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Determining Phenolic Compounds in Whisky using Direct Large Volume Injection and Stir Bar Sorptive Extraction

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Phenols, Whisky, Capillary GC-MS, LVI, Solvent Vent, TDU, SBSE, Deconvolution

ABSTRACT
In this study, a method was developed for quantitative determination of seven phenolic compounds in scotch whisky. Two different whisky brands were analyzed by Stir Bar Sorptive Extraction (SBSE), based on novel EG-Silicone Twisters, combined with thermal desorption-gas chromatography-mass spectrometry (TD-GC-MS). Direct Large Volume Injection (LVI) -GC-MS was used as reference method. Optimized methods for LVI-GC-MS and SBSE-TD-GC-MS analysis were used for quantitative determination of the target compounds: phenol, o-,m-, and p-cresol, guaiacol, 4-ethylguaiacol, and 4-ethylphenol. Both methods were evaluated regarding linearity of calibration, reproducibility, and limits of detection (LOD), or limits of quantification (LOQ), for the target compounds. These values were calculated for pure whisky (40 % v/v, ethanol/water). Target compound LODs for the SBSE-TD-GC-MS method range from 1.2 ng/mL (guaiacol) to 6.9 ng/mL (4-ethylguaiacol) based on extraction of 5 mL ethanol/water sample. LODs of LVI-GC-MS range from 90 ng/mL (phenol) to 210 ng/mL (4-ethylguaiacol) based on injection of 20 µL ethanol/water sample. Coefficients of determination (R^2) for the calibration curves were found to be higher than 0.999 for the SBSE-based method and between 0.991 and

0.999 for the LVI method. Recoveries of phenolic compounds in ethanol/water matrix using the EG-Silicone Twister were calculated to be between 12.2 % (guaiacol) and 56.8 % (4-ethylguaiacol) with relative standard deviations from 4.2 % to 8.9 %. Comparable quantitative results were achieved using SBSE and LVI to determine concentrations of target compounds in two different whisky brands. Relative standard deviations ranged from 0.8 to 5.4 % for SBSE and 1.6 to 6.2 % for LVI. For GC separation a fast narrow-bore column FFAP was chosen. An MS deconvolution software (IFD™ mass spectral deconvolution algorithms) was applied for quantification of coeluting analytes and analytes masked by matrix.

Introduction

It is well known and documented that phenolic compounds contribute significantly to the smoky and peaty flavor of a whisky. These compounds are even used as indicators when assessing the quality of a peated whisky. The main sources of phenolic compounds are the peating (smoking) process, the kilning (thermal degradation) process, as well as maturation (ageing) in oak barrels. The critical compounds are: Phenol, cresols (o-/p-/m-cresol), xylenols, ethylphenols and guaiacol [1].

The analysis of whisky flavour compounds can be accomplished using GC-MS in combination with sample preparation techniques for extraction and analyte concentration, If the sample could be injected directly without sample preparation, the total time needed for analysis could be reduced significantly. Recently, large volume injection (LVI) of whisky samples in combination with GC-MS was introduced successfully by MacNamara and his colleagues [3]. When combining programmed temperature vaporization (PTV) injection with solvent vent mode, the ethanol-water matrix of whisky can be removed efficiently in the injector. Following the solvent vent step, analytes are transferred highly efficiently to the GC column by rapidly heating the injection port in splitless mode. Up to 20 µL of whisky sample can be directly injected into the Cooled Injection System (CIS) PTV-type inlet without injection speed programming [3]. Up to 100 µL whisky was successfully introduced at a reduced injection rate of 12 µL/min [4]. For optimized conditions recovery higher than 90 % has been reported with good area reproducibility versus added internal standards [4]. An automated liner exchange device (GERSTEL ALEX) is highly recommended to periodically replace the GC-liner when necessary and prevent contamination of the inlet for samples containing non-volatile matrix.

The extraction and enrichment technique Stir Bar Sorptive Extraction (SBSE) is an alternative analysis method for flavour profiling in whisky. SBSE is based on principles similar to Solid Phase MicroExtraction (SPME). Both techniques generally rely on partitioning of analytes between a sorbent phase and a liquid sample phase, resulting in extraction and concentration of the analytes in the sorbent phase depending on the partitioning coefficient. Due to both the much larger sorbent phase volume of the PDMS-based Twister and the active stirring, the extraction efficiency can be up to 250 times higher than for PDMS-based SPME fibers [1]. Following extraction, the coated stir-bar is thermally desorbed in a flow of carrier gas, releasing and transferring the analytes to the GC system for analysis. SBSE is commercialized under the name GERSTEL Twister™. The most widely used Twister phase is polydimethylsiloxane (PDMS), which is non-polar. A novel sorbent phase based on ethylene glycol- (EG) modified silicone developed for SBSE is now available and was used in this work.

Experimental

Standards and whisky samples. Phenol, o-, p-, m-cresol, guaiacol, 4-ethylphenol and 4-ethylguaiacol >99 % pure in ethanol were obtained from Sigma-Aldrich. A stock solution containing all target analytes at 100 ng/µL in 99 % pure ethanol was prepared. The calibration solutions for large volume injection (LVI) were prepared by spiking stock solution in ethanol/water (40 % v/v) matrix. For SBSE, the stock solution was spiked into 20 % (v/v) ethanol/water matrix to obtain required calibration concentrations. The stock solution was stored in a refrigerator at 4°C. Two commercially available single malt scotch whisky brands, whisky A (46 % v/v) and whisky B (40 % v/v), were purchased.

Instrumentation. The TD-GC/MS analysis was performed using a Thermal Desorption Unit (TDU) combined with a MultiPurposeSampler (MPS) equipped with a 10 µL syringe and a Cooled Injection System (CIS 4) programmed temperature vaporization (PTV) type inlet (all from GERSTEL). An Agilent 6890N gas chromatograph with a 5795B inert XL (triple axis) mass selective detector (MSD) was used. The entire analysis system was operated under

MAESTRO software control integrated with Agilent ChemStation software using one integrated method and one integrated sequence table.

