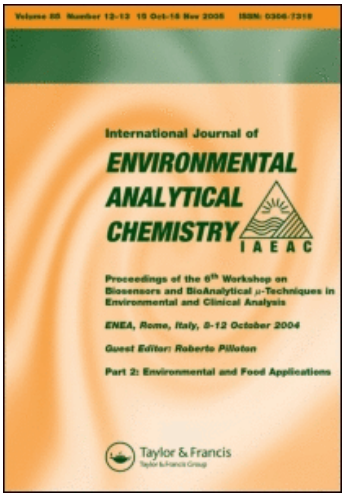

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Spectrophotometric Determination of Phenols in Water Samples by the GHPSAM Method

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SPECTROPHOTOMETRIC DETERMINATION OF PHENOLS IN WATER SAMPLES BY THE GHPSAM METHOD

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The generalized H-point standard-additions method (GHPSAM) is proposed in order to obtain the phenol concentration in water samples when the matrix is completely unknown. The procedure involves solid-phase extraction in BondElut PPL cartridges and data handling of the UV-visible spectrophotometry measurements. The spectral regions where the unknown interferent behaviour can be considered as linear are found and the analyte concentration free from bias error is estimated. The percentages of recovery of phenols in spiked samples were similar to those obtained by HPLC. Cresols or chlorophenols can be also determined in real samples by this method. The concentration range tested was 0.075 – 12.5 mg L^{-1} and the limits of detection found were in the 2.4 – 5.4 μg L^{-1} range. The method has been applied to real harbour water samples. The results obtained are compared to those provided by HPLC.

Keywords: GHPSAM; solid-phase extraction; UV-visible spectrophotometry; phenols

INTRODUCTION

Phenol and its derivates are serious water pollutants. Small amounts of phenols directly influence taste and smell of water. The environmental pollution proceeds from industrial sources by the manufacture of dyes, papers, plastics, drugs, and antioxidants or from the use of phenols as pesticides and insecticides. Laws in most countries limit the concentration of phenols in drinking water. The upper limit for total phenol in drinking water is fixed at 0.5 μg/L by the EU-Directive 80/778, in bathing water was fixed at 50 μg/L by 76/160/CEE and surface water intended for the abstraction of drinking water was fixed at 1–100 μg/L by 75/440/CEE.

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A rapid, accurate and sensitive procedure is required for phenol determination in water. The reference method is based on the oxidative coupling reaction with 4-aminoantipyrine (4-AAP) and absorbance measurement at 510 nm[1]. This reagent has some disadvantages as the para-substituted phenols can not be determined and it also requires preliminary distillation of the sample to separate the interferents. The detection limit is 0.5 μg/L with chloroform extraction method and 1 μg/L with direct photometric method.

However, the definitive method is the coupling of gas chromatography and mass spectrometic detection with a previous extraction step, such as liquid-liquid extraction[2], extractive two-phase isobutoxy derivatization with subsequent solid-phase extraction[3], solid-phase microextraction[4] or membrane solid-phase extraction[5]. The range of detection limits of these methods is 0.1 – 1 μg/L.

Other analytical methods proposed for the determination of phenols include spectrotrophotometric procedures involving the reaction with iodine monobromide[6], gas chromatography-FID[1,7], HPLC[8,9], electrochemical[10]and chemiluminescent[11] techniques. FIA assemblies with on-line solid-phase extraction have been described but using the 4-AAP reaction[12,13]. Moreover, an ultraviolet multiwavelength absorptiometry method (UVMA) has been used to correct the background signal when directly measuring in the UV-visible range[14]. The range of detection limits of these methods is 0.2 – 50 μg/L.

Our research group has demonstrated how the generalized H-point standard addition method (GHPSAM)[15,16] can estimate with a very low error the analyte concentration in a sample where unknown interferents are present. The method is based on the location of linear spectral intervals for interferences in the entire spectral region measured.

In the present study, the GHPSAM is proposed as an alternative to the existing methods to estimate the concentration of the phenols (phenol, o-cresol, m-cresol, p-cresol, 4-chlorophenol and 4-chloro-3-methylphenol) in natural waters and in wastewaters. The analytical method is based on solid-phase extraction and on the direct measurement of the absorbance of the compounds. The method allows for directly enriching and quantifying phenolic compounds in water in the presence of unknown interferents in a wide range of concentrations.

