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Optimisation of stir bar sorptive extraction applied to the determination of volatile compounds in vinegars

Enrique Durán Guerrero, Ramón Natera Marín, Remedios Castro Mejías *, Carmelo García Barroso

Analytical Chemistry Department, Faculty of Sciences, University of Cádiz, P.O. Box 40, E-11510, Pol. Río San Pedro, Puerto Real, Cádiz, Spain

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Abstract

Stir bar sorptive extraction (SBSE) was evaluated for analysing volatile compounds in vinegar. The extraction and desorption analytical conditions have been optimised using a two-level factorial design expanded further to a central composite design. This chemometric tool is very appropriate in screening experiments where the aim is to investigate several possibly influential and/or interacting factors. For the extraction step, the optimum analytical conditions were: sample volume 25 ml without dilution, sampling time 120 min, NaCl content 5.85 g, and stirring speed 1250 rpm. For the desorption step, the optimised analytical conditions were: desorption temperature 300 °C, cryofocusing temperature −140 °C, flow of helium 75 ml min^{-1}, and desorption time 10 min. The SBSE procedure developed shows detection limits, and linear ranges adequate for analysing this type of compounds. The repeatability values obtained were lower than 10%.

SBSE is a very simple, solvent-free, fast technique with better sensitivities, in general, than SPME. However, a disadvantage of this technique is that, up to now, the stir bar offers a limited enrichment capability for polar compounds because is only available with PDMS coating.

Keywords: Stir bar sorptive extraction; Vinegar; Volatile compounds; Two-level factorial design; Central composite design

1. Introduction

Vinegar is now a product of high reputation, much appreciated in gastronomy. Due to the diversity of vinegars on the market and the increase in demand, it has been considered necessary to investigate reliable analytical methods to establish criteria for determining quality and origin, since objective authentification remains an unresolved issue.

The market value of this type of product can only be sustained if chemical–physical and/or sensorial parameters are found to express differences in composition on the basis of the origin of the vinegar, manufacturing techniques and commercial type.

The flavour of vinegar depends on the raw materials (white and red wines, cider, malted barley, honey, etc.), the constituents formed during the fermentation and, in some cases, the substances formed during the ageing, so it is logical to suppose that vinegars may be characterised and differentiated by the quantitative and qualitative analysis of their volatile components.

Even today, the extraction and concentration of flavour components, prior to their GC analysis, constitute a problem that has still not been satisfactorily resolved. In recent years, there has been an increasing interest in developing new analytical techniques for the monitoring of volatile compounds in a wide variety of matrices. In the bibliography, various methods can be found for the capillary GC analysis of volatile components [1–5]. The tendency is to develop accurate, easy-to-automate, and sensitive methodologies which reduce sample handling. Sample preparation for GC analysis of less volatile compounds has been carried out mainly by liquid/liquid [1] or solid phase [2] extraction. The more volatile compounds are normally analysed by head space or by purge and trap methods [3,6]. Other preparation techniques employed include supercritical fluid extraction [7], and simultaneous distillation-solvent extraction [8], among others. All these sample preparation methods present several disadvantages, such as excessive cost and time, the possible generation of artefacts, etc.

Stir bar sorptive extraction (SBSE) is a recently developed technique [9–12] in which a stir bar coated with 50–300 μl of polydimethylsiloxane (PDMS) is employed to extract analytes from a variety of matrices. The extraction mechanism is similar

* Corresponding author. Tel.: +34 56 01 63 63; fax: +34 56 01 64 60.
E-mail address: remedios.castro@uca.es (R.C. Mejías).

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to that of solid phase microextraction (SPME) based on PDMS sorption [13]. A magnetic stirring bar is added to the sample to promote the transfer of analytes to the polymer coating and, after a predetermined extraction period, the analytes are thermally desorbed in the GC injector.

The advantage of SBSE is the much higher mass of PDMS available, which results in high recoveries and higher sample capacity. The applications developed with SBSE have shown low detection limits and good repeatability [12,14,15], which confirm the great potential of this technique.

The present paper describes the optimisation of a stir bar sorptive extraction and thermal desorption procedure coupled to capillary gas chromatography–mass spectrometry for the determination of volatile compounds in vinegar.

