Alternative sorptive extraction method for gas chromatography determination of halogenated anisoles in water and wine samples

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Abstract

An alternative sorptive microextraction method for the determination of five halogenated anisoles in water and wine matrices is proposed. Analytes were concentrated in an inexpensive and disposable piece of bulk polydimethylsiloxane (PDMS), desorbed with a small volume of organic solvent, and determined by gas chromatography with electron-capture detection (GC-ECD) or tandem mass spectrometry (GC-MS/MS). The influence of several factors on the efficiency of extraction and desorption steps was investigated in detail and the observed behaviour justified on the basis of thermodynamics and kinetics of the solid-phase microextraction technique. Under optimised conditions, analytes were first extracted in the headspace (HS) mode, at room temperature, for 2.5 hours and then desorbed with 1 mL of n-pentane. This extract was further evaporated to 50 μL. The overall extraction yield of the procedure ranged from 40 to 55% and the limits of quantification remained between 0.5 and 20 ng L^{-1}, depending on the compound considered and the detection technique. Precision and linearity of the method were excellent for all species with both GC-ECD and GC-MS/MS detection. Matrix effects were evaluated with different water and wine samples; moreover, the suitability of the PDMS sorbent for storage of analytes, under different conditions, was demonstrated.

Keywords: anisoles, polydimethylsiloxane, sorptive extraction, gas chromatography.

1. Introduction

The presence of halogenated anisoles in tap water and wine is a matter of concern for consumers and producers because of their unpleasant taste and flavour. The main sources of these off-flavours in both matrices are the chlorine-based disinfectants added to tap water distribution systems and the bleaching solutions used during production of cork stoppers, washing of oak barrels, etc. In the above situations, breakdown products from humic acids and/or lignin may be first oxidized to chlorinated phenols, as well as brominated ones if a source of bromide is available, and the corresponding anisoles may then be produced through bio-methylation reactions [1,2]. Application of chlorinated pesticides in cork oak forests and the use of 2,4,6-tribromophenol as flame retardant could also contribute to the presence of halogenated anisoles in the environment of wine cellars, with the consequent risk of wine contamination. Sensorial threshold levels of anisoles depend on several factors, such as their degree of halogenation, the type of matrix and the perception skills of each person. It is known that consumers will reject wines containing concentrations of 2,4,6-trichloroanisole (TCA) over 10

ng L^{-1}, whereas, an even lower threshold has been reported for the same compound in tap water [3-5]. Fortunately, the perception limits for other haloanisoles are significantly higher [6,7].

Methods for the determination of halogenated anisoles in water and wine samples rely on the use of gas chromatography with electron-capture detection (GC-ECD) or hyphenated to mass spectrometry (GC-MS) [8-10]. In both cases, a previous extraction step is required to achieve quantification limits in the low ng L^{-1} region. Therefore, sample preparation remains as the key step that controls the overall performance of most procedures developed for the determination of anisoles. Solid-phase extraction (SPE), closed-loop stripping (CLSA) and pervaporation [11-13] have been successfully applied to the concentration of halogenated anisoles from liquid matrices. Moreover, different microextraction techniques: solid-phase microextraction (SPME) [4,7,10,14], stir-bar sorptive extraction (SBSE) [5,15,16] and more recently single-drop microextraction (SDME) [17] have also proved to be effective enrichment approaches. The main advantages of SPME are the availability of different sorbents and the fact that there is no need for instrumental modifications at the level of the injector in the gas chromatograph. Polydimethylsiloxane (PDMS) and divinylbenzene-Carboxen-polydimethylsiloxane (DVB-CAR-PDMS) coated SPME fibres show the best performance for anisoles extraction. On the other hand, SBSE provides higher extraction efficiencies than SPME, therefore, when used in combination with thermal desorption, it allows obtaining lower quantification limits.

In addition to PDMS coated fibres and stir bars (Twisters), the bulk polymer has been used as an effective device for in-field monitoring studies aimed at measuring time-weighted average levels of several organic compounds in the aquatic environment [18,19]. Moreover, it has also been applied to direct [20,21] and headspace sorptive extraction (HSSE) of priority pollutants [22], and natural products [23] from discrete samples in the laboratory. The advantages of using bulk PDMS as sorbent are: (1) the possibility of customizing the volume of polymer for each particular application, (2) the availability of different formats (lays, tubes, rods) and, (3) the very low cost of the sorbent in comparison with SPME fibres and Twisters. The latter feature makes it possible to use a new piece of sorbent for each extraction, which avoids problems associated with carry-over and cross contamination, allows simultaneously processing as many samples as desired, and provides the possibility of considering the extraction sorbent for analytes storage purposes.

The aim of this study was to assess the suitability of rods of bulk PDMS, produced on an industrial scale and cut in the laboratory, for the extraction of five halogenated anisoles from liquid (water and wine) samples. The effect of different variables on the performance of the process was investigated and a set of working conditions proposed after taking into consideration: (1) their influence on the yield of the extraction and (2) the simplicity of the experimental set-up. Figures of merit of the method were calculated using GC-ECD and gas chromatography combined with tandem mass spectrometry (GC-MS/MS), which are the most commonly used techniques for the determination of halogenated anisoles.

