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Advantages of monolithic over particulate columns for multiresidue analysis of organic pollutants by in-tube solid-phase microextraction coupled to capillary liquid chromatography

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ABSTRACT

The performance of a monolithic C_{18} column (150 mm × 0.2 mm i.d.) for multiresidue organic pollutants analysis by in-tube solid-phase microextraction (IT-SPME)-capillary liquid chromatography has been studied, and the results have been compared with those obtained using a particulate C_{18} column (150 mm × 0.5 mm i.d., 5 μm). Chromatographic separation has been carried out under isocratic elution conditions, and for detection and identification of the analytes a UV-diode array detector has been employed. Several compounds of different chemical structure and hydrophobicity have been used as model compounds: simazine, atrazine and terbutylazine (triazines), chlorfenvinphos and chlorpyrifos (organophosphorous), diuron and isoproturon (phenylureas), trifluralin (dinitroaniline) and di(2-ethylhexyl)phthalate. The results obtained revealed that the monolithic column was clearly advantageous in the context of multiresidue organic pollutants analysis for a number of reasons: (i) the selectivity was considerably improved, which is of particular interest for the most polar compounds triazines and phenyl ureas that could not be resolved in the particulate column, (ii) the sensitivity was enhanced, and (iii) the time required for the chromatographic separation was substantially shortened. In this study it is also proved that the mobile-phase flow rates used for separation in the capillary monolithic column are compatible with the in-valve IT-SPME methodology using extractive capillaries of dimensions similar to those used in conventional scale liquid chromatography (LC). On the basis of these results a new method is presented for the assessment of pollutants in waters, which permits the characterization of whole samples (4 mL) in less than 30 min, with limits of detection in the range of 5–50 ng/L.

1. Introduction

Recent decades have brought increasing concerns for potential adverse effects resulting from the production, use and disposal of several organic chemicals. Many of such compounds can enter the environment, disperse and persist in water, air, soils, sediments and organisms. Many often, organic pollutants are released through regulated and unregulated discharges to water resources. Thus, protecting the integrity of water resources has become one of the most essential environmental issues, as recognized by the international legislation. The European Commission and the Environmental Protection Agency of the United States of America have listed the most toxic and persistent pollutants, as well as the maximum permissible levels into the aquatic environment [1,2].

The increasing demand of analytical results for monitoring environmental pollution make necessary the development of rapid, simple and cost-effective analytical procedures. From an analytical point of view, two types of difficulties are typically encountered when monitoring water quality. First, owing to the low concentration levels fixed by the authorities for organic pollutants, high sensitive analytical methodologies are required. Second, since the target compounds belong to different chemical groups, a complete characterization of a sample usually requires two or more separate analytical methods with different data objectives [3].

As regards the sensitivity, suitable results are obtained if the analytes are previously preconcentrated using some form of extraction. Traditionally, gas chromatography (GC) coupled with mass spectrometry (MS) detection has been the option preferred for the separation and identification of organic pollutants. Nowadays, liquid chromatography (LC) is gaining popularity because it facilitates the integration of the sample processing in the chromatographic system. As an example, the coupling of in-tube solid-phase microextraction (IT-SPME) in in-valve mode with LC enables the direct analysis of several classes or organic pollutants in waters [4,5]. Another approach to improve the analytical performance is the reduction of the column diameter dimensions

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(micro-, capillary-, nano-LC). The combination of the in-valve IT-SPME methodology to capillary LC enables the simultaneous identification and quantification at sub-μg/L levels of several organic pollutants [6,7].

Monolithic columns have emerged as an alternative to traditional packed-bed columns for high efficiency separations in LC. The main advantages of monolithic columns are good permeability and fast mass transfer, versatile surface chemistry, easy fabrication and fritless design [8]. The advantages of monolithic columns in capillary LC have been extensively exploited in the biomedical field, especially in the analysis complex mixtures of peptides for proteome analysis [9]. In principle, the high efficiency and resolution of monolithic capillary columns make them ideal for assessing environmental pollution. However, most of the described studies deal with the preparation of the columns or with theoretical aspects of the separations [10]. Monolithic capillary columns have also been used as the extractive media for on-line enrichment by SPE using the precolumn technique [11] or by IT-SPME [12]. In all instances, the proposed methods were applied to the analysis of a single class of pollutants.