The parameters that affect the extraction of the analytes from vinegar into the into PDMS coated stir bars and the conditions affecting thermal desorption are investigated using a chemometric approach based on the use of an optimum set of experiments (experimental design) which allows the simultaneous variation of all experimental factors studied, and the distinguishing of interactions among them that are not detectable with the classical experimental methods [16,17]. For the extraction step, we evaluate the effects of experimental parameters such as sample volume, salting out effect, stirring speed, sampling time, and dilution of the sample on the SBSE. For the desorption into the GC, the factors evaluated were desorption temperature, desorption time, helium flow, and cryofocusing temperature in the PTV injector. In both cases, the effects of these parameters were evaluated using a two-level factorial design expanded further to a central composite design. This chemometric tool is very appropriate in screening experiments where the aim is to investigate possibly influential and/or interacting factors. The juxtaposition of a two-level design with a star design (the centres of the two designs coincide) gives a composite design. It is one of the most useful designs for estimating a multifactor response surface [16,17], which keeps to a minimum the number of experiments while providing the information needed.

2. Experimental

2.1. Vinegar samples

A Commercial Sherry vinegar sample was used to optimise the extraction and desorption conditions in order to determine various vinegar aroma and flavour compounds of varying volatilities and functionalities. After optimisation, several vinegars were analysed following this methodology.

2.2. Chemicals and reagents

All the aroma standards used in this study were supplied by Merck (Darmstadt, Germany) and Sigma (Steinheim, Germany). 4-Methyl-2-pentanol was employed as internal standard. NaCl was purchased from Scharlau (Barcelona, Spain).

2.3. Sample preparation

The extractions were carried out with 10 mm × 0.5 mm (length × film thickness) PDMS commercial stir bars, supplied by Gerstel (Mülheim a/d Ruhr, Germany). After optimisation, and for each SBSE analysis, a volume of 25 ml of sample (natural and synthetic vinegar) was pipetted and placed into a 100-ml Erlenmeyer flask with 5.85 g of NaCl and 50 μl of a solution of 4-methyl-2-pentanol (2.27 g/l in Milli-Q water containing 80 g/l of acetic acid). The Erlenmeyer flask was placed on a 15 position magnetic stirrer (Mülheim a/d Ruhr, Germany). The stir bar was stirred at 1250 rpm at 25 °C for 120 min. After removal from the vinegar sample, the stir bar was placed for a few seconds in distilled water in order to remove NaCl and gently dried with a lint-free tissue. Then, it was transferred into a glass thermal desorption tube and then thermal desorption was carried out.

2.4. Apparatus

The coated stir bars were thermally desorbed using a commercial TDS-2 thermal desorption unit (Gerstel) connected to a programmed-temperature vaporisation (PTV) injector CIS-4 (Gerstel) by a heated transfer line. The PTV was installed in an Agilent 6890 GC-5973 MS system (Agilent Technologies, Palo Alto, CA, USA). An empty baffled liner was used in the PTV. The thermodesorption unit was equipped with a MPS 2L autosampler (Gerstel) capable of handling the program for 98 coated stir bars. The desorption temperature was programmed from 40 to 300 °C (held for 10 min) at 60 °C min^{-1} under a helium flow (75 ml min^{-1}) and the desorbed analytes were cryofocused in the PTV system with liquid nitrogen at −140 °C. Finally, the PTV system was programmed from −140 to 300 °C (held for 5 min) at 10 °C s^{-1} for analysis by GC–MS. Capillary GC–MS analyses in the electron impact mode were performed on an Agilent 6890 GC-5973N MS system (Agilent, Little Falls, DE, USA), equipped with a DB-Wax capillary column (J&W Scientific, Folsom, CA, USA), 60 m × 0.25 mm I.D., with a 0.25 μm coating. The carrier gas was helium at a flow rate of 1.0 ml min^{-1}. The GC oven was programmed as follows: held at 35 °C for 10 min, then ramped at 5 °C min^{-1} to 100 °C. Then it was raised to 210 °C at 3 °C min^{-1} and held for 40 min. The mass detector operated in EI+ mode at 70 eV in a range of 30–400 amu.

Peak identification was carried out using the Wiley library by analogy of mass spectra and confirmed by retention indices of standards when they were available or by retention data from the literature. Quantitative data from the identified compounds were obtained by measuring the molecular ion relative peak area in relation to that of 4-methyl-2-pentanol, the internal standard.

