



## Article

# Volatile Sulphur Compounds in Wine Distillates by Stir Bar Sorptive Extraction-Gas Chromatography-Mass Spectrometry

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**Abstract:** A Stir Bar Sorptive Extraction-Gas Chromatography-Mass Spectrometry (SBSE-GC-MS) method has been optimized and validated for the determination of eight volatile sulphur compounds in wine distillates: diethyl sulphide (DES), dimethyl disulphide (DMDS), diethyl disulphide (DEDS), 2-thiophenecarboxaldehyde (TC), dibutyl sulphide (DBS), dipropyl disulphide (DPDS), dipropyl sulphide (DPS), and dimethyl trisulphide (DMTS). After optimization by  $2^4$  factorial design, the SBSE-GC-MS extraction conditions were as follows: a polydimethylsiloxane twister (10 mm  $\times$  0.5 mm), 35 °C as the extraction temperature, 10 mL as the sample volume, 7% (*v/v*) as the alcoholic grade, 47 min as the extraction time, 10% (*w/v*) of NaCl, and 1% (*w/v*) of EDTA (ethylenediaminetetraacetic acid). Under optimal conditions, adequate analytical figures of merit were obtained for eight of the ten compounds initially considered, with low quantification and detection limits and relative standard deviations for inter-twister and inter-day repeatability values ranging from 7.5 to 21.8% and from 7.2 to 27.5%, respectively. The methodology was applied to 34 wine distillates (continuous column distillation and distillation in pot still) elaborated for the production of Brandy de Jerez: 15 aged distillates aged for different periods of time in American oak wood and 19 non-aged distillates. The most significant volatile sulphur compounds were DBS, DMDS, and DPS. The Cluster Analysis (CA) on the volatile sulphur compounds grouped the samples according to the use of sulphur dioxide. In general, lower amounts of volatile sulphur compounds were found in the aged samples, although the high standard deviations obtained highlight that their contents depend on multiple factors related to the elaboration process.



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**Keywords:** volatile sulphur compounds; wine distillates; sulphur dioxide; Brandy de Jerez; SBSE

## 1. Introduction

Volatile sulphur compounds (VSCs) are a group of compounds of diverse chemical nature, mainly thiols, mono- or polysulfides, and thiol-esters, which can be part of the composition of foods and beverages. They are, mainly, aromatic compounds and, although they are usually found in very low concentrations (in the order of  $\mu\text{g/L}$ , or even  $\text{ng/L}$ ), they usually present low perception thresholds. The presence of VSCs in food and beverages is associated with defects in their organoleptic characteristics [1]. In general, their odours are unpleasant (garlic, onion, asparagus, rotten eggs, etc.), although there is a small group of VSCs that present pleasant odours such as dimethyl sulphide, which can have a beneficial effect in the organoleptic characteristics of wine, enhancing its fruity notes, an effect that depends on its concentration [2].

In the case of grape-derived beverages, these compounds are produced by two main routes: enzymatic and non-enzymatic [3]. In the enzymatic pathway, they are formed from hydrogen sulphide produced by yeasts during the winemaking process from inorganic sulphur compounds such as sulphates or sulphites, or from organic sulphur compounds such as glutathione or cysteine. The non-enzymatic pathway occurs mostly during the processing and storage stages, and involves chemical reactions catalyzed by light and/or the temperature of sulphur compounds present in the wine [4].

In distillation, being compounds with a low boiling point (below 90° Celsius), they pass, mainly, from the wine to the distillate in the first stage of the process (head fraction) together with other undesirable aromatic compounds. The wine distillate obtained in the central stage of the process (heart fraction) is richer in desirable aromatic compounds and has a lower concentration of VSCs [5,6]. In addition, their concentrations may be modified during the distillation stage according to the specific conditions employed [7].

Brandy de Jerez is produced in southern Spain from wine spirits that are aged in oak wood casks for specific durations. Its volatile composition depends on the starting grape, the fermentation conditions, the conservation of the wine obtained, the distillation process, and the aging period in oak wood. Among these conditions for the fermentation and conservation of the wine until the moment of its distillation, we find the use of sulphur dioxide as a preservative, which affects both the starting wine and the distillate obtained [8].

In relation to the VSC determination, the methods of analysis of these compounds in wine distillates present certain difficulties due to factors such as the complexity of the sample matrix, the high alcohol content (over 30% alcohol by volume (ABV)), the low levels of concentration of these compounds in distilled beverages, and their high reactivity [3]. Because of this, the methods of analysis found in the literature usually present a first stage of extraction and concentration before their analysis stage by GC. For the extraction of VSCs in wines and wine distillates, liquid–liquid extraction [3], static headspace [3], counter-current supercritical fluid extraction [9], purge and tramp concentrators [10], solid-phase extraction (SPE) [5], solid-phase microextraction (SPME) [3,11], headspace solid-phase microextraction (HS-SPME) [1,5,12–14], and Stir Bar Sorptive Extraction (SBSE) [15] have been used.

SPME and SBSE techniques have certain advantages over other extraction techniques, since they do not require solvents; they simultaneously combine the extraction and concentration of analytes in a single step; they are simple and fast techniques that require a low sample volume; and they are easily combined with analytical techniques such as GC. SBSE has a larger sorbent phase and higher sensitivity and is more robust than SPME [16], which makes it an ideal green analytical method for determining the concentration of volatile minor compounds such as VSCs at a stage prior to their analysis.

The most common detection system used in the analysis of VSCs in wine and distillate samples is MS [2,11,14,17,18], although other types of more specific detectors such as chemiluminescent detectors [19], atomic emission detectors [1], and pulsed flame photometric detection [12] are also found.

There are few recent papers that focus their studies on the analysis of VSCs in brandy samples [1,5,20,21], and there have been no studies on Brandy de Jerez samples. It is for this reason that the aim of this paper was the optimization of an SBSE-GC-MS method for the quantitative determination of volatile sulphur compounds in wine distillates and brandy samples. After optimization and validation, the analytical methodology was applied to a high number of distillates employed for the elaboration of Brandy de Jerez.

## 2. Materials and Methods

### 2.1. Distillates

A wine distillate from a local winery spiked with all volatile sulphur compounds considered in the present study at a concentration of 1 µg/L was employed to optimize the SBSE conditions. After optimization and validation, several wine distillates (head fraction, heart fraction, non-aged distillate, and aged distillate) subjected to the addition of different amounts of SO<sub>2</sub> from different local companies were analyzed (Appendix A, Table A1).

