

**GERSTEL**

AppNote 3/2011

## Using Three Types of Twister Phases for Stir Bar Sorptive Extraction of Whisky, Wine and Fruit Juice

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### KEYWORDS

EG-Silicone Twister, Stir Bar Sorptive Extraction (SBSE), Thermal Desorption, GC-MS, Whisky, Wine, Multivitamin Juice, pH Stability

### ABSTRACT

This paper describes a novel ethylene glycol- (EG) and silicone based combined sorbent phase developed for stir bar sorptive extraction (SBSE) using the GERSTEL Twister™. EG-Silicone, polyacrylate (PA), and polydimethylsiloxane (PDMS) Twisters were used separately to perform SBSE on whisky, white wine and multivitamin juice in order to determine the usefulness of these phases for generating qualitative flavor profiles of beverages. The Twisters were subsequently thermally desorbed and the analytes determined using gas chromatography-mass spectrometry (GC/MS) based on both polar and non-polar GC columns. The pH stability of the EG-Silicone Twister was studied in wine samples and in aqueous standards. The EG-Silicone Twister extracted a broader range of substances from whisky, wine and multivitamin juice compared with PA Twister and PDMS. Most phenols and polar aromatic compounds could be extracted with EG-Silicone and PA Twisters. It was found that SBSE based on EG-Silicone phase results in the extraction of significantly larger amounts of the polar compounds than the PDMS- or PA based Twisters. The EG-Silicone Twister also showed good extraction efficiency for other polar compounds such as more volatile esters and fusel alcohols. Due to its PDMS basis, non-polar compounds

such as long carbon-chain ethyl esters, lactones, and terpenes are extracted with good recovery as well.

## INTRODUCTION

Stir bar sorptive extraction (SBSE) is based on principles similar to solid phase micro-extraction (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. Following extraction, the coated stir-bar is thermally desorbed in a flow of carrier, releasing and transferring the analytes to the GC system for analysis.

The most widely used Twister phase is polydimethylsiloxane (PDMS), which is non-polar. It has been reported that extraction efficiency of the PDMS-based Twister can be up to 250 times higher than for PDMS-based SPME fibers [1] due to the much larger sorbent phase volume, improved phase ratio and improved phase contact during extraction, all of which enable more efficient extraction and extraction of larger volumes. Successful applications of SBSE include extraction and analysis of VOCs, PAHs, pesticides, and off-odors in water; drugs of abuse such as Tetrahydro-cannabinol (THC), barbiturates and benzodiazepines; phthalates and various metabolites in biological fluids; flavor compounds, preservatives, trichloroanisole, pesticides, and fungicides in food and beverages [2-6].

For polar compounds with an octanol-water partition coefficient ( $K_{o/w}$ ) lower than 10,000, it has been found that recoveries gradually decrease with decreasing  $K_{o/w}$  when using PDMS-based Twisters. Among the more hydrophilic solutes are, for example, polar pesticides, alcohols, esters, and phenolic compounds. Although recoveries could successfully be improved for many polar pesticides by adding 30 % NaCl (w/w) into the water sample [7, 8], the salting-out technique does not necessarily help for all polar compounds and there has increasingly been demand for a Twister with a more polar phase.

Two new Twisters with more polar phases are now available from GERSTEL: The Polyacrylate (PA) Twister and the Ethylene Glycol (EG)-Silicone Twister. These new Twisters extract polar compounds more efficiently than the PDMS Twister due to their polar nature. In addition, the EG-Silicone Twister, since it is silicone based, will also efficiently extract non-polar compounds.

## EXPERIMENTAL

*Samples.* Scotch whisky (40 % EtOH v/v); white wine, sauvignon blanc (13 % EtOH v/v) and multivitamin juice.

*Instrumentation.* The TD-GC/MS analysis was performed using a Thermal Desorption Unit (TDU) combined with a MultiPurpose Sampler (MPS) and a Cooled Injection System (CIS 4) programmed temperature vaporization (PTV) type inlet (all GERSTEL). An Agilent 6890N gas chromatograph with a 5975B 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.*

TDU: 40 mL/min solvent vent (0.5 min)  
*EG-Silicone and PA Twister:*  
40°C (0.5 min); 120°C/min;  
220°C (5 min)  
*PDMS Twister:*  
40°C (0.5 min); 120°C/min;  
270°C (5 min)  
PTV: split 1:10  
-100°C (0.5 min); 12°C/s;  
300°C (5 min)

*Polar separation*

Column: 15 m ZB-FFAP (Phenomenex)  
 $d_i = 0.25$  mm  $d_f = 0.25$   $\mu$ m  
Pneumatics: He, constant flow = 1.4 mL/min  
Oven: 50°C (2 min); 5°C/min;  
60°C; 10°C/min;  
165°C; 20°C/min, 250°C (5 min)

*Non-polar separation*

Column: 30 m ZB-5 (Phenomenex)  
 $d_i = 0.25$  mm  $d_f = 0.25$   $\mu$ m  
Pneumatics: He, constant flow = 1.2 mL/min  
Oven: 60°C (2 min); 5°C/min;  
200°C; 10°C/min; 300°C (5 min)