In the present study, we have compared the potential utility of silica-based particulate and monolithic columns for multiresidue organic pollutants analysis by capillary LC, using IT-SPME for on-line enrichment of the analytes. The columns have been evaluated not only in terms of resolution capabilities, but also for their suitability to be used in an on-line system that integrates analytes enrichment, separation and detection. To our knowledge, this is the first time that the IT-SPME methodology has been used in combination with a capillary monolithic column. Conditions for IT-SPME were those previously optimized in [6]. Several compounds of different chemical structure and hydrophobicity have been used as model compounds (Table 1): simazine, atrazine and terbutylazine (triazines), chlorfenvinphos and chlorpyrifos (organophosphorous), diuron and isoproturon (phenyl ureas) trifluralin (dinitroaniline) and di(2-ethylhexyl)phthalate (DEHP). These compounds are considered priority substances in monitoring water quality [1]. On the basis of the results obtained, a new method is presented for assessing water pollution. The reliability of the proposed method has been tested by analysing several waste waters.

2. Experimental

2.1. Reagents and solutions

All reagents were of analytical grade. Simazine, atrazine, terbutylazine, chlorfenvinphos, trifluralin and DEHP were obtained from Sigma (St. Louis, MO, USA). Chlorpyrifos, diuron and isoproturon were obtained from Dr. Ehrenstorfer (Augsburg, Germany). Acetonitrile was of HPLC grade (Scharlau, Barcelona, Spain).

The stock solutions of the individual compounds (10.0 μg/L) were prepared in water. Working solutions were prepared by dilution of the stock solutions with water.

2.2. Equipment and chromatographic conditions

The capillary chromatographic system used consisted of a LC isocratic capillary pump (Jasco Corporation, Tokyo, Japan) and a UV–vis diode array detector (Agilent, 1200 series) equipped with a 80 nL flow cell. The analytical signal was recorded between 190 and 400 nm. Samples were injected via a six-port injection valve equipped with a GC capillary column which acted as the injection loop.

For the separation of the analytes a Zorbax SB C_{18} (150 mm × 0.5 mm i.d., 3.5 μm) column (Agilent) and a Onyx Monolithic C_{18} (150 mm × 0.2 mm i.d.) column (Phenomenex, Torrance, CA, USA) were used. The mobile-phase was a mixture of acetonitrile/water (60:40, v/v). Different mobile-phase flow rates in the range 4–15 μL/min were assayed. All solvents were filtered through 0.45 μm nylon membranes (Teknokroma, Barcelona, Spain) before use.

2.3. IT-SPME procedure

For on-line IT-SPME of the analytes a GC TRB-5 capillary column of 40 cm length with 0.32 mm i.d., coated with 5% diphenyl-95% polydimethylsiloxane (PDMS) (3 μm coating thickness) was used (Teknokroma, Barcelona, Spain). This capillary column was connected to a conventional six-port injection valve and used as the injection loop. Capillary connections to valve were facilitated by the use of 2.5 cm sleeve of 1/16 in. polyether ether ketone (PEEK) tubing; 1/16 in PEEK nuts and ferrules were used to complete the connections. Aliquots of 4.0 mL of the samples were manually loaded into the system by means of a 1.0-mL precision syringe [6]. After sample loading, 100 μL of ultrapure water was passed through the capillary in order to flush out the residual sample. Next, the valve was manually rotated, so the analytes were desorbed from the extractive phase of the GC capillary with the mobile-phase, and transferred to the analytical column for separation and detection. All the experiments were carried out in triplicate and at room temperature.

2.4. Real water samples

Real waste water samples collected at different water treatment plants of the Comunidad Valenciana (Spain) were directly analysed (without filtration). After the arrival to the laboratory, water samples were stored in dark in brown glass flasks at 4 °C until analysis. Each sample was analysed in triplicate and at room temperature.

