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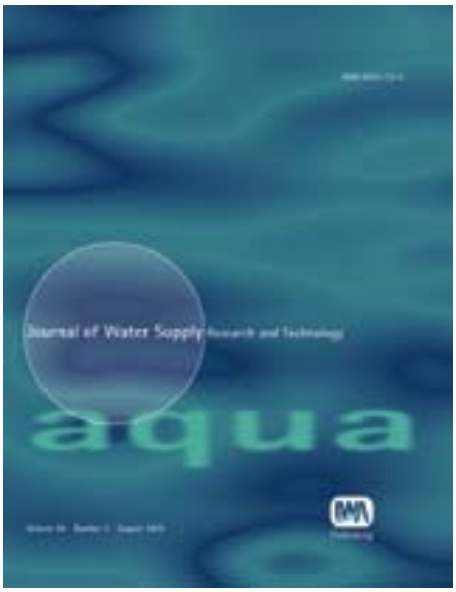

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Determination of chlorinated organic compounds in aqueous matrices

B. Pavoni, A. Giacometti and M. Bragadin

ABSTRACT

Thirteen pure volatile, semi-volatile and non-volatile chlorinated organic compounds of molecular weights ranging from trichloroethylene (MW = 131.39 g mole^{-1}) to hexachlorobenzene (MW = 284.78 g mole^{-1}) were determined in aqueous matrices by GC-ECD. After 10% salt addition, different extraction tests were performed using fibres whose adsorbing phase was based on microsphere carbon particles characterized by a constant size. Five experimental parameters were optimized: extraction temperature and time, position of the fibre in the GC injector port, desorption temperature and time. The optimized analytical protocol was employed to determine the efficiency of a real activated carbon adsorption plant to remove organic chlorinated pollutants from an industrial wastewater at ng l^{-1} levels.

Key words | aqueous matrix analysis, environmental analysis, extraction techniques, organochlorine compounds, solid phase microextraction, water analysis

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INTRODUCTION

Organochlorine compounds may be industrial effluent contaminants (Jya-Jyun & Shinn-Yow 2000; Shawwa *et al.* 2001) because they are used on a large scale as important industrial intermediates and solvents, in textile industries, in paper mills (Hileman *et al.* 1994) and for dry cleaning. Some of them are toxic or can have harmful health effects on humans and might be responsible for cancer, mutations and damage to the endocrine system and therefore are listed among the US-EPA priority organic pollutants. In general, because of their chemical structure, they are slowly biodegraded, so that they disperse and accumulate in the environment. They represent a category comprising the most persistent organic micropollutants present in waters (Cancho *et al.* 1999). To detect in real samples the low levels normally fixed by regulatory limits, a preconcentration step is needed prior to the widely used GC-ECD (gas chromatography electron capture detector) analysis (Fiorani 1983; Huang *et al.* 1997). Analytical protocols might be subdivided into two steps: the first one concerns the isolation of the analytes from the matrix and their preconcentration. Classical methodologies involve liquid–liquid extraction for non-volatile compounds, solid phase extraction for semi-volatile compounds and 'purge and trap' (Arthur *et al.* 1992*a*; Potter & Pawliszyn 1992, 1994) or headspace analysis for volatile compounds (Arthur *et al.* 1992*a*; Louch *et al.* 1992; Shirey *et al.* 1994).

The solid phase micro extraction (SPμE) technique (Pawliszyn 1997; Peñalver *et al.* 1999) was introduced and developed by Pawliszyn and co-workers as a practical alternative to the more tedious and labour-intensive classical sample enrichment methodologies. For solid (Sarrión *et al.* 1998), liquid (Aguilar *et al.* 1999; Cancho *et al.* 1999; Pavoni *et al.* 2006) and gaseous (Pawliszyn 1997; Peñalver *et al.* 1999) samples this technique integrates sampling, extraction and preconcentration. It employs fused-silica fibres coated with polymeric stationary phases to extract target analytes on the basis of the partition equilibrium between fibre and sample. SPμE requires no solvent or complicated apparatus; it needs only small volumes of sample, it is very simple, fast, easily automated,

doi: 10.2166/aqua.2009.040

portable, and inexpensive while it provides good results over a wide range of analyte concentrations. It minimizes sample handling, which is the greatest source of contamination and error during analyses.

Like classical methodologies, SPμE comprises two steps. First, the target analytes are extracted from the sample matrix by exposing the fibre for a predetermined period of time. This can be accomplished either by direct immersion of the SPμE fibre into the sample or by headspace solid-phase microextraction (HS- SPμE). The amount of analyte extracted by the SPμE fibre can be determined by several parameters: for example, the characteristics of the fibre coating, the temperature and time of the extraction process, the addition of salt or organic solvent to the sample, pH modification, agitation of the sample and sample volume. During the second step, the fibre is retracted from the sample and the analytes retained in the fibre are desorbed in an analytical instrument to be separated, detected and quantified. Usually, this step is carried out by introducing the fibre in a hot GC injector port where thermal desorption takes place; owing to the high temperature, the affinity of analytes for the fibre coating decreases so that they are released (Arthur *et al.* 1992*a*,*b*; Louch *et al.* 1992; Potter & Pawliszyn 1992; Shirey *et al.* 1994; Huang *et al.* 1997; Nilsson *et al.* 1997).