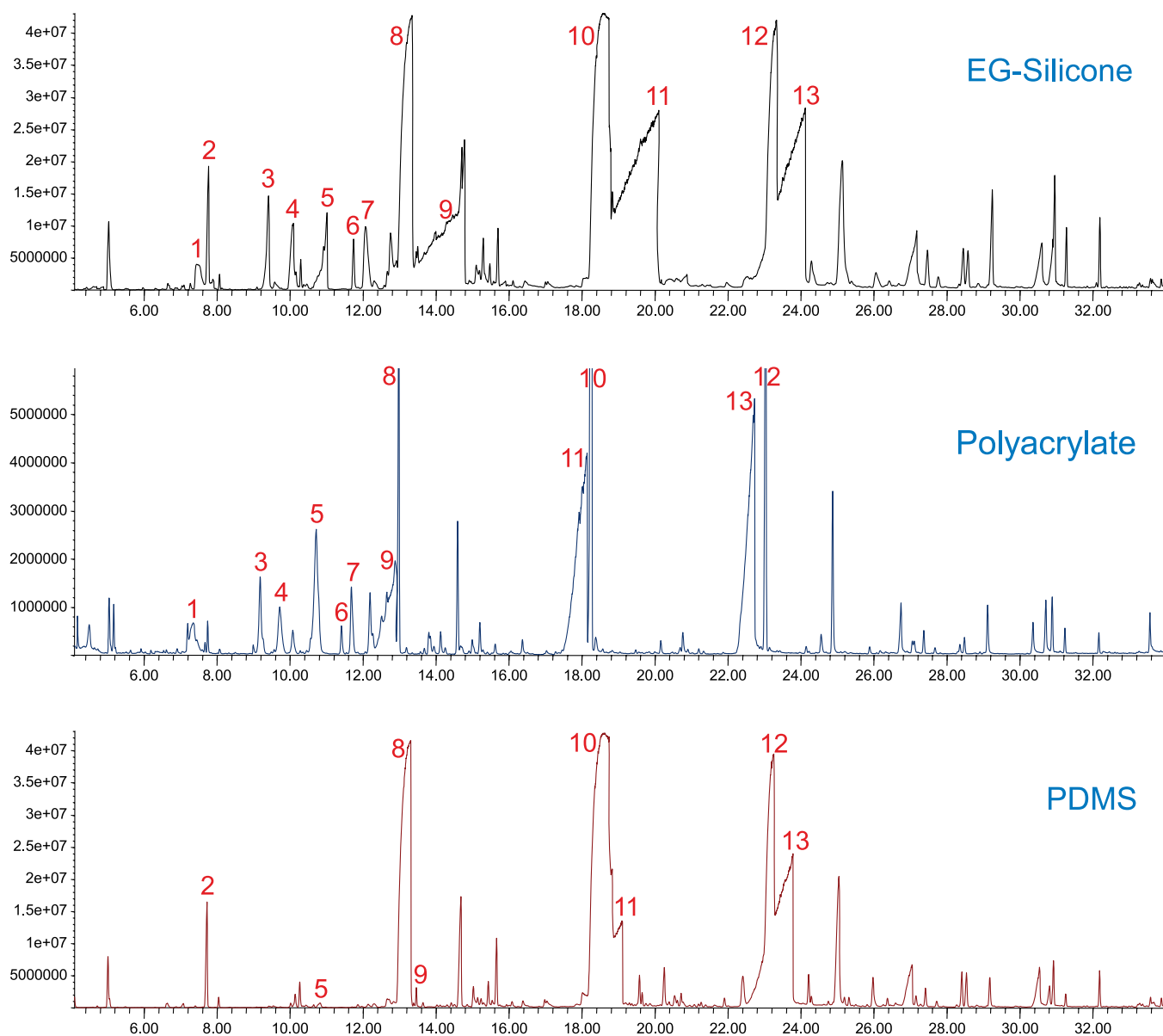
The PA and EG-Silicone Twisters retain some water during extraction from aqueous samples. In order to eliminate excess water prior to GC/MS analysis, the TDU is operated in solvent vent mode and the water is evaporated at low initial temperature, for example at 30-40 °C and ambient pressure (0 kPa) for a pre-determined time before the temperature ramp for the thermal desorption starts. As a result of using the TDU solvent vent mode introduction of water into the GC/MS system is avoided or significantly reduced.

An alternative way to reduce water background is to allow the Twisters to dry in a dry atmosphere for approximately 15 minutes. In this work, we used the TDU solvent vent for water removal because it is an automated process, which delivers more reproducible and reliable results.

Extraction of aqueous samples using an EG-Silicone or a PA Twister is performed in exactly the same way as when it is done with a PDMS Twister. Aqueous sample was transferred into a 10 mL headspace vial. The Twister was added and the vial was sealed with a screw cap. The extraction was performed at room temperature for 60 min. while stirring at 1000 rpm on a multiple position magnetic stirrer. After the extraction

had been completed, the Twister was removed from the sample with a magnetic rod and briefly rinsed with HPLC-grade water. After carefully drying it with a lint-free tissue, the Twister was stored in a 1.5 mL vial. The Twister was finally placed in a TDU glass liner and the liner stored on an MPS sample tray for GC/MS analysis.

*Scotch Whisky.* The EG-Silicone Twister is especially well suited for the extraction of polar compounds, which form hydrogen bonds, for example phenols and similar substances. In figure 1, a comparison of three chromatograms from three extractions of a whisky using different Twisters is shown.



**Figure 1.** Whisky extraction chromatograms obtained using EG-Silicone, Acrylate and PDMS Twisters, non-polar column separation. 5 mL whisky sample (20 % EtOH (v/v), 1:1 dilution with water), 1000 rpm for 1 hour at room temperature. Peak identification: 1. Phenol; 2. C6 Acid ethyl ester; 3. o-Cresol; 4. p-Cresol; 5. Phenethyl alcohol; 6. o-Ethylphenol; 7. 2,4- Xylenol; 8. C8 Acid ethyl ester; 9. C8 Acid; 10. C10 Acid ethyl ester; 11. C10 Acid; 12. C12 Acid ethyl ester; 13. C12 Acid.

The EG-Silicone Twister extraction provided the best recovery for phenols, ethyl esters and fatty acids from whisky. It is clearly seen that the EG-Silicone Twister extracts more compounds, and in greater amount, especially in the first region of the chromatogram up to 13 minutes. In table 1, peak areas are listed for the annotated compounds shown in the chromatograms. It is clearly seen that the peak areas that result from the EG-Silicone Twister extraction are an order of magnitude higher than the compound peaks obtained using the PA or PDMS Twisters for almost all compounds. Due to its polydimethylsiloxane basis, the EG-Silicone Twister also has high affinity for non-polar analytes like long carbon-chain ethyl esters and acids. When comparing the chromatograms from the EG-Silicone- and PDMS Twister extractions, it becomes clear that the EG-Silicone Twister extraction (top chromatogram) results in the same number of peaks in the region after 25 minutes, but the peaks are significantly larger and recoveries significantly better.

**Table 1.** Peak Areas of marked peaks obtained from extraction using three different Twister types.

Peak No.	Compounds	Extracted Ion [m/z]	Peak Areas		
			EG-Silicone	PA	PDMS
1	Phenol	94	1.1E+07	2.3E+06	6.0E+04
2	C6 Acid ethyl ester	88	1.8E+06	2.8E+05	7.6E+06
3	o-Cresol	108	1.5E+07	1.7E+06	1.8E+05
4	p-Cresol	108	1.1E+07	1.4E+06	1.6E+05
5	Phenethyl alcohol	91	2.4E+07	7.9E+06	1.6E+06
6	o-Ethylphenol	107	9.3E+06	6.1E+05	2.1E+05
7	2,4-Xylenol	107	1.7E+07	1.3E+06	4.3E+05
8	C8 Acid ethyl ester	88	1.5E+08	4.0E+06	1.4E+08
10	C10 Acid ethyl ester	88	2.3E+08	1.2E+07	2.3E+08
12	C12 Acid ethyl ester	88	1.1E+08	5.0E+06	7.0E+07

Table 2 shows the extraction efficiency (recovery in %) for selected whisky components: phenol, o-cresol, cis-whisky lactone and eugenol, obtained with three types of Twisters from spiked water samples. The highest recovery for phenol and o-cresol was obtained using an EG-Silicone Twister: 5.7 % and 9.8 %, respectively. The PDMS Twister gave high extraction efficiency for non-polar compounds like lactone and eugenol: 24.3 % and 32.9 %, respectively. In direct comparison with the PA Twister, the EG-Silicone Twister provided higher sensitivity for whisky lactone (6.1 %) and eugenol (29.5 %). These results prove that the EG-Silicone Twister extracts phenolic substances very efficiently and that it is also highly suitable for many non-polar compounds.