2. Experimental

2.1. Standards and materials

Acetone, ethyl acetate, n-pentane, diethyl ether, methanol, ethanol, dichloromethane and isooctane (trace analysis quality), as well as sodium chloride, sodium hydroxide, sodium thiosulphate and tartaric acid were acquired from Merck (Darmstadt, Germany). Standards of 2,4-dichloroanisole (DCA), TCA, 2,4,6-tribromoanisole (TBA), 2,3,4,6-tetrachloroanisole (TeCA) and pentachloroanisole (PCA) were purchased from Aldrich (Milwaukee, WI, USA) and Supelco (Bellefonte, PA, USA). The internal standard, 4-iodoanisole (IA), was supplied by Aldrich. Individual solutions of each compound were

prepared in acetone, further dilutions and mixtures of them were made in the same solvent. The stock solution of IA was prepared in acetone and then diluted with isooctane.

PDMS rolls (20 m length x 2 mm diameter) were purchased from Goodfellow (Bad Nauheim, Germany). Rods with a length of 10 mm were cut in the laboratory with a sharp blade. After that, they were weighed and those with mass differences higher than 2% were discarded. The nominal volume of each rod was 31 μL, similar to the amount of PDMS incorporated in a Twister (10 mm length, 0.5 mm film thickness). Before being used for analytes extraction, rods were soaked with a mixture of dichloromethane: methanol (1:1) for 15 min and then conditioned overnight at 250 ºC under a flow of nitrogen (ca. 50 mL min^{-1}).

2.2. Sample preparation

Spiked and non-spiked water and wine samples were used in this study. In the first case, ultrapure, tap, river and treated wastewater (obtained from an urban sewage plant equipped with primary and secondary treatments) were considered. White and red wine samples, from different geographic areas of Spain, were purchased in local markets. Synthetic wine was prepared by addition of tartaric acid (3.5 g L^{-1}) to 12% ethanol solutions in ultrapure water, followed by adjustment of pH to 3.5 by addition of NaOH 1M [9]. Tap water was spiked with sodium thiosulphate (ca. 40 mg L^{-1}) to remove any residual chlorine. All samples, except ultrapure water, were passed through glass fiber filters. Extractions were carried out in 100 mL capacity glass vessels furnished with PTFE-lined septa and aluminium caps. Vessels and caps were purchased from Sugelabor (Madrid, Spain). A rod of PDMS was fixed to the septum with a stainless steel pin (i.d. 0.7 mm), and dipped in the sample or maintained in the headspace (HS) of the vessel, depending on the selected extraction mode. The effect of temperature on the performance of the process was investigated by placing the extraction vessel, containing the sample and the PDMS sorbent, into an oven with a temperature control precision of ± 2 ºC. After finishing the concentration step, PDMS rods were transferred to 2 mL volume GC vials. Analytes were recovered with 1 mL of an appropriate solvent, using sonication (5 min) to enhance the efficiency of the desorption. Details regarding manipulation of the rods during the desorption step have been provided elsewhere [22].

Under optimised conditions, 80 mL of a spiked sample (water or wine) and 24 g of sodium chloride were placed in each vessel. Analytes were extracted in the HS mode, at room temperature for 2.5 hours. In a further step, they were recovered from the PDMS sorbent with 1 mL of n-pentane. This extract was spiked with the internal standard (a solution of IA in isooctane) and evaporated until a final volume of 50 μL under a gentle stream of nitrogen. A scheme of the sample preparation process is shown in Fig. 1.

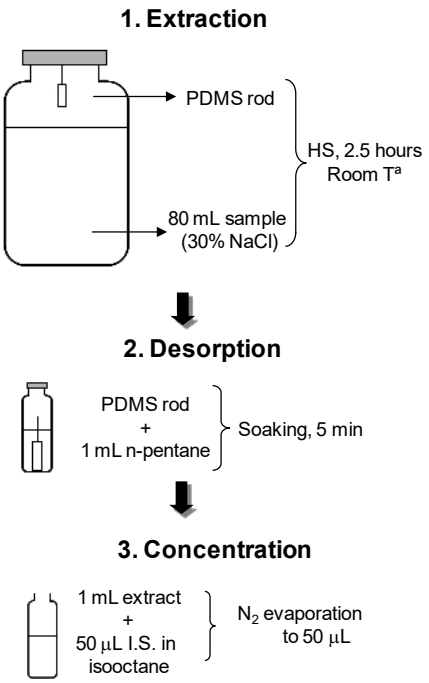

Fig. 1. Scheme of the sample preparation procedure.

