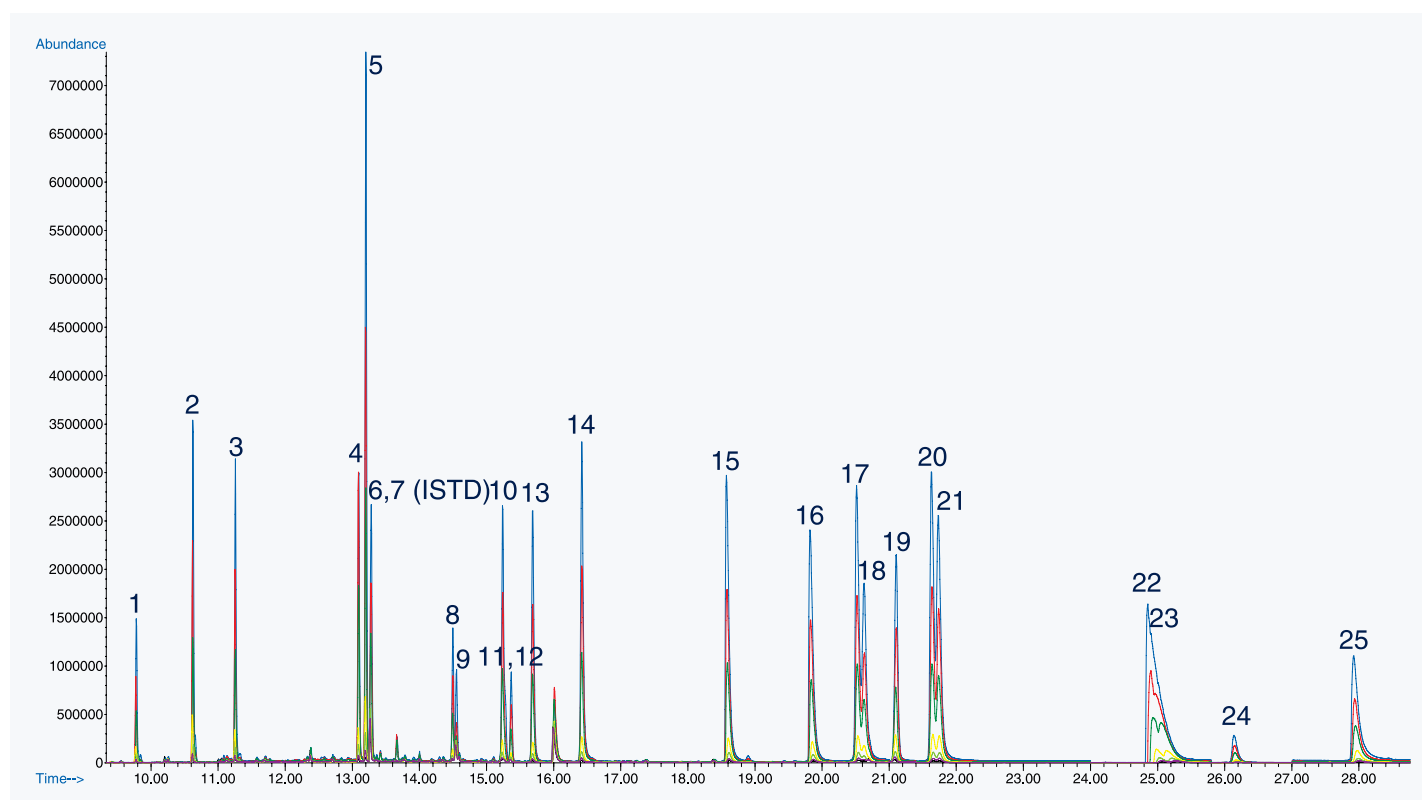

Figure 3: Selected ion monitoring (SIM) chromatograms obtained at 7 calibration levels based on extractions with EG-Silicone Twister. Column: Stabilwax-DA (30 m x 0.25 µm x 0.25 mm), Restek, splitless.

Table 2: List of target compounds identified in the SIM chromatogram based on extraction with EG-Silicone Twister.