**Table 2.** Recovery in % for selected whisky standard substances obtained with three types of Twisters.

Whisky standards	Log $K_{o/w}$	EG-Silicone	PA	PDMS
Phenol	1.46	5.7	4.2	3.0
o-Cresol	1.95	9.8	5.2	1.5
cis-Whisky lactone	2.00	6.1	1.7	24.3
Eugenol	2.27	29.5	3.3	32.9

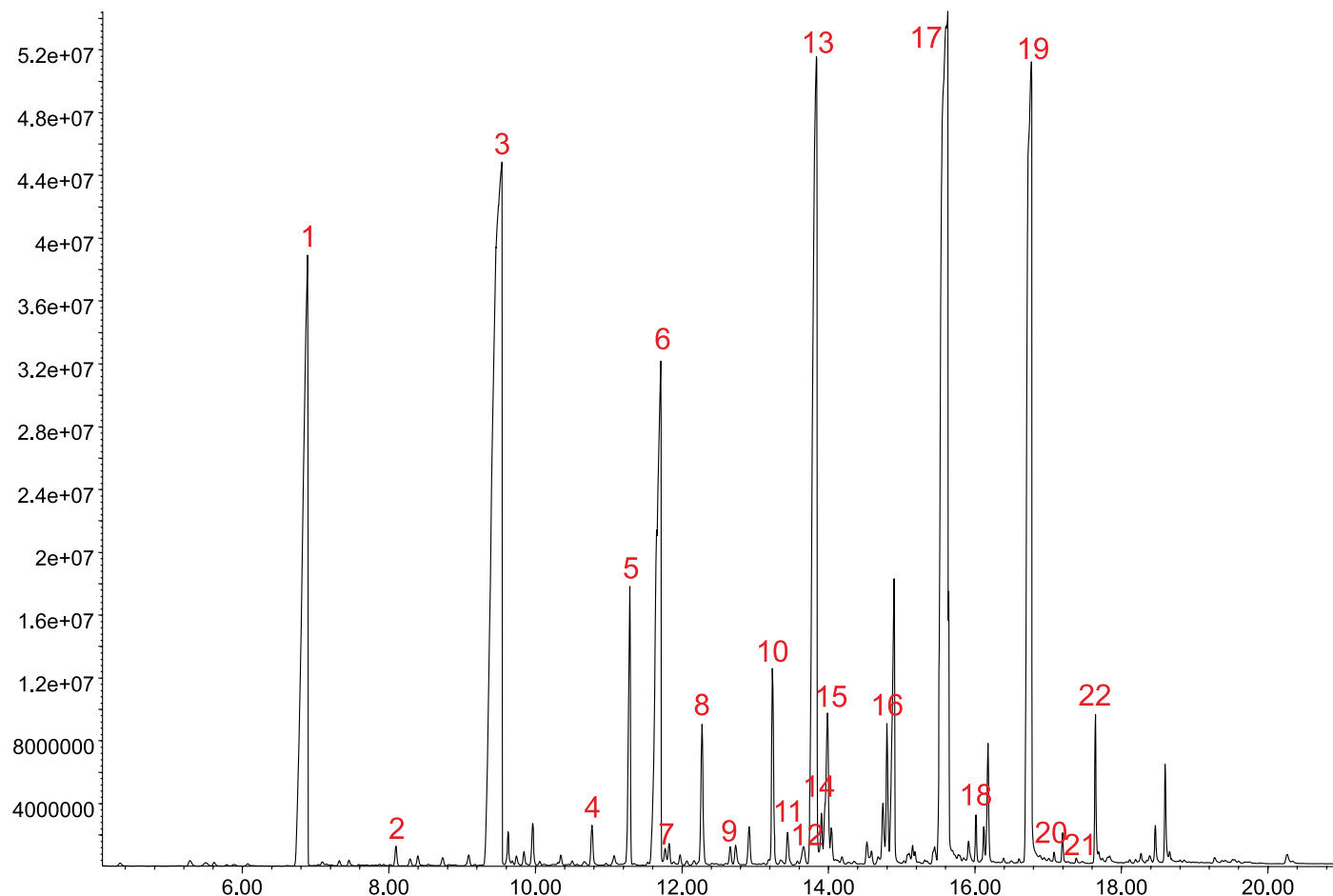
As is clearly seen in table 3, a significantly larger number of phenols and aromatic compounds were extracted from the whisky sample with the EG-Silicone Twister than with the PDMS Twister. The total number of extracted compounds is 126 for the EG-Silicone Twister and 92 for the PDMS Twister. For the other compounds classes, both Twisters extract a similar number of compounds, but the EG-Silicone Twister generally gives better recovery.

**Table 3.** Whisky compounds extracted by SBSE using the PDMS and EG-Silicone Twister respectively.

Compound class	PDMS	EG-Silicone
Phenols and aromatic compounds	14	40
Fusel alcohols	10	10
Fatty acids	11	11
Aliphatic acid ethyl esters	15	15
Other esters	22	22
Lactones	1	2
Acrolein derivates	7	7
Terpenes and norisoprenoids	6	7
Miscellaneous	6	12
Total	92	126

In order to achieve better separation of polar compounds from the whisky sample, a ZB-FFAP column was subsequently used. The resulting chromatogram is shown in figure 2, the whisky profile was obtained based on extraction with an EG-Silicone Twister. Table 4 lists the proposed compound names identified with the mass spectral database (Wiley6n). All identified peaks have a hit quality higher than 80.

The plausibility of the identification was checked against literature to ensure that the reported compounds were known to be present in whisky. Using the polar column, the peaks for acids, phenols and other polar compounds show a better peak shape. Many important whisky compounds (vanillin, ethyl vanillate, etc.), which were covered by broad co-eluting acid peaks when using the ZB-5 non-polar column, were now well separated and could easily be identified.



**Figure 2.** SBSE-TD-GC/MS chromatogram, polar column separation, resulting from an EG-Silicone Twister extraction of a 5 mL whisky sample diluted 1:1 with water (20 % EtOH v/v). Sample extracted for 1 hour at room temperature and 1000 rpm.

