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Trace enrichment of phenols by on-line solid-phase extraction and gas chromatographic determination

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Abstract

An on-line gas chromatographic pretreatment module for the preconcentration/determination of phenols in waters is proposed. A solid-phase extraction system using different sorbents packed in a minicolumn is coupled on-line with a gas chromatograph equipped with flame ionization detection (FID). The XAD-2 sorbent selected provides detection limits from 0.3 to 2 μg/l for 100 ml of water at an acid pH. The relative standard deviations for eleven analyses of samples containing 10 μg/l phenols were 2.3–4.5%. The proposed method can be used for the routine analysis of natural and drinking waters containing phenols at trace levels.

Keywords: Preconcentration; Solid-phase extraction; Phenols

1. Introduction

Phenol and substituted phenols such as clorinated derivatives and related aromatic compounds are produced widely in many industrial processes and can be the source of serious health hazards if released into the environment through accidental spillage or poor disposal practices. Many phenols, particularly chlorophenols, have a bad reputation due to their toxicity and persistency; this has given rise to the need for methods allowing phenol concentrations of a few micrograms-per-millilitre in the environment to be detected [1]. Phenolic compounds in the aquatic environment can be handled and analysed by various methods. Liquid–liquid extraction is being gradually superseded by solid-phase extraction (SPE) for the separation of phenols from water in many methods because of the wide availability of selective sorbent materials, and also to avoid the need for disposal of organic solvents. This technique involves sorption of phenols from a large amount of water on a suitable sorbent and their desorption by solvent elution [2]. Macroreticular Amberlite XAD resins [3], polystyrene [4], activated carbons [5], C_{18}-modified silica [6,7] and graphitized carbon black [8] have been used as sorbents for this purpose. In these methods, phenols are usually determined by liquid chromatography (LC) with UV [4–7] or mass spectrometric detection [8]. Recently, solid-phase microextraction was used for the determination of phenols at trace levels [9–11]. This technique is based on the partitioning of analytes between a sample matrix and the stationary phase coated on a fused-silica fibre housed in the needle of a microsyringe; the analytes are thermally desorbed by introducing the needle into the heated injector of a gas chromatograph. Capillary gas chromatography (GC) is the separation technique of choice when a

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compound is amenable to analysis without prior derivatization; in fact, GC features high separation efficiency, sensitivity and selectivity. Brinkman et al. [12] have proposed several methods for the trace-level determination of GC-amenable organic micropollutants in water. They developed an on-line SPE–GC–mass spectrometry instrument for use as an automated water analyser [13]. The loaded volume is lower than that typically used in SPE–LC (ca. 100 ml) thanks to the superior performance of GC detectors, relative to LC detectors; the analytes are preconcentrated on a precolumn and, following a clean-up step, desorbed with 50–100 μl. This method requires several injection valves, on-column injection and three columns (retention gap, retaining precolumn and analytical GC column). With FID detectors, analyte recoveries range from 70 to 110%, with a detection limit of 50 ng/l.

The flow-injection technique was employed for the determination of phenols in polluted water with chemiluminescence detection [14]. Our group developed an automatic module that enables liquid–liquid extraction, derivatization and gas chromatographic determination of phenols in water [15,16].

The problems associated with liquid–liquid extraction (viz. poor recoveries and high solvent consumption in manual procedures or complicated manifolds in their automatic counterpart) can be overcome by SPE methods. The main aim of this work was to develop a rapid, straightforward SPE method for the determination of phenols at concentrations of few micrograms-per-millilitre in waters, and to couple it with a gas chromatograph equipped with a conventional FID detector. Several sorbents were tested in order to select the best analytical conditions for the determination of phenols at low levels; in this way, no derivatization reaction was needed to improve chromatographic separation/detection and extractability of phenols from waters, nor was an electron capture detector required to increase sensitivity.