No.	Compound	No.	Compound	No.	Compound
1	2-Isopropyl-3-methoxypyrazine	10	2,4-Dimethylphenol	19	4-Chloro-3-methylphenol
2	2-Isobutyl-3-methoxypyrazine	11	4-Methylphenol	20	3,4,5-Trichlorophenol
3	2-Methylisoborneol (MIB)	12	3-Methylphenol	21	2,4,5-Trichlorophenol
4	2,4,6-Trichloroanisole (TCA)	13	2,6-Dichlorophenol	22	2,3,5,6-Tetrachlorophenol
5	Geosmin	14	2,4-Dichlorophenol	23	2,3,4,6-Tetrachlorophenol
6	2-Chlorophenol	15	2,4,6-Trichlorophenol	24	2,4,6-Tribromophenol
7	2-Chlorophenol-3,4,5,6-d4 (ISTD)	16	2,3,6-Trichlorophenol	25	2,3,4,5-Tetrachlorophenol
8	2-Methylphenol	17	2,3,5-Trichlorophenol		
9	Phenol	18	2,4-Dibromophenol		

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Phenol is highlighted in the table because insufficient linearity was achieved due to an enhanced background value for phenol. The instrument used for this work is often used for customer samples and was available only for a short period of time, so this matter could unfortunately not be pursued further. Presumably, it would have been a matter of cleaning the inlet system properly. In a previously reported work (GERSTEL AppNote 2/2012) excellent linearity and very low background were demonstrated for both phenol and cresols using a similar system with an FFAP column. 3- and 4-methylphenol are equally greyed out in the table because they co-elute (peak no. 11 and 12 in the chromatogram).

Since they both have the same mass-to-charge ratio, it is difficult to determine them individually. As a result, these three compounds were not evaluated further.

The carryover and blank values were also tested. In figure 4, it can be seen that the chromatogram shows little carryover effect after the second desorption with the same EG-Silicone twister except for peak 9 (phenol) as explained earlier. The instrument blank afterwards shows the same peak for phenol. No phenol peak was found in the Twister blank chromatogram obtained directly after conditioning.
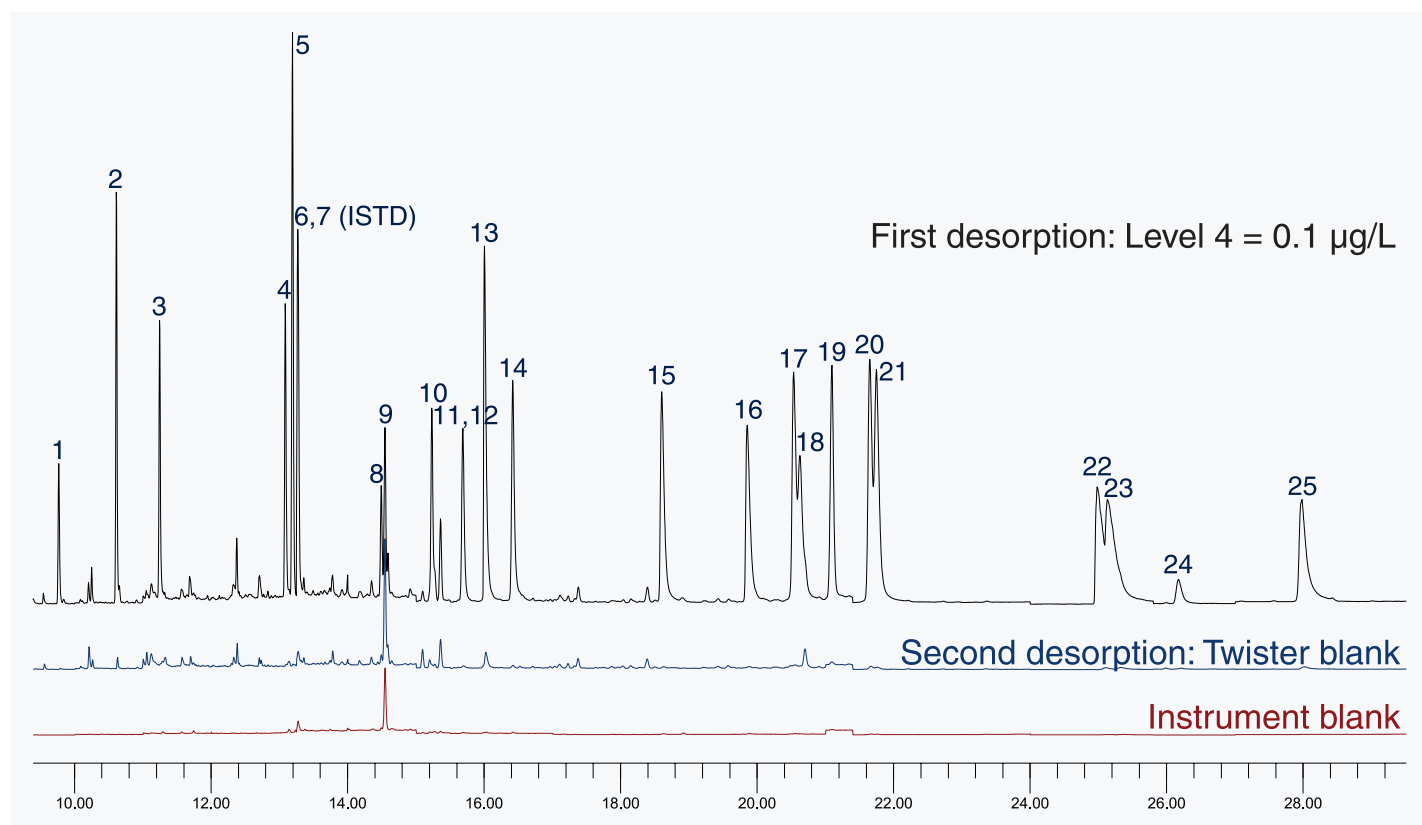