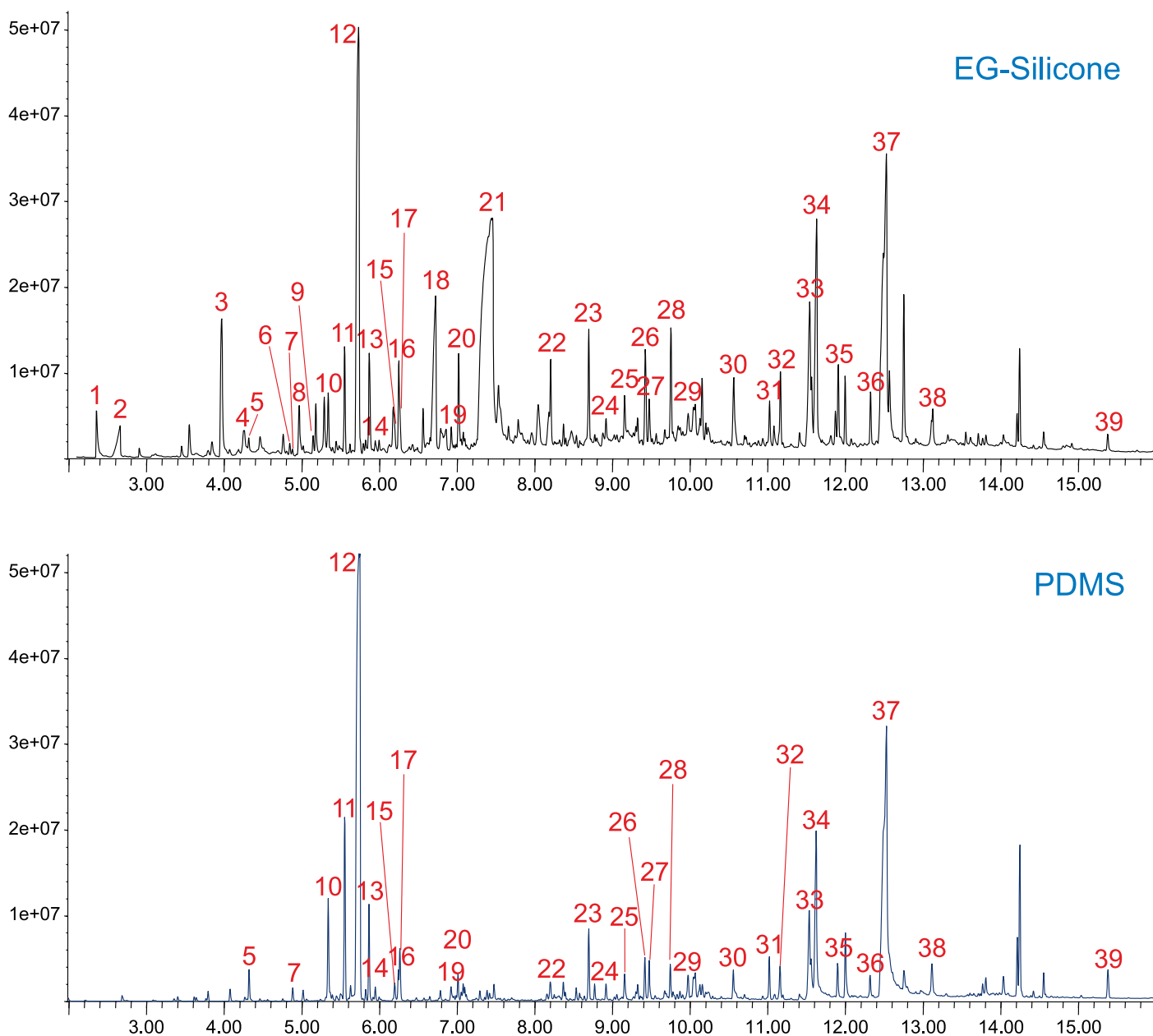
**Table 4.** Tentatively identified compounds found in Scotch whisky by Twister extraction and GC/MS analysis using a ZB-FFAP Column.

Peak No.	Proposed Identity	Peak No.	Proposed Identity	Peak No.	Proposed Identity
1	C8 Acid ethyl ester	9	trans Whisky lactone	17	C10 Acid
2	C9 Acid ethyl ester	10	o-Cresol	18	Farnesol
3	C10 Acid ethyl ester	11	p-Ethylguaiacol	19	C12 Acid
4	1-Decanol	12	d-Nerolidol	20	Vanillin
5	Phenethyl acetate	13	C8 Acid	21	Ethyl vanillate
6	C12 Acid ethyl ester	14	o-Ethylphenol	22	C14 Acid
7	Guaiacol	15	2,4-Xylenol		
8	Phenethyl alcohol	16	p-Ethylphenol		

**Multivitamin Juice.** Extraction of multivitamin juice or of other fruit juices is often negatively influenced by fruit pulp, which blocks analyte access to the extraction phase and/or hinders phase separation following the extraction. In contrast, the SBSE process for multivitamin juice is very easy to perform. 10 mL sample was directly filled into a 10 mL vial, the Twister was added and the sample stirred for 1 hour at 1000 rpm. Both EG-Silicone- and PDMS Twisters were used for the extraction.

As can be seen in the chromatograms in figure 3, the EG-Silicone Twister extracts more compounds than the PDMS Twister and with better recovery. The

peaks obtained using the EG-Silicone Twister are significantly bigger. In the chromatogram obtained with EG-Silicone Twister, 39 peaks were clearly identified. Nine compounds were not at all found or identified using the PDMS Twister: formic acid, acetic acid, furfural, furfural alcohol, 2-Hydroxycyclopent-2-en-one, 3-Methyl-2,5-Furandione, 5-Methyl-2-furfural, 2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one and Hydroxymethylfurfurole (HMF). Most of these compounds are furfurals and derivatives of furan. Moreover, the peaks for these nine compounds were very large using EG-Silicone Twister extraction, for example furfural (No. 3) and HMF (No. 21).



**Figure 3.** Multivitamin juice chromatogram obtained from EG-Silicone and PDMS Twister, non-polar column separation. 10 mL sample, 1000 rpm, 1 hour, room temperature.

**Table 5.** Identified compounds found in multivitamin juice by Twister extraction and GC/MS analysis using a ZB-5 Column.

Peak No.	Proposed Identity	Peak No.	Proposed Identity	Peak No.	Proposed Identity
1	Formic acid	14	gamma-Terpinene	27	Nerolidol
2	Acetic acid	15	alpha-Terpinolene	28	Methoxyeugenol
3	Furfural	16	Linalool	29	alpha-Cubebene
4	Furfural alcohol	17	Apple oil	30	C14 Acid
5	Isoamyl acetate	18	2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	31	Nootkatone
6	2-Hydroxycyclopent-2-en-one	19	4-Terpineol	32	8-Hydroxy-6-methoxy
7	alpha-Pinene	20	alpha-Terpineol	33	9-Hexadecenoic acid
8	3-Methyl-2,5-Furandione	21	Hydroxymethylfurfurole (HMF)	34	C16 Acid
9	5-Methyl-2-furfural	22	Eugenol	35	Limetin
10	beta-Myrcene	23	trans-Caryophyllene	36	Xanthotoxin
11	delta-3-Carene	24	alpha-Humulene	37	Linoleic acid
12	d-Limonene	25	Valencene	38	Isopimpinellin
13	Isoamylbutyrate	26	Elemicin	39	Squalene

Some important terpenes in the multivitamin juice were found with both Twisters, these are listed in table 6. Eight terpenes were selected and their peaks integrated based on extracted ion chromatograms (EICs). The EIC masses used and the resulting peak areas are also listed in table 6. It can be seen that EG-Silicone- and PDMS Twisters give similar extraction efficiency for the terpenes judging by the very similar peak areas obtained using the two Twisters. For more polar alcohol-terpenes linalool, 4-terpineol, alpha-terpineol, and nerolidol, the EG-Silicone Twister does provide better recovery than the PDMS Twister; conversely, for monoterpenes like alpha-pinene, beta-myrcene, delta-3-carene and d-limonene the PDMS Twister gives better recovery.