### 2.2. Chemicals and Reagents

The commercial standards, diethyl sulphide (DES), 98%; dimethyl disulphide (DMDS), 99.0%; diethyl disulphide (DEDS), 99%; 2-thiophenecarboxaldehyde (TC), 98%; dibutyl sulphide (DBS), 98.0%; dipropyl disulphide (DPDS), 98%; dipropyl sulphide (DPS), 99%; thiophene (T), 99%; dimethyl trisulphide (DMTS), analytical standard; Ethyl methyl sulphide, (EMS) 96%; and 1-pentanethiol (P), 98%, were supplied by Merck (Darmstadt, Germany). Thiophene (T) was employed as internal standard. Some chemical and physical properties of all of these volatile compounds are shown in Table 1. NaCl and AEDT were purchased from Scharlau (Barcelona, Spain). Ethanol (analytical grade) was obtained from Merck (Darmstadt, Germany), whereas ultrapure water was obtained using a Milli-Q gradient water purification system (18.18 MΩ/cm at 25 °C; total organic content less than 10 µg/L).

**Table 1.** Some of the physical and chemical properties of the volatile sulphur compounds studied <sup>1</sup>.

Compounds	Molecular Weight (g/mol)	Boiling Temperature (°C)	Melting Temperature (°C)	Partition Coefficient (Log K <sub>ow</sub> )	Aromatic Descriptor
Ethyl methyl sulphide (EMS)	76.16	65.0–67.0	−104.8	1.54	cabbage, garlic, sulphur
Diethyl sulphide (DES)	90.19	92.1	−103.9	1.95	garlic, ethereal
Thiophene (T)	84.14	84	−39.4	1.81	benzene
1-Pentanethiol (P)	104.22	126.6	−75.69	2.74	meaty, strong garlic
Dimethyl disulphide (DMDS)	94.20	109.72	−84.67	1.77	garlic, onion, sulphurous
Dipropyl sulphide (DPS)	118.24	142–143	−102.5	2.84	unpleasant
Diethyl disulphide (DEDS)	122.3	152	−101.5	2.41	cabbage, carbide, roasted onion, rubber, sulphur
Dibutyl sulphide (DBS)	146.3	182–189	−80	4.50	green, unpleasant
Dimethyl trisulphide (DMTS)	126.3	165–175	−85	1.87	cabbage, fish, onion, sulphur
Dipropyl disulphide (DPDS)	150.3	193–195	−85.6	3.84 *	onion, garlic
2-Thiophenecarboxaldehyde (TC)	112.15	198	<10 °C	1.56	sulphurous

<sup>1</sup> Data obtained from PubChem, <https://pubchem.ncbi.nlm.nih.gov>, accessed on 10 January 2025. National Institutes of Health, National Center for Biotechnology Information, U.S. National Library of Medicine, USA. \* Estimated.

Individual stock standard solutions of each sulphur compound were prepared by weight in ethanol.

From these, two global standard solutions containing all the analytes at high concentrations (A: EMS, P, DPS, DBS, and DPDS; and B: DES, DMDS, DEDS, DMTS, and TC) were prepared in ethanol. Working solutions were prepared by diluting different amounts of these global solutions in ethanol. All these solutions were kept at 4 °C.

### 2.3. Sample Preparation

After optimization, the specific SBSE procedure employed was as follows: 10 mL of sample diluted to 7% (v/v) with ultrapure water was pipetted into a 50 mL Erlenmeyer flask closed with parafilm and spiked with 100 µL of a solution of thiophene (IS, 0.1043 g/L

in ethanol). NaCl at 10% (*w/v*) and 1% (*w/v*) ethylenediaminetetraacetic acid (EDTA) were also added. A 10 mm commercial PDMS stir bar (0.5 mm film thickness) was employed for the extraction. Each sample was agitated at 1100 rpm at a temperature of 35 °C for 47 min on a multi-position magnetic stirrer (Mulheim a/d Ruhr, North Rhine-Westphalia, Germany). After the extraction, the PDMS stir bar was removed, washed with distilled water, and gently dried. Then, it was transferred into a glass thermal desorption tube for thermal desorption.

#### 2.4. Apparatus

A commercial thermal desorption unit (TDU, TDS-2, Gerstel, Mülheim and der Ruhr, North Rhine-Westphalia, Germany) equipped with a CIS-4 (cooled injection system, Gerstel) was used for the programmed thermal desorption (from 40 °C to 300 °C, held for 10 min and at 60 °C/min) under helium flow at 75 mL/min. After desorption (splitless for 2 min), the sulphur volatiles were cryofocused in the CIS-4 system employing liquid N<sub>2</sub> at –140 °C. After cryofocusing and for the analysis by GC-MS, the CIS-4 was programmed from –140 °C to 300 °C (held for 5 min) at 10 °C/s.

Capillary GC-MS analyses in the electron impact mode (EI+ at 70 eV) were performed using an Agilent 6890 GC-5973N MS system (Agilent, Little Falls, DE, USA). The mass detector worked in a range from 30 to 400 amu.

A DB-Wax capillary column (J&W Scientific, Folsom, CA, USA), 60 m × 0.25 mm I.D., with 0.25 µm coating was used. The program of the GC oven was as follows: Temperature held at 35 °C for 10 min, and then ramped up to 100 °C at 5 °C/min. After that, the oven temperature was elevated to 210 °C at 3 °C/min and kept for 40 min. Helium was employed as carrier gas at a flow rate of 1.0 mL/min.

The MS signal identification was performed by analogy with mass spectra (with a minimum of 90% similarity) from commercial standards and those from Wiley 7N Edition Library [22] and confirmed by their retention times. Each volatile sulphur compound was quantified using selective ion monitoring mode (Table 2). Quantitative data were obtained by measuring the molecular ion area in relation to that of the internal standard (T).

**Table 2.** Volatile sulphur compounds studied. Information employed for their identification and quantification.

Compounds	CAS Number	Retention Time (min)	Quantifying Ion	Qualifier Ions
Ethyl methyl sulphide (EMS)	624-89-5	6.899	76	61, 48, 47
Diethyl sulphide (DES)	75-78-3	9.179	90	75, 47
Thiophene (T)	110-02-1	14.477	84	58, 45
1-Pentanethiol (P)	110-66-7	15.955	104	70, 55, 42
Dimethyl disulphide (DMDS)	624-92-0	16.931	94	79, 45
Dipropyl sulphide (DPS)	111-47-7	17.169	118	89, 43
Diethyl disulphide (DEDS)	110-81-6	23.026	122	94, 66
Dibutyl sulphide (DBS)	544-40-1	26.057	146	61, 56
Dimethyl trisulphide (DMTS)	3658-80-8	28.779	126	110, 79, 45
Dipropyl disulphide (DPDS)	629-19-6	29.711	150	108, 43
2-Thiophenecarboxaldehyde (TC)	98-03-3	39.778	112	111, 39

For calibration, six levels of concentration, covering the expected concentration range, were tested in triplicate for each sulphur volatile compound.