2.3. Equipment

Anisoles were determined by GC-ECD or GC-MS/MS. In the first case, an Agilent 6890 gas chromatograph (Wilmington, DE, USA) equipped with a micro-electron-capture detector (micro-ECD) was used. The GC-MS/MS system consisted of a Varian CP 3900 gas chromatograph (Walnut Creek, CA, USA) connected to an ion-trap mass spectrometer (Varian Saturn 2100). Both systems were furnished with autosampler injectors. Two different capillary columns, an Agilent HP-5 (30 m x 0.32 mm I.D.; d_f: 0.25 μm) and an Agilent HP-35 (30 m x 0.25 mm I.D.; d_f: 0.25 μm), were considered for separation of analytes. Columns were operated at constant helium flow rates of 1.4 and 1.0 mL min^{-1}, respectively. Isooctane standards, containing increased concentrations of target species and a fixed level of IA, and extracts from PDMS rods (2 μL volume) were injected in the splitless mode (1 min), with the oven temperature programmed as follows: 70 ºC (1 min), ramp to 280 ºC at 12 ºC min^{-1} and hold at 280 ºC for 10 min. Operating under these conditions, both columns provided baseline separations for all species. The most significant difference observed in the corresponding chromatograms was that IA eluted before TCA in the HP-5 column, whereas the reverse order was observed in the HP-35 one.

The ion-trap mass spectrometer was operated in the electron impact mode (70 eV). The most intense signals in the spectrum of each anisole, appearing at $[M]^+$ or $[M-15]^+$ m/z units, were chosen as parent ions, isolated with a m/z window of ± 3 units and submitted to collision induced dissociation. The working MS/MS conditions, as well as m/z ratios for parent and product ions, are summarised in Table 1.

Compound	Molecular ion (m/z)	Parent ion (m/z)	Excitation storage level (m/z)	Excitation amplitude (V)	Product ions (m/z)[a]

DCA	178	163	70	1.36	133,135
TCA	212	197	85	1.62	167,169
IA	234	234	100	0.42	219
TeCA	246	246	105	1.48	229, 231
TBA	346	346	150	1.50	329, 331
PCA	280	265	115	1.36	235, 237

Table 1. Summary of MS/MS working conditions. [a]Used as quantification ions

3. Results and discussion

3.1. Desorption conditions

Preliminary optimisation experiments were carried out with ultrapure water spiked at the 2 μg L^{-1} level. On the basis of results reported for SPME fibres [10] and bulk PDMS [22], analytes were extracted overnight at 50 ºC in the HS mode. Rods were then soaked for 5 min with 3 consecutive fractions (1 mL each) of n-pentane or ethyl acetate, and extracts were injected in the GC-ECD system without any further concentration step. For both solvents, relative standard deviations for responses of target species remained below 6% (n= 4 replicates). With ethyl acetate, approximately 85% of the total amount of each compound concentrated in the PDMS rod was recovered with the first mL of solvent, whereas a slightly higher desorption yield (ca. 90%) was achieved with the same volume of n-pentane. Dichloromethane and diethyl ether were also tested as desorption solvents; however, they did not improve the yield provided by n-pentane, which was retained for further experiments. Since rods were employed as disposable sorbents, only 1 mL of solvent was used for analytes desorption.

Quantification limits of the method are determined by the efficiency of the extraction step and the volume of solvent required to recover the analytes from PDMS rods. Therefore, the possibility of concentrating the 1 mL n-pentane extracts to a lower volume was investigated. The process was carried out at room temperature, under a gentle stream of nitrogen. Evaporation to dryness, followed by reconstitution of the residue with a small volume of solvent, led to severe losses of DCA and TCA; however, the problem could be overcome by addition of isooctane (50-100 μL, containing IA at the 200 μg L^{-1} level), as a keeper, to the n-pentane extracts. The internal standard (IA) was used to compensate for differences in the volume of concentrated extracts. Fig. 2 compares the responses obtained for aliquots of the same mixture of anisoles in n-pentane (TeCA was not included in this study) before and after concentration from 1 to 0.1 or 0.05 mL. As appreciated, the evaporative concentration process did not affect to the ratios between analytes and internal standard peak areas.

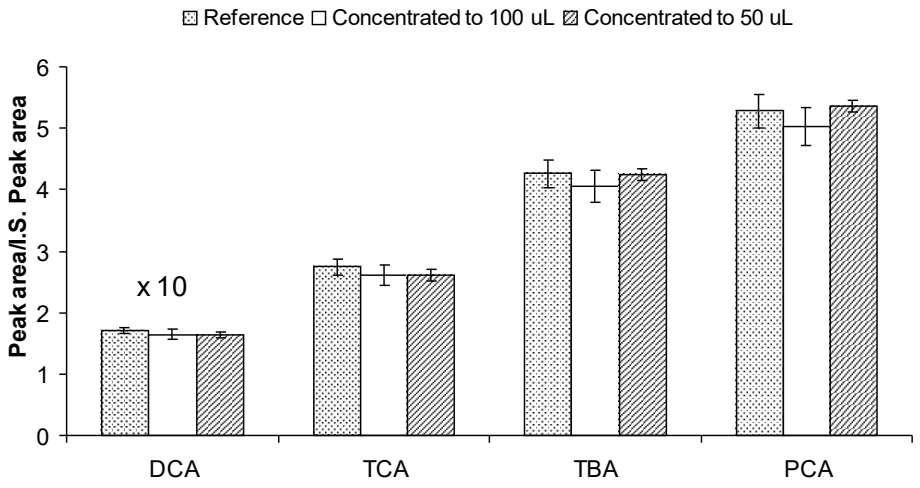

Fig. 2. Evaluation of potential losses of anisoles after concentration of 1 mL n-pentane extracts to different final volumes, n= 3

replicates.