2. Experimental

2.1. Chemicals

Phenols (phenol, *p*-cresol, 2,5-dimethylphenol, 2-*tert.*-butylphenol, 4-chlorophenol, 2,4-dichlorophenol, 3,4-dichlorophenol, 2,4,6-trichlorophenol, pentachlorophenol and *m*-nitrophenol) and methyl nonanoate (internal standard) were obtained from Aldrich-Chemie (Madrid, Spain). Ethyl acetate, ethanol, methanol, acetone and *n*-hexane, all in HPLC grade, were purchased from Romil Chemical (Loughborough, UK). Polygosyl-bonded silica reversed-phase sorbent with octadecyl functional groups (RP-C_{18}), 40–63 μm, Darco 20–40 mesh granular activated carbon and XAD-2 styrene–divinylbenzene, 50–100 μm, were supplied by Sigma (Madrid, Spain), Aldrich-Chemie and Serva Feinbiochemica (Heidelberg, Germany), respectively.

Stock standard solutions containing 10 g/l of each phenol were prepared in 99.9% acetone and stored in glass-stoppered bottles at 4°C. Appropriate volumes of these stock solutions were diluted with Milli-Q water to prepare more dilute solutions containing phenols at the microgram-per-millilitre level at pH 3.

2.2. Pretreatment module and interface unit

The proposed continuous system consists of a Gilson Minipuls-2 peristaltic pump fitted with poly(vinyl chloride) and Solvaflex pumping tubes for water and organic solvent (ethanol), respectively; two Rheodyne 5041 injection valves; PTFE tubing (0.5 mm I.D.) for coils; and a displacement bottle for pumping ethyl acetate. A custom-made adsorption column packed with XAD-2, activated carbon or RP-C_{18} was also employed.

The sorbent column for SPE was made from poly(tetrafluoroethylene) capillaries (3 mm I.D.). The end-caps were formed by fitting 30 mm×0.5 mm I.D. PTFE tubing into a 10 mm×1 mm I.D. PTFE tube, which facilitated insertion into the continuous system, and both ends were sealed with a small swab of cotton wool to prevent material losses. The sorbent column was conditioned by passing 1 ml of ethanol, followed by 1 ml of Milli-Q water.

The interface unit was constructed from a standard injection valve (Knauer 633200) similar to that used for coupling an extraction unit to a gas chromatograph [16], with an injected volume of 5 μl (internal volume and loop volume, 2.5 and 2.5 μl, respectively). The connection between the injection port of the chromatograph and the valve consisted of a 10 cm× 0.3 mm I.D. stainless-steel tube with a needle soldered at one end for inserting the loop contents

into the injection port of the instrument (via the septum). The carrier gas inlet was split into two streams that were directly connected to the valve and the chromatograph injection port. The inlet was shut by a stopcock, so the instrument could be used for manual injections while allowing the nitrogen stream to follow its normal route through the instrument.

2.3. Gas chromatographic conditions

A Hewlett-Packard Series 5890 A gas chromatograph equipped with a flame ionization detector (FID) was used. The analytical column was a 15 m×0.53 mm I.D., 3.0 μm HP-1 [100% cross-linked poly(dimethylsiloxane)] fused-silica column. Chromatograms were recorded on a Hewlett-Packard 3392 A integrator.

The optimal conditions for gas chromatography were established by using a mixture of 10 mg/l of each phenol and 20 mg/l of internal standard (methyl nonanoate) in ethyl acetate and standard syringe injection. The temperature programme of the chromatographic oven was held at 60°C for 3 min, ramp to 86°C at 6°C/min, held at 86°C for 6 min, ramp to 200°C at 12°C/min held for 2 min. A packed column injection port, heated at 220°C, with a HP series 530-μ column liner (glass inserts) was used; the detector temperature was kept at 250°C. Sample injection was done in the splitless mode; injection volumes of 2 or 5 μl for off-line or on-line analysis, respectively, were employed. Nitrogen at a flow-rate of 15 ml/min was used as the carrier gas.