#### 2.5. Experimental Design

For the optimization of the SBSE conditions, a 2<sup>4</sup> two-level factorial design, using the statistical Computer Package Statgraphics Centurion 19.0 (Statpoint, VA, USA) was chosen. According to the bibliography [16,23] and the authors' previous experience [24,25], four

possible significant factors were selected: extraction time, temperature, alcoholic degree, and sample volume. Total chromatographic area and number of chromatographic peaks were fixed as experimental responses to be optimized. All the SBSEs were carried out using 1% EDTA, 10% NaCl, and agitation at 1100 rpm.

This  $2^4$  design involved seventeen experiments performed in duplicate and in random order to provide protection against the possible effects of lurking variables. The values corresponding to the high (+) and low (−) points for each factor were as follows: 10 and 25 mL for sample volume; 30 and 100 min for extraction time; 25 and 35 °C for temperature; and 5 and 25% (*v/v*) for alcoholic content. A central point (65 min as extraction time, 30 °C as temperature, 15% as alcohol content, and 17.5 mL as sample volume) was also considered (Table 3).

**Table 3.** Factor levels. Optimization of SBSE conditions.

<b>First Experimental Design, <math>2^4</math></b>					
<b>Factor</b>	<b>Low (−)</b>	<b>High (+)</b>	<b>Center</b>	<b>Axial (−<math>\alpha</math>)</b>	<b>Axial (+<math>\alpha</math>)</b>
Temperature (°C)	25	35	30		
Extraction time (min)	30	100	65		
Sample volume (mL)	10	25	17.5		
Alcoholic content (% <i>v/v</i> )	5	25	15		
<b>Second Experimental Design, rotatable CCD</b>					
Extraction time (min)	15	45	30	8.8	51.2
Alcoholic content (% <i>v/v</i> )	2.5	10	6.25	0.95	11.6

After determining the significant variables, a second experimental design (a rotatable central composite design (CCD) with  $\alpha = 1.4142$ ) considering only extraction time and alcoholic content was selected. Table 3 shows the levels for the different factors considered in each experimental design.

### 2.6. Validation SBSE Methodology

After optimization, the SBSE methodology was validated. For this, detection and quantification limits, linear ranges, correlation coefficients, and inter-twister and inter-day repeatability were calculated.