Analysis conditions LVI-ALEX

CIS 4:	
Liner	3 % Rxi-1 (Polydimethylsiloxane) on 80/100 Silcoport W, d_i = 2 mm
Injection	20 µL, 10 µL/s
Pneumatics	2 min solvent vent (200 mL/min) splitless
Temperature	20 °C (2.2 min); 10 °C/s; 320 °C (10 min)

Analysis conditionsSBSE

TDU:	
Temperature	40°C (1 min); 720°C/min; 220°C (5 min)
Pneumatics	40 mL/min solvent vent (1 min) splitless
CIS 4:	
Temperature	-100°C (2 min); 12°C/s; 280°C (5 min)
Pneumatics	solvent vent, 20 mL/min
Liner	quartz wool deactivated, d_i = 2 mm

Analysis conditions

GC:	
Oven	50 °C (2 min); 5 °C/min; 60 °C; 10 °C/min; 165 °C; 20 °C/min; 240 °C (10 min)
Column	25 m CP-FFAP (Varian) d_i = 0.15 mm d_f = 0.25 µm
Pneumatics	He, constant pressure = 362 kPa, initial flow = 1.4 mL/min
MSD	EI mode, scan, 30-350 amu, threshold 150

Solvent vent Large Volume Injection (LVI). Removal of the ethanol-water matrix is the critical issue when a large volume of aqueous sample is directly injected into a GC system. The GERSTEL Cooled Injection System (CIS) is a PTV-type inlet, which enables removal of aqueous sample matrix at ambient or sub-ambient temperature when operated in Solvent Vent mode. The CIS inlet liner used for this work was packed with 3 % Rxi-1 (Polydimethylsiloxane) on 80/100 Silcoport W. The packing was supported on a small plug of deactivated quartz wool placed at the bottom of the liner. 20 µL of standard solution or whisky sample was injected using a programmed injection speed of 10 µL/s. Initial inlet temperature was set to 20°C and the vent flow was set to 200 mL/min for 2 min. After a 2 min. solvent vent step, the inlet pneumatic control switched to splitless mode and the CIS inlet was heated using a temperature program transferring the analytes to the GC column [3].

Solvent vent Twister desorption. For thermal desorption of a Twister that contains a polar sorbent, for example an EG-Silicone Twister, it is recommended to select the mode “TDU solvent vent” in the Gerstel MAESTRO Software. The Ethylene Glycol (EG)-Silicone Twister does show an uptake of small amounts of water during extraction of aqueous phases due to its polar nature. This water can be evaporated and vented by operating the TDU in solvent vent mode prior to thermal desorption of the analytes. Water is evaporated at low initial temperature, e.g. 30 to 40°C, for a short period of time, typically 0.5 min, and vented at high flow through the split vent. During venting, the pressure is set to zero kPa for best possible evaporation efficiency. The TDU solvent vent mode eliminates, or significantly reduces, introduction of water into the GC/MS system to help ensure that ice blockage of the CIS during cryofocussing is avoided. An alternative way to reduce the introduction of water from the EG-Silicone Twister phase is to let the Twisters dry in a clean atmosphere at room temperature for approx.15 minutes. Since the process is fully automated, TDU solvent vent is the preferred method of water removal for more reproducible and reliable results. Following the vent time, the split valve is switched to splitless mode before the temperature ramp for thermal desorption starts. The desorbed analytes are transferred quantitatively into the CIS liner.

Sample extraction

Twisters should be conditioned in a Thermal Conditioner (TC) using a flow of nitrogen at 220°C for 30 to 60 min before usage. Sampling was performed as follows: A 5 mL aliquot of a spiked ethanol/water (20 % v/v) solution or diluted whisky (1:1 dilution with HPLC grade water) sample was pipetted into a 10 mL vial. A Twister was added to the vial before sealing it with a screw cap with septum. SBSE extraction was performed at room temperature for one hour while stirring at 800 rpm on a multiple position magnetic stirrer. Following the extraction step, the Twister was removed from the sample using a magnetic rod and briefly immersed in HPLC grade water. After careful drying with a lint-free tissue, the Twister was stored in

a sealed 2 mL vial. Prior to analysis, the Twister was placed in a TDU glass liner, which was transferred a suitable sample tray on the MPS autosampler.

Identification and quantification of whisky target compounds. All target compounds, their major fragment ions as well as the masses and associated relative abundances are listed in Table 1. Each obtained data file was analyzed using IFD™ mass spectral deconvolution algorithms (Ion Signature Technology). The software identifies and quantifies compounds based on the mass spectral patterns of at least three ions per compound. Based on the given ion masses and the associated expected relative abundances (Table 1), the deconvolution software provides a list of the compounds found in the standard total ion chromatogram (TIC) and generates a reconstructed ion chromatogram (RIC), which contains only the target analytes. This process is more comprehensive than selected ion monitoring (SIM) because the software identifies and discards contributions to the spectra that originate from compounds other than the target compounds [4].

Table 1. Retention times, ions and relative abundances (% RA) for Whisky target compounds.

No.	Compound	CAS	RT, min	Main ion	Ion 1 (% RA)	Ion 2 (% RA)	Ion 3 (% RA)
1	Guaiacol	90-05-1	15.72	109	124 (84)	81 (59)	53 (15)
2	o-Cresol	95-48-7	16.86	108	107 (98)	77 (33)	79 (29)
3	Phenol	108-95-2	16.90	94	95 (12)	66 (29)	65 (22)
4	4-Ethylguaiacol	2785-89-9	17.12	137	152 (40)	122 (11)	
5	p-Cresol	106-44-5	17.44	107	108 (102)	77 (29)	79 (30)
6	m-Cresol	108-39-4	17.50	108	107 (87)	77 (33)	79 (32)
7	4-Ethylphenol	123-07-9	18.04	107	108 (8)	122 (34)	77 (16)

Results and Discussion

Direct Large Volume Injection (LVI)

Standard solution calibration. Standard solutions for calibration were prepared from spiked 40 % ethanol/water mixtures in order to simulate the whisky matrix. Calibration standards were provided for levels 0.1, 0.2, 0.5, 1.0, and 2.0 ng/µL. For each level, the measurement was performed in three replicates. Figure 1 shows calibration curves for all seven target compounds.