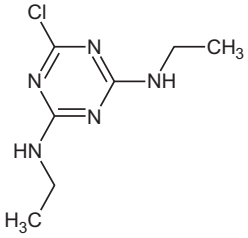
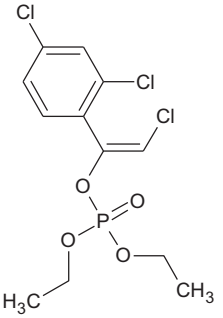
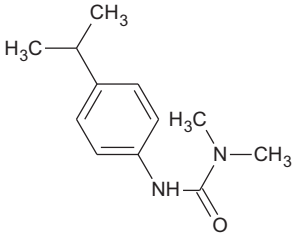
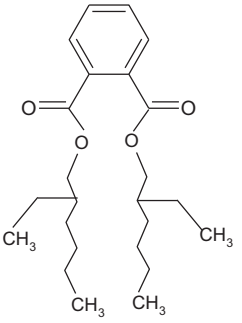
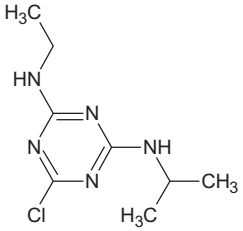
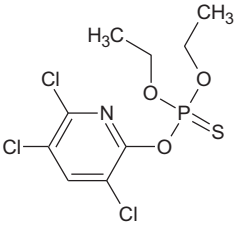
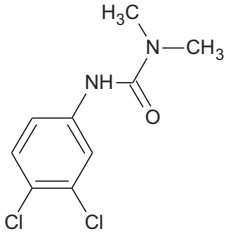
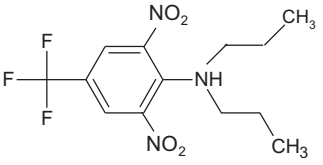
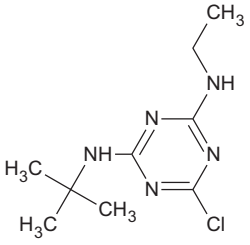
3. Results and discussion

3.1. Optimization of the separation

The separation of the tested organic pollutants was carried out under isocratic mode. After preliminary studies, a mixture acetonitrile/water (60:40, v/v) was selected as the mobile-phase, and then, different mobile-phase flow rates were assayed. In these assays different solutions of the individual analytes as well as different mixtures were used. The concentration of the analytes ranged from 1 to 5 μg/L.

Mobile-phase flow rates in the range 10–15 μL/min were tested for separation of the analytes in the particulate column. Higher flow rates were not assayed to prevent high backpressures, which could negatively affect the IT-SPME device. In all instances, suitable separation for the tested compounds was achieved with the only exception of atrazine and diuron, which eluted at the same retention time. In an attempt to improve the resolution between atrazine and diuron different acetonitrile/water and methanol/water mixtures were also tested. However, these compounds eluted at almost identical retention times under all conditions assayed. As a compromise between separation and time of analysis a flow-rate of 12 μL/min was selected as the best option. Examples of the chromatograms obtained under such conditions are shown in Fig. 1. It should be noted that the *x*-axis represents the total run time, that is, the time necessary for desorption of the analytes from the SPME capillary, for transfer them to the analytical column, and for chromatography. A baseline disturbance was observed at the beginning of the chromatograms, which is a chromatographic profile typically found when using the in-valve IT-SPME technique. The baseline disturbance is due to the inclusion of the SPME capillary column in

Table 1
Chemical structures of the tested compounds.

Compound		Compound	
Simazine		Chlorfenvinphos	
Isoproturon		DEHP	
Atrazine		Chlorpyrifos	
Diuron		Trifluralin	
Terbutylazine			

the chromatographic flow scheme. After sample loading, the residual sample in the capillary is sent to waste by flushing water. When rotating the valve, the excess of water is carried over by the mobile-phase, causing at the working wavelength a drop in the signal. As observed in Fig. 1, the drop of the baseline occurred from 2.5 to 4.9 min, which is consistent with the internal volume of the SPME capillary (≈32 μL) and the mobile-phase flow rate. Indeed, all the analytes were eluted from analytical column at higher retention times and therefore, the drop in the base line did not disturb the identification of the analytes.