In the present work, after 10% NaCl addition to the sample, we optimize five experimental parameters of SPμE: temperature and time of extraction, position of fibre in the GC injector port, temperature and time of desorption. The optimized operative parameters were applied to analyse the target organic chlorinated compounds (Table 1) in an industrial effluent to ng l^{-1} levels. Then, the efficiency of a real activated carbon adsorption plant was assessed in removing from an industrial effluent the target chlorinated pollutants (Pavoni *et al.* 2006).

METHODS

Materials and reagents

Reagents used were: sodium chloride 99.9% AnalaR® (BDH), methanol for spectroscopy (UV-FLUO) 99.9% RS degree (Carlo Erba reagents), acetone pesticide grade 99.8% (BDH), and Milli-Q water (WP 4100 reagent grade water purifier-SMEG). Chemicals used to wash glassware were concentrated detergent Contrad 2000 (BDH), sulphuric acid 98% AnalaR® (BDH) and ammonium persulfate 98% (Aldrich).

Table 1 | The 13 examined organic chlorinated compounds and some of their physicochemical characteristics

Substance		MW* (g mole^{-1})	Bp† °C	log K‡$_{ow}$ –	Dipole§ D
Volatile	1,1,1-trichloroethane	133.41	75.0	2.49	1.57
	Carbon tetrachloride	153.82	76.5	2.73	0.00
	Trichloroethylene	131.39	86.7	2.42	0.90
	1,1,2-trichloroethane	133.41	112.5	2.17	1.25
	Tetrachloroethylene	165.83	121.0	2.88	0.00
	1,1,2,2-tetrachloroethane	167.86	144–146	2.39	1.40
	1,3-dichlorobenzene	147.01	172–173	3.53	1.48
	1,4-dichlorobenzene	147.01	173	3.37	0.00
	1,2-dichlorobenzene	147.01	178–180	3.38	2.25
Non-volatile	1,2,4-trichlorobenzene	181.45	214.0	4.05	1.54
	1,2,3-trichlorobenzene	181.45	218.5	4.07	3.08
	Hexachloro-1,3-butadiene	260.76	215.0	4.90	0.00
	Hexachlorobenzene	284.78	324.5‖	5.50	0.00

*MW = molecular weight (g mole^{-1}).
†bp = boiling point (°C).
‡log K_{ow} = logarithm of octanol-water partition coefficient (dimensionless).
§D = dipole moment (Debye).
‖It sublimes.

Adsorbates

The 13 examined organic chlorinated compounds and some of their physicochemical characteristics are listed in Table 1.

Optimization of the analytical method

Two kinds of fibre coating were tested: polydimethylsiloxane (PDMS, 100 μm thick), from now on here referred to as Fibre 1, which is a polymer presenting a high affinity for non-polar compounds and the more recent, porous and adsorbent material, Carboxen blended in PDMS (PDMS/Carboxen, 75 μm thick), or Carbowax, from now on here referred to as Fibre 2.

Five different factors influencing efficiency, sensitivity and precision of SPμE technique were tested: position of the fibre in the injector of the gas chromatograph, desorption temperature and time, extraction temperature and time. Each parameter, in turn, was optimized by scanning its value domains while keeping fixed all other variables. Results were reported on graphs in which every point was the average of three measures and the error bars represented the standard deviation.

Analytical instruments, glassware and laboratory equipment

Solid phase microextraction (SPμE)

For the experiments, the following equipment was used: a SPμE holder and fibre (Supelco) (Pawliszyn 1997); glass vials of 20 ml with PTFE/Silicone septa (Boussahel *et al.* 2002); small PTFE lined magnets (10 × 3 mm, Aldrich); and a magnetic stirrer (BE 32-Bicasa model). The thermostatic bath (Haake 3 M) was connected to a thermostated glass cell to keep the temperature of the magnetically stirred samples within a ± 1°C range, checked with a thermometer (ASTM 88 C GB 4).

Gas-chromatographic equipment

For the analyses a Hewlett Packard 5890 series II plus gas chromatograph (GC) equipped with an electron capture detector (ECD) was used. Auxiliary gas was a mixture of argon-methane (5%), with a flow rate of 50 ml min^{-1}, while the septum (i.e. injector) cleaning gas was helium, with a flow rate of 30 ml min^{-1}. The carrier gas was helium, with a flow rate of 0.8 ml min^{-1}. Volatile compounds were chromatographically separated with medium polarity capillary column VOCOL 60 m × 0.25 (i.d.) mm × 1.5 μm (Supelco), and high boiling compounds with a non-polar capillary column HP Ultra 1 crosslinked methyl silicone gum 25 m × 0.2 (i.d.) mm × 0.33 μm (Hewlett Packard). Chromatographic data were processed with the 'HP Chemstation' software (Hewlett Packard).