**Table 6.** Peak area responses of Terpenes resulting from Twister extractions.

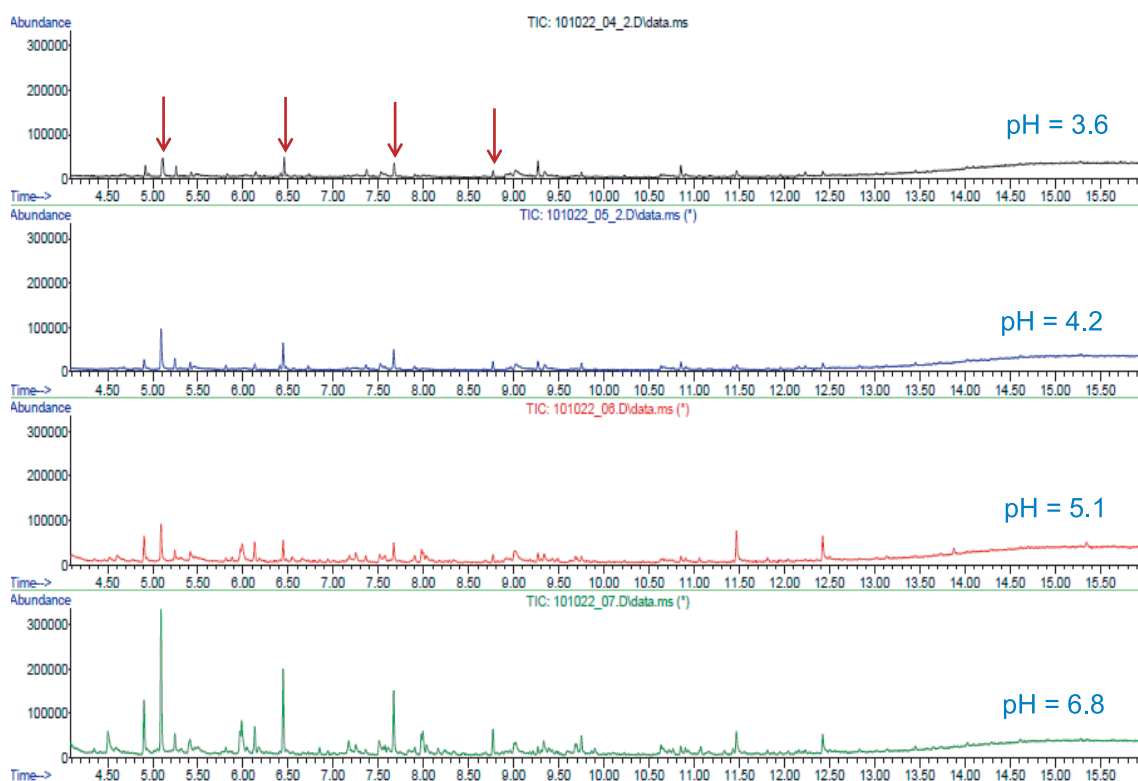
Peak No.	Compounds	Extracted Ion [m/z]	Peak Areas	
			EG-Silicone	PDMS
7	alpha-Pinene	93	1.7E+05	3.9E+05
10	beta-Myrcene	93	1.4E+06	2.6E+06
11	delta-3-Carene	93	2.8E+06	4.7E+06
12	d-Limonene	68	1.3E+07	1.8E+07
16	Linalool	71	1.5E+06	4.3E+05
19	4-Terpineol	71	4.3E+05	2.7E+05
20	alpha-Terpineol	59	1.5E+06	4.3E+05
27	Nerolidol	69	5.2E+05	4.8E+05

*White Wine (Sauvignon Blanc): pH Stability.* It has been shown in the application examples listed above that the EG-Silicone Twister is well suited for extraction of both whisky and multivitamin juice. The appearance of chromatograms and blanks, as well as the extraction efficiency, remain stable even after many extractions as long as the Twisters are kept properly conditioned. Twisters that had been used for extraction of white wine, however, showed a significant increase in the number and size of blank peaks. Several extraction conditions were tried, e.g. sample dilution (1:10 and 1:20 with water), headspace extraction and adjusting the pH value. It was finally determined that the acidity of the white wine was the reason for the observed phase damage.

White wine ranges in pH value from 2.9 to 4.2. The sauvignon blanc, which was used in this study, had

a pH value of 3.2, lower than the pH of the whisky samples analyzed (4.0) and lower than the multivitamin juice (3.8).

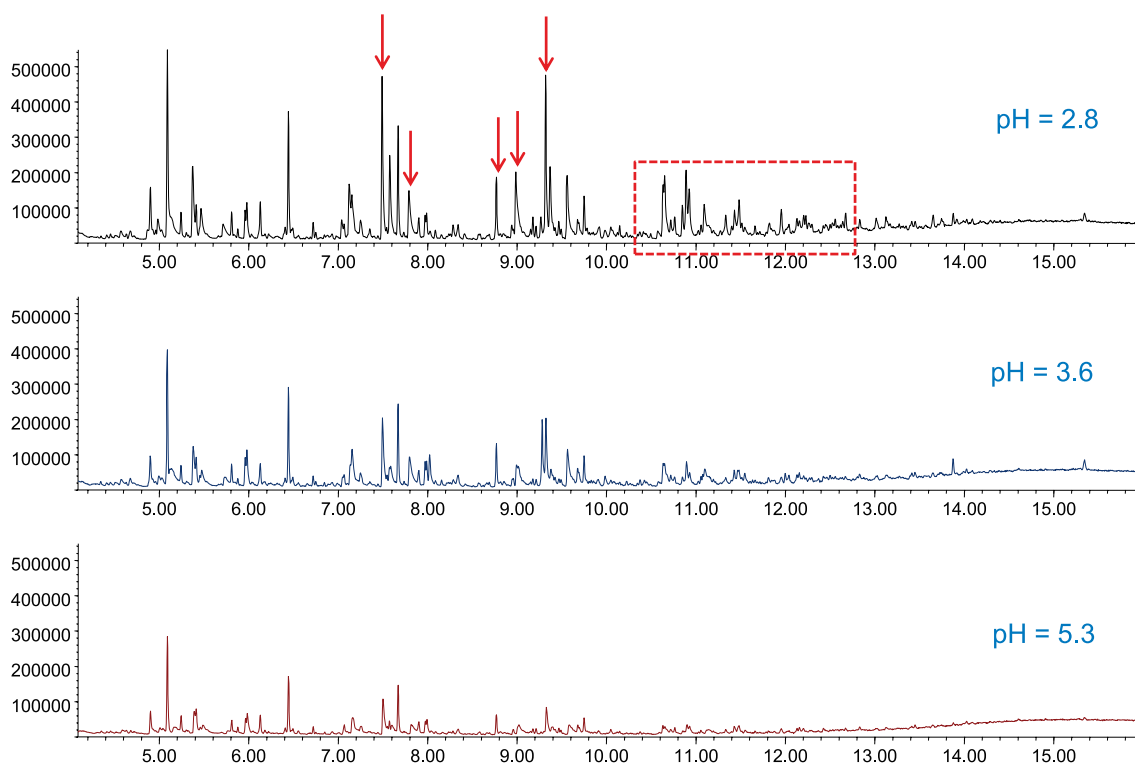
In order to avoid phase damage and to determine the acceptable pH range for working with the EG-Silicone Twister, white wine samples were neutralized by adding 1.0 molar NaOH to reach pH values of 3.6, 4.2, 5.1 and 6.8 respectively. After sample extraction for 1 hour and subsequent conditioning, the blank chromatograms were compared. Figure 4 shows a stacked view of the obtained chromatograms. The siloxane peaks increased in number and size with increasing pH value. The pH limit for EG-Silicone Twister in neutralized wine sample is found to be 3.5 to 5.1. Within this pH range phase damage is clearly limited. The blank peaks increase significantly at higher pH values.