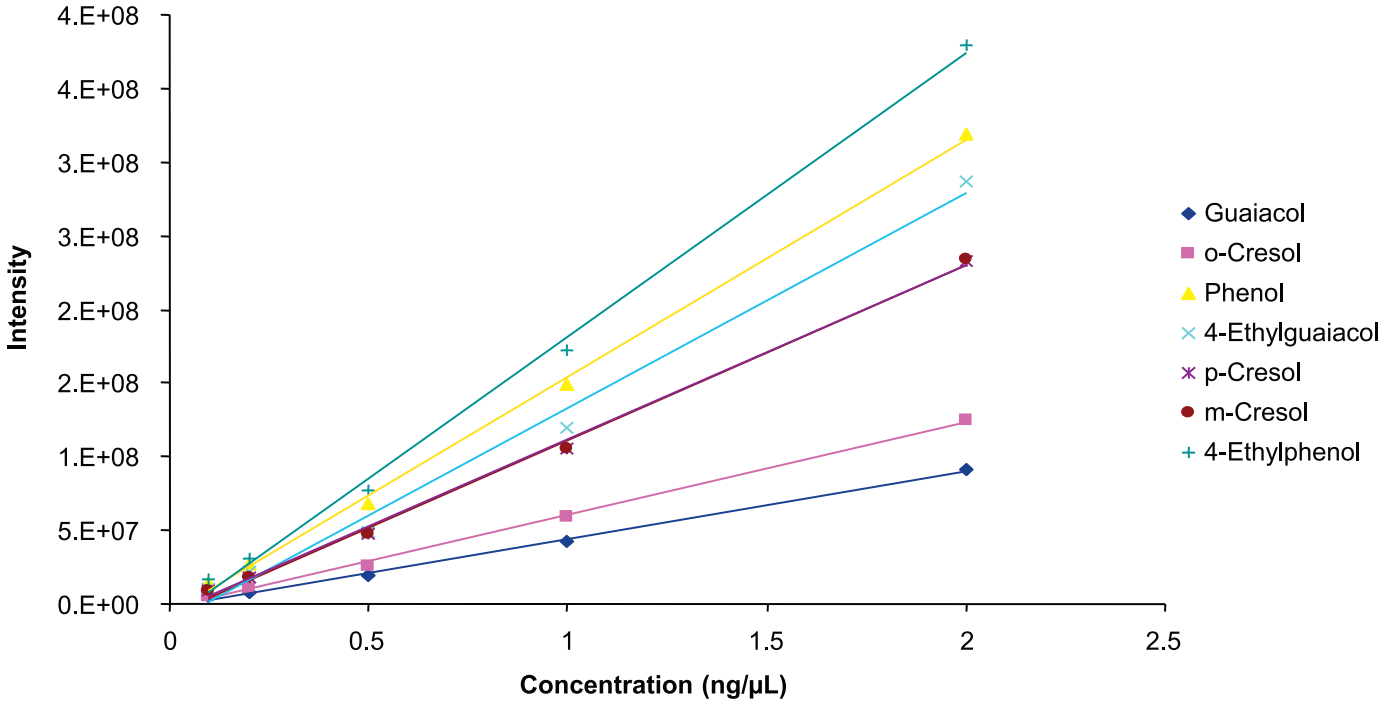

Figure 1. Calibration curves for seven target compounds obtained by LVI-GC-MS of spiked 40 % (v/v) ethanol/water mixtures in the range from 0.1 to 2.0 ng/µL.

Limits of detection (LOD) and limits of quantification (LOQ) were calculated according to DIN 32 645 using the calibration function method [5]. A K-factor value of three was used, which means that 33.3 % is the maximum acceptable uncertainty. As can be seen in Table 2, the LODs achieved using LVI-GC-MS range from 0.09 ng/µL (phenol) to 0.21 ng/µL (4-ethylguaiacol); LOQs range from 0.24 ng/µL (phenol) to 0.53 ng/µL (4-ethylguaiacol). The achieved coefficients of determination (R^2) for the calibration curves ranged between 0.991 and 0.999.

Table 2. Limits of detection and limits of quantification (ng/µL) as well as the coefficient of determination (R^2) for the target compounds (calculated for pure whisky 40 % (v/v) ethanol/water (n=4)).

	Guaiacol	o-Cresol	Phenol	4-Ethylguaiacol	p-Cresol	m-Cresol	4-Ethylphenol
LOD	0.12	0.10	0.09	0.21	0.11	0.11	0.12
LOQ	0.32	0.28	0.24	0.53	0.30	0.31	0.32
R^2	0.997	0.998	0.999	0.991	0.998	0.997	0.997

Whisky samples. In order to determine the concentrations of seven phenolic compounds, a 20 µL sample of pure whisky was injected directly without further sample preparation. Two commercially available single malt whisky brands were analyzed, each injected in triplicate. In Figure 2, the total ion chromatograms (TICs) resulting from the whisky brands are shown.

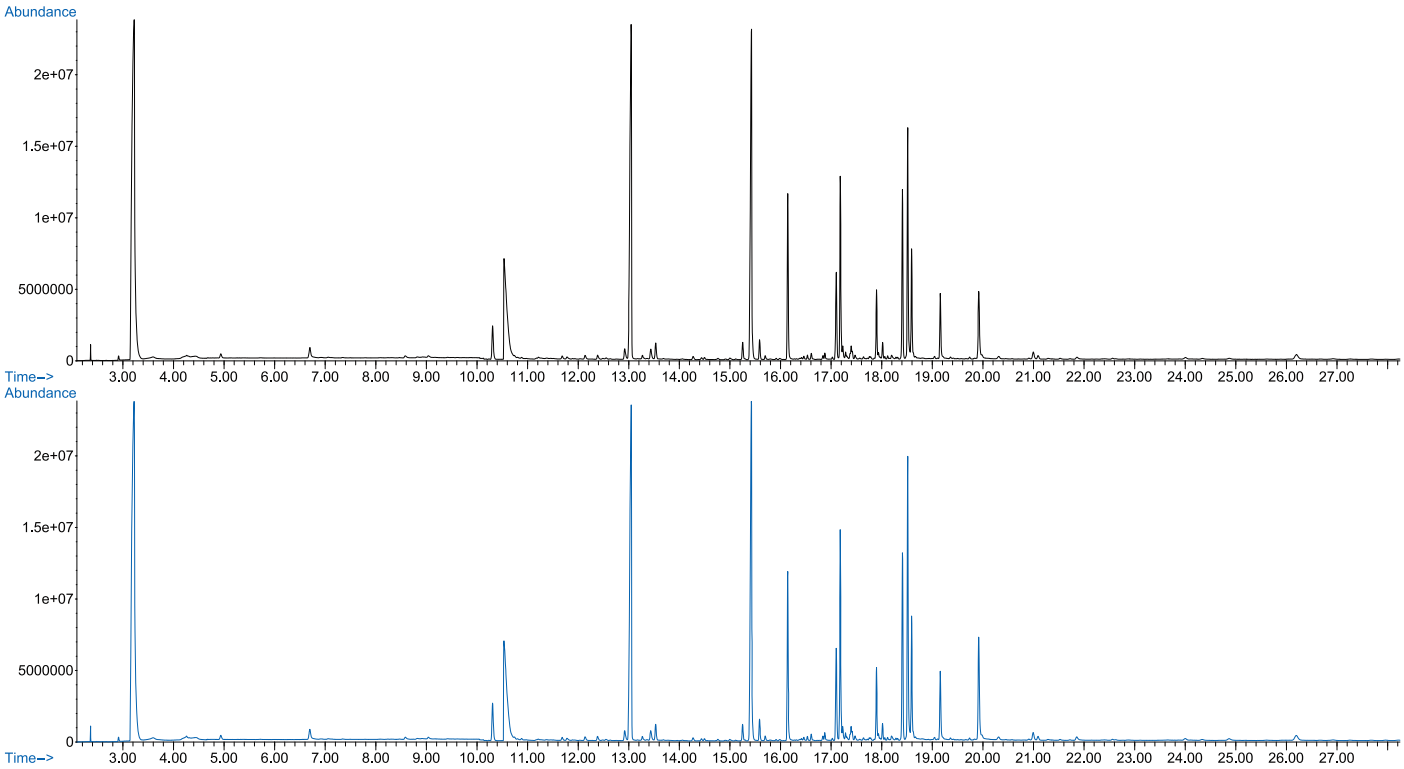

Figure 2. Total ion chromatograms resulting from direct injection of 20 µL samples of two whisky brands. Top: Brand A (46 % v/v), bottom: Brand B (40% v/v).

