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Analysis of phenolic compounds in effluent by solid-phase extraction and gas chromatography–mass spectrometry with direct on-column benzylation: sensitive negative ion chemical ionisation gas chromatography–mass spectrometry detection of phenyl benzyl ethers

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Abstract

A procedure for the extraction of eight phenolic compounds in effluent from various tertiary sewerage treatment plants in the Sydney area using a non-ionic polystyrene–divinylbenzene polymeric sorbent is described. Good recoveries were obtained for these phenols which differ widely in polarity. The performance of this new sorbent is superior to that of graphitised carbon black. The determination of the phenols was carried out by direct on-column derivatisation in GC with a recently developed reagent, 3,5-bis(trifluoromethyl)benzyldimethylphenylammonium fluoride (BTBDMAF). Benzyl derivatives of phenols allow very sensitive detection of phenols by GC–MS in the negative ion CI mode at ppt levels.

Keywords: Phenols; Polystyrene–divinylbenzene polymer

1. Introduction

Phenolic compounds are common pollutants in aquatic environments as a result of industrial outfalls and degradation of pesticides. These pollutants are required to be detected at trace levels by most environment protection authorities. In addition to the requirement for a sensitive determination technique, an effective preconcentration step is required to reach the sub ppb detection level necessary for the detection of these compounds in water.

There has been a gradual increase in the use of solid-phase extraction (SPE) as a sample preparation and preconcentration step in phenol analysis, as it overcomes many of the disadvantages of liquid–liquid extraction (LLE). The sorbents which have been studied include octadecyl (C_{18}) bonded silica [1–5], graphitised carbon black (GCB) [5–9] and, recently, polystyrene–divinylbenzene polymers [10–14].

Although C_{18}-bonded silica is the most widely used sorbent, it has a limited ability to adsorb the more hydrophilic phenols, such as phenol, 4-nitrophenol and 2-chlorophenol. The recovery and breakthrough volume for these phenols in tap water were found to be low with this sorbent [5]. A method for the extraction of phenols with GCB cartridges was developed by Borra et al. [5] and was found to be

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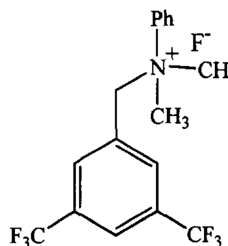
generally more efficient than the use of C_{18}. A 2 l tap water sample concentrated on a 250 mg GCB cartridge gave good recoveries for all phenolic compounds including most of the hydrophilic ones, except for phenol which has a breakthrough volume of 200 ml. However a dramatic reduction in the efficiency of GCB cartridges was observed in the extraction of hydrophilic phenols from environmental waters which typically contain large amounts of humic substances [8].

Polystyrene–divinylbenzene polymeric (XAD) sorbents have recently become commercially available in cartridge form for sample preconcentration. Puig and Barcelo [15] carried out a comparative study of the performance of four SPE sorbents (three polystyrene–divinylbenzene polymeric sorbent and one graphitised carbon sorbent) for the extraction of phenolic compounds from ground water and found that polystyrene–divinylbenzene polymeric (XAD type) sorbents gave better breakthrough volumes and analyte recoveries than porous graphitised carbon.

The extracted phenols are often separated and determined by reversed-phase liquid chromatography coupled with either a UV detector or an electrochemical detector. Although these detection methods provide the sensitivity required, there are many problems associated with interfering compounds. GC–MS represents a better determination method as it not only has the advantage of providing mass spectral confirmation but also offers a more selective determination of phenolics at low analyte levels via the selective ion monitoring (SIM) mode.

In order to improve the gas chromatographic peak shape of the phenols, they are commonly derivatised either before or after extraction, or with an on-column reagent in the GC injector port. In a previous communication [16], the preparation of an efficient benzylating reagent (BTBDMAF) (1)



for direct on-column derivatisation of phenols in GC–MS was described. It was found that the resulting phenol derivatives not only had improved peak shapes but produced signals of much higher total ion current (TIC) than both the free phenols and the corresponding methyl derivatives.