Standard solutions used for the optimization of SPμE

For volatile chlorinated compounds, calibration lines for quantification were drawn by using the standard solution 8500-6634 'Halogenated Volatiles Mixture' (HVM, Hewlett Packard), with an average concentration of 100 μg ml^{-1} in methanol; 0.5 ml of concentrated HVM standard solution was brought to 1 l in Milli-Q water. Starting from this solution, five more standard solutions were prepared: the first one by diluting 200 ml of the solution to 1 l, and the others by further dilutions following the same procedure. For non-volatile chlorinated compounds, a mixture of 1,2,3-trichlorobenzene 99% (Aldrich), 1,2,4-trichlorobenzene 99% (Aldrich), hexachloro 1,3-butadiene 97% (Aldrich) and hexachlorobenzene 99% (Aldrich) at an average concentration of 100 μg ml^{-1} in acetone was prepared. First, 5 ml of concentrated standard in acetone was diluted to 1 l. Then, the dilution procedure was the same as that followed for the volatile chlorinated compounds. Therefore, for volatile chlorinated compounds the concentration range was 10 μg l^{-1} – 1.6 × 10^{-2} μg l^{-1}, while for non-volatile chlorinated compounds the range was 100 μg l^{-1} – 1.6 × 10^{-1} μg l^{-1}. The flasks were sealed with a Teflon lined plug and the solutions were left at room temperature for several hours. Then such solutions were stored in refrigerator at 4°C. Milli-Q water blank samples were run to check the absence of interfering compounds.

SPμE fibre conditioning

SPμE fibres needed a thermal treatment before use to avoid the occurrence of spurious gas-chromatographic peaks due

to residual interfering substances adsorbed on their surface. Fibres were conditioned by exposing them to the flow of the septum cleaning gas in the hot chromatographic injector. The fibre position within the gas-chromatographic injector was optimised in conjunction with the desorbing time and temperature. Optimal fibre conditioning parameters were 1 h at 250°C for Fibre 1 and 30 min at a temperature of 280°C for Fibre 2. For both fibres, blank samples were run under analytical conditions to ensure absence of any extraneous peak in the chromatogram. Three desorption cycles were normally sufficient to obtain a clean chromatogram (i.e. free from spurious peaks). In order to avoid memory effects and ghost peaks between analyses, fibres were 'banked' after each analytical run.

Analysis of organic chlorinated compounds

Volatile compounds were determined by HS-SPμE using Fibre 2; 2 g of sodium chloride and 10 ml of sample were set in a 20-ml magnetically stirred vial inside a thermostated cell at 50°C, together with the SPμE holder. After 15 min of thermal equalization, the fibre was exposed from the holder to the headspace vapours above the sample for 45 min; this was then withdrawn into the holder inserted into the GC injection port and the fibre exposed for about 5 min to the carrier gas. Gas-chromatographic conditions were: injector temperature: 240°C; pressure on column head: 120 KPa; temperature programme: 35°C constant for 10 min, then 4°C min^{-1} up to 210°C, constant for 10 min; detector temperature: 300°C.

Non-volatile compounds were determined using direct immersion SPμE and Fibre 1; 4 g of sodium chloride and 20 ml of sample in a 20-ml magnetically stirred vial were set in a thermostatic cell at 50°C. The SPμE holder was kept inside the solution for 15 min to attain thermal equilibrium; then the fibre was directly exposed to the sample for 20 min, retracted and quickly exposed to the carrier gas in the hot GC injector port for 5 min. Gas-chromatographic conditions were: injector temperature: 240°C; pressure on column head: 80 KPa; temperature programme: 80°C for 3 min, 20°C min^{-1} up to 165°C; constant for 18 min, 20°C min^{-1} up to 290°C; constant for 7 min; detector temperature: 300°C.

Detection limits and reproducibility

Due to the linear relationship between the analyte quantity extracted by the fibre and the concentration of the solution (Arthur & Pawliszyn 1990; Arthur *et al.* 1992*b*; Potter & Pawliszyn 1994), a calibration line with optimized parameters was constructed for all target analytes. For both volatile and non-volatile organic compounds, calibration curves were determined by repeating the same injection of standard four times for each point. The origin was set (0,0) because blank signal was always zero (Potter & Pawliszyn 1992; Nilsson *et al.* 1997).

Limits of detection (LOD) were calculated as signal-to-noise ratio equal to 3 whereas limits of quantification (LOQ) were considered twice that of LOD (Arthur *et al.* 1992*b*; Potter & Pawliszyn 1992).