In Figure 3, the reconstructed ion chromatogram (RIC) of the target compounds as well as the TIC of whisky brand A obtained with IFD software are shown.

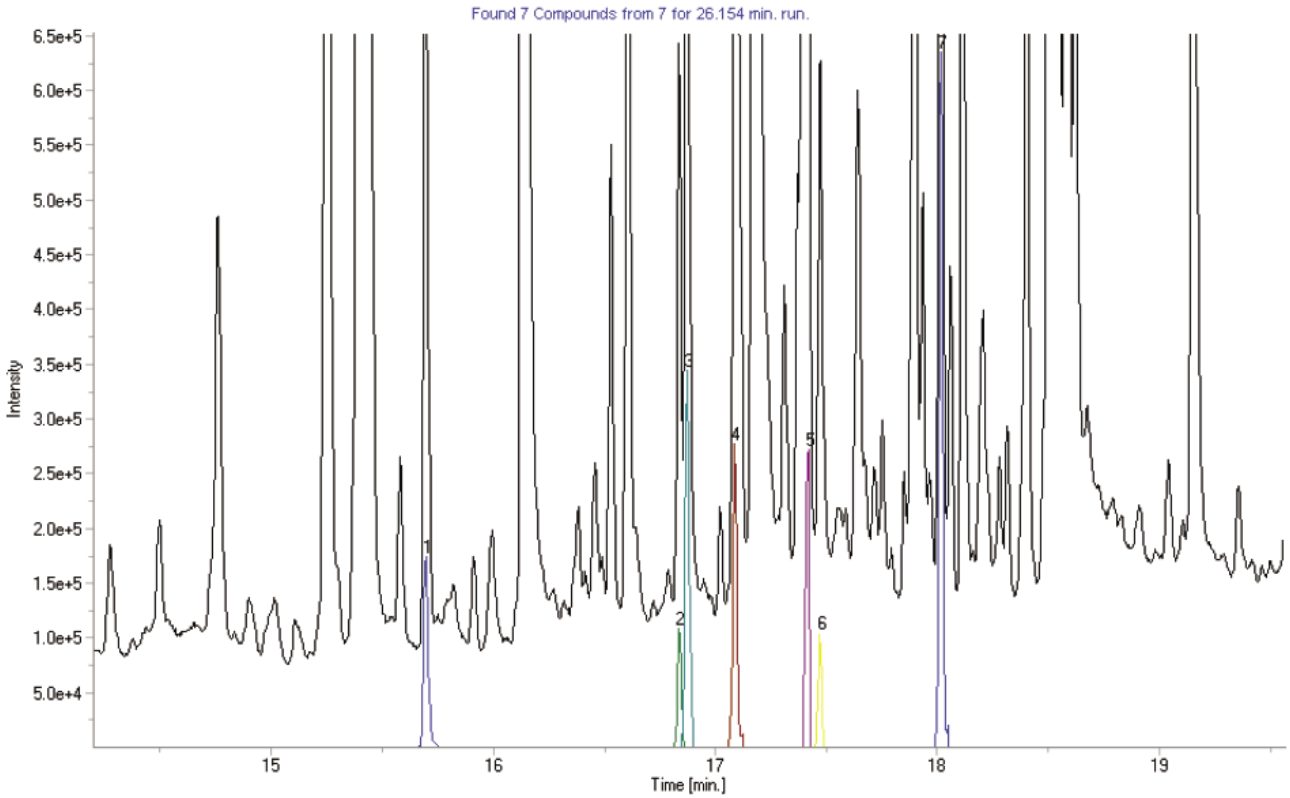

Figure 3. RIC and TIC resulting from a 20 µL injection of whisky brand A (46% v/v).

Table 3 lists the determined concentrations of seven phenolic compounds in the two whisky brands and the percent relative standard deviations (% RSDs). For the seven compounds, the % RSDs obtained using LVI-GC-MS range from 1.6 to 6.2 for both whisky types. This is a highly acceptable results given that the determined concentrations are at the lower end of the linear range.

Table 3. Concentrations (ng/µL) of phenolic compounds in two whisky brands, and the associated % RSDs, determined using LVI-GC-MS based on injection of 20µL samples of whisky (n=3).

	1 Guaiacol	2 o-Cresol	3 Phenol	4 4-Ethylguaiacol	5 p-Cresol	6 m-Cresol	7 4-Ethylphenol
Whisky A	3.7	3.4	3.7	1.3	4.2	1.1	2.5
% RSD	3.2	4.1	4.3	4.7	3.8	3.2	2.3
Whisky B	4.1	3.6	4.8	1.6	5.1	1.5	3.2
% RSD	3.1	6.2	3.2	5.3	4.1	1.6	3.5

Stir Bar Sorptive Extraction (SBSE)

Phenolic compounds in whisky can be determined with great sensitivity using the SBSE technique. In this study, a novel Ethylene Glycol-Silicone Twister was used due to the higher extraction efficiency for phenolic compounds of the more polar EG-Silicone phase in comparison to the PDMS phase.

SBSE Calibration. Calibration of the SBSE-based method was performed by adding Twisters into synthetic whisky samples (acidified ethanol/water, 20 % v/v) at three different concentration levels: 0.01, 0.1 and 1.0 ng/µL. The pH value was adjusted to 3 with hydrochloric acid (HCl), the pH-value found in whisky at which the phenolic compounds are present in their non-dissociated form. Each concentration level of spiked samples was prepared in duplicate and all spiked samples extracted with individual EG-Silicone Twisters. Six EG-Silicone Twisters were used in total. Sampling and instrument parameters for analysis of calibration standards and whisky samples were identical. All samples were extracted simultaneously using a multi-position magnetic stirring plate for best possible productivity.

Total ion chromatograms (TICs) obtained from extractions with EG-Silicone Twisters of spiked ethanol/water samples (20 % v/v) are shown in figure

4. Chromatograms of standards show good reproducibility even when using different Twisters. Coefficients of determination (R^2) for the compounds were found to be between 0.997 and 0.999.