In the present work, the efficiency of the polystyrene–divinylbenzene polymeric sorbent for the extraction of phenolic compounds from waste water was studied. The determination of the phenols by direct on-column derivatisation in GC–MS (using negative ion CI ionisation) with the newly developed reagent was examined.

2. Experimental

2.1. Reagents and chemicals

2-Chlorophenol, 2,4,6-trichlorophenol and 2,4-dinitrophenol were purchased from Aldrich (Milwaukee, WI, USA); 2,4-dichlorophenol was obtained from Sigma (St. Louis, MO, USA); phenol from May and Baker (Dagenham, UK); 4-nitrophenol from Riedel-de Haen (Seelze, Germany); *p*-cresol from the British Drug Houses (London, UK); and pentachlorophenol was from Chem Service (West Chester, PA, USA). Individual standard solutions were prepared in methanol and two working mixed standard solutions were also prepared in methanol containing 10 mg/l and 100 mg/l, respectively of each analyte. The standard solutions were stored in the dark at 4°C.

2,4,6-Tribromoanisole was used as an internal standard for GC–MS determinations and was prepared according to standard procedures [17] from 2,4,6-tribromophenol. 2-Fluorophenol was obtained from Aldrich and used as an internal standard for HPLC determinations. Tetramethylammonium hydroxide (TMAOH) was purchased from Aldrich and BTBDMAF was prepared as described previously [16].

All solvents were HPLC grade and were obtained from EM Science (Darmstadt, Germany). All HPLC solvents were filtered through a 0.2 μm PTFE membrane filter (Micro Filtration Systems, Dublin, CA, USA) prior to use. Water was purified using a Milli-Q purification system (Millipore, Bedford, MA, USA) and was filtered through a 0.2 μm

cellulose nitrate membrane filter (Micro Filtration Systems). Trifluoroacetic acid was obtained from BDH (Poole, UK).

2.2. Extraction apparatus

Water samples were preconcentrated by the use of LiChrolut EN extraction cartridges containing 200 mg of sorbent and were obtained from Merck (Darmstadt, Germany). The extractions were carried out using a Baker (J.T. Baker) SPE-12G vacuum manifold system. 300 mg GCB cartridges were used for comparison purposes and were obtained from Alltech (Australia).

2.3. Instrumentation

GC–MS analyses for exploratory work were conducted on a Hewlett-Packard (Palo Alto, CA, USA) 5890 gas chromatograph equipped with an HP 7673A autosampler and an HP Model 5971A mass-selective detector. An HP-1 (Hewlett Packard) 12 m×0.22 mm fused-silica capillary column with a film thickness of 0.33 μm was used and helium was employed as the carrier gas. The data were analysed using HP Chemstation software.

GC–MS analyses for low spiked level samples were carried out on a Finnigan MAT (San Jose, CA, USA) GCQ GC equipped with a Finnigan MAT CTC autosampler Model A200S and a GCQ MS detector. Analytes were separated using a BPX-5 (SGE) 30 m×0.22 mm fused-silica capillary column with a film thickness of 0.25 μm. Helium was employed as the carrier gas and methane as the reagent gas. The data were analysed using the GCQ Data Processing software supplied with the GCQ MS detector.

Injector liners were cleaned with methanol and silanised with a solution of 5% dimethyldichlorosilane (DMCS) in toluene.

Liquid chromatographic experiments were performed using an LKB (Bromma, Sweden) Model 2249 gradient pump equipped with an LKB Model 2157 autosampler and a Waters (Milford, MA, USA) Model 490E programmable multiwavelength detector. Separation was carried out using a Pharmacia (Uppsala, Sweden) stainless-steel column (250×4 mm I.D.) containing 2.5 μm Spherisorb ODS packing (Superpac).

2.4. Chromatographic conditions and detection

The GC analyses were carried out in splitless mode under the following conditions: injector temperature 260°C, detector temperature 280°C, injection volume 1 μl (with three washes between each injection), oven equilibration time between runs 0.5 min. The oven temperature was held at 60°C for 1 min initially, then increased to 140°C at 15°C/min, and to 280°C at 25°C/min and held at that temperature for 2 min.

The parameters for the HP mass-selective detector were as follows: solvent delay 4 min, scan parameters m/z 50–500, threshold 1500; ion 227 was selectively monitored.