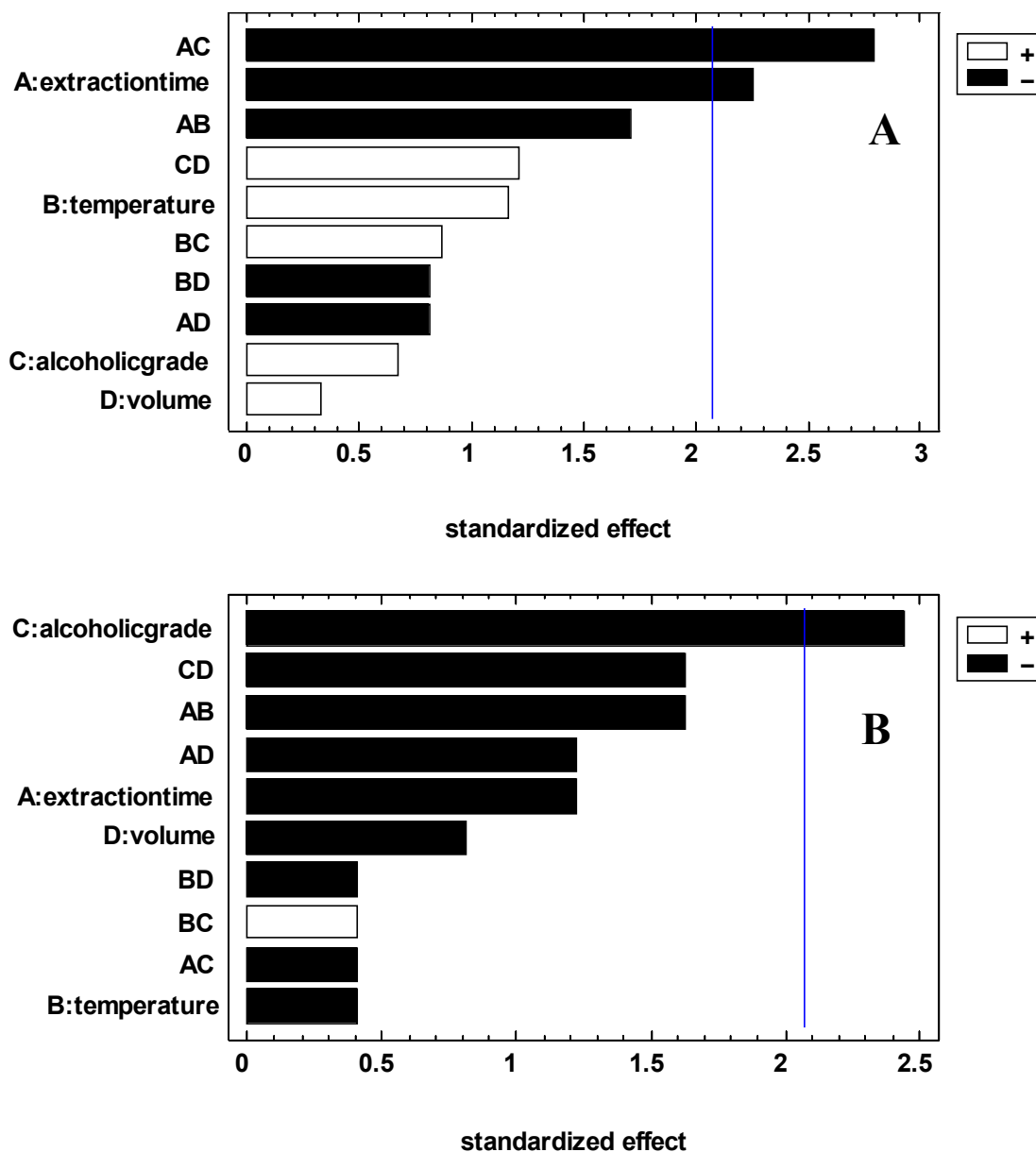
## 3. Results and Discussion

### 3.1. Optimization of the Extraction Conditions

Some factors such as the addition of EDTA (1%), NaCl (10%), and agitation (1100 rpm) were set according to previous studies. The addition of EDTA during the extraction of volatile sulphur compounds has demonstrated positive effects on their stability against oxidative phenomena [26], whereas the use of agitation and a certain amount of NaCl to enhance the SBSE efficiency [12,15] are clearly established. Firstly, a full factorial design ( $2^4$ ) was employed for screening the variables that may influence the SBSE procedure for the determination of volatile sulphur compounds in wine distillates. The variables considered were the extraction time, sample volume, extraction temperature, and alcoholic grade. The range studied for all of them is presented in Table 3. All of these parameters have shown that they must be carefully studied according to the matrix and the physical and chemical properties of analytes when applying the SBSE methodology. In the case of beverages with a high amount of ethanol, the study of the dilution of the sample previous to the SBSE analysis in order to reduce its alcohol content is crucial. Davis and Qian [27] have shown that there is a marked decrease in the detectability of some volatile sulphur compounds by

SPME when ethanol is present in the sample. For the extraction temperature factor, its high and low values were fixed, taking into account that high temperatures may cause thermal degradation problems and that low temperatures may give low chromatographic signals in the case of volatile compounds with low boiling temperatures.

The total chromatographic area and number of volatile sulphur compounds detected were considered as the experimental responses. The data were evaluated by an analysis of variance at the 5% significance level and the results are shown in Figure 1 ( $p < 0.05$  indicated by blue line).



**Figure 1.**  $2^4$  factorial design. Pareto diagram for total chromatographic area (A) and number of compounds detected (B).

As can be seen, for the total chromatographic area, the extraction time factor and the extraction time and alcoholic grade double interaction were significant at  $p < 0.05$ , whereas the alcoholic grade factor was the only significant variable for the number of compounds detected. In both cases, their effects were negative, that is, better chromatographic responses were obtained at lower values of these factors. Regarding the significant double interaction for the total chromatographic area, at lower extraction times, the chromatographic response

increased as the alcohol content increased, while only a slight decrease was observed at high extraction times. This seems to indicate that when low extraction times are used, the dilution effect by the addition of water to the samples is more significant than that of a higher SBSE efficiency at a low ethanol content. However, if high extraction times are used, both effects (dilution versus lower extraction competence) are compensated for.

Taking into account these first results, the extraction temperature variable was fixed at 35 °C, whereas the sample volume was set at 10 mL. A second experimental design considering only the extraction time and alcoholic grade was carried out. For this, a response surface design (composite central design,  $\alpha = 1.4142$ ) was selected. Table 3 shows the studied values for extraction time and alcoholic grade. These values were set taking into account the previous results from the first design.

In this case, the total chromatographic area was significantly affected by both variables, with a positive sign. However, neither of them was significant for the number of compounds detected. According to all of the results, the optimized SBSE conditions were fixed as follows: 35 °C as the extraction temperature, 10 mL as the sample volume, 7% (v/v) as the alcoholic grade, 47 min as the extraction time, 10% (w/v) of NaCl, and 1% (w/v) of EDTA. A volume of 100 µL of a solution of thiophene (IS, 0.1043 g/L in ethanol) was also added.

### 3.2. Method Validation

Once the parameters of the SBSE technique for volatile sulphur compounds in distillates were optimized, the method was analytically validated. First, the linearity range of each compound was determined from its calibration curve. For calibration, six concentration levels were used, in triplicate, at 7% (v/v) alcoholic grade of each volatile sulphur compound to be studied and covering the range of concentrations expected to be found in the samples (Appendix A, Table A2). In general, good correlation coefficients were obtained, with values ( $r^2$ ) greater than 0.991 in eight of the ten compounds studied. EMS and P showed erratic relative chromatographic area values and their calibration curves could not be established. The calibration curve equations for the remaining eight sulphur compounds are shown in Table 4. 1-pentanethiol together with 1-propanethiol and 1-butanethiol had previously shown poor linearity in a study of the determination of volatile sulphur compounds in fruit brandies by SPME [11], whereas ethyl methyl sulphide exhibits the lowest boiling point and octanol-water partition coefficient (Log  $K_{ow}$ ) of all of the sulphur compounds considered in this work, which could explain these anomalous chromatographic values (Table 1).

Subsequently, the detection and quantification limits (DL and QL) for each sulphur compound were calculated as three and ten times, respectively, the standard deviation of the y-intercept of the regression lines divided by its slope [28]. As can be seen, the DL and QL values found were between 0.04–0.93 µg/L and 0.13–3.1 µg/L, respectively (Table 4). In general, lower DL and QL values were obtained for those volatile sulphur compounds with higher Log  $K_{ow}$  values (Table 1). This is logical considering the apolar character of PDMS.

Finally, the inter-twister and inter-day repeatability values for each compound were evaluated (Table 4). For this purpose, the same sample prepared in absolute ethanol at intermediate concentrations in the linear range for each compound was analyzed under the optimized SBSE conditions on different days (3 days) and with five different twisters each day. The corresponding RSD values obtained for the inter-twister and inter-day repeatability are shown in Table 4. The RSD values obtained were from 5.9 to 21.8% for the inter-twister repeatability and from 7.2 to 27.5% for the inter-day values. 1-Pentanethiol exhibited high RSD values, which could be due to possible instability problems that were observed during the calibration phase. The values obtained demonstrate the high precision of the SBSE method optimized with values around 20% or lower.

**Table 4.** Validation study.

Compound	Concentration Range (µg/L)	Calibration Curve (r <sup>2</sup> )	DL (µg/L)	QL (µg/L)	Repeatability (%)		Recovery (%)
					Inter-Twister	Inter-Day	
EMS	-	-	-	-	15.4	14.5	-
DES	1.00–25.0	0.0009x + 0.0058 (0.9961)	0.9293	3.0977	8.1	12.1	116.4
P	-	-	-	-	36.5	38.2	-
DMDS	0.10–30.0	0.0027x + 0.0018 (0.9958)	0.1830	0.6101	6.3	7.2	110.1
DPS	0.10–1.00	0.0057x + 0.0011 (0.9963)	0.0396	0.1321	14.4	22.1	116.8
DEDS	0.10–1.00	0.0133x – 0.0007 (0.9909)	0.0676	0.2254	5.9	13.8	119.4
DBS	0.025–5.00	0.0055x + 0.0073 (0.9972)	0.1678	0.5595	21.8	27.5	109.3
DMTS	0.25–10.0	0.0089x + 0.0002 (0.9980)	0.2376	0.7921	7.5	10.6	113.6
DPDS	0.10–1.00	0.0167x – 0.0002 (0.9966)	0.0382	0.1274	9.6	26.5	108.8
TC	0.25–15.0	0.0006x + 0.0004 (0.9970)	0.4893	1.6310	18.7	27.4	84.8

For recovery, a non-aged distillate sample was spiked with a global standards solution at five levels of concentration. These concentrations coincided with those employed in the calibration phase. The slopes of the lines obtained for each compound were compared with those corresponding to the calibration (*t* criterion). In general, there was no significant difference between both slopes at  $p \leq 0.05$ . The recovery values ranged from 84.8% for TC to 119.4% for DEDS, which corroborate the accuracy of the SBSE method developed.