2.5. Experimental design

The standard approach to the analysis of the experimental design data is to calculate and evaluate a list of the main effects and interaction effects supported by an ANOVA table, indicating which effects are significant. For data manipulation, the Statgraphics Statistical Computer Package “Statgraphics Plus 5.0” for Windows 98 was used.

Table 1
Factor levels

Factor	Low (−)	High (+)	Centre	Axial (−α)	Axial (+α)
Sample volume (ml)	20	40			
Stirring speed (rpm)	500	1500	1000	190	1800
Extraction time (min)	30	120	75	2.5	147
NaCl (M)	2.0	4.0	3.0	1.4	4.6
Dilution	0.0	1.0	0.5	0.0	1.3

Optimisation of extraction conditions.

In this study, we chose a sequential exploration of the response, which was carried out in two stages. In the first stage, we wished to establish the relative influence of the factors and their interactions on the number of chromatographic peaks detected and on the total chromatographic area obtained. Five factors were selected as potentially affecting the SBSE extraction: time of extraction, sample volume, stirring speed, ionic strength effect from adding different amounts of NaCl, and dilution of the sample.

This last factor was considered taking into account that the presence of sample matrix can change not only the distribution coefficient, but also the equilibrium time in sorptive extraction [13]. In wines, the ethanol content appears to interfere in the SPME technique [18–20]. Since acetic acid is one of the major constituents of vinegars, it may compete with the volatile compounds in the extraction. In a previous study [4], using SPME, the data obtained showed that although the absolute chromatographic areas decreased as the acetic acid content increased, the compound area/I.S. area ratio remained constant, so the acetic acid concentration did not affect the analytical data. On the other hand, analyses are greatly simplified when samples can be generously diluted, by preventing overloaded peaks and detector saturation, but high sensitivity detection methods are required.

Consequently, a factorial design of 2^{5-1} was chosen. This design involves 16 experiments undertaken in random order to provide protection against the effects of lurking variables. These experiments were carried out in triplicate. The values corresponding to the high (+), and low (−) points for each factor are shown in Table 1.

In the second stage, this two-level factorial design was expanded to a star design. A central composite design (CCD, with $\alpha = 1.607$) was obtained, since the centres of the two separate designs were coincidental. Table 1 lists the values given to each factor.

Then, the desorption conditions were also optimised following a similar process (factorial design of 2^4, and then, a central composite design with $\alpha = 1.078$). In this case, four factors were selected: desorption temperature and time, helium flow and cryofocusing temperature. Table 2 lists the values given to each factor.

3. Results and discussion

3.1. Extraction condition optimisation

Time of extraction, sample volume, stirring speed, dilution of the sample, and the ionic strength effect from adding different amounts of NaCl were evaluated to achieve the best overall analytical conditions. Number of chromatographic peaks and total chromatographic area were selected as experimental responses for optimising.

3.1.1. Screening by a 2^{5-1} factorial design

The initial screening design served to detect those variables having the most influence on the experimental responses (number of chromatographic peaks and total chromatographic area).

The data obtained for these parameters were evaluated by ANOVA at the 5% significance level. These results can be shown by bar charts (Fig. 1). In these graphics, the data are presented in chart form with the causes depicted in rank order.

Extraction time, stirring speed, NaCl concentration, and dilution were significant parameters (at $p < 0.05$) for both number of chromatographic peaks and total area. Sample volume was only significant, with a modest effect, for total area.

Extraction time was the most influential variable for total area and number of peaks. All significant factors affected both responses with a positive sign with the exception of dilution of the sample, which, as can be expected, affected them with a negative sign.

The SBSE efficiency is also affected by the interrelated variables, as shown in Fig. 1. The interaction between the factors extraction time and stirring speed appears statistically significant, with a positive sign, for both the number of peaks detected and the total area. For this latter experimental response, the inter-

Table 2
Factor levels

Factor	Low (−)	High (+)	Centre	Axial (−α)	Axial (+α)
Desorption temperature (°C)	250	330	290	247	333
Desorption time (min)	4	12			
Helium flow (ml min^{-1})	50	150			
Cryofocusing temperature (°C)	−150	−10	−80	−155.5	−4.5

Optimisation of desorption conditions.