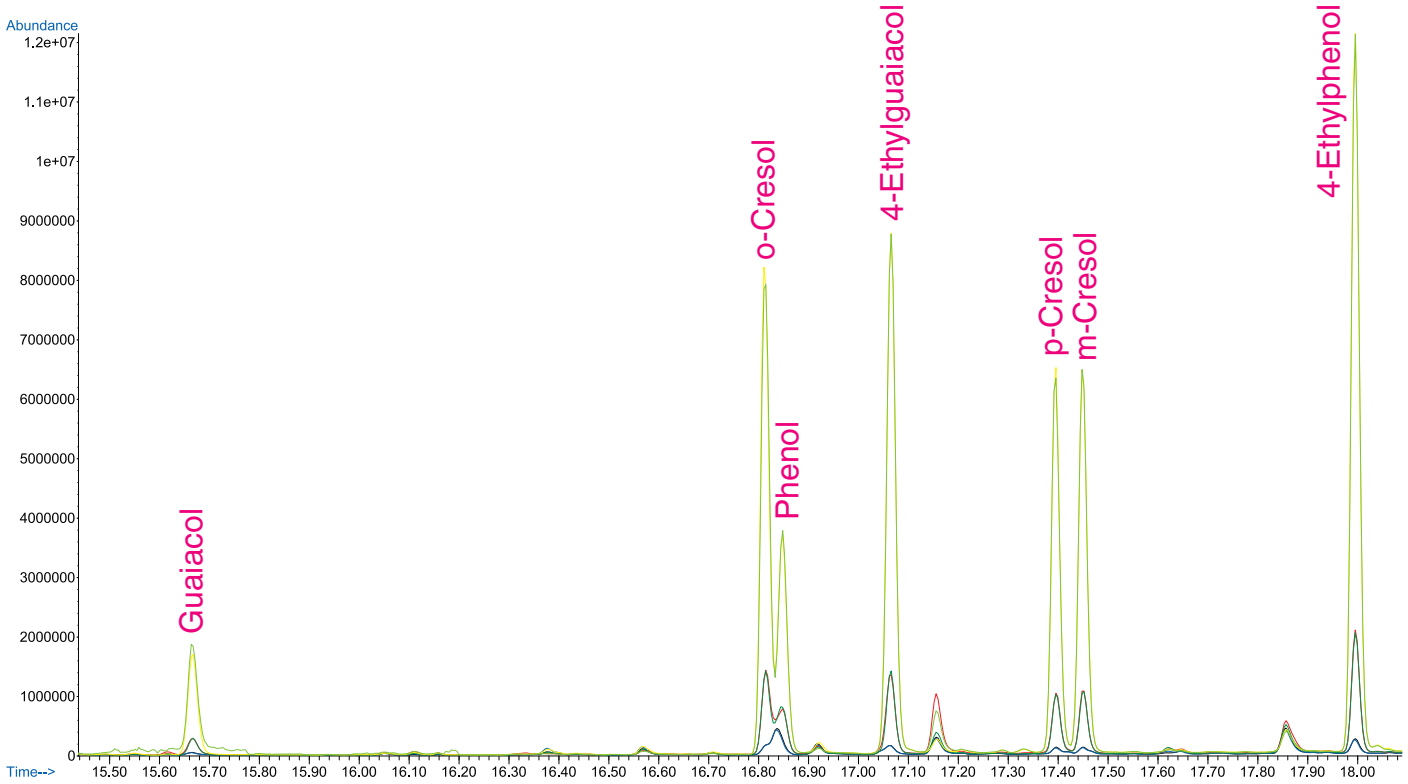

Figure 4. Total Ion Chromatograms (TICs) obtained with SBSE using EG-Silicone Twisters showing seven phenolic compounds at 0.01, 0.1 and 1.0 ng/µL respectively in 5 mL synthetic whisky [20 % (v/v) ethanol/water, pH = 3], split 1:20.

Whisky samples. Total ion chromatograms (TICs) obtained from extractions with EG-Silicone Twister of 5 mL samples of whisky brands A and B (1:1 diluted with HPLC water) are shown in Figure 5.

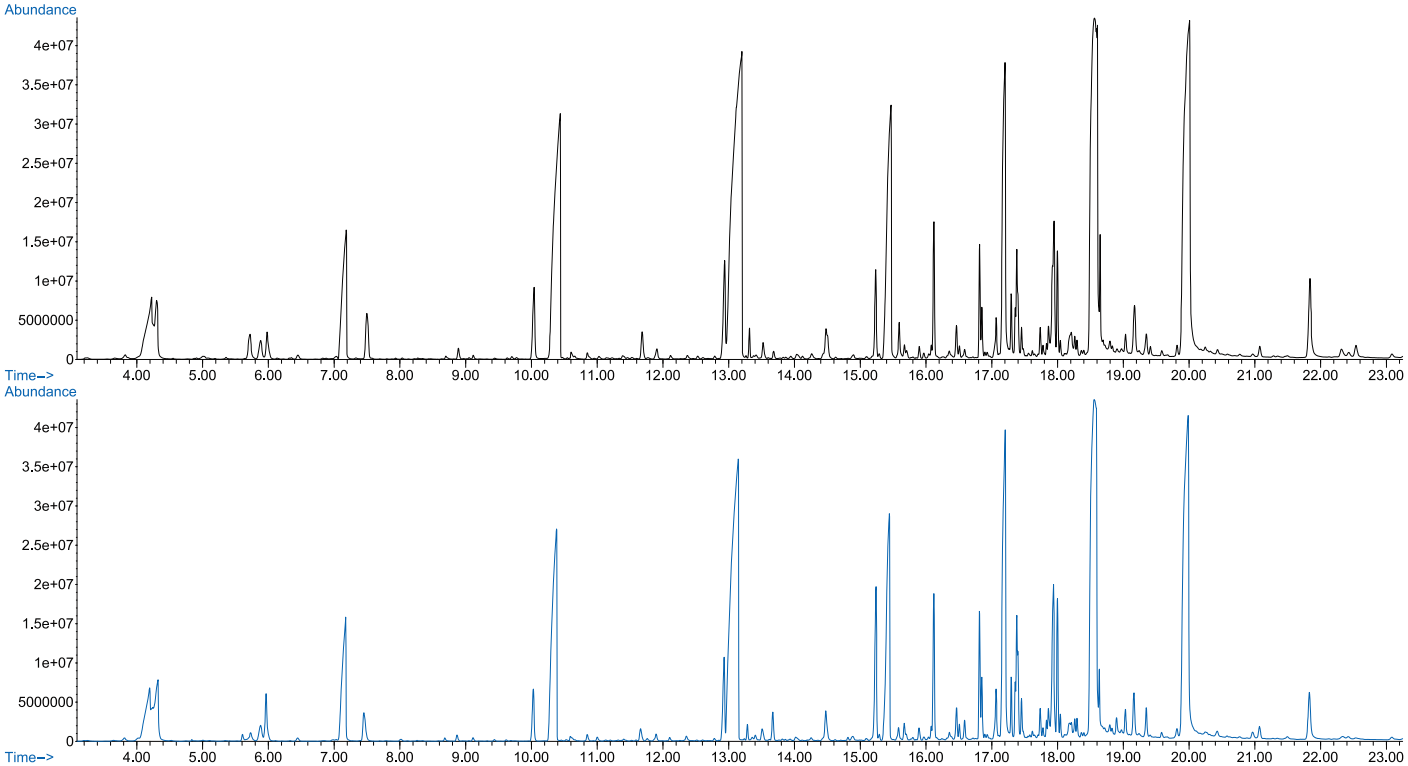

Figure 5. Total ion chromatograms of 5 mL samples of two whisky brands (1:1 diluted with HPLC water) extracted with SBSE using EG-Silicone Twister. Top: Brand A (23 % EtOH v/v), bottom: Brand B (20 % EtOH v/v).