### 3.3. Comparison with Other Analytical Methodologies

Considering that there are no previous works on volatile sulphur compounds in wine distillates using SBSE-GC-MS, the developed methodology was compared with other analytical techniques applied to different alcoholic beverages.

In terms of the DL values, the present methodology exhibited improved values with respect to methods such as the determination of DES, DMDS, DPS, DMTS, and DPDS in whisky by HS-SPME-AED; DES and DMDS in wine by HS-GC-pFPD; and DES, DEDS, and DMDS in wine by HS-GC-SCD with cryofocusing (Table 5).

However, some authors [11,13,14] obtained, in some cases, lower DL values employing HS-SPME. In these studies, divinylbenzene/carboxen/polydimethylsiloxane (DVB/CAR/PDMS) arrow fibers and carboxen-polydimethylsiloxane (CAR/PDMS) and (DVB/CAR/PDMS) fibers, which have slightly higher polarity and higher retention capacity than PDMS, were used. The DL and QL values obtained in the present work were, in general, low enough to quantify the eight VSCs studied (Appendix A, Table A2). If it were necessary to improve the sensitivity of the present methodology, it could be achieved using Tandem Mass Spectrometry, also known as MS/MS or MS2.

On the other hand, the current analytical methodology presented recovery, repeatability, and reproducibility values similar to those based on SPME (Table 5), using extraction times and temperatures similar to this one, but with the advantage that, in the case of SBSE, several extractions can be easily performed in parallel.

Therefore, the SBSE-GC-MS method developed can be truly used to identify and quantify eight volatile sulphur compounds in grape distillate samples at very low concentrations.



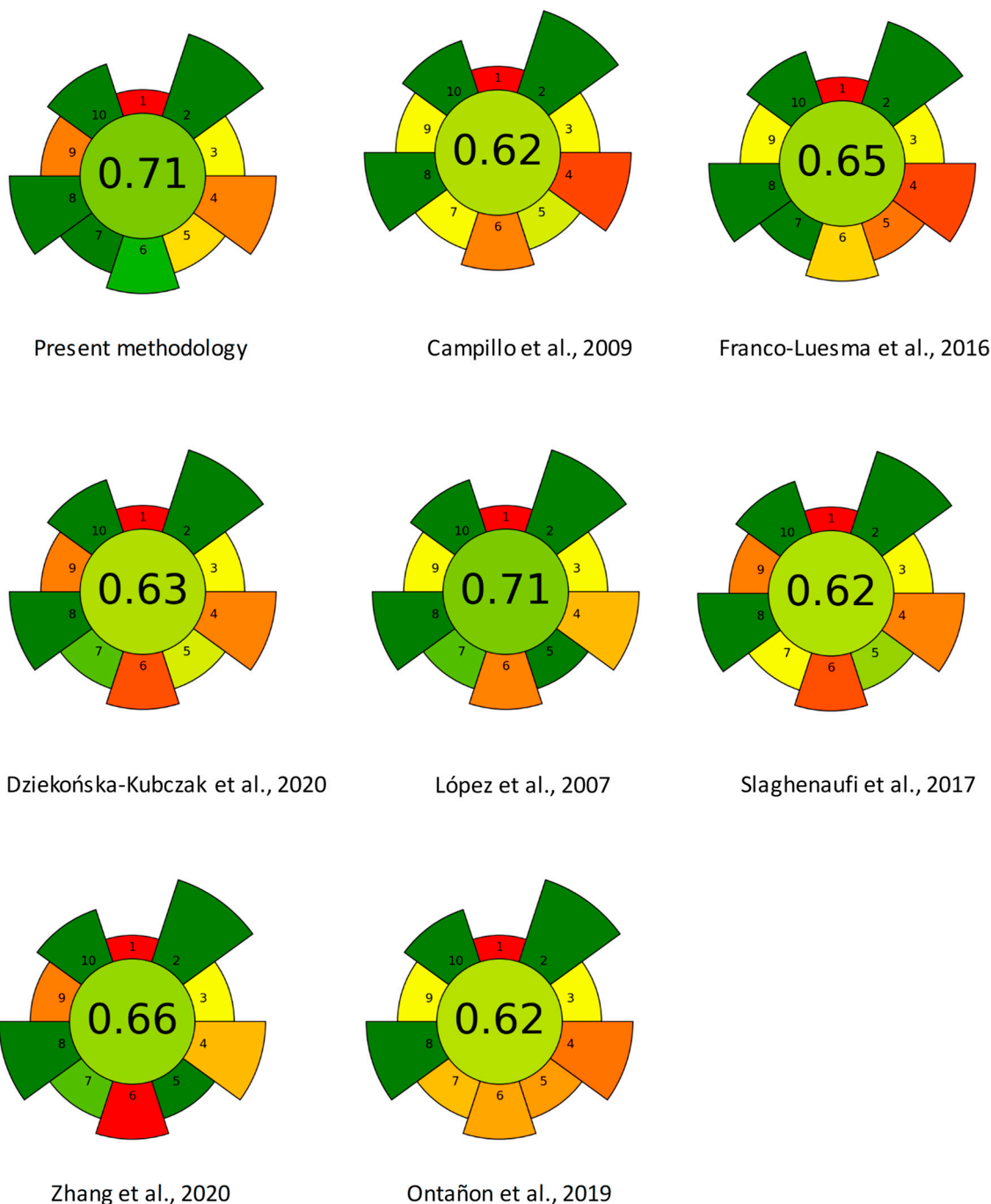
**Table 5.** Analytical comparison with previous methodologies.