Figure 4: Selected ion monitoring (SIM) chromatograms resulting from EG-Silicone Twister extractions: First desorption after extraction of a water sample spiked at 0.1 µg/L (blue); Second desorption using the same Twister for the Twister blank chromatogram (red); The instrument blank chromatogram without Twister (green). Stabilwax-DA (30 m x 0.25 µm x 0.25 mm), splitless.

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SBSE Recovery of Phenolic Compounds when using the EG-Silicone Twister

In order to determine the SBSE extraction efficiency for each compound, splitless liquid injections into the CIS were performed for comparison. A 6-point calibration for the liquid injection method was performed covering the concentration range from 0.05 ng/µL to 5 ng/µL in acetone. Each concentration level was analyzed in triplicate. The injection volume used was 1 µL. The squared correlation coefficients (R^2) were found to be in excess of 0.999, which shows excellent linearity.

The amount of extracted analytes was calculated using the linear equation obtained from liquid calibration curves. Recovery was calculated by dividing extracted amount of each compound with the total amount spiked into the water sample. Average recoveries were obtained at the seven Twister calibration levels (0.01 - 0.75 µg/L). At each concentration level, five replicate measurements were done. The relative standard deviations (RSDs) were found to be between 1% and 8% (table 3). Average recoveries ranged from 17% (2-methylphenol) to 127% (2, 3, 5-tricholorophenol).

It can be seen in figure 5 that with the exception of the five off flavor compounds 2-isopropyl-3-methoxypyrazine, 2-isobutyl-3-methoxypyrazine, 2-methylisoborneol, geosmin and 2,4,6-trichloroanisole, average recoveries increase with increasing log $K_{o/w}$ value. For the series 2-chlorophenol, dichlorophenols, trichlorophenols and tetrachlorophenols, solubility in water decreases with increasing number of halogens in the molecule.

Table 3: Average recoveries (%) of phenolic and off flavor compounds determined at seven concentration levels listed with the associated relative standard deviations (% RSD) achieved using EG-Silicone Twister (n=5). Compounds are listed according to their log $K_{o/w}$ value.

| Compound	Average Rec (%)	RSD (%)	Log $K_{O/w}$ *
2-Methylphenol	17	8.1	2.06
2-Chlorophenol	26	5.9	2.16
2-Isopropyl-3-methoxypy-razine	27	4.8	2.37
2,4-Dimethylphenol	30	6	2.61
4-Chloro-3-methylphenol	53	2.9	2.7
2,6-Dichlorophenol	56	3.6	2.8
2,4-dichlorophenol	74	1.8	2.8
2-Isobutyl-3-methoxypyra-zine	28	6.4	2.86
2,4-Dibromophenol	96	2.3	3.29
2-Methylisoborneol	34	4.1	3.31
2,4,6-Trichlorophenol	115	4.3	3.45
2,3,6-Trichlorophenol	123	3.4	3.45
2,3,5-Trichlorophenol	127	4.2	3.45
3,4,5-Trichlorophenol	104	1.3	3.45
2,4,5-Trichlorophenol	123	1.7	3.45
Geosmin	81	1.9	3.57
2,4,6-Trichloroanisole	73	3.5	4.01
2,3,5,6-Tetrachlorophenol	115	6.1	4.09
2,3,4,6-Tetrachlorophenol	112	5.4	4.09
2,3,4,5-Tetrachlorophenol	111	2	4.09
2,4,6-Tribromophenol	103	5.7	4.18