RESULTS AND DISCUSSION

Since SPμE is based on an equilibrium partitioning process, the greatest amount of analyte will be extracted when the equilibration time is completed or, more practically, when concentrations are very close to equilibrium (Potter & Pawliszyn 1992). Stirring the sample reduces this time because it facilitates diffusion towards the fibre for both direct immersion and head-space extraction. Compounds with low distribution constants require longer equilibration times. In such cases, normally an extraction time shorter than the optimum 'equilibration time' was selected. In this instance, exposure time was controlled very well to

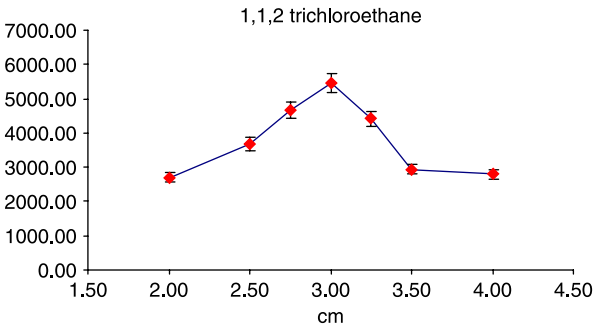

Figure 1 | Results for the variation of the fibre position in the GC injector port for 1,1,2-trichloroethane. Numbers in the abscissa are centimetres while the ordinate are GC-ECD output, i.e. 'area counts'.

Table 2 | Effects of the desorption temperature in the GC injector port for two selected compounds. Numbers in table are GC-ECD output, i.e. 'area counts' (experimental error is within 5%), while italic numbers mean highest value

	1,1,1-trichloroethane		Tetrachloroethylene	
Desorption temperature (°C)	**Fibre 1**	**Fibre 2**	**Fibre 1**	**Fibre 2**
190	29,837	7,422	65,668	4,472
200	32,574	8,506	78,250	10,156
210	32,863	8,847	81,239	32,671
220	*33,266*	9,095	*86,042*	59,959
230	28,968	10,028	84,444	78,442
240	26,093	*10,139*	83,682	*103,623*
250	25,182	8,527	80,502	102,374
260	24,220	8,238	78,427	101,159
270	23,965	8,232	75,849	99,876
280	22,182	8,229	72,336	96,032
290	21,880	8,207	68,745	95,163
300	18,639	8,197	63,898	94,018

ensure reproducible results. Extraction temperature needs optimization because it affords two opposite effects. While high temperature enhances analyte diffusion towards the fibre (or vapour pressure in the case of HS-SPμE), on the other hand it also reduces the distribution constant because absorption on fibre is an exothermic process. Most studies (Peñalver *et al.* 1999) showed that mineral salt addition, usually NaCl, positively affects the retention of some analytes into the fibre coating because it increases the ionic strength of the sample while reducing analyte solubility in water. This effect is not general and depends on analyte polarity, salt concentration and sample matrix.

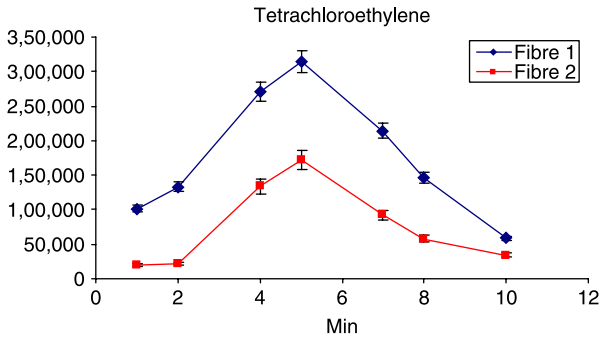

Figure 2 | Effects of increasing desorption times in the GC injector port for tetrachloroethylene. Numbers in the abscissa are minutes while the ordinate are GC-ECD output, i.e. 'area counts'.

Fibre position in the GC injector port

Normally, the position of the fibre in the GC injector port affects the yield of detected analyte. The flow of the carrier gas within the injector port helps to scavenge analytes from the fibre by moving them to the GC column. Insert liners with low volumes are required to assure rapid transfer of desorbed analytes to the GC column. Five positions were tested, while all other parameters were maintained constant. For the sake of simplicity, only Fibre 1 and low boiling compounds were used, inasmuch as in these experiments the injector geometry is the only key factor, not the type of fibre or the kind of analyte (Arthur *et al.* 1992*b*).

Results for one selected compound (1,1,2-trichloroethane) are reported in Figure 1, where 'distance' refers to the fibre position along the SPμE holder. As shown in Figure 1, the highest analyte quantity was desorbed when the fibre was allocated at *c.* 3 cm (i.e. in the central position of the injector port), whereas desorption sensibly decreased when displacing the fibre from such an optimum. This position was kept constant during all the following experiments.

Determination of desorption temperature

The values obtained by changing only the desorption temperature are reported for two selected analytes in Table 2. In this series of experiments to avoid memory effects, prior to each test a blank thermal desorption of the fibre was always accomplished.

For low boiling compounds, optimum desorption temperature was 220°C for Fibre 1 and 240°C for Fibre 2.