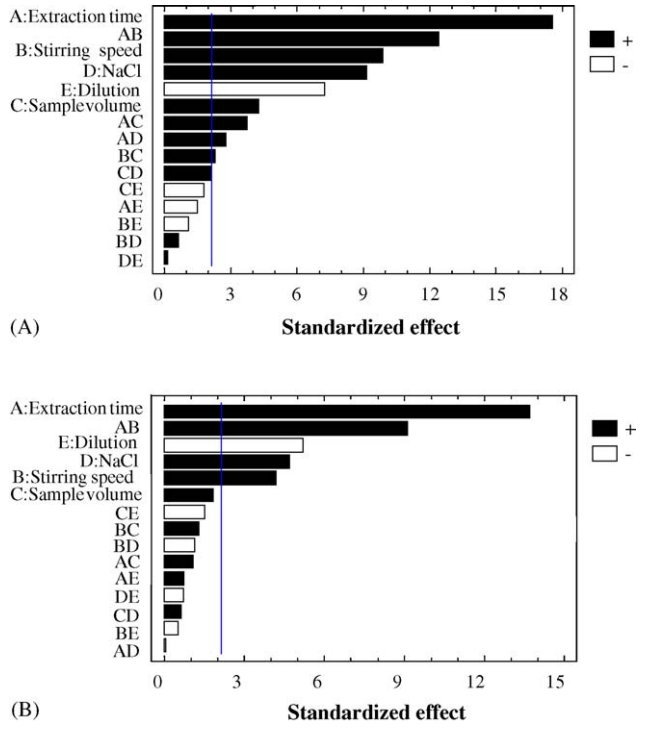

Fig. 1. Pareto chart of main effects in the factorial 2^{5-1} design for total area (A) and chromatographic peak number (B). Optimisation of extraction conditions.

actions between extraction time and sample volume and NaCl were also significant.

3.1.2. Optimisation by a central composite design

As can be seen, the SBSE technique is affected by interrelated parameters. For an optimisation design, it is advisable to keep the number of parameters as small as possible in order to avoid very complex response models and large variability. Since sample volume was not shown to have a statistically significant influence on the considered responses (total chromatographic area and number of chromatographic peaks), in order to estimate curvature in response surfaces, we decided not to retain this factor. For the central composite design (CCD), the four parameters utilised were: extraction time, stirring speed, NaCl, and dilution of the sample. The sample volume was set at 25 ml. The axial values for these parameters are located on a sphere surrounding the two-level factorial design (Table 1).

After the CCD, as expected from the screening experiments, the extraction time appeared as statistically significant main effect, having a strong positive influence for both total area and number of chromatographic peaks (Table 3).

Stirring speed and NaCl showed a significant and positive influence on both experimental responses whilst dilution of the sample was statistically negative for them. In general, no problems of overloaded peaks and detector saturation were observed when the sample was injected without dilution.

For both experimental responses, among the two factor interactions, the extraction time and stirring speed interaction was the most statistically significant.

Table 3
Main effects and interactions in the central composite design for number of chromatographic peaks and total area

Effect	Number of chromatographic peaks		Total area	
	F ratio	*p*-value	*F* ratio	*p*-value
A: Extraction time	100.98	0.0000[a]	48.29	0.0000[a]
B: Stirring speed	15.36	0.0004[a]	20.19	0.0001[a]
C: NaCl	7.46	0.0099[a]	17.39	0.0002[a]
D: Dilution	14.44	0.0006[a]	7.01	0.0122[a]
AA	30.80	0.0000[a]	23.08	0.0000[a]
AB	22.89	0.0000[a]	15.08	0.0005[a]
AC	0.37	0.5495	2.26	0.1416
AD	1.07	0.3074	3.53	0.0688
BB	40.02	0.0000[a]	49.35	0.0000[a]
BC	1.00	0.3235	0.44	0.5125
BD	1.96	0.1709	0.28	0.5972
CC	0.80	0.3780	0.02	0.8907
CD	4.96	0.0326[a]	5.45	0.0257[a]
DD	2.78	0.1044	9.26	0.0045[a]

Optimisation of extraction conditions.
[a] Values are significant at $p < 0.05$.