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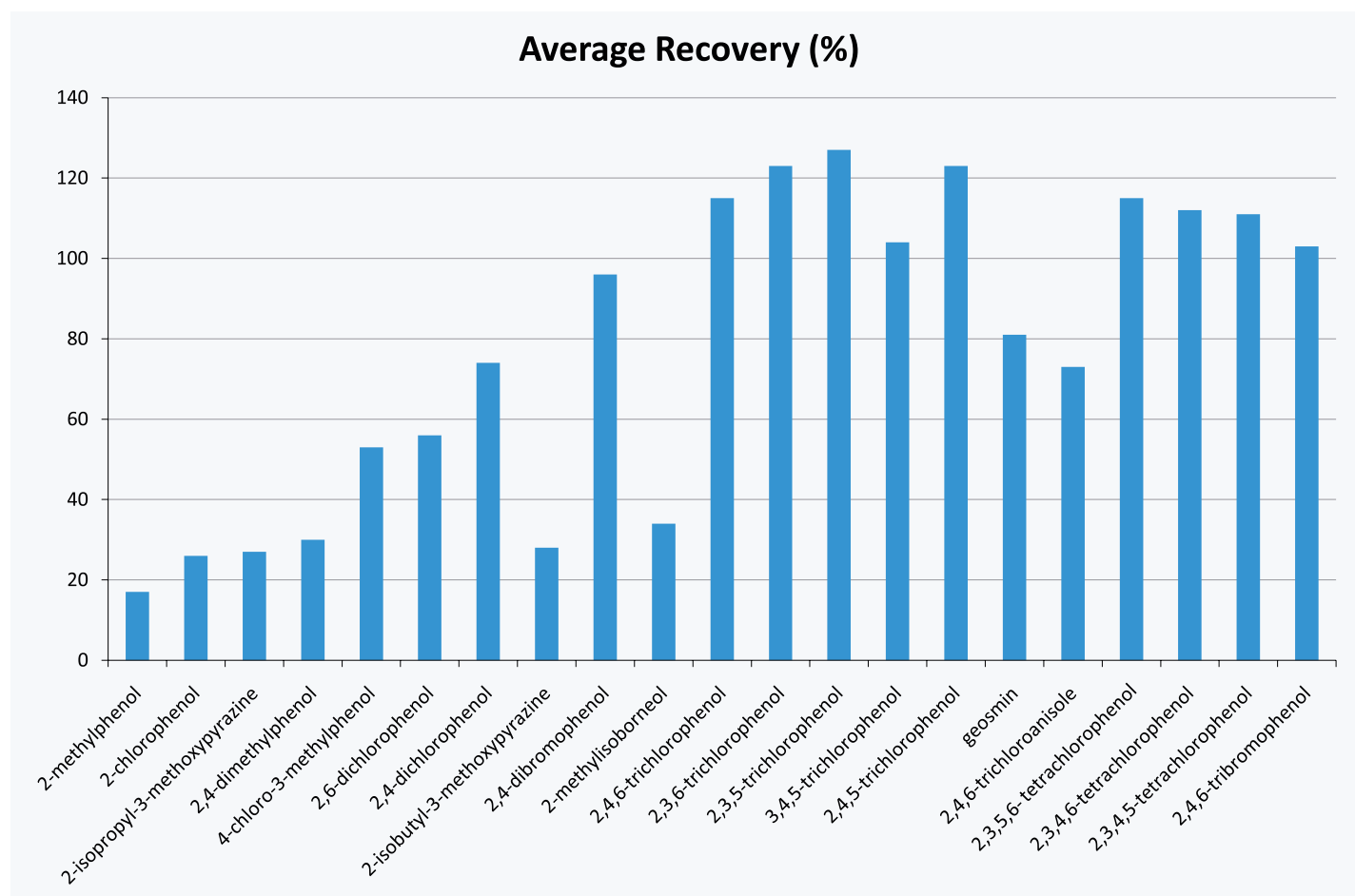
Figure 5: Average recoveries of phenolic and malodor compounds obtained from seven calibration levels extracted with EG-Silicone Twister. Compounds are listed with increasing $K_{o/w}$ value from left to right.