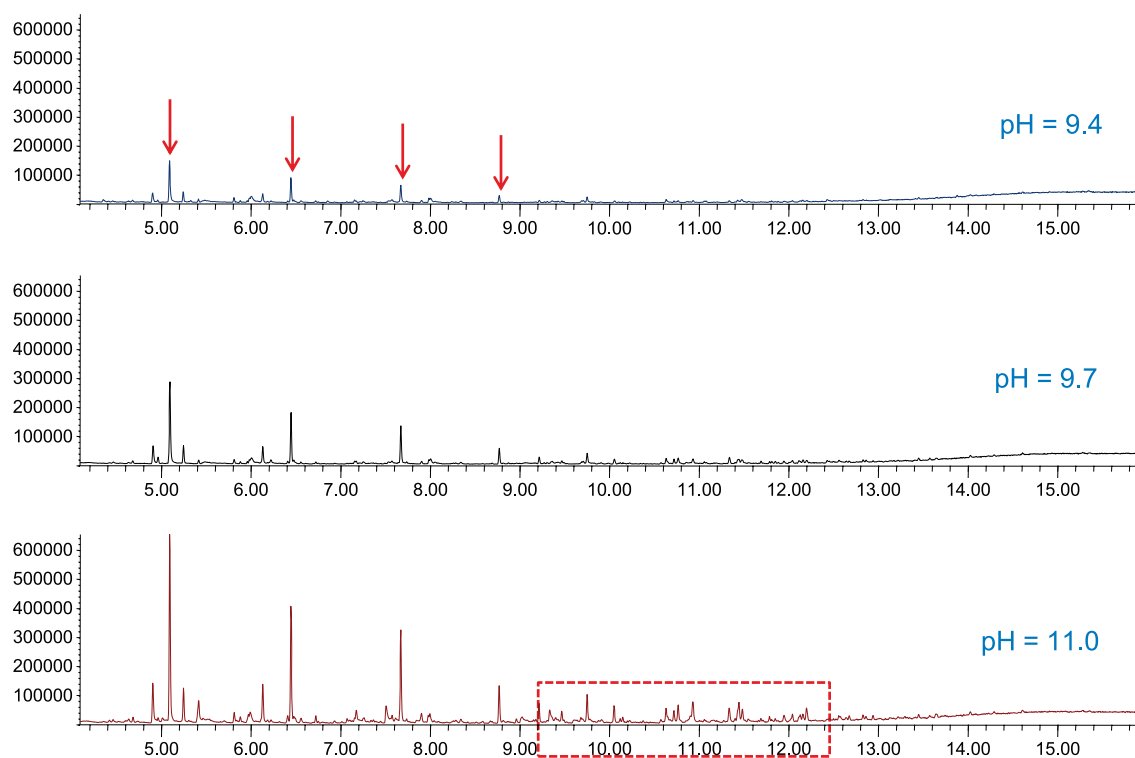
**Figure 4.** Blank chromatograms of EG-Silicone Twisters after wine extraction at different pH values and subsequent conditioning. The arrows indicate the siloxane peaks, which increase in size with increasing pH value.

The pH limit for the use of EG-Silicone phase in aqueous matrix was also determined. HPLC-grade water samples were adjusted to a range of pH values. 0.1 molar HCl was added to reach pH 2.8, 3.6, 4.0 and 5.3, respectively, and 0.1 molar NaOH was added to reach pH 9.4, 10.0 and 11.0. Twisters were then added and the adjusted samples stirred for 1 hour. After extraction, all Twisters were conditioned at 220°C for 1 hour and blank chromatograms were recorded. The comparisons show that the polyglycol blank peaks increased with decreasing pH (Fig. 5) and the siloxane peaks increased with increasing pH value (Fig. 6). In aqueous matrix, the acceptable pH range for using the EG-Silicone Twister was found to be 3.5 to 10.00.





**Figure 5.** Blank chromatograms of EG-Silicone Twisters after water sample extractions at different pH values and subsequent conditioning. The arrows and dashed lines show the polyglycol peaks that increase in size with decreasing pH value.