EXPERIMENTAL

Apparatus and reagents

For the measurements a Hewlett-Packard HP8453 UV – visible diode-array spectrophotometer (Palo Alto, CA, USA) equipped with a 1-cm pathlength quartz cell was used. The spectrophotometer was interfaced to a Hewlett-Packard Vector XM 5/90 personal computer.

The chromatography system consisted of a quaternary pump (Hewlett-Packard, 1050 series) and an automatic sample injector (Hewlett-Packard, 1050 series). For detection, a UV detector (Hewlett-Packard, 1100 series) was used; the UV signal was monitored at 220 nm.

The following reagents were used: phenol (Panic, Spain), o-cresol (Merck, Germany), m-cresol (Merck), p-cresol (Merck), 4-chlorophenol (Aldrich-Chemie, Germany) and 4-chloro-3-methylphenol (Aldrich-Chemie), methanol (Lichrosolv, Germany), acetonitrile (Baker, Holland). The solutions were prepared in water (nanopure, Sybron, Barnstead, Spain). The extraction cartridges were BondElut™ PPL (6 mL/500 mg) (Varian, USA).

A Lichospher 100 RP_{18} 5 μm, 125 mm × 4 mm I.D. (Merck) column was used. The mobile phase was an acetonitrile-water mixture (40:60, v/v) at a flow-rate of 1 mL/min. The volume of sample injected was 20 μL. All solvents were filtered with nylon membranes, 0.45 μm (Tecknokroma, Spain) and degassed with helium before use.

Procedure

In previous research, the solid-phase extraction using BondElut™ PPL cartridges was optimised for phenolic compounds (unpublished own work).

The extraction columns were previously conditioned by drawing through 2 mL of methanol, followed by 5 mL of acidic water (H_3PO_4) at pH = 3.

The acidic phenolic solutions (H_3PO_4 was used to set the pH of the solutions to 3) were transferred to the cartridge and washed with 1 mL of acetonitrile-water (25:75 v/v). After that, the phenolic compounds were eluted from the column with 3 mL acetonitrile-water (50:50 v/v). The absorbance between 220–400 nm was recorded.

Harbour samples were spiked with phenol (0.075–0.75 mg L^{-1}) or with a phenolic compound (0.03 and 0.12 mg L^{-1}); the pH was adjusted with a concentrated H_3PO_4 solution to 3. The range of processed water volume varied between 100 – 1000 mL; the analytes were preconcentrated in the solid-phase extraction cartridge as described above.

To develop the calculations for the GHPSAM, programs written in VisualBasic language (Microsoft Excel®) were used.

RESULTS AND DISCUSSION

Location of the spectral linear intervals for the unknown interference

As explained in the appendix A, the GHPSAM is based on the selection of three wavelengths where the signal of the unknown interference can be linearly related

to the wavelength. Two methods have been proposed to carry out the selection[15,16]. The first one is described in the appendix A and is preferred due to the simplicity of the calculations. The horizontal intervals of wavelengths for the $A''_{S,j}/M''_j$ quotient plots are selected, being $A''_{S,j}$ the second derivative of the sample spectrum and M''_j the second derivative of the molar absorption coefficient of the phenolic compound, obtained from standard solutions.

First of all, the applicability of the recovery assays in this type of sample was evaluated. The UV – visible spectra of phenol solutions, water samples and spiked-samples showed that the absorbance values were additive. Then, it was concluded that no reaction takes place with the species present in these samples. This fact allowed the study of spiked samples because the spiked amount of analyte did not suffer any change.

Figure 1(a) shows the spectra of standard solutions with 10 mg L^{-1} of the studied analytes: phenol, o-cresol, m-cresol, p-cresol, 4-chloro-phenol and 4-chloro-3-methylphenol. The spectra of water samples and spiked samples with 10 mg L^{-1} of phenol after the concentration step for different processed water volume (range 100 – 1000 mL) are presented in Figure 1(b). One can see the small analyte signal and interferent signal ratio.