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Linearity, Limits of Detection and Limits of Quantification for both methods

Limits of detection (LODs) and limits of quantification (LOQs) of all compounds achieved with both Twisters were calculated according to DIN 32 645 based on the calibration curve [10]. LODs were calculated according to Eq. (1):

$$x_{LOD} = \frac{s_y}{b} \; t_{f,\alpha} \sqrt{\frac{1}{N_a} + \frac{1}{N_c} + \frac{\overline{x}^2}{\sum (x_i - \overline{x})^2}}$$

(1)

s_y = residual standard deviation

b = slope of the linear calibration curve

$t_{f,\alpha}$ = the value of student t-distribution at freedom of f and significant level of α (here α = 0.05, single side)

$f = N_c - 2$

N_a = number of multiple analyses of a sample (here N_a = 5)

N_c = number of calibration concentration level

$\overline{x}$ = mean of the standard concentrations x_i

LOQs were calculated according to Eq. (2):

$$x_{LOQ} = k \; \frac{s_y}{b} \; t_{f,\alpha} \sqrt{\frac{1}{N_a} + \frac{1}{N_c} + \frac{(k \; x_{LOD} \; \overline{x})^2}{\sum (x_i - \overline{x})^2}}$$

(2)

k = factor for calculating the limit of quantification (k-Factor represents the maximum acceptable relative uncertainty)

Here a k-factor value of 3 was used for all calculations, which means that 33.3% is the maximum acceptable uncertainty. The summary of LODs and LOQs of selected compounds determined for the two types of Twister is listed in Table 4 along with the squared correlation coefficients (R^2).

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Table 4: LODs and LOQs (µg/L) for phenolic and off flavor compounds and their linear squared correlation coefficients (R², N=5) achieved with derivatization-PDMS-SBSE and EG-Silicone-SBSE respectively.

	Compound	LOD (µg/L)		LOQ (µg/L)		R²	
		EG-Silicone	PDMS	EG-Silicone	PDMS	EG-Silicone	PDMS
1	2-Isopropyl-3-methylpyrazine	0.024	0.039	0.08	0.12	0.999	0.997
2	2-Isobutyl-3-methylpyrazine	0.027	0.033	0.09	0.1	0.998	0.996
3	2-Methylisoborneol (MIB)	0.024	0.017	0.08	0.06	0.999	0.997
4	2,4,6-Trichloroanisole (TCA)	0.021	0.035	0.07	0.1	0.999	0.998
5	Geosmin	0.021	0.011	0.07	0.04	0.999	0.999
6	2-Chlorophenol	0.03	0.032	0.1	0.1	0.998	0.998
8	2-Methylphenol	0.022	n.a.	0.07	n.a.	0.999	n.a.
10	2,4-Dimethylphenol	0.027	0.053	0.09	0.16	0.998	0.996
13	2,6-Dichlorophenol	0.035	0.018	0.11	0.06	0.998	0.998
14	2,4-Dichlorophenol	0.035	0.025	0.11	0.07	0.998	0.997
15	2,4,6-Trichlorophenol	0.032	0.02	0.11	0.07	0.997	0.997
16	2,3,6-Trichlorophenol	0.036	0.029	0.12	0.09	0.997	0.997
17	2,3,5-Trichlorophenol	0.033	0.014	0.11	0.05	0.997	0.996
18	2,4-Dibromophenol	0.007	0.021	0.03	0.07	1	0.996
19	4-Chloro-3-methylphenol	0.024	0.016	0.08	0.05	0.999	0.998
20	3,4,5-Trichlorophenol	0.033	0.032	0.11	0.1	0.998	0.995
21	2,4,5-Trichlorophenol	0.03	0.054	0.1	0.14	0.997	0.994
22	2,3,5,6-Tetrachlorophenol	0.032	n.a.	0.1	n.a.	0.997	n.a.
23	2,3,4,6-Tetrachlorophenol	0.034	n.a.	0.11	n.a.	0.996	n.a.
24	2,4,6-Tribromophenol	0.03	0.015	0.1	0.05	0.998	0.995
25	2,3,4,5-Tetrachlorophenol	0.03	0.023	0.1	0.07	0.998	0.993