3.2. Extraction conditions

The effect of different factors on the performance of the extraction step was investigated using ultrapure water samples spiked with anisoles at the 0.150 μg L^{-1} level (1.5 μg L^{-1} for DCA). Extractions were carried out in 100 mL vessels, and different sample volumes, temperatures, ionic strength values and sampling modes were considered. In order to minimise sorption and cross-contamination problems, and also to simplify the set-up of the extraction step, sample stirring with a magnetic bar was not considered. Analytes were desorbed from PDMS rods with 1 mL of n-pentane, the extract evaporated to a final volume of 50 μL, and 2 μL injected in the GC-ECD system.

3.2.1. Sampling mode

Kinetics of sorptive extraction (SE) processes change depending on the position of the sorbent: HS or direct exposure to the sample. Both modes have been proposed for the extraction of anisoles from aqueous samples with SPME fibres [4,7,10] and PDMS coated Twisters [5,15,16]. Considering similar conditions to those proposed for the latter device (2 hours sampling at room temperature), the efficiency of the direct mode represented less than 5% of that achieved in HS. When the sampling step was extended overnight (14 hours), and vessels were maintained at higher temperatures (50 and 80 ºC), at least still twice higher signals were obtained in the HS mode than with direct sampling.

3.2.2. Ionic strength and sample volume

The effect of the ionic strength on the efficiency of the HSSE was evaluated with 80 mL samples containing sodium chloride at four different levels, between 0 and 30%. Extractions were performed in duplicate, at room temperature for 2.5 hours. For non-ionic species, their distribution constants between aqueous samples and PDMS sorbents increase with the ionic strength of the sample; however, the kinetics of mass transference decreases at high salt concentrations [24]. Experimental data showed that the amount of each anisole concentrated in the PDMS rod increased slowly, but steadily, with the ionic strength of the sample. On average, twice higher signals were measured for samples containing a 30% of sodium chloride than those found for samples without salt addition.

Fig. 3 shows the effect of sample volume on the efficiency of the HSSE. A proportional relationship between anisoles responses and sample volume was observed. This behaviour can be explained on the basis of two different contributions. One is the extraction capability of the rod, which is a function of the high volume of PDMS, as a consequence the extracted amount of each analyte increased with its total mass in the sampling vessel. The second contribution is related to the decrease in the HS of the vessel, which minimised the fraction of analytes remaining in the vapour phase.

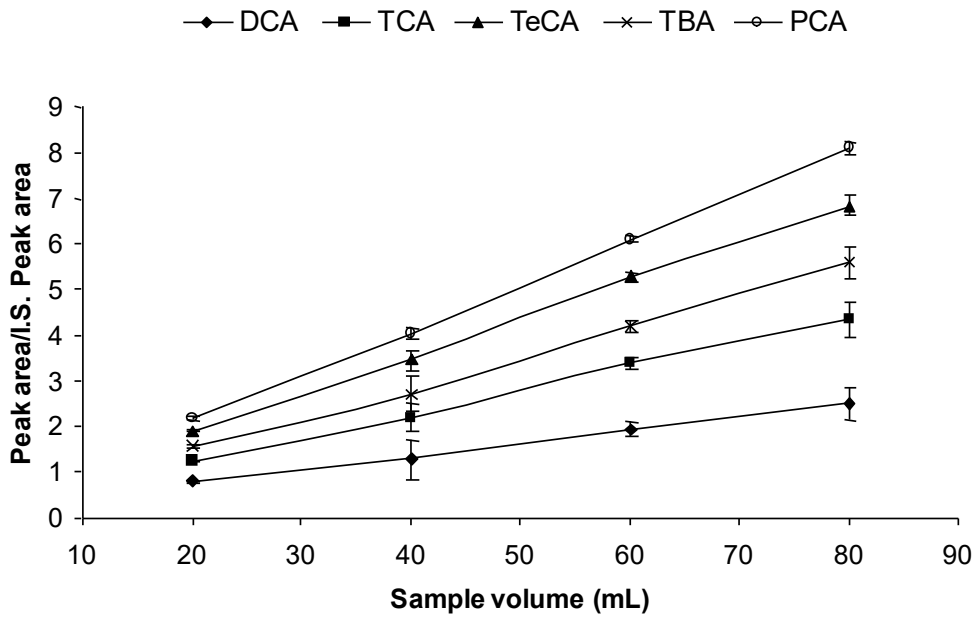

Fig. 3. Effect of sample volume on the yield of the HSSE for water samples containing a 30% of NaCl. Room temperature extraction for 2.5 hours, n= 3 replicates.