In Figure 2, an example of $A''_{S,j}/\varepsilon''_j$ vs. λ_j plot for spiked and non-spiked water samples is shown. As the theoretical basis establishes, in the interval where this quotient is constant, the spectral interferent behaviour can be considered as linear. The selection of three wavelengths within this interval will yield the analyte concentration free of bias error. In spite of the noise, the signals in the interval 260–290 nm were considered as adequate for the calculation of phenol concentration. The possible divisions by zero (inflection points for the analyte, see Figure 1) must be considered in order to eliminate them because of the abnormal high or low ratio values that can be obtained.

The $A''_{S,j}/\varepsilon''_j$ vs. λ_j plots provide previous estimation of the concentration of the analytes that is equal to the constant ordinate value. Nevertheless, those predictions are affected by an error, since they are obtained using second derivatives and the signal to noise ratio is increased. Then, these values are not definitive, but they are suitable to select the linear interval of the interference and to obtain an initial estimation of the concentration of the analyte.

For the interval 260–290 nm, an additional study of the spectral interference linearity was carried out, see appendix B, because the absorption maximum of the analyte spectrum was included in it[17]. The wavelength couples lying on both sides of the analyte maximum that presented the same absorbance for the analyte ($A_{Xj} = A_{X,k}$) were selected. The difference between the absorbances $\Delta A_{Xj,k}$ at these wavelengths (λ_j and λ_k) was constrained to be lower than 2.5 %. Dividing $\Delta A_{S,j,k}$ by the corresponding $\Delta\lambda_{j,k}$, we will obtain a value, that will be