The GCQ MS was operated in negative ion chemical ionisation (NICI) mode and the parameters were as follows: solvent delay 4 min, scan parameters m/z 30–550; and the negative phenylate ions were selectively monitored.

Phenols were chromatographed on the HPLC with premixed methanol–acetonitrile (A) (10:90, v/v) and water acidified with TFA (B) (0.05%, v/v), the latter was made up daily. The initial eluent composition was 30% A and 70% B, which was increased linearly to 35% A over 5 min and then to 75% A over another 15 min. The composition remained at 75% A for 10 min before it was decreased linearly to 30% over 5 min. The flow-rate was held at 1.0 ml/min. The separation was monitored at 280 nm initially and then switched to 230 nm after 15 min.

2.5. Extraction procedure

The LiChrolut EN cartridge was preconditioned with 10 ml of acetone, 3 ml of methanol and 3 ml of acidified water (pH 2). The cartridge was not allowed to go dry after the preconditioning step.

50 ml of effluent was spiked with a known amount of the working mixed phenol standard and the pH of the sample was adjusted to 2 with 5 M HCl. The sample was agitated for 5 min and then poured into a reservoir connected to the preconditioned LiChrolut EN cartridge. The sample was allowed to pass through the cartridge at no more than 5 ml/min.

Vacuum was applied when necessary and turbid samples were centrifuged before passing through the cartridges. The sample container was rinsed with 3 ml acidified water (pH 2) and this washing passed through the cartridge at the same flow-rate. The sorbent was then washed by slowly passing 1 ml of 40% aqueous methanol through the cartridge and finally dried by blowing nitrogen through the cartridge for 5 min.

The cartridge was eluted with three 2.5 ml aliquots of a mixture of acetonitrile–methanol (50:50, v/v). 5 to 10 min was allowed between each elution. Initial phenol determination was carried out using HPLC-UV. The combined eluate was basified with 150 μl of a 0.5 mol/l methanolic solution of TMAOH to minimise evaporation losses of volatile analytes and 10 μg of 2-fluorophenol added as an internal standard. The eluate was concentrated to approximately 1 ml under a gentle stream of nitrogen and was acidified with 30 μl of 5 *M* HCl. 20 μl of the final extract was injected into the HPLC system.

For GC–MS determination, the combined eluate was basified with 50 μl of a 0.2 *M* methanolic solution of BTBDMAF, 5 μg of 2,4,6-tribromoanisole added as internal standard and then concentrated to approximately 1 ml. 1 μl of the final extract was injected directly into the GC. HPLC confirmations were carried out on the GC samples to ensure that complete derivatisations were achieved. The GC samples were acidified with 10 μl of 5 *M* HCl and 10 μg of 2-fluorophenol added. 20 μl of the acidified extract was injected into the HPLC system.

3. Results and discussion

3.1. Optimisation of the sample preconcentration process

Waste water samples with low levels of particulate matter were passed through the cartridges without the aid of vacuum to allow for maximum interaction time between analytes and sorbent. For turbid samples, low level vacuum was applied so that the flow-rate was maintained at a similar level as the low particulate samples (approximately 5 ml/min). Unlike most other SPE cartridges and disks, no significant clogging was experienced even when concentrating large sample volumes or turbid samples.

Polar non-target compounds adsorbed by the sorbent would normally be eluted from the cartridge with the target phenols. However, the presence of these acidic interfering compounds in the final extracts decreased the efficiency of the on-column derivatisation and much larger excesses of the reagent were required to achieve complete derivatisation of the phenols. These compounds also coeluted with the polar phenols during HPLC analyses. Therefore a wash step with an aliquot of 1 ml 40% aqueous methanol was incorporated into the procedure to remove non-target compounds. Analysis of this aliquot showed that negligible amount of the target phenols were eluted. After the cleanup step, elution of the analytes with a mixture of acetonitrile–methanol (50:50) was found to be selective and resulted in a negligible amount of interference. The HPLC and GC–MS chromatograms are shown in Fig. 1.