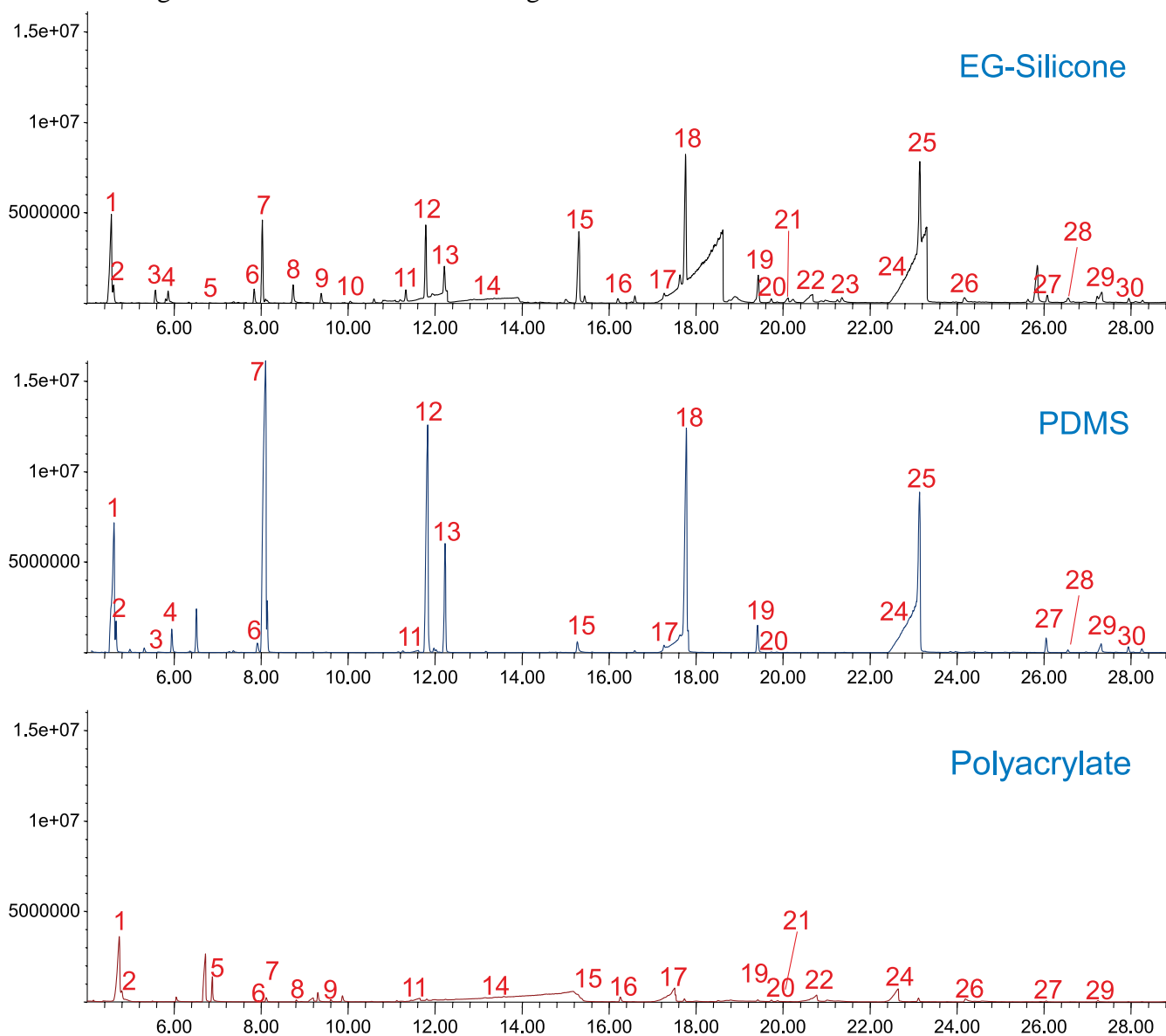
**Figure 6.** Blank chromatograms of EG-Silicone Twisters after water sample extractions at different pH values and subsequent conditioning. The arrows and dashed lines show the siloxane peaks that increase in size with increasing pH value.

If an EG-Silicone Twister is used outside the pH range suggested here, blank peaks will increase significantly in size up to a factor 10 or more. Additionally, the Twister will lose its extraction efficiency due to phase damage and will no longer be useable. The reason for the difference in acceptable pH range between white wine and water samples is not yet fully understood.

*White Wine (Sauvignon Blanc): Profile.* EG-Silicone-, PA- and PDMS Twisters were used to extract a broad range of volatile compounds and generate a flavor profile of the white wine. Subsequently, the extraction results for the three Twister types were compared. PA- and PDMS Twisters can be added directly to the wine sample without modifying the sample. Prior to extraction with EG-Silicone Twister, the wine sample needed to be neutralized to pH 3.6 in order to avoid break-down of the Twister phase. Chromatograms were obtained using both ZB-5 (non-polar) and ZB-FFAP (polar) columns, the tentatively identified wine compounds are listed in Table 7. Except for the oven programs and column flow rates used, all conditions for TDU, CIS, and MSD were the same for all analyses performed.

A stacked view comparison of chromatograms from extractions using different Twisters is shown in figure

7. It can be seen that the EG-Silicone Twister extracts a larger number of individual substances (30 tentatively identified peaks) from wine than the PDMS and PA Twisters. Substances like furfural, cis- and trans-4-hydroxymethyl-2-methyl-1,3-dioxolane, glycerin, malic acid, methyl 2,3-dihydroxybenzoate are only found in the EG-Silicone- and PA Twister based chromatograms. Furthermore, most peaks are much larger in the EG-Silicone Twister-based chromatogram than in the PA Twister-based chromatogram. The EG-Silicone Twister extracts acids much more efficiently from wine than the PDMS Twister, see peaks No. 11, 17, 20, 22, and 24 as well as alcohols like 2,3-butanediol (No. 3), 1-hexanol (No. 6), and Phenethyl alcohol (No.15). PDMS Twisters, conversely, extract larger amounts of esters compared to EG-Silicone Twister (see No. 4, 7, 12, 13, 18, 25).