For the EG-Silicone Twister, LODs range from 0.007 µg/L (2,4-dimethylphenol) to 0.036 µg/L (2,3,6-trichlorophenol) and LOQs range from 0.03 µg/L to 0.12 µg/L. The squared correlation coefficients (R²) are larger than 0.996. For the PDMS Twister used in combination with derivatization, LODs range from 0.011 µg/L (geosmin) to 0.054 µg/L (2,4,5-trichlorophenol) and LOQs range from 0.04 µg/L to 0.14 µg/L with R² higher than 0.993. Both SBSE methods meet the requirements of EU water framework directive, which regulates that the concentration of individual phenols in drinking-water should not exceed 0.1 µg/L. Both the techniques described in this work achieve much lower LOQ values than the maximum concentration limits of 1-10 µg/L specified in the Germany federal law gazette for surface and coastal waters.

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Table 5 lists LODs reported in literature for the determination of phenols in water using different sample preconcentration methods in combination with different analytical techniques. By comparison, the SBSE-TD-GC-MS methods based on two different types of Twisters presented in this work achieve low limits of detection (LODs) and low relative standard deviation (RSD %)

Table 5: Literature data for the determination of phenols in water [5].

Method	LOD (µg/L)	RSD (%)	Derivatization reagent	Real Sample
LLE-GC-MS (EPA 625)	1,5 - 42	-	Pentafluorobenzyl bromide	Municipal and industrial waste-water
SPE-CE-DAD	28 - 399	6.7 - 12.3	-	Wastewater
SPE-HPLC-IFD	0.0012 - 66.58		Sodium 1-naphthalenesulfo-nate	Wastewater
SPME-GC-MS	0.052 - 9.1	3,3 - 20	-	Groundwater and surface water
SPME-HPLC-UVD	0.25 - 3.67	1.52 - 6.38	-	River water and wastewater
SBSE-TD-GC-MS	0.1 - 0.4	6 - 27	Acetic anhydride	Groundwater and lake water
PDMS Twister	0.011 - 0.054	1.0 – 13.6	Acetic anhydride	Drinking water
EG-Silicone Twister	0.007 - 0.036	0.7 – 11.8	-	Drinking water

Drinking Water
After method validation for derivatization-PDMS-SBSE and EG-Silicone-SBSE, two tap water samples from England (Wakefield) and Germany (Mülheim an der Ruhr) were analyzed using the EG-Silicone Twister method.

The tap water samples were modified with 5% Methanol and the pH value adjusted to pH=4. Each water sample was analyzed in triplicate and the average concentration calculated from the linear calibration curves. The SIM chromatograms of tap water from England and Germany are shown in figure 6. Only geosmin and 2-methylphenol could be quantified in the Wakefield tap water at concentrations of 0.030 µg/L and 0.028 µg/L respectively. None of the target compounds were found at levels above their respective LOQs in the Mülheim an der Ruhr tap water.