In order to prevent losses of volatile phenols during the eluate concentration step, the eluates were basified with BTBDMAF for GC–MS determinations and tetramethylammonium hydroxide (TMAOH) for HPLC determinations. The analytes in the presence of these reagents form ion-pair complexes which are less volatile than the free phenols.

3.2. Recovery studies

External standards were prepared by adding known amounts of the phenols and the internal standard to 7.5 ml mixtures of methanol–acetonitrile (1:1, v/v) and evaporating them to 1 ml. Extraction experiments were initially carried out on 50 ml Milli-Q purified water samples. Background phenol was observed in all blank samples and the recoveries for phenol given below have been corrected. The signal was confirmed to be phenol by both EI and CI mass spectrometry. The origin of this phenol contamination was unknown as background phenol was also found in blank samples extracted with a LLE process using a different set of equipment in another section of this laboratory. Extraction of purified water samples spiked with 20 ppb of each of the eight target phenols gave excellent recoveries for all the phenols (90 to 100%), including the hydrophilic

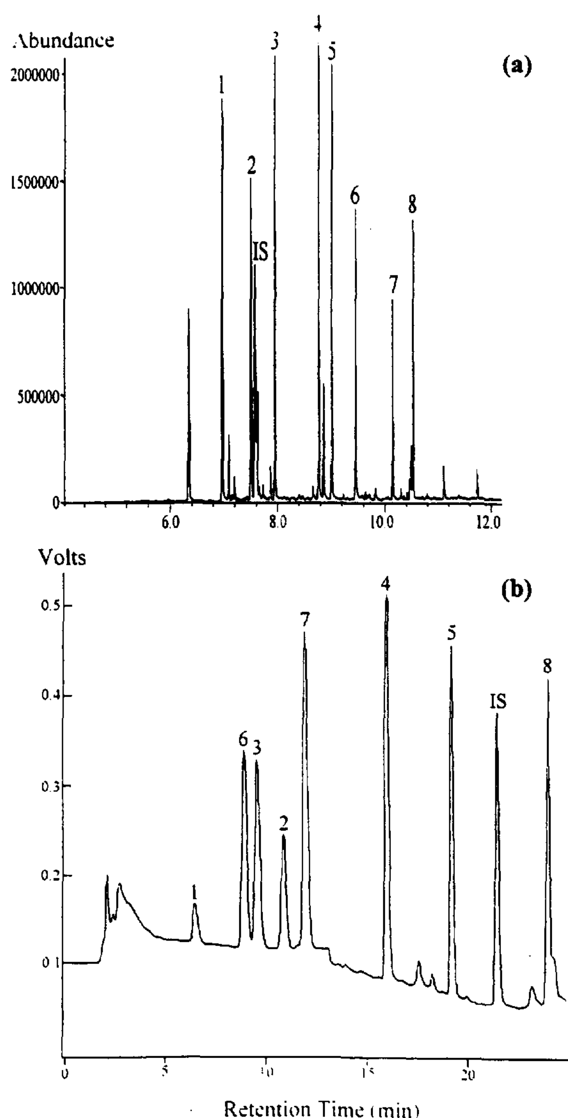


Fig. 1. (a) GC–MS (+ ion EI/SIM mode) chromatogram after on-column derivatisation of a 50 ml waste water sample spiked with 200 ppb of each phenol; (b) HPLC–UV chromatogram of the same sample (the free phenols were analysed). Compounds: 1= phenol; 2=*p*-cresol; 3=2-chlorophenol; 4=2,4-dichlorophenol; 5=2,4,6-trichlorophenol; 6=4-nitrophenol; 7=2,4-dinitrophenol; 8=pentachlorophenol (derivatives of the above phenols shown in the GC–MS chromatogram).

phenols, and 80% for pentachlorophenol. The recoveries are listed in Table 1. Increasing the volume of the eluent failed to improve the recovery of pentachlorophenol. Acidification of eluent with trifluoroacetic acid improved its recovery slightly but also eluted interfering compounds that coeluted with some of the target analytes during analysis.