The mobile-phase flow rates assayed for separation of the target compounds with the monolithic column ranged from 4 to 10 μL. Best results were achieved at a flow rate of 4 μL/min. Using such flow-rate all the analytes were satisfactorily resolved as observed in Fig. 2, and thus, lower flow rates were not assayed. As in the chromatograms obtained with the particulate column, a drop in the base line was observed at the working wavelength. In this instance, the distortion was significantly broader (from 2.5 to 11 min) because a lower mobile phase flow rate was used. As a result, the analytes started to

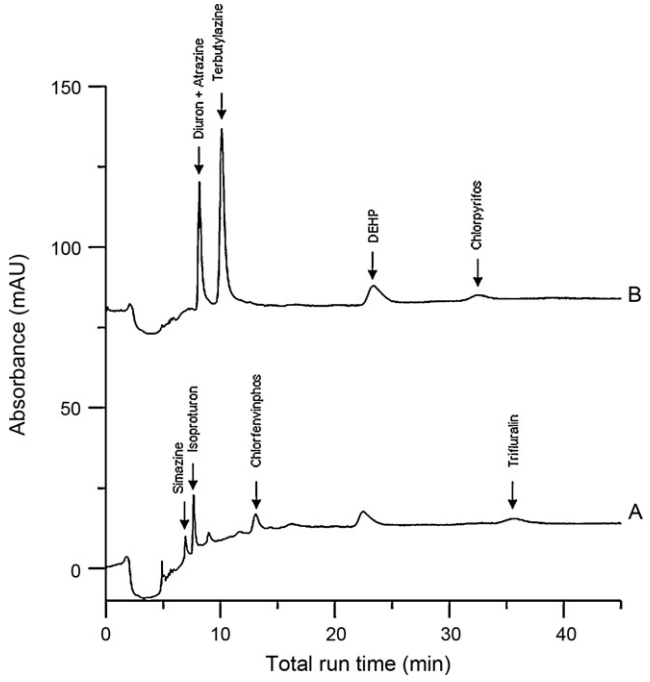


Fig. 1. Chromatograms at 230 nm obtained with the particulate column for a mixture of: (A) simazine (4 μg/L), isoproturon (4 μg/L), chlorfenvinphos (4 μg/L), and trifluralin (1 μg/L); (B) diuron (4 μg/L), atrazine (4 μg/L), terbutylazine (2 μg/L), DEHP (5 μg/L) and chlorpyrifos (2 μg/L). Volume of sample, 4 mL. For other details, see text.

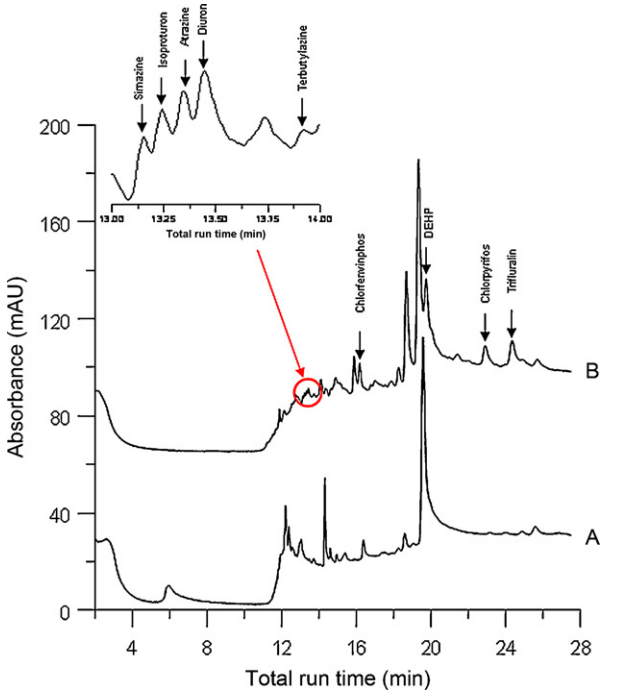


Fig. 2. Chromatograms at 230 nm obtained with the monolithic column for: (A) a blank, and (B) a mixture of simazine (2 μg/L), isoproturon (2 μg/L), diuron (2 μg/L), atrazine (2 μg/L), terbutylazine (1 μg/L), chlorfenvinphos (2 μg/L), DEHP (2.5 μg/L), chlorpyrifos (1 μg/L) and trifluralin (1 μg/L). For other details, see text.

elute from the analytical column at retention times higher than 13 min.