Methodology	Matrix	Analytes	Precision (%)		Recovery (%)	$r^2$	DL ( $\mu\text{g/L}$ )	QL ( $\mu\text{g/L}$ )	Ref.
			Repeat.	Reprod.					
SBSE-GC-MS	Grape distillate	DES, DMDS, DPS, DEDS, DBS, DMTS, DPDS, TC	5.9–21.8	7.2–27.5	84.76–119.39	>0.9955	0.0382–0.9293	0.127–3.098	Present study
HS-SPME-GC-AED	Whisky	DES, DMDS, DPS, DMTS, DPDS	4.2–8.8				0.045–1.4		[1]
HS-GC-pFPD	Wine	DES	<4		89–128	>0.99	0.527		[4]
HS-SPME-GC-MS	Fruit brandy	DES, DMDS, P, DPS, DEDS, TC, DBS, DPDS			78.02–129.13	>0.9640	0.003–0.063	0.009–0.208	[11]
HS-SPME-GC-pFPD	Wine	DES, DMDS	<10	10–20	97–114	>0.9914	0.2–0.9		[12]
HS-SPME-GC-MS	Wine	DES, P, DPS, DMDS, DEDS, DPDS, DMTS, TC	2.0–15.8	9.9–33.0	90.2–113.3	>0.9933	0.023–0.283	0.077–0.942	[13]
HS-SPME arrow-GC-MS	Chinese liquor (Baijiu)	DMTS	10.75	8.78	96.97	0.9946	0.0030		[14]
HS-GC-SCD (with cryofocusing)	Wine	DES, DMDS, DEDS				>0.998	0.05–0.1		[19]

DES: diethyl sulphide; DMDS: dimethyl disulphide; DPS: dipropyl sulphide; DEDS: diethyl disulphide; DBS: dibutyl sulphide; DMTS: dimethyl trisulphide; DPDS: dipropyl disulphide; TC: 2-thiophenecarboxaldehyde.

Regarding the green character of the SBSE-GC-MS method, the Analytical Greenness Calculator (AGREE) was used [29]. In this, the greenness and efficiency of each analytical method is evaluated and an overall global score from 0 to 1 is established (0, low; 1, high).

In the case of the present methodology, this global score was 0.71, equal to that reported by López et al. [12] using HS-SPME-GC-pFPD for the determination of DES and DMDS in wines (Figure 2). Both methodologies are characterized by the use of low sample volumes, no hazardous materials, no solvents, and low energy consumption. The lowest global scores were obtained by Campillo et al. [1], Ontañón et al. [19], and Slaghenaufi et al. [13], with analytical methodologies characterized by higher waste volumes, lower hourly sample throughputs, and/or a higher degree of complexity of the detection system. The aspect that received the lowest score for all of the methodologies was that related to the offline collection and determination, since the samples require transportation from the distillation point or the winery to the laboratory to be analyzed by GC.



**Figure 2.** Green character assessment of the present work and different analytical methodologies from bibliography (Table 5): Campillo et al., (2009) [1]; Franco-Luesma et al., (2016) [4]; Dziekońska-Kubczak et al. (2020) [11]; López et al. (2007) [12]; Slaghenaufi et al. (2017) [13]; Zhang et al. (2020) [14]; Ontañón et al. (2019) [19]. Colour codes: red: very low green character; orange: low green character; yellow: medium green character; green: high green character.

### 3.4. Application to Real Samples

The optimized and validated SBSE–GC–MS method was applied for the analysis of thirty-four different samples obtained under different conditions (Appendix A, Table A1). Each sample was analyzed in duplicate. The results are shown in Appendix A (Table A2). Low standard deviations for each sample were obtained, indicating good precision values. DES was not detected in any sample, whereas DEDS was only detected in four samples. The most significant volatile sulphur compounds found in the samples were DBS, DMDS, and

DPS, DMTS and TC were detected in a low number of samples from both column and pot still distillation. The mean concentrations for DBS and DMDS were  $642.1 \pm 696.8$   $\mu\text{g/L}$  and  $185.8 \pm 452.1$   $\mu\text{g/L}$ , respectively. The high standard deviations associated with the mean values obtained for all of the volatile sulphur compounds implies that their concentrations depend on several different factors such as raw wine, specific conditions for distillation, and possible aging in wood, among others.

Ledauphin, Basset, Cohen, Payot, and Barillier [30] found dimethyl disulphide (DMDS, from 50 to 500  $\mu\text{g/L}$  of pure alcohol (PA)), dipropyl sulphide (DPS), dibutyl sulphide (DBS, from 20 to 100  $\mu\text{g/L}$  of PA), dipropyl disulphide (DPDS), and 2-thiophenecarboxaldehyde (up to 1000  $\mu\text{g/L}$  in some samples), among other volatile sulphur compounds, in Cognac samples, whereas dimethyl sulphide (DMS) was detected in brandy samples [10]. 2-thiophenecarboxaldehyde was also found by Xiang et al. [5] in the heart and tail fractions of a spirit obtained from Spine grape wine.

In order to evaluate the similarity among all of the samples, taking into account the content of volatile sulphur compounds considered in the present work, the data were subjected to a Cluster Analysis (CA) considering the squared Euclidean distance as a metric and the Ward method as an amalgamation rule. As can be seen in Figure 3, the samples seem to be grouped according to the use of sulphur dioxide, with three groups: one of them with distillates without  $\text{SO}_2$  and aged in wood, and two others with  $\text{SO}_2$ . Guerrero-Chanivet et al. [31] found that the addition of sulphur dioxide during alcoholic fermentation had the higher influence on the aromatic and phenolic profile of distillates obtained using different distillation methods and aged for 14 and 28 months in oak wood. In the present study, samples 25, 27, 29, and 31 correspond to samples 24, 26, 28, and 30, respectively, after different periods of aging in wood. Out of all of them, 26, 28, and 30 were obtained from wines subjected to the addition of  $\text{SO}_2$ . As can be observed in Table A2, in general, all of the volatile sulphur compounds were found to be decreased in the aged samples compared to unaged ones. In this sense, Zhou et al. [32] found that the content of sulphur volatile compounds together with alcohols, aldehydes, and terpenes decreased with aging time in different brandy samples. In this sense, De La Burgade et al. [33] found that dimethyl sulphide increased in Shiraz wines during accelerated bottle aging and that those increases were higher when more impermeable closures were employed, suggesting that its formation depends on the redox status of the wine. The same behaviour was observed for dimethyl disulphide by Jiménez-Lorenzo et al. [34] in a Viognier wine subjected to darkness under anoxic conditions for 9 weeks at a temperature of 50 °C. During aging in wood, the evolution of the redox potential depends on several factors: the amount of dissolved oxygen at the beginning of aging; the level of oxygen permeability through the wood; the amounts of compounds (phenolic compounds and volatile compounds, mainly) released from the wood; the temperature; and the rate of oxygen consumption [35]. According to this, all of these factors could determine the content of volatile sulphur compounds in distillates during their aging in wood.