3.2.3. Extraction time

The effect of sampling time on the yield of the HSSE was evaluated in the range between 0.25 and 8 hours, at room temperature and 50 ºC. Fig. 4 shows the mean results obtained for duplicate extractions. The values on the y axis correspond to the overall efficiency of the extraction procedure, defined as the ratio between the amount of each anisole in the extract from the PDMS sorbent and that added to the sample. The first was determined by external calibration, using standards in isooctane containing increased levels of the analytes and, the same fixed amount of internal standard (IA) as that added to extracts from PDMS rods. At room temperature, equilibrium was achieved after 2.5 hours of sampling, and the yield of the HSSE varied between 40 and 55%. Moreover, there was a direct correlation between the extraction efficiency and the octanol-water partition coefficient of each anisole (log K_{ow} values: 3.4 for DCA, 3.9 for TCA, 4.2 for TBA, 4.5 for TeCA and 5.0 for PCA). At 50 ºC, the kinetics of the extraction was faster and equilibrium was achieved after 1 hour of sampling; however, the yield of the extraction decreased considerably. Taking into account these results and the possibility of simultaneously processing of as many samples as required, 2.5 hours of sampling at room temperature were selected as the final extraction conditions. This sampling period is longer than those reported for SPME fibres when applied to the determination of same analytes [3,7,10,26], however, it remains similar to that proposed for SBSE [5,16].

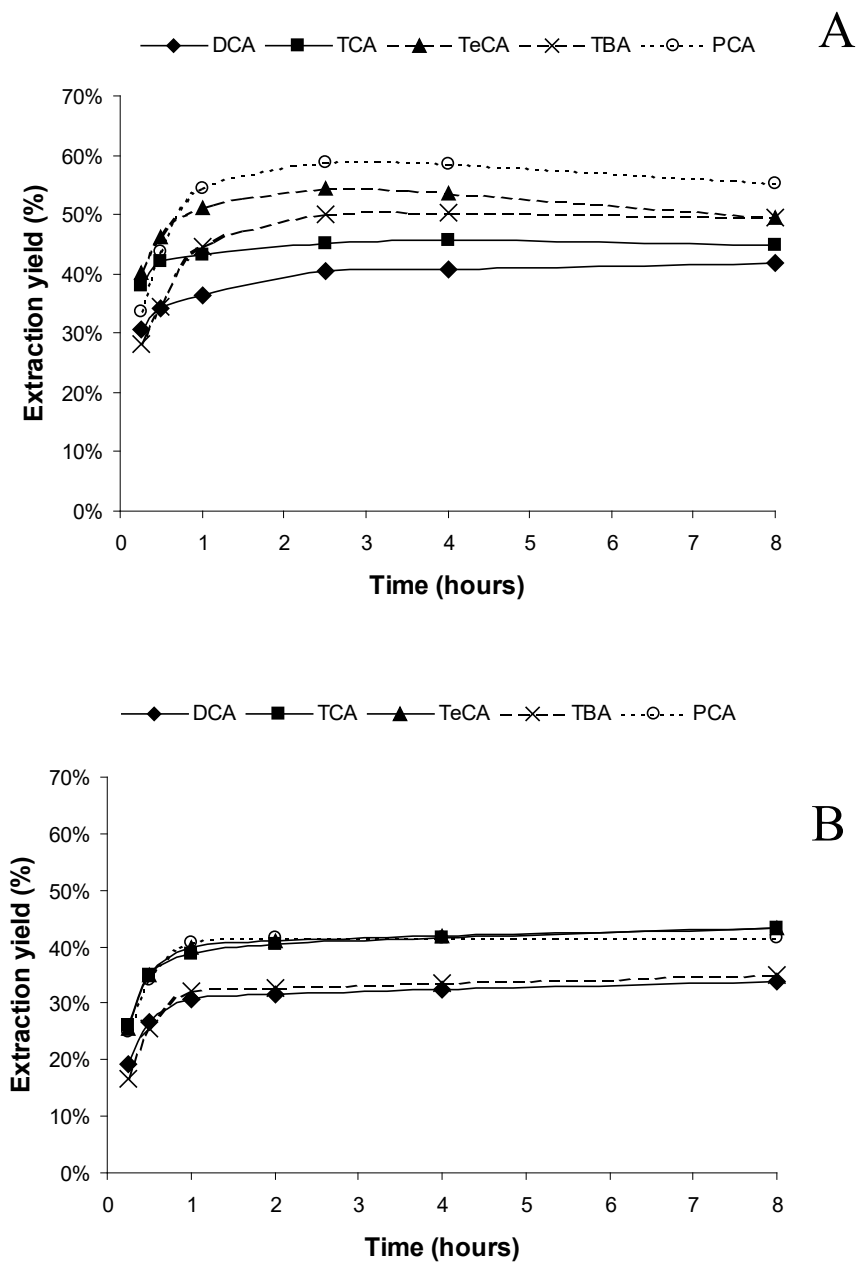

Fig. 4. Time course of the HSSE at room temperature (A) and at 50 ºC (B). Average data for duplicate extractions.

3.3. Precision, linearity and quantification limits

Figures of merit of the proposed method were evaluated using GC-ECD and GC-MS/MS. Precision studies were accomplished with water samples spiked at different concentration levels between 5 and 50 ng L^{-1}, and extracted the same day (repeatability studies) or on different days (reproducibility evaluation). Relative standard deviations (RSDs) in the responses measured for target species remained below 10%. The only exception was the data obtained for DCA under reproducibility conditions, by GC-MS/MS, Table 2.