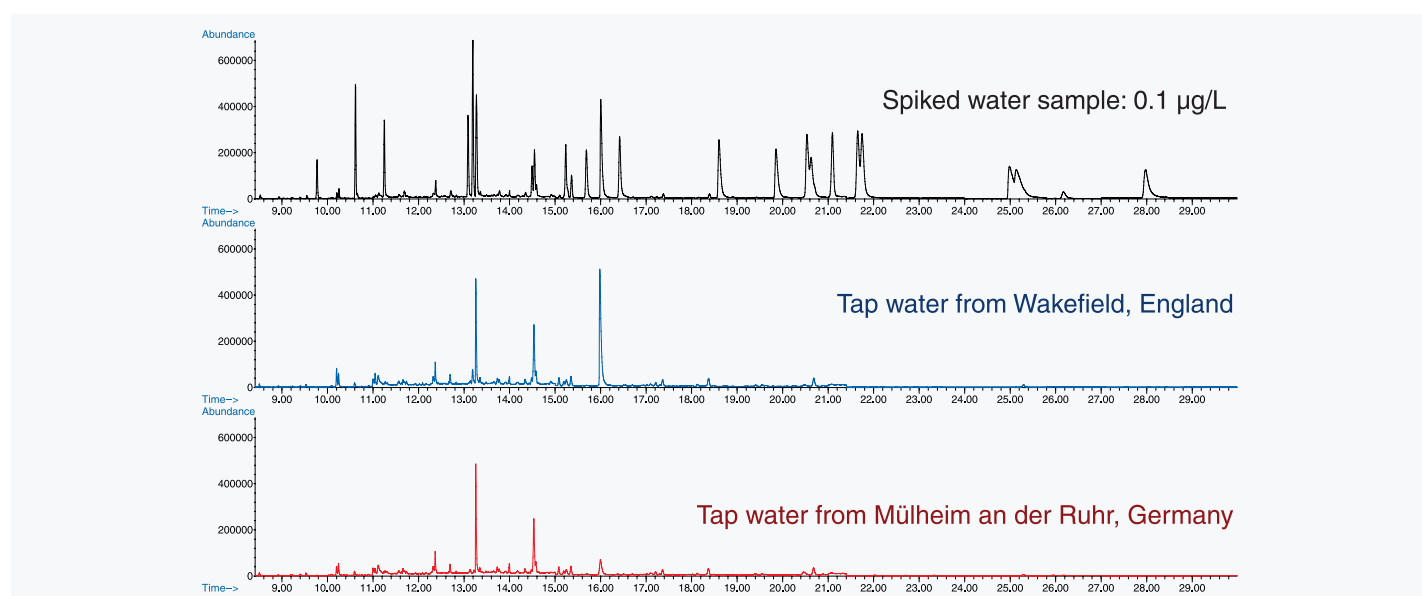**Figure 6:** SIM chromatograms obtained from a water sample spiked at 0.1 µg/L (black), tap water from Wakefield, England (blue) and tap water from Mülheim an der Ruhr, Germany (red) using EG-Silicone-SBSE.

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Conclusion

SBSE-TD-GC/MS methods for the determination of phenols and off flavor compounds in water using two types of Twister were compared and validated. SBSE based on the PDMS Twister used in combination with derivatization and SBSE based on the EG-Silicone Twister used without derivatization both gave similar results: Low limits of detection and quantification, good linearity and repeatability, and negligible carryover.

Based on the low limits of detection, simplicity of use, low cost and high quality of results, SBSE-TD-GC/MS using the GERSTEL LabWorks Platform is a highly suitable tool for the determination of phenols and off flavor compounds in water. The use of a multi-position stir plate enables simultaneous extraction of many samples ensuring high throughput while reducing the amount of time needed for sample preparation.

Acetylation derivatization combined with PDMS Twister extraction is a well-known and proven method for determination of phenols

that enables the use of a standard DB-5 equivalent column for GC/MS, which means the system can easily be used for applications such as pesticide or VOC analysis. The effort required for the derivatization work is very limited. Deuterated internal standards were not used in this study, but might provide additional robustness for more dirty samples such as wastewater. The PDMS Twister's maximum desorption temperature of 300 °C enables better and more complete conditioning, lower background and overall the PDMS Twister offers better long-term stability than the EG-Silicone Twister.

EG-Silicone Twister allows direct extraction from water samples without a derivatization step, saving time and resources. Since non-derivatized analytes are extracted, the recovery is more easily determined using liquid injection of the standard solution as reference. In this work it was found that a 5 min. desorption at 220 °C is sufficient for complete desorption of both phenols and the determined off flavors compounds.

Table 6: Summary of the SBSE-TD-GC-MS methods used for phenols in water with each type of Twister used.

	PDMS Twister	EG-Silicone Twister
Sample Volume (mL)	10	10
Derivatization Reagent	Acetic anhydride + Potassium carbonate	-
Extraction time (h)	2	2
Thermal Desorption	270 °C, Splitless	220 °C, Solvent Vent
Column	Rxi-5ms, 30 m x 0.25 mm x 0.25 μm	Stabilwax-DA, 30 m x 0.25 mm x 0.25 μm
LOD (μg/L)	0.011 – 0.053	0.007 – 0.035
LOQ (μg/L)	0.06 – 0.16	0.03 – 0.11
R^2	>0.993	> 0.996
RSD %	1.0 – 13.6	0.7 – 11.9
Recovery %	-	17 – 127

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