Table 3 | Results of the extraction temperature for one selected low boiling compound (1,1,1-trichloroethane) using Fibre 2. Numbers in table are GC-ECD output, i.e. 'area counts' (experimental error is within 5%), while italic numbers mean highest value

	1,1,1-trichloroethane	
Extraction temperature (°C)	**Headspace**	**Immersion**
20	55,190	6,290
30	59,907	9,038
40	*75,470*	11,786
50	62,550	*15,761*
60	45,283	9,872
70	28,016	7,183

Table 4 | Results of the extraction temperature for one selected high boiling compound (1,2,4-trichlorobenzene). Numbers in table are GC-ECD output, i.e. 'area counts' (experimental error is within 5%), while italic numbers mean highest value

Extraction temperature (°C)	1,2,4-trichlorobenzene
20	36,523
30	104,530
40	140,738
50	*166,837*
60	117,283
70	81,428
80	22,350

Similar experiments were run for high boiling compounds by using Fibre 1 only. In this case, optimum desorption temperature was 240°C. Generally, the injector would be set at the maximum temperature permitted by the stability of both fibre coating and analytes. Higher desorption temperatures decreased the analyte quantity, probably because of thermal decomposition.

Determination of desorption time

Once the optimum desorption temperature had been determined, the desorption time was determined by exposing the fibre inside the injector, at increasing times (Arthur *et al.* 1992*a*,*b*) as shown in Figure 2 for one selected compound (tetrachloroethylene).

Optimal desorption time can be affected by several parameters such as injector temperature, position of the fibre, and carrier gas flow rate; usually a few minutes are adequate for most compounds. Analytes such as high molecular weight compounds would require a higher desorption temperature than the optimized one; they might be retained in the fibre coating and then appear in the following analyses giving rise to the so-called carryover effect. Higher desorption times may help to reduce this problem. However in our case, no ghost peak was ever detected. For both high and low boiling point compounds (either with Fibre 1 or Fibre 2), maximum peak area was reached after 5 minutes of exposure time. For longer desorption times, peak areas decreased, again probably due to thermal decomposition.

Determination of extraction temperature

A suitable temperature for extracting analytes from the samples into the fibre coatings was optimized in both operating conditions; that is, when immersing the fibre inside the solution and when exposing the fibre to the headspace above the solution. The quantity of analyte adsorbed onto the fibre is influenced by temperature because this changes the analyte diffusion velocity in solution and the partitioning constant between the polymeric coating and the sample. Furthermore, the higher the partitioning constants, the higher the time necessary to reach equilibrium.

As shown in Table 3 for one selected low boiling compound (1,1,1-trichloroethane), like the other parameters investigated so far, the amount of extracted analyte displayed a maximum. In most cases, for Fibre 2 such maximum was located around 40–50°C and decreased on both sides of this optimum (Arthur *et al.* 1992*b*; Huang *et al.* 1997; Nilsson *et al.* 1997). Trends for high

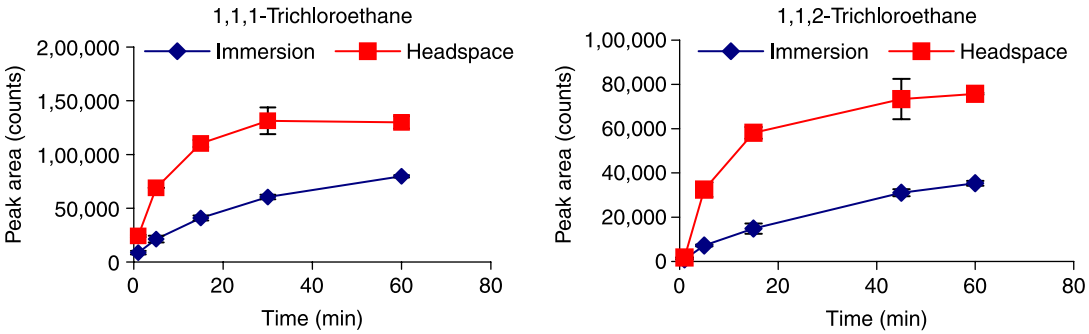

Figure 3 | Optimization of the Fibre 2 extraction time for two chosen compounds (1,1,1-trichloroethane and 1,1,2-trichloroethane). Numbers in the abscissa are minutes while the ordinate are GC-ECD output, i.e. 'area counts'.

Table 5 | Optimized parameters for Fibre 1 and Fibre 2 coatings. Desorption time and % NaCl were set at 5 min and 10%, respectively, in all cases

	Volatile compounds				Non-volatile compounds
	Fibre 1		Fibre 2		Fibre 1
Parameters	Immersion	Headspace	Immersion	Headspace	Immersion
Desorption temperature (°C)	220	220	240	240	240
Extraction temperature (°C)	50	40	50	40	50
Extraction time (min)	25	20	60	45	20

boiling compounds (only direct immersion and Fibre 1) are exemplified in Table 4 for one selected compound (1,2,4-trichlorobenzene); the optimum extraction temperature was set at 50°C.