Figure 6 shows an overlay of a reconstructed ion chromatogram (RIC) of target compounds obtained using IFD software and the TIC of whisky brand A.

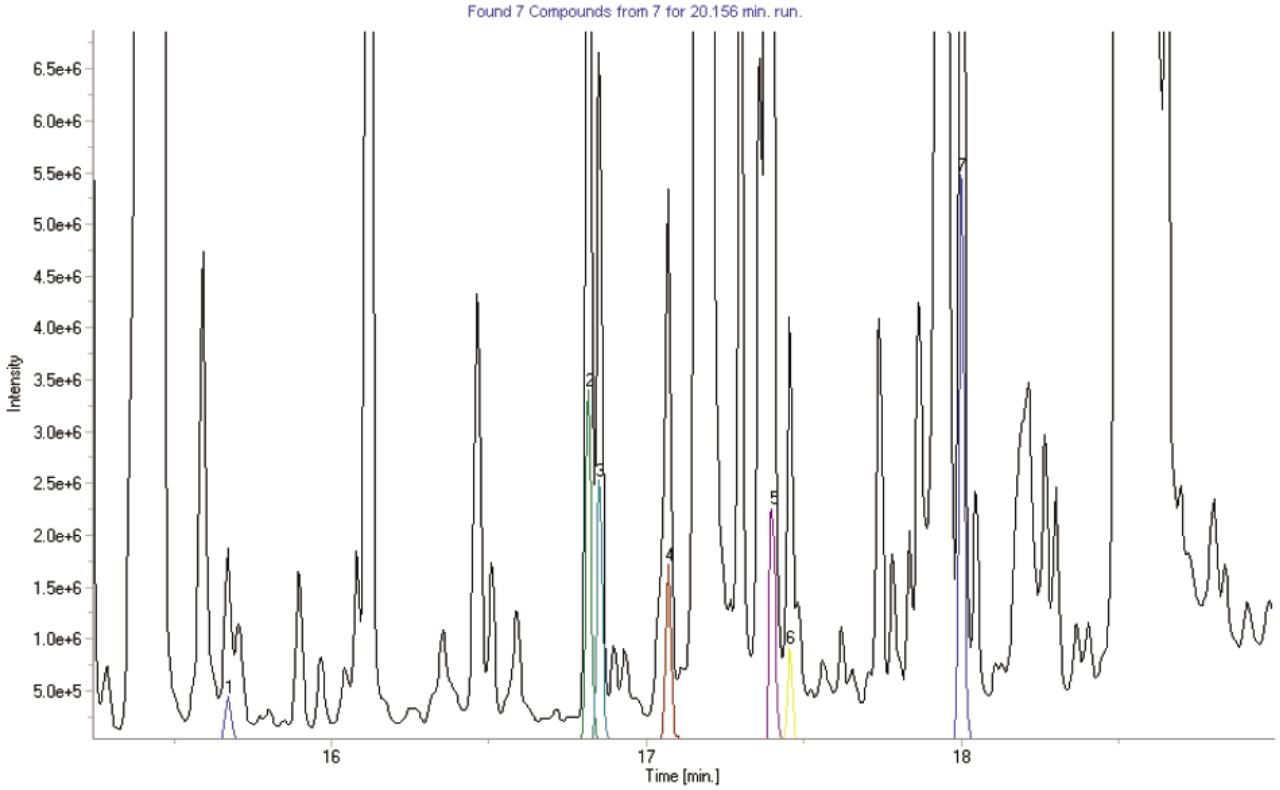

Figure 6. Overlay chromatograms of RIC and TIC of a 5 mL sample of whisky brand A (1:1 diluted with HPLC water, 23 % EtOH v/v) obtained with SBSE using the EG-Silicone Twister.

For quantification, each whisky sample was analyzed in triplicate and the target compound concentrations calculated from average peak areas using a 3-point calibration curve established using Twister extractions of spiked ethanol/water (20 % v/v). The whisky was diluted 1:1 with water to approximately 20 % v/v ethanol concentration prior to extraction. The calculated concentrations were therefore multiplied by a factor of two to back-calculate the concentration levels of the phenolic compounds in whisky (Table 4). Percent relative standard deviation (% RSD) ranged from 0.8 to 5.4, proof of good Twister to Twister reproducibility.

Table 4. Concentrations (ng/µL) of phenolic compounds and associated percent relative standard deviations (% RSD) determined in two whisky brands using SBSE with EG-Silicone Twisters (n=3).

	1 Guaiacol	2 o-Cresol	3 Phenol	4 4-Ethylguaiacol	5 p-Cresol	6 m-Cresol	7 4-Ethylphenol
Whisky A	2.6	3.5	3.5	1.3	2.6	1.0	2.5
% RSD	3.3	2.6	0.8	2.3	4.1	2.6	0.9
Whisky B	2.6	3.9	4.4	1.0	3.6	1.5	2.8
% RSD	4.2	5.4	3.3	4.4	4.2	3.6	4.5

Limits of detection and limits of quantification. In order to determine both the LOD and the LOQ achieved for each target compound using SBSE and the EG-Silicone Twister, calibrations at lower concentration levels were required. The EG-Silicone Twister was added to 5 mL samples of spiked ethanol/water (20 % v/v) at concentration levels of 8, 20, 40 and 100 ng/mL. Each level was determined twice. Extraction of eight Twisters was performed simultaneously; the total time used was 60 min. Table 5 shows LODs and LOQs for seven target compounds and the linearity of the calibration curve. Detection limits of EG-Silicone Twister based SBSE-TD-GC-MS range from 1.2 ng/mL (guaiacol) to 3.47 ng/mL (4-ethylguaiacol) and quantification limits range from 1.65 ng/mL to 9.33 ng/mL calculated for pure whisky with 40 % (v/v) ethanol. Linear correlation coefficients were between 0.999 and 1.000.

Table 5. LODs and LOQs (ng/mL) for target compounds and their linear correlation coefficients (R^2) [calculated for pure whisky 40 % (v/v) ethanol/water (n=4)].