All of this seems to indicate that aging in wood exerts a certain decreasing effect on the content of sulphur compounds, although further studies and a larger number of samples are necessary in order to obtain conclusive results on the effect of aging in wood on the content of this type of volatile compound in distillates.

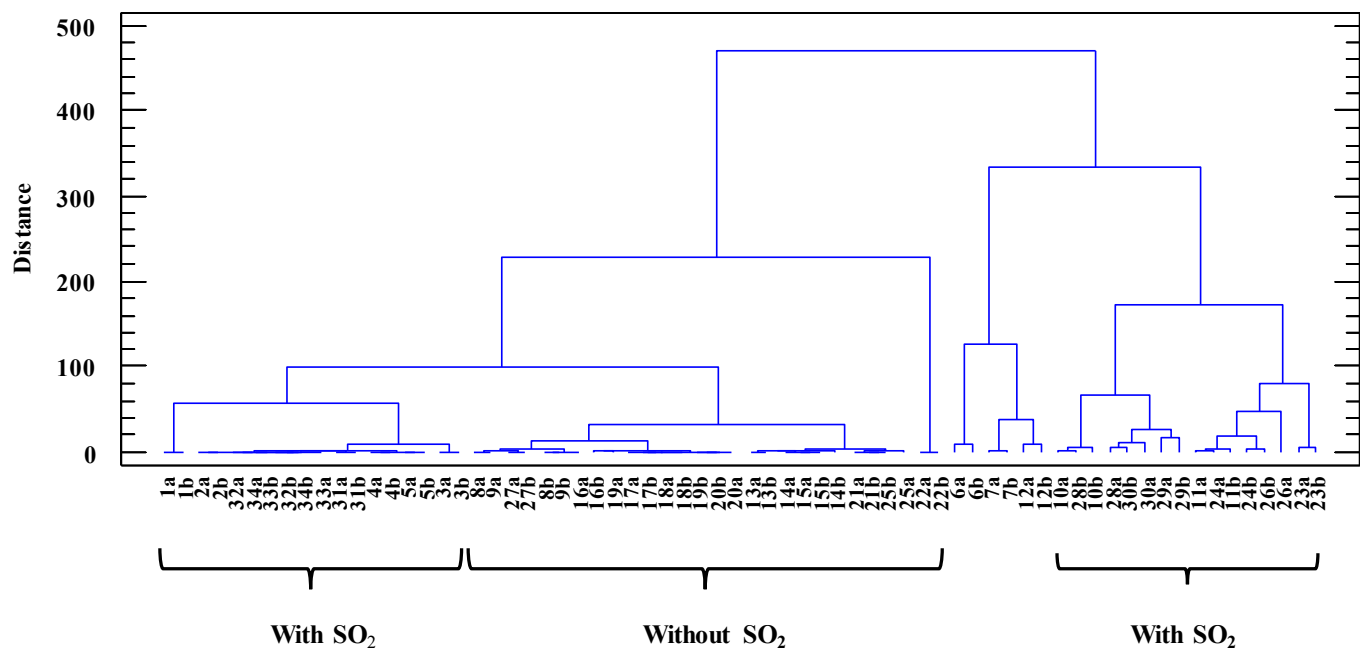


Figure 3. Cluster Analysis according to content in volatile sulphur compounds. Codes in Table A1.

#### 4. Conclusions

To our knowledge, no methods have been published for the analysis of volatile sulphur compounds in wine distillates using SBSE-GC-MS. The method was successfully validated and shown to be suitable for the determination of eight volatile sulphur compounds: DES, DMDS, DPS, DEDS, DBS, DMTS, DPDS, and TC. The proposed method had a good analytical performance when compared with other analytical methodologies optimized and validated for similar analytes in similar samples. After optimization and validation, it was successfully applied for the analysis of 34 wine distillate samples. The most significant volatile sulphur compounds found in the samples were DBS, DMDS, and DPS. In relation to the possible influence of aging in wood on the volatile sulphur compound content, the preliminary results seem to indicate that these exhibit a decreasing tendency during the aging of distillates in wood.

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## Abbreviations

The following abbreviations are used in this manuscript:

ABV	Alcohol by volume
EMS	Ethyl methyl sulphide
DES	Diethyl sulphide
T	Thiophene
P	1-Pentanethiol
DMDS	Dimethyl disulphide
DPS	Dipropyl sulphide
DEDS	Diethyl disulphide
DBS	Dibutyl sulphide
DMTS	Dimethyl trisulphide
DPDS	Dipropyl disulphide
DL	Detection limit
QL	Quantification limit
SPE	Solid Phase Extraction
SPME	Solid Phase MicroExtraction
HS-SPME	Headspace-Solid Phase MicroExtraction
SBSE-GC-MS	Stir Bar Sorptive Extraction-Gas Chromatography-Mass Spectrometry
HS-GC-SCD	Headspace-Gas Chromatography-Sulphur Chemiluminescent Detection
HS-SPME-GC-AED	Headspace-Solid Phase MicroExtraction-Gas Chromatography-Atomic Emission Detection
HS-SPME-GC-pFPD	Headspace Solid-Phase Microextraction-Gas Chromatography-Pulsed Flame-Photometric Detection
TDU	Thermal desorption unit
EDTA	Ethylenediaminetetraacetic acid
CA	Cluster Analysis
PDMS	Polydimethylsiloxane
VSCs	Volatile sulphur compounds

## Appendix A

**Table A1.** Information about samples studied.

Code	Distillation Fraction	Alcohol Content (ABV)	SO <sub>2</sub> Addition*	Distillation Type	Aging
1	Head	85%	High	Continuous column distillation	No
2	Heart	77%	Very low	Continuous column distillation	No
3	Heart	77%	Medium	Continuous column distillation	No
4	Head	77%	High	Continuous column distillation	No
5	Head	85%	High	Continuous column distillation	No
6	Head	85%	-	Distillation in pot still	No
7	Head	70%	-	Distillation in pot still	No
8	Heart	70%	-	Continuous column distillation	No
9	Heart	70%	Low	Continuous column distillation	Yes
10	Heart	77%	-	Continuous column distillation	No
11	Head	95%	-	Continuous column distillation	No
12	Heart	65%	-	Continuous column distillation	No
13	Heart	35%	-	Continuous column distillation	Yes
14	Heart	35%	-	Continuous column distillation	Yes
15	Heart	35%	-	Continuous column distillation	Yes
16	Heart	35%	-	Continuous column distillation	Yes
17	Heart	35%	-	Continuous column distillation	Yes
18	Heart	35%	-	Continuous column distillation	Yes
19	Heart	35%	-	Continuous column distillation	Yes

Table A1. Cont.