It should be noted that the chromatograms of Figs. 1 and 2 show different unidentified peaks, which is a common feature of procedures based on large-volume sample injections [6,7]. None of such

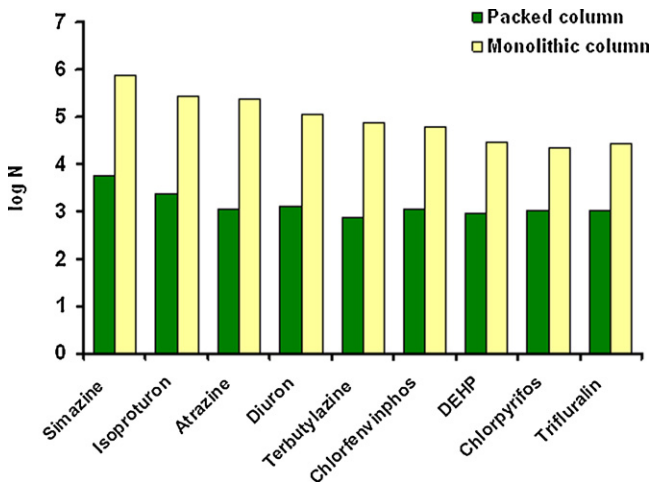


Fig. 3. Log N obtained for the compounds assayed with the two columns tested ($n = 3$). The concentrations used for calculation of N with the packed column and the monolithic column were those of Figs. 1 and 2, respectively. For other details, see text.

peaks was detected when processing acetonitrile instead of aqueous solutions and, therefore, it was concluded they corresponded to impurities and/or degradation products of the chemicals and of nanopure water used to prepare working solutions. According to the literature highly ubiquitous contaminants such as phthalates other than DEHP, carboxylic acids and/or phenol derivatives may be some of the unidentified peaks [13,14]. In spite of the presence of such peaks, the peaks of the analytes could be clearly identified through the joint evaluation of their retention times and their UV spectra.

3.2. Comparison of the separation performance

The separation performance of the two columns tested was evaluated by comparing the number of plates, N, and the analysis time [15] for concentrations of the analytes in the 1–5 μg/L range. According to the above results, the mobile phase flow-rate used with the particulate column was 12 μL/min, whereas for separations into the monolithic column the flow-rate was 4 μL/min.

In Fig. 3 are depicted the values of log N calculated for each of the analytes with the two columns tested. As deduced from this figure, values of log N of about 3 were found for most of the analytes with the particulate column, although slightly higher values were obtained for the most polar compounds simazine ($\log N = 3.8$) and isoproturon ($\log N = 3.4$). The values obtained with the monolithic column showed a marked dependence with the retention of the analytes; log N values ranged from 4.45 for the late eluting compound trifluralin to 5.9 for simazine. This means that the efficiency of the monolithic column is clearly superior for the tested analytes, especially for the most polar compounds (triazines and phenylureas). For such compounds, the number of plates obtained were of about 2 orders of magnitude higher with the monolithic column. The peak asymmetry factors were also calculated for 10% peak height, and the results are listed in Table 2. In most instances, the values obtained were more favourable with the monolithic column.

As regards the analysis time, the most retained compound trifluralin was eluted at 34.6 min and 24.5 min with the particulate and the monolithic columns, respectively. These results indicate that when using the monolithic column, and taking into account the delay time introduced by the IT-SPME device, the analytes eluted in a window time of 13 min; complete separation of the three triazines and the two phenylureas was achieved in 1 min, as shown in Fig. 2. When using the particulate column the analytes were eluted

Table 2
Peak asymmetry factors calculated from chromatograms of Figs. 1 and 2.