Fig. 2 shows the response surface plots for the total area and the number of chromatographic peaks obtained by plotting extraction time versus stirring speed. Intensive stirring is known to shorten the extraction time. At high extraction

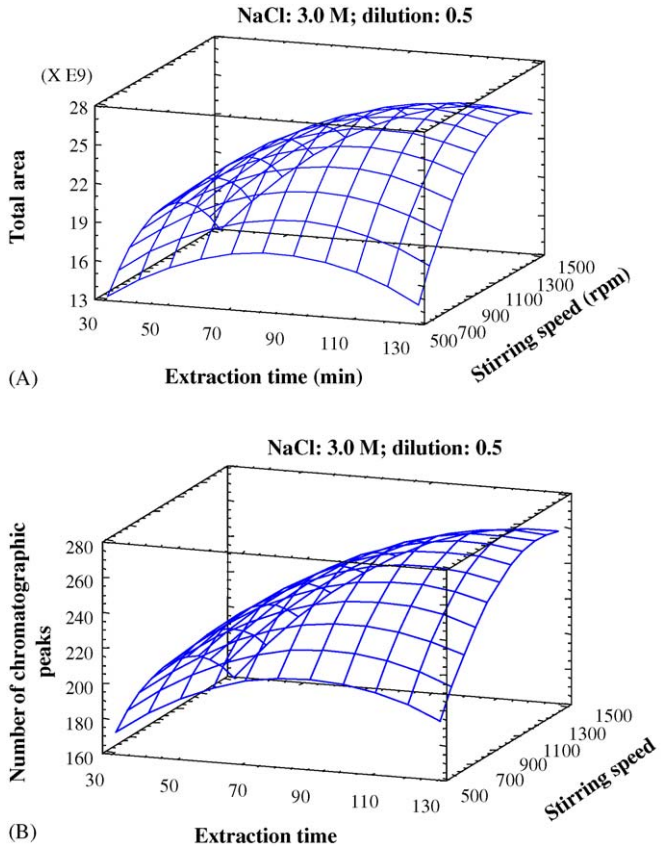

Fig. 2. Estimated response surfaces for total chromatographic area (A) and number of chromatographic peaks (B) using the central composite design obtained by plotting extraction time vs. stirring speed. Optimisation of extraction conditions.

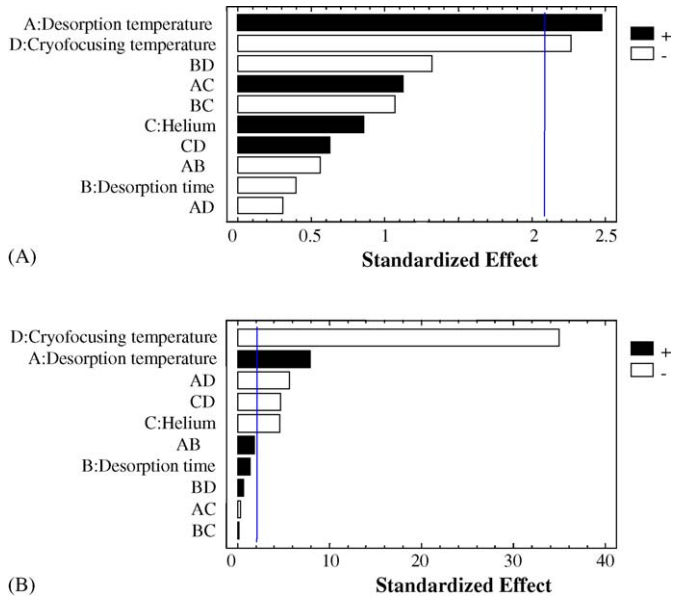

Fig. 3. Pareto chart of main effects in the factorial 2^4 design for total area (A) and chromatographic peak number (B). Optimisation of desorption conditions.

time (130 min), better experimental responses were obtained in line with increasing stirring speed. This interaction indicates that a long sampling time produces the extraction of a larger number of volatile compounds when high stirring speed is used.

In summary, after evaluation of the main factors and their interactions, the best conditions for extracting the volatile compounds of vinegar were: sample volume 25 ml without dilution, sampling time 120 min, NaCl content 5.85 g, and stirring speed 1250 rpm.

3.2. Desorption condition optimisation

Desorption time and temperature, helium flow, and cryofocusing temperature were evaluated to achieve the best overall analytical conditions. Number of chromatographic peaks and total chromatographic area were selected as experimental responses for optimising.