Code	Distillation Fraction	Alcohol Content (ABV)	SO <sub>2</sub> Addition*	Distillation Type	Aging
20	Heart	35%	-	Continuous column distillation	Yes
21	Heart	35%	-	Continuous column distillation	Yes
22	Heart	35%	-	Continuous column distillation	Yes
23	Heart	55%	Medium	Distillation in pot still	No
24	Heart	55%	-	Distillation in pot still	No
25	Heart	55%	-	Distillation in pot still	Yes
26	Heart	55%	Medium	Continuous column distillation	No
27	Heart	55%	Medium	Continuous column distillation	Yes
28	Heart	55%	Medium	Distillation in pot still	No
29	Heart	55%	Medium	Distillation in pot still	Yes
30	Heart	65%	Medium	Distillation in pot still	No
31	Heart	65%	Medium	Distillation in pot still	Yes
32	Head	96%	Medium	Continuous column distillation	No
33	Head	96%	Medium	Continuous column distillation	No
34	Heart	65%	Medium	Continuous column distillation	No

\* High: >500 mg/L; medium: about 100 mg/L; low: <100 mg/L; very low: about 20 mg/L; -: without sulphur dioxide.

Table A2. Mean concentrations (µg/L) and standard deviations for volatile sulphur compounds studied.

Code	DES	DMDS	DPS	DEDS	DBS	DMTS	DPDS	TC
1	nd	404.7 ± 6.7	<QL	<QL	nd	42.25 ± 0.38	nd	nd
2	nd	9.60 ± 0.37	nd	nd	67.48 ± 12.74	nd	1.67 ± 0.16	nd
3	nd	16.47 ± 1.44	nd	nd	13.21 ± 4.36	13.68 ± 1.79	2.40 ± 0.40	nd
4	nd	95.42 ± 3.55	<QL	nd	nd	nd	nd	nd
5	nd	96.83 ± 10.48	nd	nd	nd	nd	<QL	nd
6	nd	1656 ± 56	nd	nd	2491 ± 663	nd	29.18 ± 4.76	nd
7	nd	1626 ± 27	nd	nd	1316 ± 188	92.07 ± 1.81	53.97 ± 9.35	nd
8	nd	15.10 ± 0.48	128.6 ± 28.0	nd	237.2 ± 11.4	nd	19.87 ± 2.23	<QL
9	nd	12.90 ± 8.23	136.6 ± 43.8	nd	267.5 ± 44.8	nd	23.16 ± 2.65	<QL
10	nd	nd	153.5 ± 10.8	nd	533.5 ± 44.2	<DL	37.63 ± 6.40	87.10 ± 28.68
11	nd	nd	132.7 ± 40.4	nd	1030 ± 6	nd	56.38 ± 12.56	nd
12	nd	1568 ± 31	265.2 ± 60.6	nd	1527 ± 456	69.79 ± 7.79	42.35 ± 4.77	nd
13	nd	130.2 ± 0.8	113.9 ± 13.6	nd	916.0 ± 4.3	nd	17.59 ± 1.90	nd
14	nd	211.1 ± 2.8	123.9 ± 11.2	nd	1068 ± 111	7.25 ± 0.55	21.70 ± 5.34	nd
15	nd	124.1 ± 1.1	122.0 ± 4.5	nd	810.6 ± 85.4	6.07 ± 0.41	17.26 ± 2.71	nd
16	nd	10.14 ± 1.74	87.9 ± 31.8	nd	210.5 ± 51.7	nd	18.92 ± 5.89	16.34 ± 2.51
17	nd	6.00 ± 0.95	65.5 ± 3.1	nd	101.1 ± 23.3	nd	10.11 ± 0.43	<QL
18	nd	6.40 ± 0.90	78.61 ± 7.40	nd	94.31 ± 3.85	nd	10.77 ± 1.26	<QL
19	nd	6.98 ± 0.75	64.70 ± 6.89	nd	157.7 ± 39.7	nd	16.54 ± 5.40	nd
20	nd	6.05 ± 0.81	53.45 ± 11.81	nd	140.3 ± 36.5	nd	11.26 ± 0.56	nd
21	nd	95.29 ± 1.16	127.9 ± 7.6	<QL	665.9 ± 136.1	nd	17.29 ± 3.07	nd
22	nd	32.57 ± 0.70	88.66 ± 1.62	22.61 ± 0.39	599.0 ± 2.8	nd	14.25 ± 0.34	nd
23	nd	61.10 ± 2.58	205.2 ± 15.9	10.37 ± 2.75	2299 ± 175	nd	67.66 ± 9.18	nd
24	nd	36.81 ± 1.21	153.5 ± 49.0	nd	1794 ± 299	nd	55.58 ± 18.65	nd
25	nd	14.77 ± 9.62	133.3 ± 25.3	nd	780.2 ± 125.3	nd	25.71 ± 7.42	nd
26	nd	15.16 ± 6.21	274.4 ± 78.4	nd	1652 ± 144	nd	114.6 ± 32.5	nd
27	nd	9.70 ± 1.65	137.1 ± 4.9	nd	414.7 ± 29.7	nd	25.99 ± 3.05	nd
28	nd	14.20 ± 0.49	218.3 ± 36.4	nd	621.0 ± 64.7	nd	50.89 ± 16.46	120.5 ± 17.6
29	nd	13.87 ± 0.75	401.4 ± 133.1	nd	618.4 ± 109.0	nd	47.74 ± 23.32	183.8 ± 12.1
30	nd	18.13 ± 0.05	269.5 ± 11.9	nd	1403 ± 211	<QL	89.63 ± 12.51	132.0 ± 37.4
31	nd	<DL	nd	nd	nd	nd	nd	11.16 ± 0.49
32	nd	nd	nd	nd	nd	nd	<QL	nd
33	nd	<QL	nd	nd	nd	nd	<QL	nd
34	nd	nd	nd	nd	nd	nd	<QL	nd
Mean	nd	185.8 ± 452.2	104.0 ± 101.4	1.06 ± 1 ± 4.17	642.1 ± 696.8	7.02 ± 20.14	26.6 ± 27.7	17.0 ± 43.9

nd: not detected; <QL: below quantification limit; <DL: below detection limit.

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