2.4. Solid-phase extraction procedure

The manifold employed, depicted in Fig. 1, operated in three steps: (1) 100 ml of sample or standard solution containing 0.8–40 μg/l phenols acidified to pH 3 was passed through the sorbent column (located in the loop of IV_1) at 6.0 ml/min; in this step, phenols were retained and the sample matrix sent to waste (W_1); (2) IV_1 valve was switched and the sorbent column dried for 3 min with a stream of nitrogen introduced via the carrier line of the second valve (IV_2); simultaneously, the loop of IV_2 was filled with eluent (20 mg/l internal standard in ethyl acetate) by aspiration from a displacement bottle (water was used for the displacement); (3) IV_2 valve was switched and 75 μl of eluent injected into a nitrogen stream at a flow-rate of 1 ml/min and passed through the column to elute the phenols. The eluate containing the phenols was homogenized in a mixing coil, R (75 cm×0.5 mm I.D.). (A) For on-line analyses, the N_2 stream transported the 75-μl eluate to the interface unit (IV_3) and the loop contents (5 μl) were injected 30 s after IV_2 was switched into the nitrogen carrier gas and transferred to the chromatograph port. (B) For off-line analyses, the

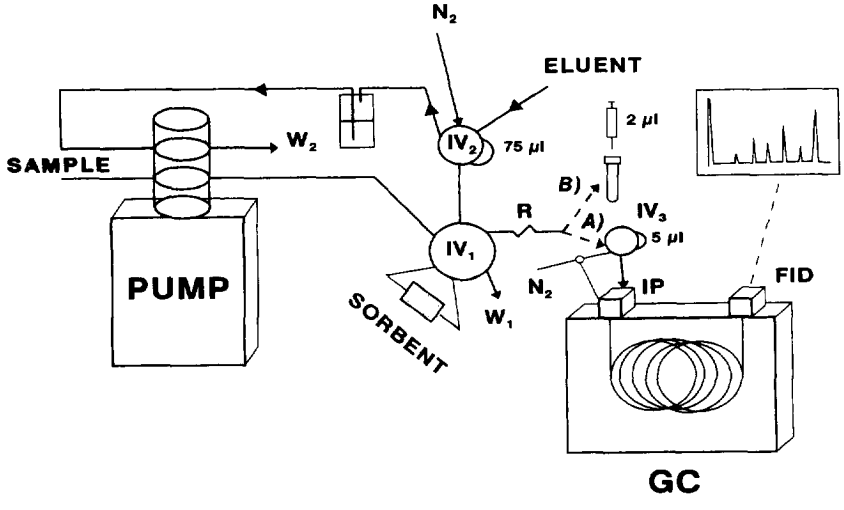

Fig. 1. Schematic diagram of the proposed continuous system for the determination of phenolic compounds in water samples. (A) On-line and (B) off-line mode. IV=injection valve; R=mixing coil; W=waste; IP=injection port; FID=flame ionization detector; GC=gas chromatograph.

eluate (75 μl) was collected in glass-vials and 2-μl aliquots were manually injected into the injection port of chromatograph. Between samples, the sorbent column was washed with 1 ml of ethanol to avoid memory effects.

3. Results and discussion

Concentrations as low as a few micrograms-per-millilitre of phenol affect the taste and odour of water and fish; for this reason, many phenols have been included in the priority pollutant list of the EU and US-EPA [17]. In this work, ten representative phenols with different functional groups (phenol, *p*-cresol, 2,5-dimethylphenol, 2-*tert.*-butylphenol, *m*-nitrophenol, 4-chlorophenol, 2,4-dichlorophenol, 3,4-dichlorophenol, 2,4,6-trichlorophenol and pentachlorophenol) were studied.

3.1. Selection of chemicals

In order to select the most suitable sorbent and eluent for the intended purpose, a manifold similar to that depicted in Fig. 1 was employed, in the off-line mode. Aliquots (2-μl) of the extract were manually injected into the chromatograph by means of a syringe.