Compound	Packed column	Monolithic column
Simazine	2.80	1.02
Isoproturon	2.23	1.11
Atrazine	–	1.02
Diuron	–	1.84
Terbutylazine	2.06	1.33
Chlorfenvinphos	1.59	1.61
DEHP	2.07	1.33
Chlorpyrifos	0.93	2.01
Trifluralin	1.42	1.54

Table 3
LODs obtained with the two tested columns.

Compound	LOD (ng/L)	
	Particulate column	Monolithic column
Simazine	100	20
Isoproturon	200	40
Atrazine	200	40
Diuron	200	40
Terbutylazine	50	10
Chlorfenvinphos	100	20
DEHP	250	50
Chlorpyrifos	25	5
Trifluralin	10	5

in a window time of 28 min. It should be remarked that the time required for a whole chromatographic analysis was about 38 min with the packed column and 28 min with the monolithic column. The total analysis time (sample conditioning and separation) was 40 min when using the packed column and 30 min with the monolithic column.

3.3. Comparison of the limits of detection

The limits of detection (LODs), established as the concentration of analyte required to generate a signal-to-noise ratio of 3, were obtained by injecting solutions of decreasing concentrations of the analytes. Before analysing each solution, water was processed to confirm the absence of contaminants and/or memory effects. In Table 3 are listed the values obtained with the two tested columns using the optimized mobile-phase flow rates. As observed, lower LODs were obtained for all the tested analytes with the monolithic column. This is consistent with the fact that the better efficiency of the monolithic column also resulted in narrower and more intense peaks, compared with those obtained with the particulate column. The highest values were obtained for DEHP (retention time, tr = 19.7 min) because of the presence of a peak at 19.4 min. Indeed, impurities also gave more intense peaks, thus resulting in more complex chromatograms.

It should be noted that in the in-valve IT-SPME approach, the sensitivity is mainly determined by the volume of sample injected in the SPME capillary, by the type and thickness of the capillary coating, and by the capillary dimensions. The length of the SPME capillary has a negligible effect on the chromatographic separations in conventional scale LC. However, at the low mobile phase flow rates used in capillary LC, the dimensions of the SPME capillary strongly affects the time of residence of the analytes in the chromatographic system, as stated in the above sections. Indeed, a reduction of the SPME capillary length would reduce extra band broadening due to IT-SPME, but it would also reduce the amount of analyte that could be extracted from the sample. The results of Table 3 demonstrate that the low flow rate used with the monolithic column did not cause a degradation of S/N ratios due to extra band broadening inside the SPME capillary, when compared with the separation with the packed column. Therefore, SPME capillary dimensions can be the same that those used at higher flow rates, such as the used with the particulate column. In other words, the separations with the monolithic columns are compatible with conditions that proportionate maxima sensitivity in the in-valve IT-SPME technique.

According to the above results, the monolithic column was found to be clearly superior in terms of efficiency, sensitivity and speed for multiresidue analysis of organic pollutants.

3.4. Analytical performance of the IT-SPME-capillary LC with the monolithic column approach

The described IT-SPME-capillary LC with the monolithic column method was applied to standard solutions of the analytes in order to evaluate its analytical performance. The concentrations assayed as well as the results obtained are listed in Table 4. The results of this table indicate that the proposed conditions provided suitable linearity within the tested concentration ranges. The intraday and interday relative standard deviations (RSDs) ranged from 2% to 16%, and to 8% to 19%, respectively. These values can also be considered satisfactory taking into account the working concentration levels. The reproducibility of the retention times was also evaluated for two monolithic columns of different batches, and the results were suitable (see Table 5).

The reliability of the IT-SPME-capillary LC with the monolithic column was tested by analysing several real samples collected at different water treatment plants. Untreated samples were directly introduced into the IT-SPME device and separated in the monolithic column under conditions described above.

Table 4
Analytical data obtained by the IT-SPME capillary LC method with the monolithic column.