3.2.1. Screening by a 2^4 factorial design

The data obtained for these parameters were evaluated by ANOVA at the 5% significance level. These results can be shown by bar charts (Fig. 3).

Desorption temperature, with positive sign, and cryofocusing temperature, with negative sign, were significant (at $p < 0.05$) for total area and number of chromatographic peaks. Flow of helium was only significant for, with a modest effect, the number of chromatographic peaks.

Desorption time was insignificant for both experimental responses.

In this case, the two-factor interactions were insignificant for total area and had a very modest effect for number of chromatographic peaks.

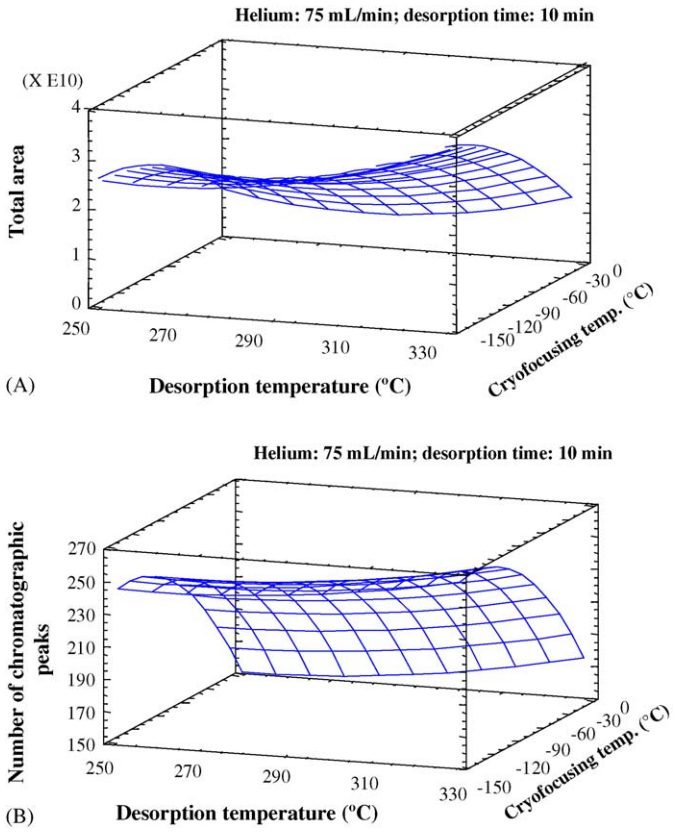

Fig. 4. Estimated response surfaces for total chromatographic area (A) and number of chromatographic peaks (B) using the central composite design obtained by plotting desorption temperature vs. cryofocusing temperature. Optimisation of desorption conditions.

3.2.2. Optimisation by a central composite design

Taking into account these results and that is advisable to keep the number of parameters as small as possible, we decided not to retain desorption time and flow of helium for this statistical study. They were set at 10 min for desorption time and 75 ml min^{-1} for helium flow, respectively.

For the central composite design (CCD), the two parameters utilised were: desorption and cryofocusing temperatures. The axial values for these parameters are located on a sphere surrounding the two-level factorial design (Table 2).

After the CCD, as expected from the screening experiments, both factors were significant for total area and number of chromatographic peaks. Desorption temperature and cryofocusing temperature interaction was only significant for total area.

Fig. 4 shows the response surface plot for the total area obtained by plotting desorption temperature versus cryofocusing temperature. At high desorption temperature (330 °C), better experimental response was obtained in line with decreasing cryofocusing temperature.

This interaction indicates that a low cryofocusing temperature produces the desorption into the GC of a larger number of volatile compounds when a high desorption temperature is used.