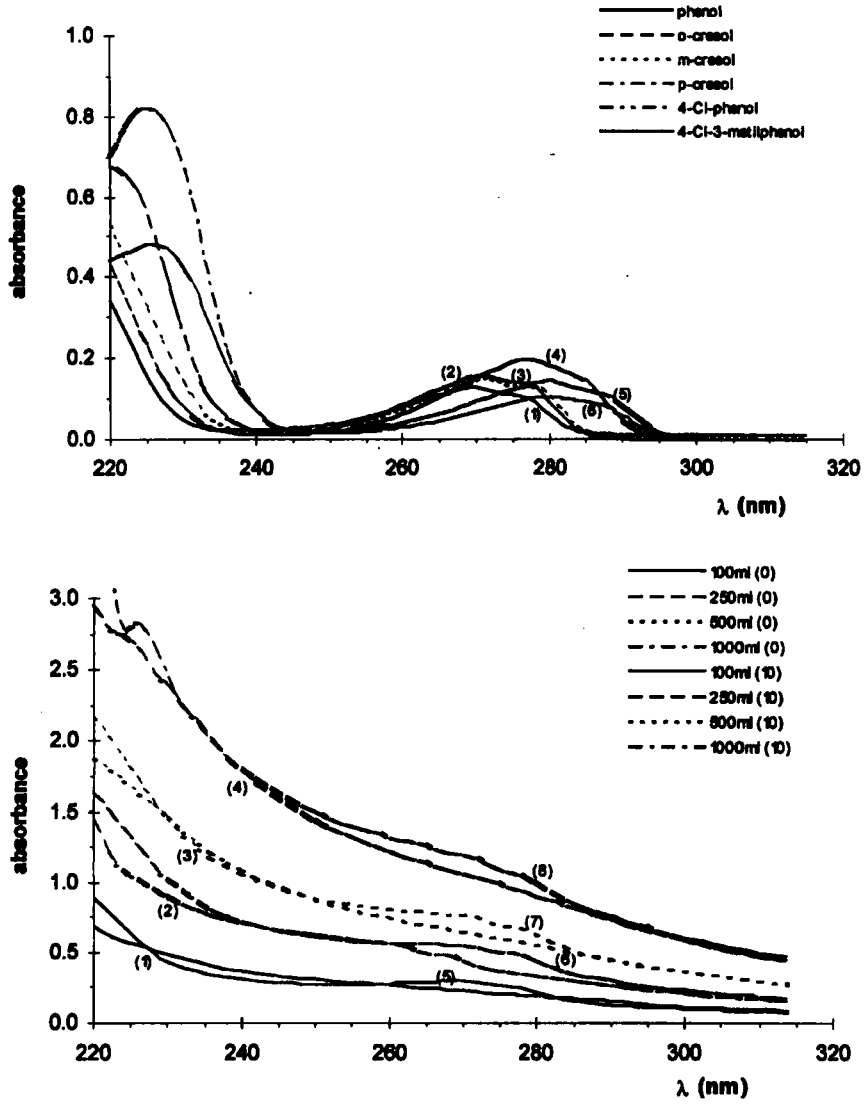

FIGURE 1 (a) UV-visible spectra of standard solutions of analytes (10 mg L^{-1}): phenol, o-cresol, m-cresol, p-cresol, 4-chloro-phenol and 4-chloro-3-methylphenol. (b) UV-visible spectra of the water samples non-spiked (0) and spiked with 10 mg L^{-1} of phenol (10) for different processed water volume (100- 1000 mL)

equivalent to the first derivative value of the sample at the maximum absorbance of the analyte if the interferent is linear. Another kind of spectral behaviour of the

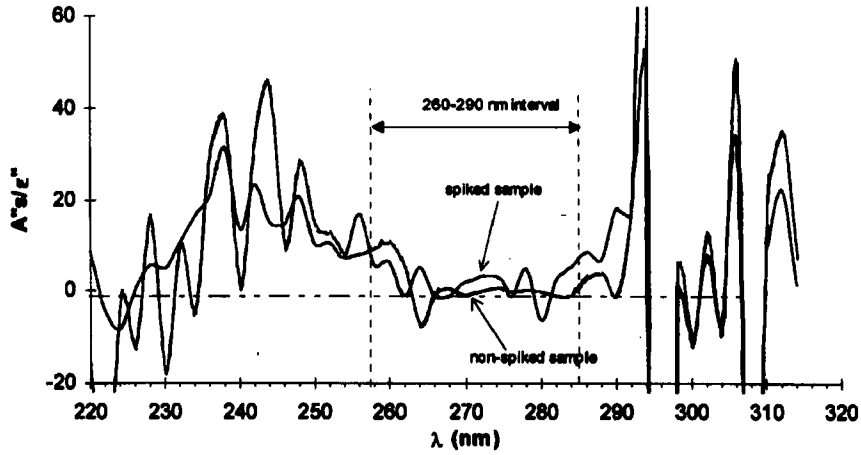

FIGURE 2 Representation $A''_{S,j}/\varepsilon''_{phenol,j}$ vs. λ_j for harbour water non-spiked and spiked sample with 0.3 mg L^{-1} of phenol (after preconcentration step ~10 mg L^{-1})

interferent will produce $\Delta A_{S,j,k}/\Delta\lambda_{j,k}$ values completely different for each wavelength increment. $\Delta A_{S,j,k}/\Delta\lambda_{j,k}$ quotients with a big variation for all possible wavelength increments (λ_j and λ_k) and/or statistically different of $(dA/d\lambda)^S_{\lambda m}$ indicate that the interferent spectrum is not linear in the wavelength range selected.

Tables I and II show the estimated values for $\Delta A_{S,j,k}/\Delta\lambda_{j,k}$ and the first-derivative spectrum values $(dA/d\lambda)^S_{\lambda m}$ for the harbour samples at the maximum absorbance wavelength of each species (λ_m). The estimated values of $\Delta A_{S,j,k}/\Delta\lambda_{j,k}$ were included in the interval $(dA/d\lambda)^S_{\lambda m} \pm 3 \times s((dA/d\lambda)^S_{\lambda m})$. The results obtained for different processed water volume are consistent. Thus, according to the theoretical background, the interference linearity at the interval 260–290 nm is confirmed.

Estimation of the concentration of the analyte

The concentration of the analyte can be obtained by applying the GHPSAM equations for 260 – 290 nm interval. The selection of the three wavelength sets (A_k, A_j, A_l) is based on the following criteria: a distance between the three wavelengths greater than 4 nm and a determination coefficient (r^2) for the resulting calibration curve ($A_k - q\,A_j - p\,A_l$ vs. c) greater than 0.995. The final predictions are obtained as an average of the results provided by the 50 absorbance increments with the highest slope of the calibration curve, see appendix A.