Three usual sorbent materials (XAD-2, activated carbon and RP-C_{18}) for conventional SPE of organic compounds were assayed for the preconcentration of phenols. Sorption tests were carried out by using a column packed with 50 mg of the sorbent tested in each case. Aqueous standard solutions (sample) containing 10 mg/l of each phenol (ten compounds) at pH 3 were passed through the sorbent column at 3.5 ml/min. Fractions of 1 ml of sample were collected before and after the column in glass vials. The phenols were then extracted with 1 ml of ethyl acetate and the extract was dried with anhydrous sodium sulphate. The solvent was chosen in terms of its extraction efficiency against the compounds studied. Finally, 2-μl aliquots of the extract were analysed by gas chromatography. After each sample was processed, the column was cleaned with ethyl acetate and water at 1 ml/min for 1 min to eliminate sorbed analytes. The sorption efficiency was assessed by comparing the amount of each compound recovered from the extract (unsorbed) with its concentration in the sample (taken to be 100%). Table 1 presents the efficiency of phenol sorption by various materials. The efficiency of sorbents, first of all, depends on the polarity of the sorbent surface. According to Rudzinski et al. [5], carbon sorbents having more polar functional groups adsorb less phenol from water because of the competitive sorption of the more polar water molecules. In our study, activated carbon provided a higher extraction efficiency for all phenols than did RP-C_{18}; however, the average sorption never reached 50%. Undoubtedly, XAD-2 was the most effective sorbent among those studied, probably because of its hydrophobic surface but also of the π-electron interactions, which favoured the adsorption of phenols from aqueous solutions. In all instances, phenol was the least efficiently extracted (21.5% for XAD-2); the other phenols were retained on XAD-2 with an efficiency close to 100%.

Table 1
Sorption efficiency (%) of phenols on different materials

Compound	XAD-2	Activated carbon	RP-C_{18}
Phenol	21.5	8.0	n.d.[a]
p-Cresol	99.0	7.8	1.6
2,5-Dimethylphenol	99.2	31.2	13.3
2-*tert.*-Butylphenol	97.3	39.0	27.2
m-Nitrophenol	98.5	23.8	n.d.[a]
4-Chlorophenol	98.0	30.7	18.0
2,4-Dichlorophenol	90.6	56.4	23.0
3,4-Dichlorophenol	99.1	39.0	15.5
2,4,6-Trichlorophenol	96.8	48.2	14.2
Pentachlorophenol	99.4	39.6	13.2

[a] n.d. = not detected.

Various sorbent columns packed with different amounts of XAD-2 (between 20 and 80 mg) were prepared as described in Section 2.2 in order to establish the optimal amount of sorbent for adsorbing the phenols. For this purpose, several calibration graphs were run by using aqueous solutions spiked with ten phenols at the 10–100 μg/l level at pH 3. Volumes (50 ml) of aqueous samples were passed through the XAD-2 column, and then eluted with 75 μl of ethyl acetate. The amount of sorbent used was influential; thus, the sensitivity was 2 times higher with 50 mg than with 20 mg. Columns containing more than 50 mg of XAD-2, required increased volumes of eluent for complete elution of the

phenols. This was confirmed by a second injection of eluent (75 μl) with no preconcentration, which gave rise to some carry-over that increased with increasing amount of sorbent above 50 mg. An XAD-2 column (18 mm×3 mm I.D.) containing 50 mg of sorbent material was selected.

n-Hexane is the most frequently used desorbing solvent for analyte desorption/transfer; however, if moderately polar or polar analytes have to be determined, experience has shown that polar solvents can be the best choice. Therefore, several organic solvents of variable polarity were assayed as eluents for phenols retained on XAD-2, namely: methanol, ethanol, ethyl acetate, acetone and *n*-hexane. For this purpose, 100 ml of an aqueous sample containing phenols at a 10 μg/l concentration was passed through the sorbent column at 3.5 ml/min. Problems caused by the presence of water in the chromatographic column were overcome by drying the sorbent column with nitrogen gas before elution. An eluent volume of 75 μl delivered at a flow-rate of 1 ml/min by means of a nitrogen stream was passed through the column in each experiment. No phenols were detected in the eluate when *n*-hexane was used as eluent. The elution efficiency of methanol, ethanol and acetone was 50% lower than that of ethyl acetate, which was the best choice and hence adopted as the desorbing solvent. As water forms an azeotrope with ethyl acetate, the drying step with nitrogen was essential.

In order to increase the precision of the method, two internal standards (naphthalene and methyl nonanoate) were assayed for addition to the eluent (ethyl acetate). As naphthalene was partially retained on the sorbent and methyl nonanoate was not retained at all, the latter was selected.