Recoveries of phenols in effluent were also determined. Triplicate blank extraction experiments were carried out on the effluent water used in this study and showed that the effluent did not contain any of the target analytes except for background phenol. Extraction experiments were carried out on 50 ml effluent samples with spiking level of 20 ppb in triplicate. HPLC analyses were carried out in addition to GC–MS analyses to confirm that the latter gave true recovery results (Table 1). The results obtained by both methods of determination were found to be comparable. It can also be seen from this table that the presence of large amounts of organic matter in the samples had little effect on the capability of the sorbent to adsorb the target phenols. Up to 400 ml of the spiked effluent samples were extracted using these cartridges with no reduction in the phenol recoveries observed.

Analysis of waste water samples which were spiked at levels near detection limits was carried out using the GCQ operating in NICI mode. SPE of samples spiked with 2 ppb of each of the phenols was carried out and analysed giving quantitative recoveries, except for 2,4-dinitrophenol (Table 2). The chromatogram is shown in Fig. 2. 2,4-Dinitrophenol was not detected using GC–MS in either CI or EI mode but was easily detected by HPLC–UV. As a result, the latter method is the preferred analytical method for 2,4-dinitrophenol as it provides lower detection limit. Waste water samples spiked with 0.2 ppb of each of the phenols were also extracted and analysed by the above method. The recoveries obtained are listed in Table 2. Recoveries for phenol and 4-nitrophenol were not determined as this spike level was below their limits of detection.

3.3. Limits of detection

Under the chromatographic conditions selected and extracting 50 ml of spiked effluent water, the predicted limits of detection (LOD) (signal-to-noise ratio=3) of the eight phenols for each of the chromatographic techniques were determined by linear extrapolation of the signals of a 2 ppb and a 20 ppb samples and are listed in Table 3. The level of background phenol was equivalent to the phenol

Table 1
Recovery of phenols from spiked Milli-Q water and waste water using the proposed method

Compound	Recovery (%)				
	Milli-Q water	Waste water			
	50 ml[a]	50 ml[a]	100 ml[b]	200 ml[b]	400 ml[b]
Phenol	98 (104)	97 (101)	103	117	111
4-Nitrophenol	110 (100)	106 (104)	86	97	112
p-Cresol	97 (100)	94 (97)	84	94	106
2-Chlorophenol	97 (96)	92 (94)	91	109	109
2,4-Dinitrophenol	123[c] (101)	130[c] (99)	91	99	105
2,4-Dichlorophenol	97 (98)	97 (99)	90	92	100
2,4,6-Trichlorophenol	97 (98)	96 (98)	89	88	101
Pentachlorophenol	79 (78)	84 (79)	81	78	84

Spiked level: 20 ppb. Analytical instrument: HP GC–MS operating in positive EI mode.
[a] Mean values obtained from duplicate measurements. Results in parentheses were obtained by HPLC–UV analysis.
[b] Mean values of triplicate measurements and determinations carried out by HPLC-UV.
[c] Results obtained from the extraction of a 100 ppb sample.

signal of a 0.2 ppb sample. This is well below the LOD for both HPLC and GC–MS (EI) determinations. However for GC–MS determination using the GCQ operating in NICI mode, quantification of samples with phenol concentrations near or below 0.2 ppb would be largely inaccurate. As a result, the value of the LOD for phenol using the GCQ was not determined by linear extrapolation but determined to be 0.6 ppb—three times the level of background phenol. This level was still lower than the LOD of the other two detection methods and thus GC–MS operating in NICI mode offered a superior method of detection for phenol as well as the chlorophenols. However, this technique was unable to provide quantitative data for 2,4-dinitrophenol at low levels.

3.4. Advantages of detection by GC–MS in the NICI mode

During the course of this work, a number of different GC detection systems were investigated. Using the same GC–MS instrument and under the same chromatographic conditions, it was found that the benzyl derivatives offered a unique advantage in the detection limits obtainable by NICI compared with normal EI mass spectral detection. The

Table 2
Recovery of phenols from waste spiked at sub-ppb levels

Compound	Spike level			
	2 ppb		0.2 ppb	
	Recovery (%)(n=4)	R.S.D. (%)	Recovery (%)(n=4)	R.S.D. (%)
Phenol	80	9.6	–[a]	–
p-Cresol	99	8.5	66	26.6
2-Chlorophenol	100	7.6	50	9.9
2,4-Dichlorophenol	106	11.8	57	15.2
2,4,6-Trichlorophenol	90	8.6	87	9.0
4-Nitrophenol	97	12.2	–[a]	–
2,4-Dinitrophenol	nd[b]	–	nd[b]	–
Pentachlorophenol	96	10.2	58	3.0

Sample volume: 50 ml. Analytical instrument: GCQ operating in negative ion CI mode.
[a] Not determined at this concentration as it is below the LOD.
[b] Not detected at this concentration.