TABLE I Values of $\Delta A_{S,j,k}/\Delta\lambda_{j,k}$ estimated in the interval 260–290 nm and value of $(dA/d\lambda)^{S}_{\lambda m}$ with λ_m = 270 nm, for phenol samples. The standard deviation (s) is also included for both values

volume water (mL)	$c_{spiked\ phenol}$ *(mg L^{-1})*	$\Delta A_{S,j,k}/\Delta\lambda_{j,k}$	$s(\Delta A_{S,j,k}/\Delta\lambda_{j,k})$	$(dA/d\lambda)^{S}_{\lambda m} \pm 3 \times s\ (dA/d\lambda)$
100	0	–0.0039	0.0005 (n = 11)	–0.0058 ± 0.0006
100	0.3	–0.0024	0.0002 (n = 11)	–0.003 ± 0.002
100	0.785	–0.0008	0.0007 (n = 11)	0.000 ± 0.002
250	0	–0.0112	0.0010 (n = 9)	–0.023 ± 0.005
250	0.3	–0.0071	0.0007 (n = 9)	–0.011 ± 0.007
500	0	–0.0095	0.0002 (n = 10)	–0.0094 ± 0.0002
500	0.06	–0.0076	0.0009 (n = 10)	–0.007 ± 0.002
1000	0	–0.0152	0.0003 (n = 10)	–0.0130 ± 0.0012
1000	0.03	–0.0155	0.0011 (n = 10)	–0.0133 ± 0.0017
1000	0	–0.0178	0.0009 (n = 11)	–0.0178 ± 0.0013
1000	0.075	–0.0128	0.0028 (n = 11)	–0.010 ± 0.003

TABLE II Values of $\Delta A_{S,j,k}/\Delta\lambda_{j,k}$ estimated in the interval 260–290 nm and value of $(dA/d\lambda)^{S}_{\lambda m}$, for cresol and chlorophenol samples. The standard deviation (s) is also included for both values

	vol. water (ml)	c_{spiked} *(mg L^{-1})*	$\Delta A_{S,j,k}/\Delta\lambda_{j,k}$	$s(\Delta A_{S,j,k}/\Delta\lambda_{j,k})$	$(dA/d\lambda)^{s}_{\lambda m} \pm 3 \times s(dA/d\lambda)$
o-cresol	250	0	–0.0061	0.0004 (n = 12)	–0.0066 ± 0.0006
	250	0.12	–0.0053	0.0005 (n = 12)	–0.0061 ± 0.0016
λ_m = 270 nm	1000	0	–0.0198	0.0016 (n = 12)	–0.023 ± 0.004
	1000	0.03	–0.0189	0.0016 (n = 12)	–0.023 ± 0.003
m-cresol	250	0	–0.0062	0.0004 (n = 10)	–0.0060 ± 0.0010
	250	0.12	–0.0050	0.0010 (n = 10)	–0.0036 ± 0.0005
λ_m = 271 nm	1000	0	–0.0197	0.0012 (n = 10)	–0.021 ± 0.003
	1000	0.03	–0.0213	0.0015 (n = 10)	–0.022 ± 0.002
p-cresol	250	0	–0.0058	0.0001 (n = 12)	–0.0054 ± 0.0002
	250	0.12	–0.0048	0.0007 (n = 12)	–0.0046 ± 0.0015
λ_m = 277 nm	1000	0	–0.0175	0.0009 (n = 12)	–0.0180 ± 0.0011
	1000	0.03	–0.0171	0.0016 (n = 12)	–0.0161 ± 0.0012
4-chloro	250	0	–0.0056	0.0001 (n = 10)	–0.0056 ± 0.0001
phenol	250	0.12	–0.0058	0.0002 (n = 10)	–0.0056 ± 0.0001
λ_m = 280 nm	1000	0	–0.0167	0.0004 (n = 10)	–0.0163 ± 0.0010
	1000	0.03	–0.0180	0.0006 (n = 10)	–0.0174 ± 0.0007
4-chloro-3-	250	0	–0.0056	0.0001 (n = 10)	–0.0055 ± 0.0001
methylphenol	250	0.12	–0.0047	0.0006 (n = 10)	–0.0046 ± 0.0010
λ_m = 280 nm	1000	0	–0.0166	0.0002 (n = 10)	–0.0154 ± 0.0010
	1000	0.03	–0.0169	0.0003(n = 10)	–0.0177 ± 0.0014

The estimated recoveries for the phenol standard solutions by the GHPSAM are presented in the Table III. The predictions were compared with the results obtained by subtracting the sample absorbance at $\lambda = 270$ nm, maximum absorbance of phenolic spectrum, to the blank solution ($A_{S,270} - A_{b,270}$). Both solutions were identically processed. As it can be seen in the table III, for the standard solutions, the results agree regardless of the sample volume used (6 – 1000 mL) and the concentration of phenol in the sample (0.0375 – 12.5 mg L^{-1}). Using these values, the variation coefficient obtained was 8.5 %.