	Guaiacol	o-Cresol	Phenol	4-Ethylguaiacol	p-Cresol	m-Cresol	4-Ethylphenol
LOD*	1.2	2.6	2.7	6.9	5.1	1.7	4.8
LOQ*	3.3	7.4	7.5	18.7	14.0	4.7	13.3
R^2	1.000	1.000	1.000	0.999	1.000	1.000	1.000

*: presented data was calculated from LODs and LOQs obtained from extractions of spiked ethanol/water matrix 20% (v/v). To compensate for the 1:1 dilution used for real Whisky samples prior to extraction, all values were multiplied by a factor of 2 to calculate the concentration values for the original Whisky sample (40% ethanol/water v/v).

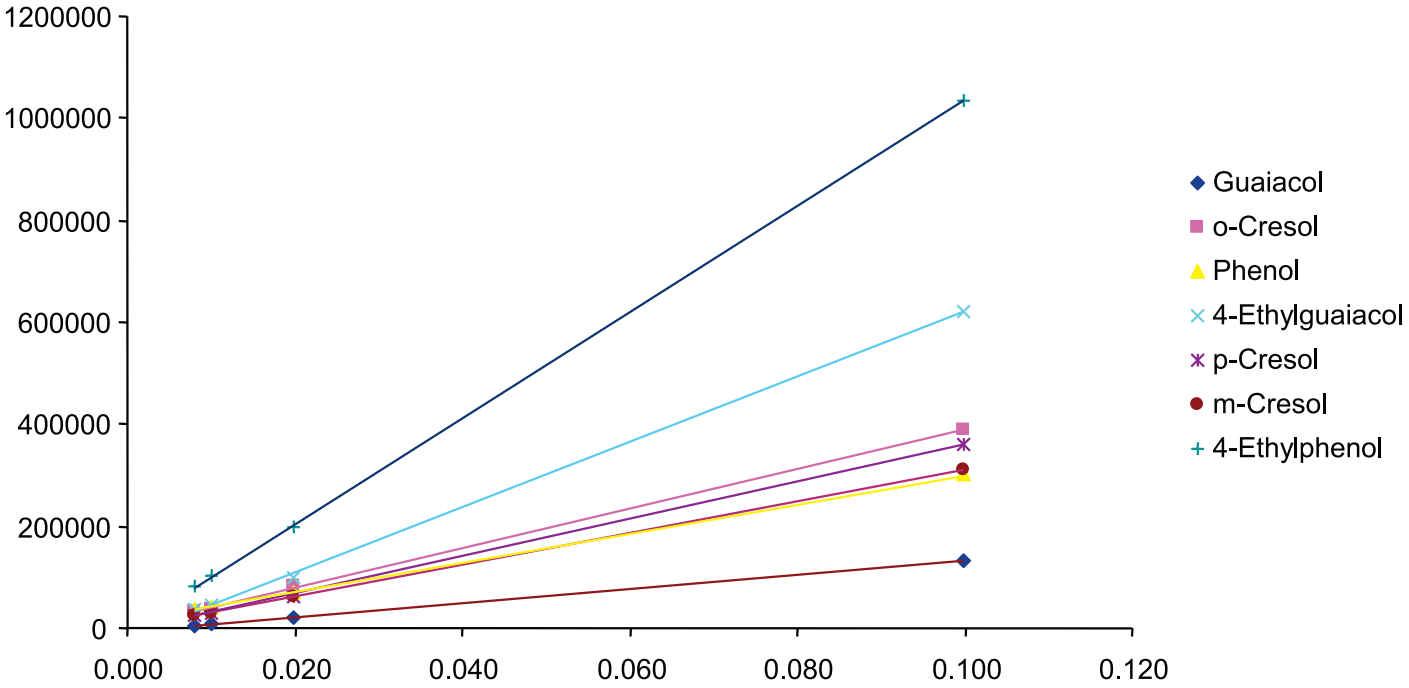

Figure 7. Calibration curves for seven phenolic compounds obtained with EG-Silicone Twister at 8, 20, 40, and 100 ng/mL in 20 % (v/v) ethanol/water matrix.

Recovery of phenolic compounds with SBSE using EG-Silicone Twister. In order to calculate the extraction efficiency for seven target compounds achieved with SBSE using the EG-Silicone Twister, a 5-point calibration using standard solutions was performed. For each level, 1 µL of the respective standard solution was injected. Concentration levels of 0.2, 0.5, 1.0, 3.0, and 5.0 ng/µL were injected directly into the thermal desorption Unit (TDU) and analyzed in triplicate.

Linearity of calibration for liquid injections into the TDU was found to be good for all seven phenolic compounds, the coefficients of determination (R^2) were found to be in excess of 0.998. The amount of extracted phenols using EG-Silicone Twisters was calculated using the linear equation obtained from the TDU liquid calibration. Recoveries were calculated by dividing extracted amounts of each compound with the total amount spiked. Average recoveries with associated relative standard deviations are listed in table 6. Achieved average recoveries of phenolic compounds were between 12.2 % (guaiacol) and 56.8 % (4-ethylphenol) with relative standard deviations ranging from 4.2 to 8.9 %.

Table 6. Average recoveries (%) of seven phenolic target compounds and the associated percent relative standard deviations (% RSD) achieved with EG-Silicone Twister in the range from 8 to 100 ng/mL spiked in 20 % (v/v) ethanol/water matrix (n=4).

	Guaiacol	o-Cresol	Phenol	4-Ethylguaiacol	p-Cresol	m-Cresol	4-Ethylphenol
Recovery	12.2	35.8	15.8	35.2	25.8	27.1	56.8
% RSD	4.2	5.8	8.9	7.4	5.8	7.3	4.3

Comparison of LVI and SBSE

Chromatographic Aspects. A simple comparison of the chromatograms shown in Figure 8 proves that SBSE provides a much broader range of extracted compounds - and with much higher sensitivity than LVI. Due to its dimethylsiloxane basis and ethylene glycol component, non-polar as well as polar compounds are extracted with the EG-Silicone Twister. Polar compounds that are extracted well are mainly substances with the ability to form H- bonds as H-donors. The higher sensitivity of the SBSE method results mainly from the larger sample volume used for Twister extractions compared to LVI.