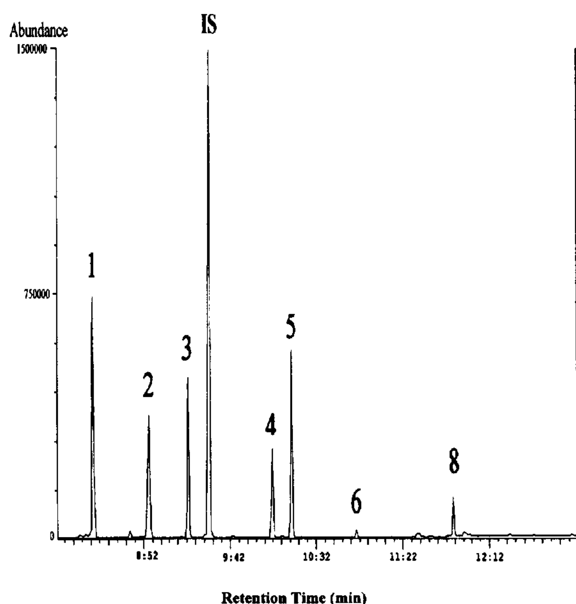


Fig. 2. GC chromatogram (NICI) of a spiked waste water sample (2 ppb) after SPE and on-column derivatisation. (Peak labels are identical to those in Fig. 1).

benzylated derivative of pentachlorophenol could be detected at 0.05 ppb with NICI, 60 and 20 times lower, respectively with HPLC–UV and EI. The increased in sensitivity extended to the whole range of phenols tested here and it allowed detection of normally NICI insensitive substances (e.g., *p*-cresol) at low levels. This sensitivity can be ascribed to the ease in fragmentation of benzyl phenol ethers into positive benzyl carbonium ions with the commitantly high yield formation of negative phenylate ions. Thus all benzyl phenol ethers detection by NICI appeared as phenylate anions and the m/z values are one lower than the parent phenols. A comparison of detection limits attainable by HPLC (UV), MS (EI) and MS (NICI) is shown in Table 3.

Although fragmentation of methyl phenol ethers also generated phenylate anions, on-column methylation of phenols resulted in signals with much lower intensity than benzylation as the methyl carbonium ions are less stable than the benzyl carbonium ions. This general attribute of benzylated derivatives may also be applied in the analysis of other substances which readily form benzyl derivatives such as acids and barbiturates. This work will be presented elsewhere.

3.5. Comparison with GCB cartridges

The extraction efficiency of effluent water using polymeric sorbent was compared with graphitised carbon black (GCB). The extraction procedure using GCB was similar to that detailed by Borra et al. [5] for the extraction of phenolic compounds from 1 l of surface water. The eluates were basified with TMAOH and analysed by HPLC–UV. The results are summarised in Table 4. The results obtained by Borra et al. [5] are also listed. GCB failed to

Table 3
Limits of detection of the various determination techniques

Compound	LOD (ppb)		
	HPLC–UV[a]	GC–MS (EI mode)[a]	GC–MS (NICI mode)[b]
Phenol	10[c]	1	0.6[e]
p-Cresol	3[c]	1	0.1
2-Chlorophenol	5[c]	0.8	0.05
2,4-Dinitrophenol	2[c]	60	nd[f]
2,4-Dichlorophenol	3[d]	0.8	0.02
2,4,6-Trichlorophenol	5[d]	0.8	0.05
4-Nitrophenol	2[d]	4	0.3
Pentachlorophenol	3[d]	1	0.05

[a] Calculated by linear extrapolation of the S/N ratios of a 20 ppb sample.
[b] Calculated by linear extrapolation of the S/N ratios of a 2 ppb sample.
[c] Detected at 280 nm.
[d] Detected at 230 nm.
[e] LOD not determined by linear extrapolation (see Section 3.3).
[f] Not detected in the analysis of a 2 ppb sample.