In summary, after evaluation of the main factors and their interactions, the optimum conditions for the desorption of volatile compounds of vinegar were: desorption temperature 330 °C, cryofocusing temperature −140 °C, flow of helium

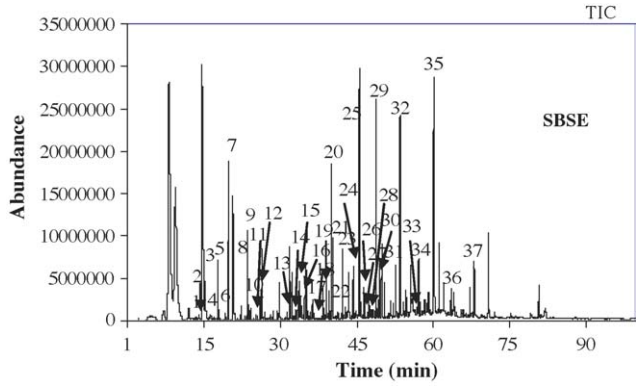

Fig. 5. Total ion chromatogram obtained for a vinegar sample by means of SBSE. 1, ethyl isobutyrate; 2, propyl acetate; 3, isobutyl acetate; 4, ethyl butyrate; 5, ethyl pentanoate; 6, 2-methyl-1-propanol; 7, isoamyl acetate; 8, ethyl hexanoate; 9, 2-methyl-1-butanol; 10, isoamyl alcohol; 11, hexyl acetate; 12, 3-hydroxy-2-butanone; 13, ethyl octanoate; 14, 2-furancarboxaldehyde; 15, decanal; 16, benzaldehyde; 17, isobutyric acid; 18, 5-methyl-2-furfural; 19, butyric acid; 20, isovaleric acid; 21, diethyl succinate; 22, α-terpineol; 23, benzyl acetate; 24, ethyl-2-phenyl acetate; 25, phenylethyl acetate; 26, hexanoic acid; 27, α-ionona; 28, benzyl alcohol; 29, 2-phenylethanol, 30, 2-ethyl-hexanoic acid: 31, 4-ethylguaiacol; 32, octanoic acid; 33, eugenol; 34, 4-ethylphenol; 35, decanoic acid; 36, diethyl phthalate; 37, lauric acid.

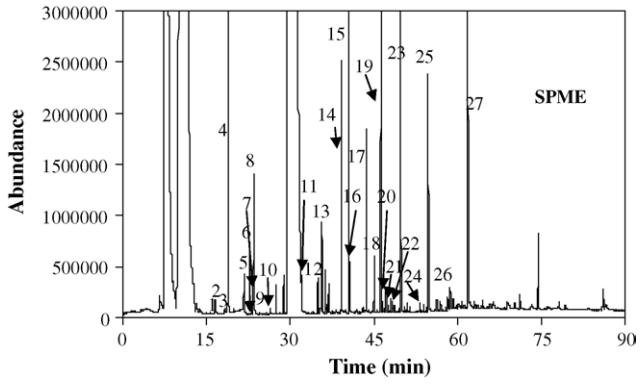

Fig. 6. Total ion chromatogram obtained for a vinegar sample by means of SPME. 1, *n*-butyl acetate; 2, ethyl pentanoate; 3, 2-methyl-1-propanol; 4, isoamyl acetate; 5, 4-methyl-2-pentanol (I.S.); 6, ethyl hexanoate; 7, 2-methyl-1-butanol; 8, isoamyl alcohol; 9, hexyl acetate; 10, 3-hydroxy-2-butanone; 11, 2-furancarboxaldehyde; 12, benzaldehyde; 13, 2,3-butanediol; 14, ethyl decanoate; 15, isovaleric acid; 16, diethyl succinate; 17, 1,1,6 trimethyl-1,2-dihydro-naphtalene; 18, ethyl-2-phenyl acetate; 19, phenylethyl acetate; 20 hexanoic acid; 21, α-ionona; 22, benzyl alcohol; 23, 2-phenylethanol; 24, 4-ethylguaiacol; 25, octanoic acid; 26, 4-ethylphenol; 27, decanoic acid.

75 ml min^{-1}, and desorption time 10 min. Taking into account the specifications from the manufacturer, the desorption temperature was finally set at 300 °C in order not to damage the stir bar.

3.3. SPME and SBSE comparative study

This analytical method was used to analyse a variety of Sherry vinegar samples supplied by different producers. Each sample was analysed in triplicate.

The chromatograms obtained using SPME and SBSE for one of the vinegar samples are shown in Figs. 5 and 6. As can be seen, SBSE exhibits better sensitivities than SPME for most of the volatile compounds. However, some of these compounds, such as acetic acid, 2,3-butanediol, ethyl decanoate, 1,1,6 trimethyl-1,2-dihydro-naphtalene, and *n*-butyl acetate, could not be identified by SBSE. This fact can be explained on the basis of the polarity of the PDMS stir bar, which offers a limited extraction capability for polar volatiles.