3.2. Optimization of experimental variables

The phenols could be uncharged at low pH because their pK_a values are generally high; however, chlorophenols have lower pK_a values than methylphenols and therefore can be ionized at low pH. Therefore, the retention of phenols is dependent on the sample pH. The effect of pH on the sorption of the ten selected phenols was studied over the range 1.5–12. The chromatographic areas obtained from 100 ml of aqueous sample spiked with phenols

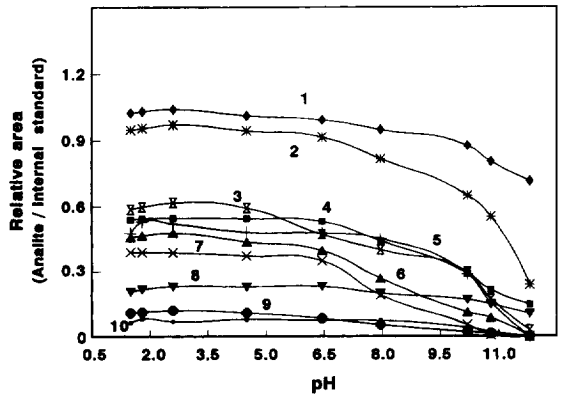

Fig. 2. Effect of pH on the sorption of phenols. 1=2-*tert.*-butylphenol, 2=2,5-dimethylphenol, 3=3,4-dichlorophenol, 4=2,4-dichlorophenol, 5=*p*-cresol, 6=2,4,6-trichlorophenol, 7=4-chlorophenol, 8=pentachlorophenol, 9=*m*-nitrophenol, 10=phenol. Concentration, 10 μg/l.

at a 10 μg/l concentration at a variable pH are compared in Fig. 2. Peak areas for pentachlorophenol and trichlorophenol decreased at low pH (about pH 5) because their pK_a values are the lowest (4.7 and 6, respectively); for the other phenols the signals remained constant over wider ranges (up to about pH 8) because their pK_a values ranged between 7 and 10.6 for 3,4-dichlorophenol and 2,5-dimethylphenol, respectively. Reproducibility also increased upon acidification. In all further work, sample solutions were acidified at pH 3. The ionic strength, adjusted with potassium nitrate, did not affect the signal up to 1.5 *M*.

The flow-rate of sample solution (100 ml) had very little effect on the signal over the range studied (0.8–6.5 ml/min). The effect of the elution process was studied by varying the nitrogen flow-rate between 0.5 and 1.5 ml/min. The phenolic compounds sorbed were eluted throughout this range, with no carry-over (i.e., elution was complete), by using an eluent volume of 75 μl. A sample flow-rate of 6.0 ml/min and a nitrogen flow-rate (eluent carrier) of 1 ml/min were thus chosen to boost the sample throughput. However, solvent changeovers (aqueous phase and ethyl acetate, from sample and eluent, respectively) required drying the sorbent column with a stream of nitrogen at 1 ml/min for 3 min. The loop of IV_2 was filled with eluent (containing 20

mg/l of the internal standard) by using a displacement bottle (see Fig. 1). The effect of the eluent volume was studied between 25 and 125 μl. Chromatographic signals increased with increasing injected volume up to 75 μl (complete elution). On the other hand, volumes above 75 μl caused the signal to decrease through dispersion of the analytes in the organic phase. Finally, for on-line coupling of the SPE to the chromatograph, a homogenization coil was required in order to ensure optimal performance of the valve interface; however, the length of this coil could be varied between 25 and 100 cm as required. Based on the above results, an injected acetyl acetate (eluent) volume of 75 μl and a 75 cm (0.5 mm I.D.) long homogenization coil (R in Fig. 1) were selected as optimal.

For mode A in Fig. 1 (on-line analysis), the flow-rate of the chromatographic carrier gas (nitrogen) was optimized by varying it between 10 and 25 ml/min. The optimal flow-rate was 16 ml/min (flow through interface valve and injection port, 11.5 and 4.5 ml/min, respectively), because neither adsorption of phenolic compounds in the lines nor distorted peaks was observed. The smallest injection volume (from the valve interface, IV_3) was 5 μl; however, because the analytical signal used was the relative area (ratio of analyte/internal standard peak area), there was no difference between injecting 2 or 5 μl in the off- or on-line mode, respectively.