Determination of extraction time

Optimum extraction time was determined for Fibre 2 for both direct immersion and headspace methods (Huang *et al.* 1997) as reported in Figure 3. Extraction time has to be long enough to guarantee that the equilibrium between the analytes and the SPμE fibre is attained. This condition should be represented by a plateau in the plot. For both Fibre 1 and Fibre 2 coatings, such an equilibrium plateau was reached faster in headspace than in direct immersion experiments. In the case of direct immersion, this different behaviour was probably caused by the formation at the solution/fibre interface of a thin stationary layer impossible to remove even by vigorously stirring the solution. Such a film hampers diffusion to the coating so that the time to reach equilibrium grows longer (Arthur *et al.* 1992*a*; Huang *et al.* 1997). Anyway, experimental extraction times were set within the 20–60 min range, as shown in Table 5.

Salt effect

The salt effect on partitioning constants and on the polymeric coating is widely documented in the literature (Arthur *et al.* 1992*b*; Louch *et al.* 1992; Zhang & Pawliszyn 1993; Aguilar *et al.* 1999). According to most papers, normally salt improves extraction; but when the concentration of sodium chloride is brought above 10%, the benefit vanishes because the partitioning constants stabilize. Results of our experiments with two chosen compounds (1,1,1-trichloroethane and 1,1,2-trichloroethane) among the examined set of chlorinated organic compounds are reported in Table 6. The data confirmed optimum concentrations for sodium chloride at 10%, above which there were no significant improvements in yields.

Final results

The final results of the optimization experiments (i.e. the optimized parameters for Fibre 1 and Fibre 2 coatings) are reported in Table 5. Desorption time and % NaCl were set at 5 min and 10%, respectively, in all cases.

Table 7 reports detection limits and correlation coefficients of calibration lines for different compounds and using two fibre coatings. As can be seen in Table 7, HS-SPμE using Fibre 2 (low boiling point compounds) yielded the lowest LODs and the highest correlation coefficients.

Analysis of a real industrial effluent

Optimized SPμE experimental conditions were used to test the removal efficiency of 13 chlorinated organic

Table 6 | Results of salt effect experiments for two selected low boiling compounds (1,1,1-trichloroethane and 1,1,2-trichloroethane). Experimental conditions: headspace, fibre 1, extraction °T = 40°C, extraction time = 20 min. Numbers in table are GC-ECD output, i.e. 'area counts' (experimental error is within 5%)

NaCl%	1,1,1-trichloroethane	1,1,2-trichloroethane
2	2,873	2,524
4	6,945	5,176
6	12,154	7,521
8	19,178	8,245
10	22,023	8,502
12	22,021	8,512
14	21,978	8,508
16	21,993	8,499

Table 7 | Limits of detection of the target compounds

		Fibre 1			
		Immersion		Headspace	
		LOD ($ng\,l^{-1}$)	R^2 –	LOD ($ng\,l^{-1}$)	R^2 –
Volatile	1,1,1-trichloroethane	13.3	0.993	1.11	0.989
	Carbon tetrachloride	5.35	0.996	0.412	0.997
	Trichloroethylene	11.2	0.969	0.799	0.979
	1,1,2-trichloroethane	166	0.996	5.36	0.996
	Tetrachloroethylene	1.71	0.999	0.138	0.991
	1,1,2,2-tetrachloroethane	17.5	0.996	0.530	0.996
	1,3-dichlorobenzene	30.7	0.935	0.699	0.979
	1,4-dichlorobenzene	35.8	0.919	1.81	0.984
	1,2-dichlorobenzene	22.8	0.925	0.591	0.993
		Fibre 2			
		Immersion		Headspace	
		LOD ($ng\,l^{-1}$)	R^2 –	LOD ($ng\,l^{-1}$)	R^2 –
Volatile	1,1,1-trichloroethane	0.9	0.991	0.3	0.995
	Carbon tetrachloride	0.1	0.999	0.01	0.999
	Trichloroethylene	0.9	0.983	0.2	0.989
	1,1,2-trichloroethane	2.0	0.999	0.4	0.999
	Tetrachloroethylene	0.8	0.996	0.1	0.997
	1,1,2,2-tetrachloroethane	0.8	0.999	0.2	0.999
	1,3-dichlorobenzene	0.8	0.935	0.2	0.990
	1,4-dichlorobenzene	1.3	0.930	0.2	0.989
	1,2-dichlorobenzene	1.8	0.925	0.1	0.996
		Fibre 1			
		LOD ($ng\,l^{-1}$)	R^2 –		
Non-volatile	1,2,4-trichlorobenzene	10	0.991		
	1,2,3-trichlorobenzene	30	0.992		
	Hexachloro-1,3-butadiene	9.0	1.00		
	Hexachlorobenzene	0.4	0.997		

LOD = limit of detection ($ng\,l^{-1}$); Detection limit has been calculated as three times signal-to-noise ratio.

compounds using five commercially available activated carbons in a $50\,m^3\,h^{-1}$ real plant samples (Pavoni *et al.* 2006). Chromatograms of the untreated wastewater are reported in Figure 4. Volatile compounds were analysed by HS-SPμE/GC-ECD (Figure 4, top) whereas non-volatile compounds were analysed by direct SPμE/GC-ECD (Figure 4, bottom).