TABLE III Recovery comparison for phenol standard solutions using nanopure water

volume water (mL)	$c_{spiked\ phenol}$ (mg L^{-1})	*% recovery GHPSAM*	*% recovery* $A_{S,270}$-$A_{b,270}$
6	6.25	100 ± 11	112.5
	12.5	75 ± 6.5	89.5
12	3.1	95 ± 10	98.5
	6.25	80 ± 8	75
18	2.1	68 ± 6	77
	4.2	82.5 ± 7.5	80
24	1.3	88 ± 8	92
	3.1	83.5 ± 7.5	78
30	1.25	96 ± 7	99.5
	2.5	94 ± 9	97.5
36	1	86 ± 8	90.5
	2.1	86 ± 7.5	89
42	0.9	84 ± 7	83
	1.8	80.5 ± 6.5	79
48	0.8	94 ± 8	94
	1.6	79.5 ± 6.5	80
100	0.375	87 ± 8	91
	0.75	82 ± 7.5	81.5
250	0.15	84 ± 8	90
	0.3	81 ± 7	85
500	0.075	82 ± 6	89
	0.15	89 ± 8	90
1000	0.0375	80 ± 6	86
	0.075	80 ± 7	88

An analysis of variance (ANOVA) was contucted. First, the influence of sample volume was evaluated. The recoveries are independent of sample volume as the results were $F_{calculated}$= 1.89 and $F_{k\text{-}1,k(h\text{-}1)}$ = 2.94 for a level of significance of α = 0.05, where *k-1* is the degrees of freedom among *k*-groups and *k(h-1)* is the degrees of freedom within groups with *h*-values. The influence of concentration of phenol was evaluated considering 5 levels of concentration being the upper limits 12.5, 2.5, 1.25 and 0.3 mg L^{-1}. These levels satisfy the basic assumptions of ANOVA: the data has to be normally distributed and the variances have to be equal for all samples (Hartley's test). The value $F_{calculated}$ = 7.48 is lower than the critical value $F_{k\text{-}1,\ k(h\text{-}1)}$ = 14.17. This indicates that the recoveries are independent of the concentration of phenol.

The independent samples t-test shows that the means obtained by the two methods are statistically similar ($t = -1.421$, 46 degrees of freedom and α = 0.162). The variances of the two methods are homogenous ($F = 0.369$, $\alpha = 0.546$).

Spiked real samples were tested by the GHPSAM. Such samples were also chromatographed. Figure 3 shows the recoveries obtained for phenol samples and phenolic derivative samples. Three values were compared: GHPSAM, HPLC and the results obtained from ($A_{S,\lambda m} - A_{b,\lambda m}$), where $A_{S,\lambda m}$ is the absorbance of the spiked sample and $A_{b,\lambda m}$ is the absorbance of the non-spiked sample at the maximum absorbance wavelength of each species (λ_m). The method based on the ($A_{S,\lambda m} - A_{b,\lambda m}$) value can only be used in recovery studies because the absorbance of the non-spiked sample is known. The GHPSAM does not need a phenol-free sample, it locates the linear interval from the register of the sample with or without phenol.

For phenol determination, the independent samples t-tests show that the means obtained by GHPSAM are statistically similar to ($A_{S,\lambda m} - A_{b,\lambda m}$) or HPLC methods ($t = 0.684$, 10 degrees of freedom, $\alpha = 0.509$ and $t = 1.128$, 10 degrees of freedom, α = 0.286, respectively). The variances of the two methods tested are homogenous ($F = 3.379$, $\alpha = 0.096$ and $F = 0.556$, $\alpha = 0.473$, respectively). For the other phenols similar results were obtained.