Compound	Linearity, $y = a + bx$ ($n = 6$)						Reproducibility[a] ($n = 3$)		Meanrecovery[b] (%) ($n = 3$)
	Wavelength (nm)	Concentration interval (ng/mL)	$a \pm S_a$	$b \pm S_b$	$S_{y/x}$	r	Intraday, CV (%)	Interday, CV (%)	
Simazine	230	0.1–10.0	38 ± 4	17.7 ± 0.7	7	0.998	10	12	93 ± 4
Isoproturon	240	0.2–10.0	27 ± 3	12.4 ± 0.3	4	0.995	16	12	98 ± 11
Atrazine	230	0.2–10.0	32 ± 5	22.6 ± 0.9	9	0.997	9	19	102 ± 7
Diuron	254	0.05–10.0	−1 ± 4	18.1 ± 0.1	6	0.996	14	16	101 ± 9
Terbutylazine	230	0.05–10.0	50 ± 20	89 ± 3	30	0.9990	11	17	84 ± 4
Chlorfenvinphos	220	0.1–10.0	11 ± 4	40 ± 1	8	0.9990	10	14	98 ± 8
DEHP	230	0.2–10.0	50 ± 5	12.5 ± 0.7	6	0.993	9	15	103 ± 10
Chlorpyrifos	210	0.02–10.0	−75 ± 13	214 ± 5	21	0.9992	7	8	100 ± 5
Trifluralin	220	0.02–10.0	8 ± 9	62 ± 2	16	0.998	2	9	103 ± 8

[a] Calculated at concentrations of 2 ng/mL for DEHP and 1 ng/mL for the other compounds.
[b] Calculated at concentrations of 2 ng /mL for simazine and chlorfenvinphos and 5 ng/mL for the other compounds.

Table 5
Comparison between the run times obtained with two monolithic columns of different batches, and through the consecutive injection (chromatograms of Figs. 1, 2 and 4 were obtained with column A).

Compound	Retention times (min)		
	Column A	Column B	
	Injections in different days ($n = 3$)	Injections in different days ($n = 3$)	Consecutive injections ($n = 3$)
Simazine	13.2 ± 0.4	12 ± 2	12.6 ± 0.1
Isoproturon	13.2 ± 0.5	12.6 ± 0.9	12.7 ± 0.1
Atrazine	13.5 ± 0.9	12 ± 2	13.0 ± 0.3
Diuron	13.8 ± 0.6	14.2 ± 0.7	13.8 ± 0.1
Terbutylazine	14.1 ± 0.3	14.3 ± 0.5	14.0 ± 0.8
Chlorfenvinphos	18 ± 1	15.6 ± 0.4	15.4 ± 0.3
DEHP	20 ± 1	21.9 ± 0.7	21.5 ± 0.3
Chlorpyrifos	22.7 ± 0.9	21.5 ± 1.6	22.5 ± 0.8
Trifluralin	24.7 ± 0.9	26.1 ± 1.4	26.7 ± 0.7