In order to choose the best performing active carbon, preliminary experiments were carried out. To establish the time necessary to attain equilibrium at room temperature between wastewater and each of the five kinds of active carbon, the SPμE technique was instrumental in determining pollutant concentrations at different times, as shown in Figure 5 for three selected compounds.

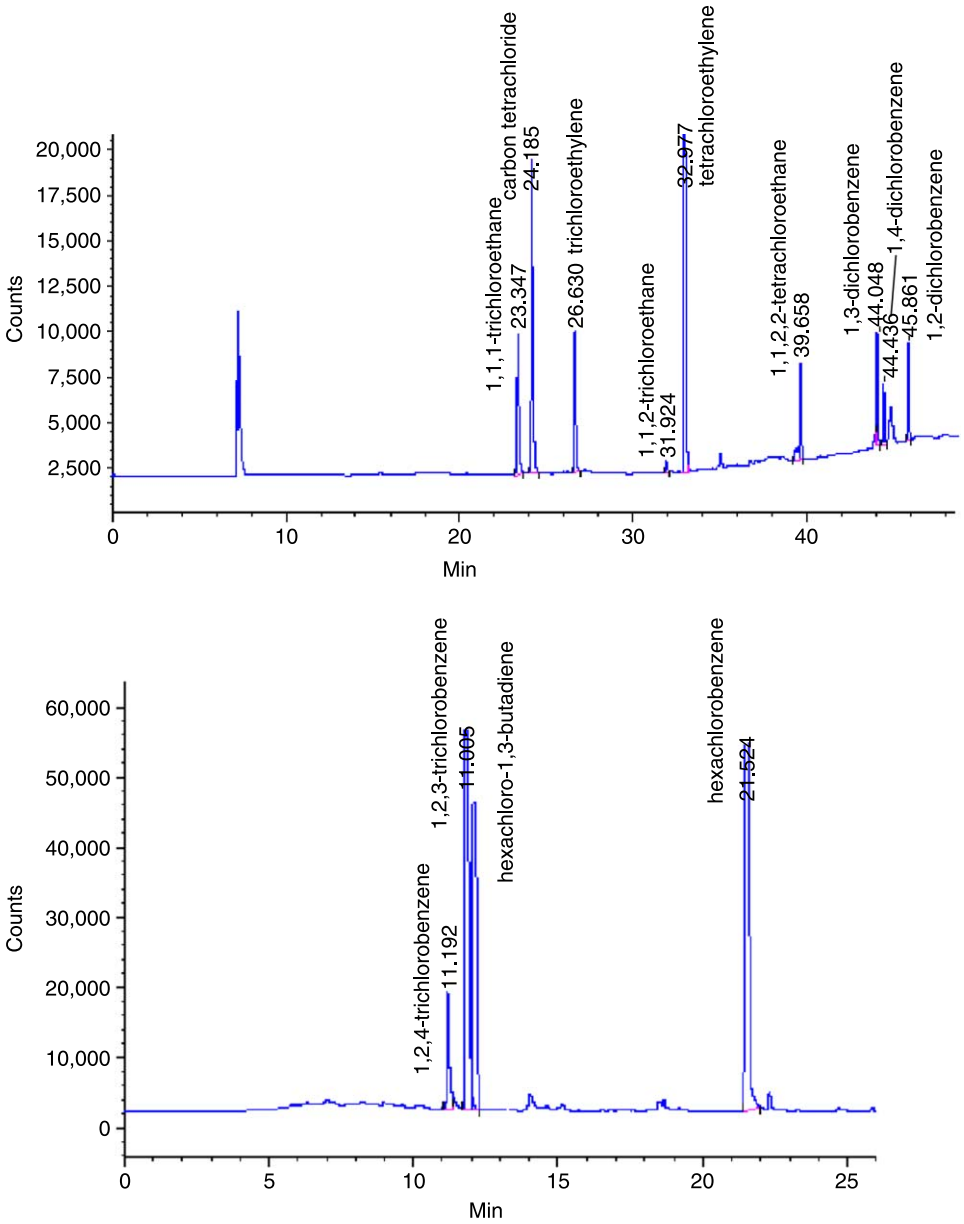

Figure 4 | Chromatograms of a real untreated wastewater analysed by HS-SPμE/GC-ECD (top) and direct SPμE/GC-ECD (bottom).

The results showed that 90% of each compound was adsorbed into the activated carbon within the first 15 min and the remaining 10% after about 1.5 h. For convenience, the selected equilibrium time was set at 2 h. Using a Freundlich model and this equilibration time, Freundlich adsorption isotherms were drawn by performing SPμE analyses. Figure 6 reports the isotherms concerning two chosen compounds where X/M represents the active carbon efficiency [X = weight of adsorbed compound (mg), M = weight of adsorbent substrate (g)] as a function of the residual pollutant concentration in solution C; the higher the straight line, the higher the efficiency.