	GC-ECD	GC-MS/MS

	Repeatability		Reproducibility	Repeatability		Reproducibility
Added level	10 ng L^{-1a}	50 ng L^{-1b}	20 ng L^{-1c}	5 ng L^{-1}	20 ng L^{-1}	10 ng L^{-1}
DCA	2.5	3.1	8.9	2.1	2.5	15.6
TCA	7.9	4.4	8.0	1.2	4.2	8.5
TeCA	10.1	4.9	5.5	5.5	4.6	9.4
TBA	10.6	3.7	7.5	6.9	2.7	9.3
PCA	8.1	5.0	3.7	8.7	5.4	8.9

Table 2. Repeatability (n= 4 replicates in the same day) and reproducibility (n=9 replicates in different days) of the HSSE procedure for water samples spiked at different concentration levels. Relative standard deviations (RSDs) given as percentages. [a] 100 ng L^{-1} for DCA,[b] 500 ng L^{-1} for DCA,[c] 200 ng L^{-1} for DCA.

Globally, RSDs were similar to, or even better than those provided by other microextraction techniques (SPME, SBSE, SDME) when applied to samples fortified with similar concentrations of anisoles [5,7,8,17]. Linearity was investigated with samples spiked at six different concentration levels from 2.5 to 250 ng L^{-1} (25 to 2500 ng L^{-1} in case of DCA using GC-ECD detection). The peak area of each compound was divided by the signal of the internal standard and plotted against its concentration in the sample. Both GC-ECD and GC-MS/MS, provided calibration graphs with correlation coefficients between 0.9960 and 0.9998, showing the existence of a linear dependence between the amount of each anisole in the extraction vessel and that transferred to the PDMS rod, Table 3.

	Correlation coefficient (R^2)		LOQ (ng L^{-1})	
Analyte	GC-ECD	GC-MS/MS	GC-ECD	GC-MS/MS
DCA	0.9980	0.9960	20	0.5
TCA	0.9994	0.9990	2.5	0.8
TeCA	0.9996	0.9996	1.5	0.5
TBA	0.9991	0.9991	1.3	1.5
PCA	0.9998	0.9990	0.8	0.5

Table 3. Linearity and limits of quantification (S/N = 10) of the method.

Quantification limits (LOQs) of the proposed method ranged from 0.5 to 20 ng L^{-1}. In the case of DCA, GC-MS/MS achieved one order of magnitude lower values than GC-ECD. For the rest of analytes, both techniques provided similar quantification limits, Table 3. Anyhow, on the basis of its higher selectivity, GC-MS/MS is recommended as detection technique. Table 4 summarizes the LOQs reported for TCA (the most commonly determined anisole and also the one exhibiting the lowest threshold level), using different sample preparation approaches followed by GC-MS or GC-MS/MS detection. The value provided by the proposed method was of the same order of magnitude as those achieved with SPME, and slightly lower than those reported for SPE and SDME. Moreover, as only a 4% of the final extract (50 μL volume) was injected in the gas chromatograph, it is expected that combining HSSE with thermal desorption of PDMS rods may compete with SBSE and CLSA in terms of quantification limits.

Matrix	Extraction technique	Sampling mode	Sampling time (min)	LOQ (ng L^{-1})	Ref
Wine	Pervaporation	-	-	15[a]	[13]
Wine	SPE	-	-	7	[11]
Wine	SPE	-	-	2	[25]
Water	CLSA	-	-	0.08[a]	[12]
Water	SPME (DVB-CAR-PDMS)	HS	40	0.3[a]	[26]
Water	SPME (DVB-CAR-PDMS)	HS	30	1.5[a]	[3]
Wine	SPME (DVB-CAR-PDMS)	HS	70	0.8	[8]
Water	SPME (PDMS)	HS	60	0.1[a]	[10]
Water	SBSE (PDMS)	Direct	120	0.1	[5]
Wine	SBSE (PDMS)	Direct	90	1	[16]
Water/wine	HSSE (PDMS)	HS	150	0.8	This work

Table 4. Summary of quantification limits (LOQs) for TCA using different sample concentration methods followed by gas chromatography with mass spectrometry detection. [a]Obtained from reported limits of detection multiplied by 3

3.4. Matrix effects

The influence of the type of matrix on the yield of the HSSE was investigated with different water and wine samples spiked with target species at 10 and 50 ng L^{-1}, respectively. In the first case, extracts were analysed by GC-MS/MS, whereas GC-ECD was used for the latter matrix. After filtration, samples were divided in several fractions and some of them fortified at the above described levels. Differences between responses measured for spiked and non-spiked (blanks) fractions of the same sample were compared with those found for ultrapure water with the same addition level. Anyhow, only TCA was detected in the non-spiked fractions of wastewater, at levels similar to the quantification limit of the proposed method, Fig. 5. Similar responses, after blank correction, were obtained for ultrapure, tap, river and wastewater, Table 5.