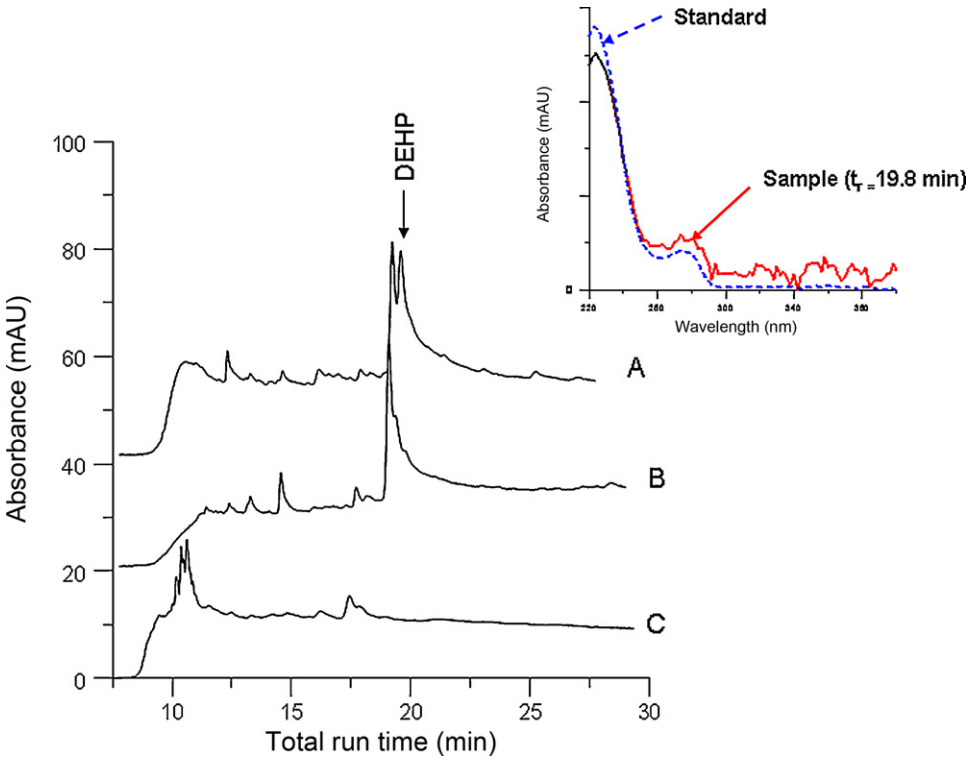


Fig. 4. Chromatograms at 230 nm obtained for three waste waters analysed by the IT-SPME capillary LC approach with the monolithic column. DEHP was identified in sample of chromatogram A, being its retention time 19.8 min. None of the tested analytes was detected in samples of chromatograms B and C. The right part of the figure shows the normalized spectra obtained for a standard solution of DEHP and that of peak identified such as DEHP in the sample of chromatogram A. Volume of sample, 4 mL. For other details, see text.

The chromatographic profiles observed for the real samples were comparable to those of the standard solutions, being DEHP the only compound detected throughout the study. As an illustrative example, in Fig. 4 is shown the chromatogram corresponding to three of the samples analysed. As observed, a peak at the run time of DEHP was observed in one of the samples (Fig. 4A). The identity of such compound was confirmed by comparing the spectrum registered at the retention time of the suspected peak with that obtained from a standard solution of DEHP (see also Fig. 4), being the mean concentration of the analyte in such sample 5 ng/L.

Recovery tests were performed by processing real samples, in which the target analytes were absent, spiked with the analytes. The concentration of each analyte in the spiked samples was calculated from peak areas in the resulting chromatograms and the calibration equations obtained for standard solutions (Table 4). Each sample was assayed in triplicate. The results are listed in Table 5. The recoveries varied from 84% to 103%, whereas the relative standard deviations obtained ranged from 4% to 11%. On the other hand, the LODs established for a real sample spiked with the analytes, and using the procedure described in the above section. No significant differences were observed between LODs in the spiked samples and the results listed in Table 3. Therefore, it was concluded that the analytical performance of the method between the real samples and standard solutions was similar.

Finally, the stability of the chromatographic system was suitable during our study, in which more than one hundred sample replicates were processed.

4. Conclusions

In this study we have evaluated the potential of capillary monolithic columns for the separation of organic pollutants, and the results have been compared with those obtained with a conventional particulate capillary column. The monolithic column was

found to be clearly superior in terms of efficiency and speed, and satisfactory resolution was achieved for compounds of very different polarities. Therefore, this kind of columns may be very useful in the context of multiresidue analysis because, nowadays, there is a well-recognized trend towards the inclusion of as many pollutants as possible in water quality control programs [2,16–20].

It has also been demonstrated for the first time that the mobile-phase flow rates used with new generations of monolithic capillary columns are compatible with the in-valve IT-SPME methodology. The combination of IT-SPME and capillary LC with the monolithic column makes possible the characterization of untreated water samples in less than 30 min (analyte enrichment and separation), and with LODs of 5–40 ng/L. Satisfactory linearity and reproducibility was also observed for concentrations of the analytes up to 10.0 ng/mL. According to the legislated values, the described method is suitable for routine monitoring water quality [1]. Indeed, the replacement of DAD detection by MS detection would render the procedure more reliable for establishing the presence of contaminants or for extending the proposed method to other classes of contaminants such as drugs or personal care products. This possibility is currently under investigation in our labs.

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