Some volatiles, for example ethyl isobutyrate, propyl acetate, ethyl butyrate, ethyl octanoate, decanal, isobutyric acid, 5-methyl-2-furfural, butyric acid, α-terpineol, benzyl acetate, eugenol, etc. could only be identified by SBSE.

3.4. Performance characteristics

3.4.1. Calibration

3.4.1.1. Linearity. In order to estimate the detection limits for a few relevant compounds, five levels of concentration were tested in triplicate; these concentrations covered the concentration ranges expected for these compounds in vinegars.

The [volatile compound/internal standard] molecular ion peak area ratio for the studied volatile compounds was used. The range of linearity studied for each compound appears in Table 4. The correlation coefficients were good ($r^2 > 0.99$).

Table 4
Linearity, detection limits, and repeatability for some volatile compounds

Compound	Linear range (μg/l)	Regression coefficient	Intercept ± SD	Slope ± SD	LOD (μg/l)	Repeat (RSD, %)
Ethyl isobutyrate	13.13–1093.75	0.9992	0.0248 ± 0.0110	0.0030 ± 0.0000	3.31	5.39
Ethyl butyrate	2.35–141.06	0.9956	0.0322 ± 0.0048	0.0035 ± 0.0001	0.71	5.27
Isoamyl alcohol[a]	0.48–100.00	0.9919	0.0133 ± 0.0042	$2 \times 10^{-5} \pm 2 \times 10^{-6}$	0.22	2.88
3-Hydroxy-2-butanone[a]	3.38–2706.24	0.9973	0.0436 ± 0.0023	$7 \times 10^{-7} \pm 2 \times 10^{-8}$	2.20	9.49
Hexan-1-ol	22.65–566.25	0.9986	0.0007 ± 0.0017	0.0041 ± 0.0000	8.60	3.45
Ethyl hexanoate	0.15–153.50	0.9983	0.0154 ± 0.0045	0.0083 ± 0.0001	0.05	4.88
Benzaldehyde	1.96–196.00	0.9988	0.0061 ± 0.0004	0.0005 ± 0.0000	0.52	4.18
Isobutyric acid[a]	2.43–121.26	0.9953	0.0107 ± 0.0179	$1 \times 10^{-5} \pm 2 \times 10^{-6}$	0.89	5.04
5-Methyl-2-Furaldehyde	9.02–2310.00	0.9944	0.0170 ± 0.0042	0.0002 ± 0.0000	4.51	6.41
α-Terpineol	0.67–66.84	0.9983	−0.0077 ± 0.0036	0.0109 ± 0.0001	0.35	8.76
Octanoic acid[a]	0.06–6.41	0.9990	0.0788 ± 0.0106	0.0004 ± 0.0000	0.03	9.80
Eugenol	1.41–236.60	0.9980	−0.0217 ± 0.0171	0.0145 ± 0.0002	0.35	4.57

[a] mg/l.

3.4.2. Detection limits and repeatability

Detection limits were calculated from the calibration curves constructed for each volatile compound, using the Alamin Computer Program [21].

The limits of detection (three times the relative standard deviation of the analytical blank values calculate from the calibration curve) obtained (Table 4) are low enough to determine these compounds in real vinegar samples, taking into account the concentrations found for them from the bibliography [22,23].

The repeatability has been evaluated by means of a series of five extractions of a Commercial Sherry wine vinegar. The mean concentrations for the studied volatile compounds, with their relative standard deviation (RSD) were calculated (Table 4). The RSD obtained ranges between 2.88–9.80%. These results corroborate the high reproducibility of this technique.

4. Conclusions

The conditions for the analysis of volatile compounds in vinegars using SBSE-TD-GC–MS have been optimised by means of a statistical approach. The detection limits and the repeatability values obtained for the studied volatile compounds are adequate for their quantitation in vinegars.

This method can be considered as an alternative to other analytical methods, such as SPME. It is a very simple, solvent-free, fast technique with better sensitivities, in general, than SPME. SPME presents some advantages with respect to SBSE, in particular because, to date, the stir bar offers a limited enrichment capability of polar compounds since it is only available with PDMS coating.

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