3.3. Calibration, sensitivity and precision

Analytical curves for aqueous samples containing different amounts of phenols prepared according to the procedure described in Section 2.4 (on-line mode) were obtained by plotting the analyte-to-internal standard peak-area ratio against the analyte concentration. The analytical figures of merit for a sample volume of 100 ml are summarized in Table 2. The slope of the calibration graph for phenol was the smallest as a result of its sorption efficiency being the lowest. Detection limits were calculated for the same sample volume as the minimum concentrations providing a chromatographic signal three times higher than background noise. Preconcentration factors increased with increasing sample volume, limited by sample availability and the operator's patience. The preconcentration factor was calculated as the ratio between the slopes of the calibration graphs obtained by using the flow system depicted in Fig. 1 (on-line mode) and the slopes obtained by manual injection of standards containing between 2 and 40 mg/l of phenols in ethyl acetate. The preconcentration factors for phenol were the lowest as a result of its sorption efficiency on the sorbent column also being the lowest (see Table 1). The mean values for nine phenolic compounds (phenol excluded) of these factors were 120, 310, 590 and 1150 for samples volumes of 10, 25, 50 and

Table 2
Characteristic parameters of the calibration graphs and analytical figures of merit of the determination of phenols

Compound	Regression equation[a]	Correlation coefficient	Linear range (μg/l)	Detection limit (μg/l)	R.S.D. (%)	Preconcentration factor[b]
Phenol	$Y=0.009+7.5\times10^{-3}X$	0.992	5–40	3	4.4	240
p-Cresol	$Y=0.039+4.9\times10^{-2}X$	0.993	2–40	0.8	3.8	1085
2,5-Dimethylphenol	$Y=-0.028+10.0\times10^{-2}X$	0.996	2–40	1	2.5	1220
2-*tert.*-Butylphenol	$Y=0.035+10.1\times10^{-2}X$	0.999	0.8–40	0.3	2.3	1150
m-Nitrophenol	$Y=0.027+9.3\times10^{-3}X$	0.994	5–40	2	4.5	1180
4-Chlorophenol	$Y=-0.020+4.1\times10^{-2}X$	0.995	3–40	1.5	4.1	1205
2,4-Dichlorophenol	$Y=-0.022+5.7\times10^{-2}X$	0.995	2–40	1	3.0	985
3,4-Dichlorophenol	$Y=-0.033+6.5\times10^{-2}X$	0.998	2–40	1	3.8	1225
2,4,6-Trichlorophenol	$Y=0.036+4.4\times10^{-2}X$	0.996	1–40	0.5	2.5	1115
Pentachlorophenol	$Y=-0.011+2.3\times10^{-2}X$	0.995	2–40	1.5	2.8	1205

[a] Y: relative area (peak area analyte/internal standard), X: concentration, in μg/l.
[b] Preconcentration factor (sampling volume, 100 ml).

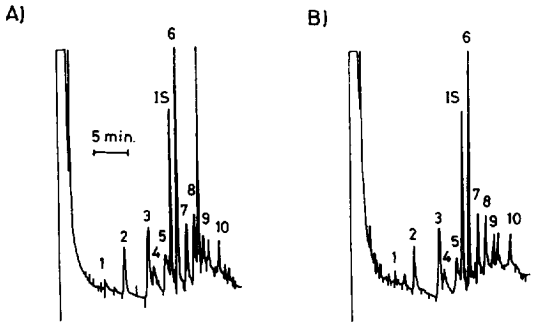

Fig. 3. Gas chromatograms for phenolic compounds spiked (10 μg/l) to river (A) and tap waters (B) after on-line trace enrichment of a 100-ml sample volume. 1=phenol, 2=*p*-cresol, 3=2,5-dimethylphenol, 4=2,4-dichlorophenol, 5=4-chlorophenol, 6=2-*tert.*-butylphenol, 7=2,4,6-trichlorophenol, 8=3,4-dichlorophenol, 9=*m*-nitrophenol, 10=pentachlorophenol, I.S.=internal standard. For other conditions, see Section 2.3.

100 ml, respectively. The precision of the method was checked on 11 samples of 100 ml spiked with each phenol at a 10 μg/l concentration. The relative standard deviations ranged between 2.3 and 4.5%.