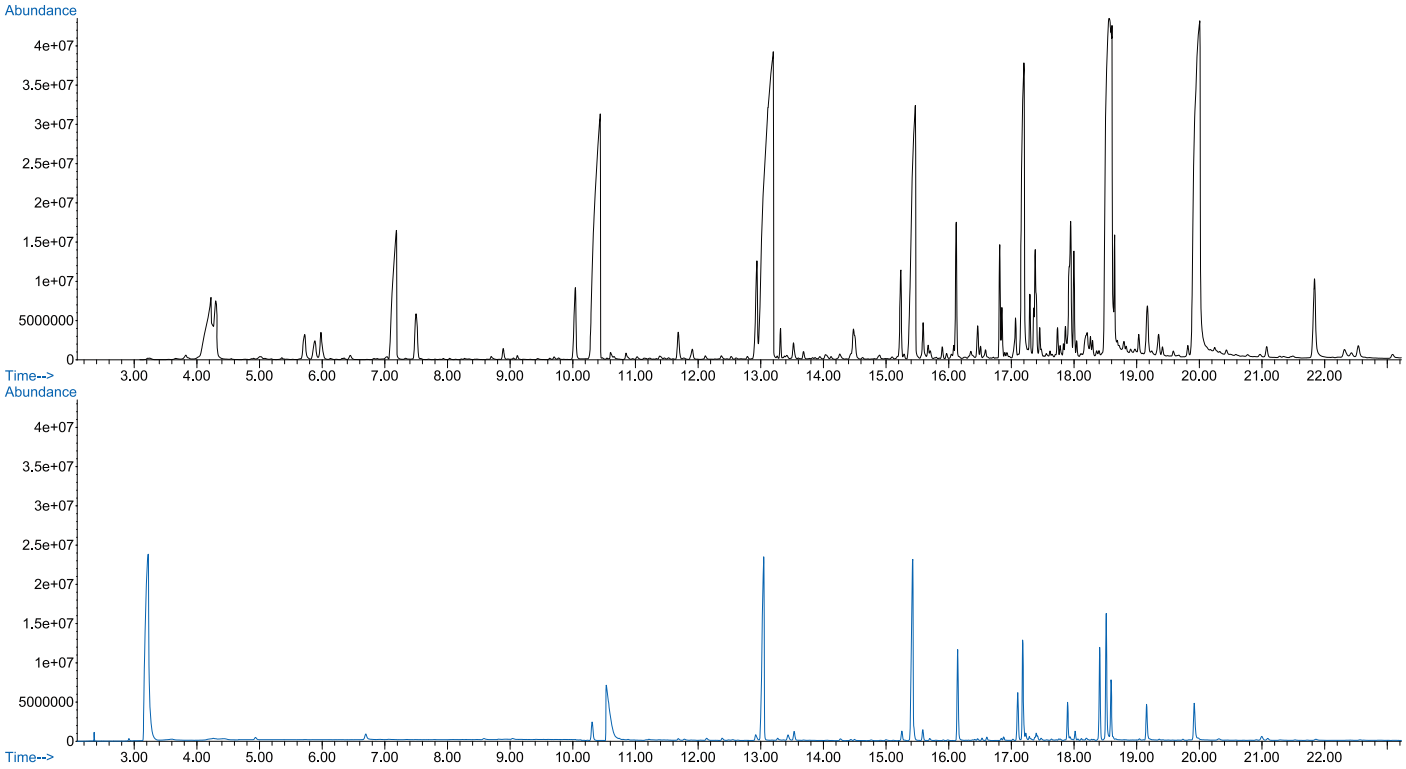

Figure 8. Total Ion Chromatograms. Top: (TICs) of 5 mL whisky brand A (23% v/v, 1:1 diluted with HPLC water) extracted with EG-Silicone Twister split 1:20; bottom: 20 µL of whisky brand A (46 % v/v); direct injection (LVI), splitless.

Limit of detection and coefficient of determination (n=4). Both SBSE and LVI show good calibration linearity for determination of phenolic compounds from an ethanol/water matrix. SBSE results in much lower LODs and LOQs, about 20-100 times more sensitive than LVI.

Table 7. LODs and LOQs (ng/mL) for the target compounds and their associated respective calibration linearity achieved for both SBSE and LVI [calculated for pure whisky 40 % (v/v) ethanol/water (n=4)].

		Guaiacol	o-Cresol	Phenol	4-Ethylguaiacol	p-Cresol	m-Cresol	4-Ethylphenol
LVI	LOD	120	100	90	210	110	110	120
	R^2	0.997	0.998	0.999	0.991	0.998	0.997	0.997
SBSE	LOD	1.16	2.62	2.68	6.94	5.10	1.66	4.84
	R^2	1.000	1.000	1.000	0.999	1.000	1.000	1.000

Comparison of quantitative results. Table 8 shows a comparison of the target compound concentrations determined in whisky brands A and B using LVI and SBSE. For most compounds, the results obtained with both techniques are identical. For example, o-cresol is found to be 3.4 and 3.5 ppm respectively in whisky A and 3.6 and 3.9 ppm respectively in whisky B; phenol is found to be 3.7 and 3.5 ppm respectively in whisky A and 4.8 and 4.4 ppm respectively in whisky B.

Table 8. Comparison of determined concentrations (ng/µL) of seven phenolic compounds in two whisky brands using SBSE and LVI respectively.

		Guaiacol	o-Cresol	Phenol	4-Ethylguaiacol	p-Cresol	m-Cresol	4-Ethylphenol
Whisky A	LVI	3.7	3.4	3.7	1.3	4.2	1.1	2.5
	SBSE	2.6	3.5	3.5	1.3	2.6	1.0	2.5
Whisky B	LVI	4.1	3.6	4.8	1.6	5.1	1.6	3.2
	SBSE	2.6	3.9	4.4	1.0	3.6	1.5	2.8

According to literature [6], heavily peated single malt whiskies contain more than 30 ppm of phenols, medium-peated about 20 ppm and lightly peated below 15 ppm. From this point of view, the test samples belong to at least medium-peated whisky. Their aroma and taste also exhibit a strong smoky impression.

Conclusion

SBSE and LVI were evaluated for quantitative determination of phenolic compounds in whisky. Both techniques show good calibration linearity and reproducibility for determining phenolic compounds in ethanol/water matrix. Comparable results were obtained using both techniques to determine concentrations of target compounds in two different whisky brands.

Large volume injection is an attractive technique because no sample preparation is needed. In principle only a PTV-type inlet, such as the GERSTEL CIS is needed in addition to the standard GC hardware. However, to avoid excessive inlet contamination with non-volatile sample matrix, use of an automated liner exchanger (ALEX) is highly recommended as liners will need to be changed more frequently. Compared to LVI, SBSE followed by thermal desorption GC requires some additional sample preparation time since it is an extraction technique, but a large number of samples can be extracted simultaneously using one or more multi-position stirring plates. This means that adding additional samples to be analyzed does not lead to an increase in the total extraction time. A thermal desorption unit (TDU) is required as additional hardware for SBSE-based analysis. The system can be calibrated without modification of the instrument since automated introduction of standards to the system can be performed directly into the TDU.

The main advantage of SBSE for this application is the increase in sensitivity achieved, resulting in lower LODs and LOQs. Furthermore, matrix introduction to the GC/MS and the resulting inlet contamination and subsequent need for frequent inlet maintenance is prevented. To keep cost per analysis under control, the PDMS Twister can be reused up to 100 times and the EG-Silicone Twister up to 50 times.

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