From these experiments, the GAC 1240 proved to be the best performing activated carbon. Using this adsorbent, breakthrough curves were determined by representing the percentage of pollutant remaining in the wastewater after exiting the adsorption bed; that is, the residual concentration, measured by SPμE analyses, as a function

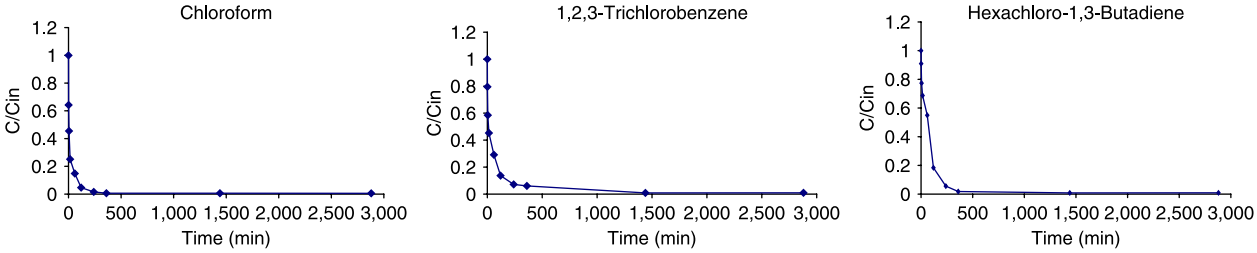

Figure 5 | Residual concentrations of three selected compounds determined by SPμE at different absorption times.

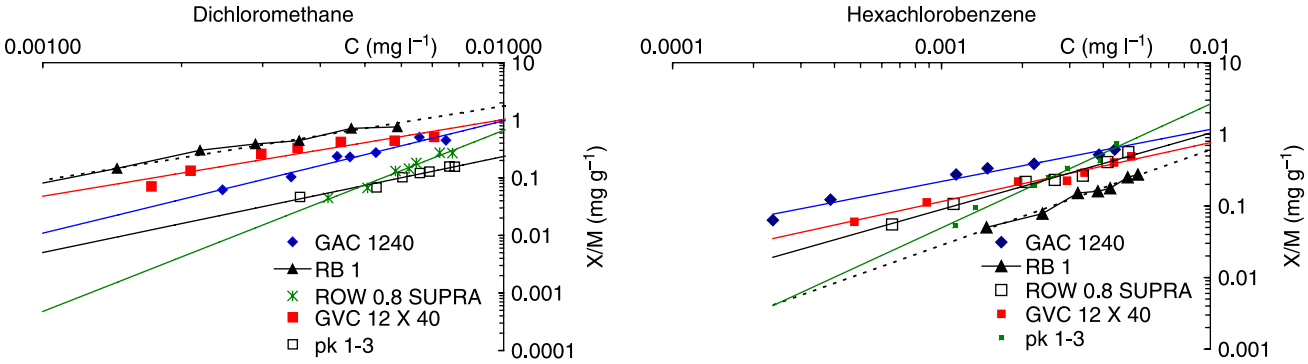

Figure 6 | Freundlich adsorption isotherms determined using SPμE.

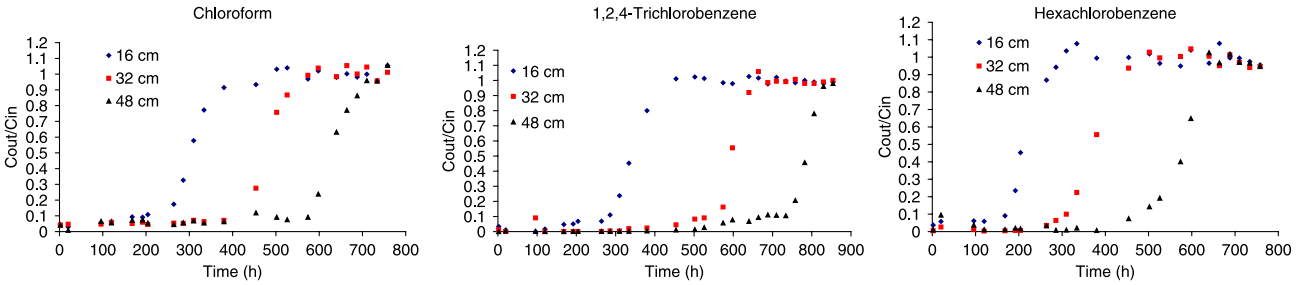

Figure 7 | Breakthrough curves for three selected chlorinated pollutants determined by SPμE.

of the service time of the activated carbon bed as shown in Figure 7 for three selected chlorinated pollutants. As explained in another article (Pavoni *et al.* 2006), a real adsorbing plant was designed using these curves.

CONCLUSIONS

Using HS-SPμE with Fibre 2 in conjunction with GC-ECD, 13 chlorinated organic compounds were determined at ng l^{-1} levels. HS-SPμE displays shorter equilibration times than direct immersion SPμE, a cleaner background, and a longer fibre life. Fibre 2 appears to be a promising coating material.

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First received 4 April 2008; accepted in revised form 7 June 2009