3.4. Water analyses

The proposed trace enrichment method was applied to the determination of the ten phenolic compounds studied in acidified well, river and tap water samples. All samples were filtered through 0.45-μm mesh (4 mm diameter) (Micron Separations, Westboro, MA, USA) to remove particulates, and adjusted to pH 3 with dilute HNO_3 before analysis. Initially, 100 ml of filtered water was analysed; however, as none of the phenols was detected, higher sample volumes (up to 250 ml) were preconcentrated in order to lower detection limits. No interferences from large amounts of foreign substances were observed for 250 ml of water (maximum volume assayed); however, no phenols were again detected. Therefore, the water samples were fortified with phenols at 10 and 20 μg/l and, after filtration, analysed by introducing 100 ml of sample into the SPE system. Fig. 3 shows the chromatograms obtained for spiked river and tap waters. As can be seen, the on-line method provides narrow peaks for the phenolic compounds; although some peaks corresponding to other organic products present in waters are present, they do not disturb the detection of the spiked phenols. Table 3 lists the percent recoveries obtained for the three different spiked water samples analysed, which ranged from 92.5 to 103.8%.

4. Conclusions

An on-line solid-phase extractor coupled to a gas chromatograph (SPE–GC) was developed for the preconcentration/determination of various phenols in waters by use of a conventional FID detector. The simplicity of the proposed method probably makes it

Table 3
Recoveries obtained from different types of water samples spiked with phenolic compounds at 10 or 20 μg/l

Compound	Well		River		Tap	
	10 μg/l	20 μg/l	10 μg/l	20 μg/l	10 μg/l	20 μg/l
Phenol	101.5±3.5	102.5±4.1	94.0±3.7	97.0±3.0	102.5±3.2	100.5±3.1
p-Cresol	99.0±3.0	100.2±3.2	95.0±2.9	97.9±3.1	96.0±2.5	101.7±2.7
2,5-Dimethylphenol	103.8±2.4	98.2±2.5	99.0±2.3	103.0±2.6	98.5±2.4	97.8±2.5
2-*tert.*-Butylphenol	102.5±2.1	97.5±2.4	102.5±2.0	99.5±2.5	103.5±2.1	95.3±2.0
m-Nitrophenol	103.0±3.6	95.5±3.8	102.7±4.5	100.3±4.1	97.6±2.8	98.2±3.9
4-Chlorophenol	94.5±3.5	103.0±4.0	101.5±3.6	102.5±3.7	96.3±3.6	94.8±2.6
2,4-Dichlorophenol	94.0±2.8	99.0±3.0	96.0±2.8	92.5±3.2	103.0±2.8	100.7±2.7
3,4-Dichlorophenol	97.5±3.2	101.5±2.9	103.0±3.4	102.0±3.1	98.5±3.5	95.5±3.2
2,4,6-Trichlorophenol	102.0±2.4	95.6±2.3	102.1±2.3	97.2±2.8	101.0±2.5	98.3±2.6
Pentachlorophenol	99.0±2.9	94.5±2.5	93.5±3.0	100.5±2.9	95.3±3.4	100.7±3.2

suitable for monitoring phenolic compounds in wastewater produced during many industrial processes such as the manufacture of plastics, dyes, drugs, antioxidants, and, especially, by the pulp industry [18]; however, this assessment requires confirmation, since the interference of oil/hydrocarbons has not been studied in this paper. The detection limits obtained (ca. 1 μg/l for 100 ml of sample) can be reduced by preconcentrating 250 ml of sample. On the other hand, incorporation of the on-line coupled module requires no alteration of the chromatograph; other reported on-line coupled SPE–GC systems, which are more complicated as they use an on-column injector and two columns in addition to the analytical one, required some changes in the chromatograph [12,13]. Problems arising from the presence of water in the chromatographic system (viz. changes in the peak shape and peak area after a number of consecutive injections) have been overcome by drying the sorbent column with gaseous nitrogen before elution. Finally, we should note that the proposed module should govern the functioning of the pumps and valves via a computer in order to accomplish full automation of the system. Otherwise, the operator's continual presence will be required and the advantages of the on-line approach will be insubstantial because the manual injection involved in the off-line mode is very simple. Therefore, the most salient contribution of this work is actually the SPE module.

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