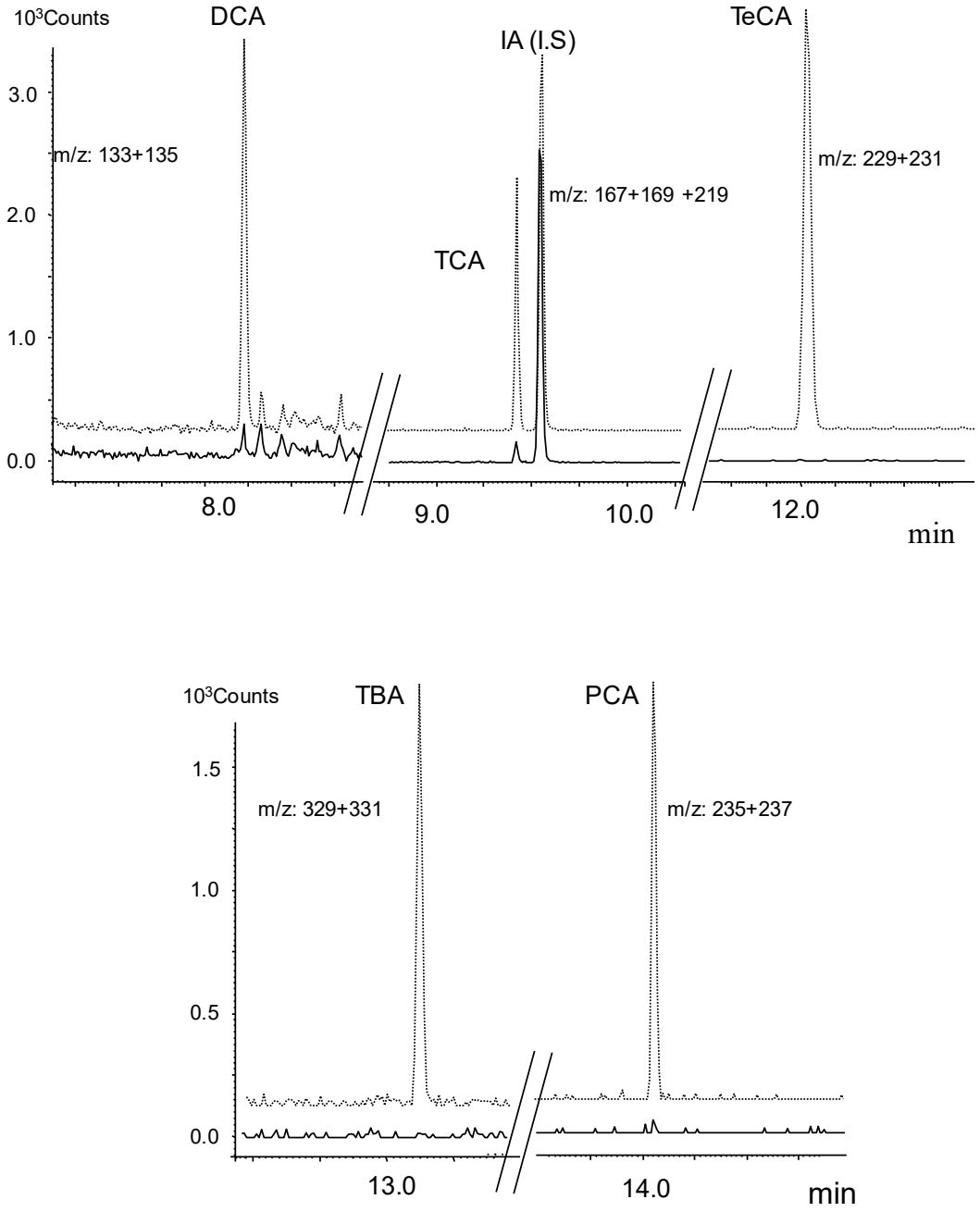

Fig. 5. Overlay of GC-MS/MS chromatograms for aliquots of a wastewater sample without (solid line) and with addition of anisoles at 10 ng L^{-1} (dotted line). Chromatograms obtained with the HP-35 capillary column.

	Relative recovery (%) ± standard deviation		
	Tap water	River water	Wastewater[a]
DCA	101 ± 2	105 ± 4	105 ± 4
TCA	96 ± 2	97 ± 7	97 ± 7
TeCA	96 ± 2	99 ± 7	99 ± 7
TBA	95 ± 2	106 ± 7	106 ± 7
PCA	92 ± 6	101 ± 5	101 ± 5

Table 5. Evaluation of matrix effects for different water samples. Relative responses to those obtained for ultrapure water, n= 4 replicates. Addition level 10 ng L^{-1}. [a] Urban wastewater

Consequently, the quantification of anisoles in water samples can be performed by external calibration. The behaviour observed for wine depended on the considered compound and sample. For the most volatile species (DCA and TCA) the efficiency of the extraction remained basically the same as for ultrapure water; however, there was a significant decrease in the responses of TeCA, TBA and PCA for some of

the investigated samples, Table 6. The composition of each particular wine appeared to have a different effect on the yield of the HSSE. Since no differences were observed between the responses measured for ultrapure water and synthetic wine, it can be assumed that ethanol did not contribute significantly to the observed behaviour, Table 6. Whatever the source of matrix effects, levels of anisoles in wine should be measured using the standard addition method, or considering the use of isotopic labelled surrogates for target species. It must also be pointed out that direct addition of IA to wine samples, rather than the n-pentane extracts from PDMS rods, cannot overcome the aforementioned problems, since they affected each analyte to a different extent.