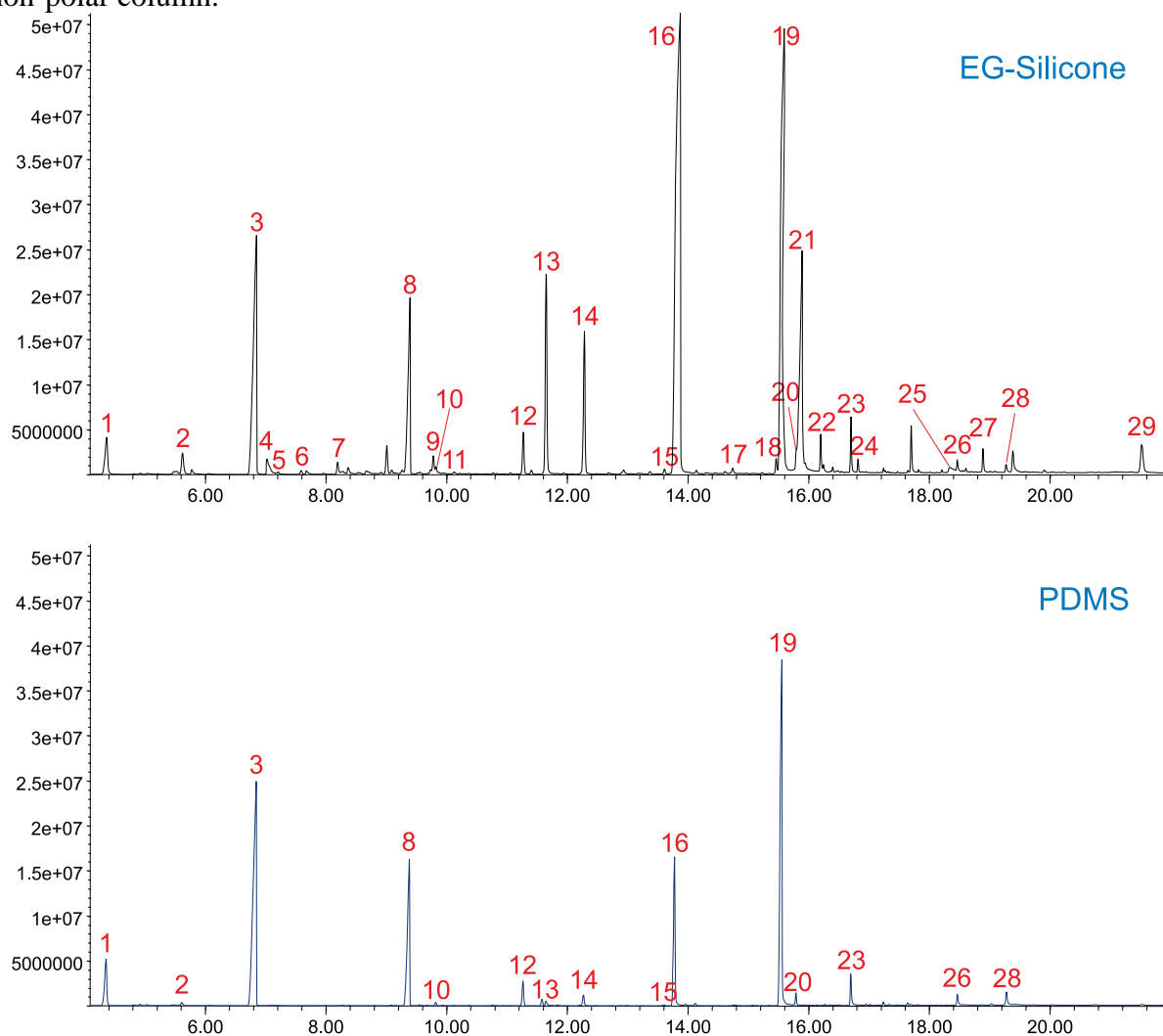


**Figure 7.** Sauvignon Blanc chromatogram profiles obtained from EG-Silicone-, PDMS- and PA Twister extractions of 5 mL samples for one hour at 1000 rpm, non-polar column separation.

**Table 7.** Tentatively identified compounds extracted from white wine using different Twisters and separated on a ZB-5 GC Column.

Peak No.	Proposed Identity	Peak No.	Proposed Identity	Peak No.	Proposed Identity
1	2-Methyl-butanol	11	C6 Acid	21	C9 Acid
2	3-Methyl-butanol	12	C6 Acid ethyl ester	22	Malic acid
3	2,3-Butanediol	13	1-Hexyl acetate	23	Methyl 2,3-dihydroxybenzoate
4	C4 Acid ethyl ester	14	Glycerin	24	C10 Acid
5	Furfural	15	Phenethyl alcohol	25	C10 Acid ethyl ester
6	1-Hexanol	16	2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	26	p-Hydroxyphenethyl alcohol
7	Isoamyl acetate	17	C8 Acid	27	2,4-Di-tert-butylphenol
8	trans-4-Hydroxymethyl-2-methyl-1,3-dioxolane	18	C8 Acid ethyl ester	28	Methyl 2,5-dihydroxybenzoate
9	cis-4-Hydroxymethyl-2-methyl-1,3-dioxolane	19	Phenethyl acetate	29	C12 Acid
10	Citraconic anhydride	20	Ethyl dl-malate	30	C12 Acid ethyl ester

To achieve better resolution and separation, of polar compounds extracted from the wine, a polar column was also used. As can be seen in figure 8, the polar column produced sharp acid peaks and enabled the separation of several key polar compounds that were covered by big co-eluting ester peaks in the chromatogram produced on the non-polar column.



**Figure 8.** Sauvignon blanc chromatogram profiles obtained from EG-Silicone- and PDMS Twister extractions of 5 mL samples for one hour at 1000 rpm, polar column separation.

Although a different column was used, the quantitative results and determined compound identities obtained from EG-Silicone- and PDMS Twister extractions were in good agreement. Some polar acids, alcohols, as well as other polar compounds could be extracted only using the EG-Silicone Twister. Additionally, 5-methyl-2-furfural (No. 11) and Hydroxymethylfurfurole (HMF) (No. 24), p-Hydroxyphenethyl alcohol (No. 27) and ethyl 3-(4-hydroxyphenyl)-propenoate (Z or E) (No. 29) were found only when combining EG-Silicone Twister extraction with separation on a polar column (Table 8).

**Table 8.** Tentatively identified compounds extracted from white wine using different Twisters and separated on a ZB-FFAP Column.

Peak No.	Proposed Identity	Peak No.	Proposed Identity	Peak No.	Proposed Identity
1	1-Hexyl acetate	11	5-Methyl-2-furfural	21	Glycerin
2	1-Hexanol	12	Phenethyl acetate	22	2,3-Dihydrobenzofuran
3	C8 Acid ethyl ester	13	C6 Acid	23	C12 Acid
4	Acetic acid	14	Phenethyl alcohol	24	Hydroxymethylfurfurole (HMF)
5	Furfural	15	Ethyl dl-malate	25	Malic acid
6	trans-4-hydroxymethyl-2-methyl-1,3-dioxolane	16	C8 Acid	26	C14 Acid
7	2,3-Butanediol	17	C9 Acid	27	p-Hydroxyphenethyl alcohol
8	C10 Acid ethyl ester	18	2,3-Dihydro-3,5-dihydroxy-6-methyl-4H-pyran-4-one	28	C16 Acid
9	cis-4-Hydroxymethyl-2-methyl-1,3-dioxolane	19	C10 Acid	29	Ethyl 3-(4-hydroxyphenyl)-propenoate (Z or E)
10	Clorius	20	2,4-Di-tert-butylphenol		

## CONCLUSION

The novel EG-Silicone Twisters and PA Twisters presented in this work enable higher extraction efficiency than traditional PDMS Twisters for polar compounds in samples like whisky, multivitamin juice and white wine. For compounds like phenols, furans, alcohols, and acids, use of EG-Silicone Twister results in the best extraction efficiency. For non-polar compounds such as terpenes and ethyl esters etc., EG-Silicone Twisters, due to their dimethylsiloxane basis, provide extraction efficiencies similar to those achieved using PDMS Twisters. By using the EG-Silicone Twister and PDMS Twister in a sequential SBSE process [7], an overall analyte profile of volatile and semivolatile organic compounds in a sample can be obtained. The pH value of the sample is a critical point for the EG-Silicone Twister. In water-based standards, the optimum pH range was found to be from 3.5 to 10.0, for wine samples from 3.6 to 7.0. Like the PDMS Twister, the extraction using the EG-Silicone Twister is easy to perform. Only a few instrumental parameters have to be adjusted, mainly because the upper temperature limit for EG-Silicone Twister phase desorption is 220 °C. Additionally operating the TDU

in solvent vent mode is important when desorbing EG-Silicone- and PA Twisters in order to remove excess water. This is needed to eliminate water from the GC/MS system since, due to their polar nature, the EG-Silicone and PA Twisters retain some water during extraction.

## ACKNOWLEDGEMENT

The authors would like to thank Dr. Kevin MacNamara, Irish Distillers, Pernod-Ricard for his kind support.

The authors would also like to thank Dr. Justus von Sonntag from the Leibniz Institut für Oberflächenmodifizierung, e.V. (Leipzig, Germany) for his contribution in developing the Acrylate Twisters.

Financial support for the development of the Acrylate Twisters by the German Ministry for Economics under the ProINNO II Grant KF 0189604VT is gratefully acknowledged.

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