Table 4
Comparison of GCB and LiChrolut EN cartridges for the extraction of phenols from waste water ($n=2$)

Compound	Recovery (%)	
	GCB[a]	LiChrolut EN
Phenol	38 (5)	101
p-Cresol	35 (nt)	97
2-Chlorophenol	11 (39)	94
2,4-Dichlorophenol	78 (89)	99
2,4,6-Trichlorophenol	79 (91)	98
4-Nitrophenol	65 (92)	106
Pentachlorophenol	78 (103)	79

Spiked level: 20 ppb, sample volume: 50 ml. Analytical instrument: HPLC–UV.
[a] Recoveries in parentheses are literature results for the extraction from surface water. nt=Not tested.

efficiently retain most of the hydrophilic phenols, such as phenol, *p*-cresol and 2-chlorophenol, with their recoveries well below acceptable levels.

3.6. Extraction method comparison

The SPE method with LiChrolut EN cartridges was carried out on two water samples of unknown provenance supplied by National Australian Testing Authority (NATA) for regular proficiency tests and spiked with unknown levels of phenol, 2-chlorophenol, 2,4-dinitrophenol and pentachlorophenol in the range of 30 to 150 ppb. Determinations were initially carried out by GC–MS, the samples were then acidified and analysed by HPLC for confirmational purposes. The results were similar to those obtained by the solvent extraction procedure that is routinely in used in this laboratory and they were in agreement with the final results supplied by the testing authority (Table 5).

3.7. Re-use of LiChrolut EN cartridges

The extraction of phenols from purified water (Milli-Q) spiked at 100 ppb was conducted in duplicate on the same cartridge three times. After each sample extraction, the cartridges were preconditioned as described in Section 2.5 before the extraction process was repeated. As the 10 ml of acetone correspond to more than 20 times the void volume of the sorbent, it should efficiently remove most of the residual organic matter remaining on the cartridges. The same experiment was also conducted on effluent samples. For both types of samples, the recoveries of the phenols remained relatively unchanged after three repeated extractions. Although the upper frits were plugged with particulate matter from the effluent samples, the flow of samples was not hindered significantly.

4. Conclusions

SPE using LiChrolut EN cartridges was shown to be very efficient for the extraction of phenols from waste water owing to the sorbents uniquely high adsorption capacity. Good analyte recoveries were obtained for the hydrophilic and polar compounds tested, which C_{18} and GCB sorbents failed to efficiently extract. Recoveries were found to remain high even for samples consisting of large amounts of organic matter. The SPE procedure described can be

Table 5
Concentrations of phenolic compounds obtained when analysing samples provided by NATA using SPE and solvent extraction

Compound	Concentration (ppb)					
	Sample 1			Sample 2		
	SPE[a]	Solvent extraction	NATA result	SPE[a]	Solvent extraction	NATA result
Phenol	63.8 (79.5)	63.8	39.7±21.0	92.0 (109.4)	86.0	60.15±29.7
2-Chlorophenol	34.6 (29.6)	42.6	42.4±7.4	93.1 (83.2)	105.4	111.00±26.8
2,4-Dinitrophenol	76.3 (81.4)	–[b]	82.7±41.6	118.1 (128.9)	–[b]	132.50±44.3
Pentachlorophenol	74.6 (66.7)	58.8	64.8±12.1	119.2 (103.3)	91.7	100.35±25.0

[a] Results in parentheses were determined by HPLC–UV.
[b] 2,4-Dinitrophenol could not be accurately quantified using the solvent extraction method.

coupled with either GC or LC detection methods. On-column derivatisation with a benzylation reagent in GC and detection with a mass spectrometer in NICI mode is able to provide detection limits at ppt levels for phenol and the chlorophenols tested. Determination of 2,4-dinitrophenol using HPLC-UV at 280 nm provided lower detection limits than those obtained by GC–MS.

This method compared favourably with the solvent extraction method routinely used in this laboratory when analysing samples provided in a NATA proficiency testing programme.

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