	Relative recovery (%) ± standard deviation				
	Synthetic wine	White wine[a]	White wine[b]	White wine[c]	Red wine[d]
DCA	102 ± 7	101 ± 6	107 ± 9	105 ± 6	88 ± 4
TCA	98 ± 6	105 ± 7	102 ± 10	98 ± 4	93 ± 5
TeCA	98 ± 5	93 ± 9	91 ± 10	87 ± 6	82 ± 7
TBA	96 ± 8	84 ± 4	81 ± 10	74 ± 6	60 ± 8
PCA	95 ± 5	85 ± 4	75 ± 12	70 ± 7	63 ± 8

Table 6. Evaluation of matrix effects for wine samples. Relative responses to those obtained for ultrapure water, n= 4 replicates. Addition level 50 ng L^{-1}. [a]Valdepeñas, [b]Ribeiro, [c]Rueda, [d]Rioja

3. 5. Stability of halogenated anisoles in PDMS rods

In-field sample concentration followed by storage of sorbent units until their analysis is one of the most challenging issues in trace analytes. Obviously, the feasibility of in-field sample preparation is determined by the stability of the analytes in the sorbent. Moreover, in practice, the simplicity of the extraction step and the cost of sorbent units, particularly when many samples have to be processed, are also relevant variables. To evaluate the stability of anisoles in PDMS rods, several aliquots of the same spiked water sample were extracted under optimised conditions. After that, rods were dried with a soft tissue and stored in closed, amber vials (1.5 mL volume), at room temperature or 4 ºC for 1-2 weeks. In another series of experiments rods were desorbed immediately after finishing the extraction step. Responses of halogenated anisoles in the extracts obtained from sorbents stored under different conditions represented between 87 and 110% of those measured for non-stored ones, Fig. 6. Therefore, PDMS rods can be considered as inert devices as regards anisoles storage. These results are in agreement with the conclusions reported by Benanou et al. for TCA and TBA using PDMS coated magnetic bars, stored at 4 ºC [5], with the additional advantage of using inexpensive sorbent devices.

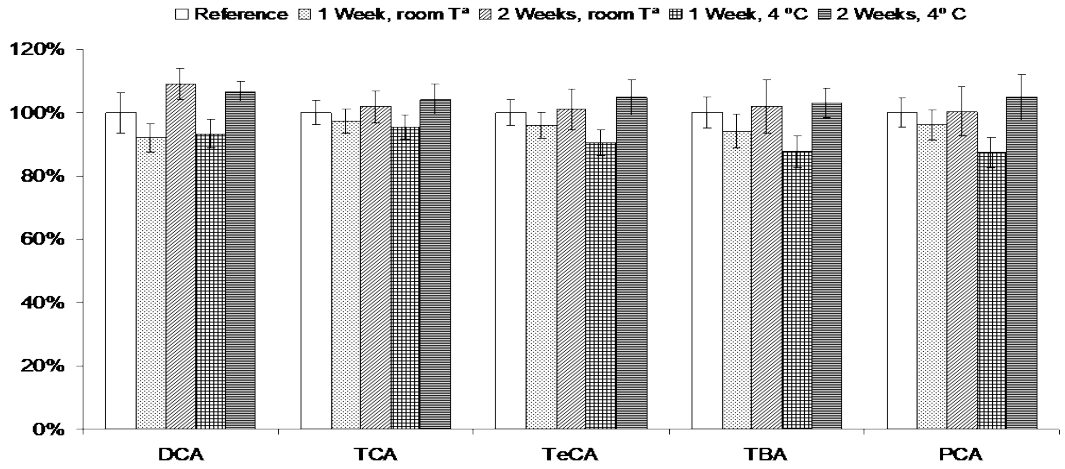

Fig. 6. Effect of storage conditions on the stability of anisoles concentrated in PDMS rods. Responses are normalised to those achieved with rods desorbed immediately after extraction.

4. Conclusions

The suitability of an inexpensive PDMS sorbent for the extraction of anisoles from aqueous matrices has been demonstrated. Extraction mode, ionic strength and sample volume were the most relevant parameters that affected the yield of the HSSE. Although the proposed method involves sampling periods between 2 and 3 times longer than those reported for SPME fibres, many samples can be extracted simultaneously, instead of one by one. Taking into consideration the stability of anisoles in the PDMS rods and the simplicity of the extraction step, samples can be concentrated in-situ and then, only the sorbent units need to be transported to the laboratory, which is a further advantage of this method. In the present form, the developed method provides excellent precision and linearity, and it is sufficiently sensitive for the determination of halogenated anisoles below their threshold levels in wine samples. Further research should be focussed on the evaluation of more efficient methods of sample introduction, e.g. thermal desorption combined on-line with GC, to achieve even lower quantification limits.

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