The GHPSAM results are in agreement with the HPLC results. The concentration factor achieved by the procedure was between 33.3 and 333 for this method, based on the measurement of the phenolic native absorption.

The GHPSAM results for harbour water samples are shown in Table IV. The estimated concentrations in the final concentrated solution and in the harbour sample are included. The calculated values for the analyte concentration (mean ± standard deviation) are consistent for the different processed water volume (100 – 1000 mL). In all cases, the estimated concentrations of phenol and of its derivates in the harbour water samples are similar to the limit of detection. The

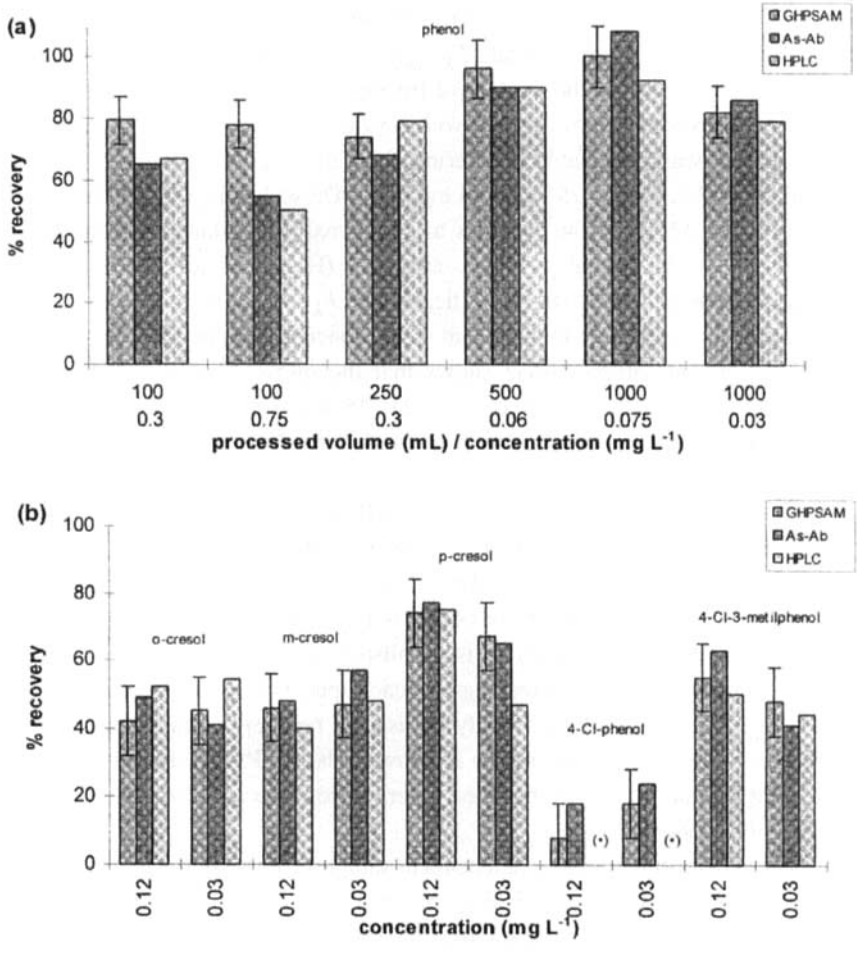

FIGURE 3 Comparison of the recoveries for harbour samples spiked with phenol (a) and spiked with other phenolic compounds (b). The values compared were obtained by the GHPSAM, by the difference of absorbances between spiked ($A_{S,\lambda m}$) and non-spiked ($A_{b,\lambda m}$) samples at the maximum absorbance wavelength of each species (λ_m) and by HLPC. The symbol (•) indicates a signal inferior to the limit of detection

limits of detection were calculated as $3s_a/b$, being s_a the standard deviation of the intercept and b the slope of the calibration curve of the phenolic compound. By the use of the maximum concentration factor of the liquid-solid proposed method these values were: 2.4 μg/L (phenol), 4.8 μg/L (o-cresol), 2.8 μg/L (m-cresol), 1.2 μg/L (p-cresol), 5.4 μg/L (4-chloro-phenol) and 4.8 μg/L (4-chloro-3-methylphenol). Detection limits achieved were similar to those of other proposed methods.

TABLE IV Estimated predictions for the final concentrated solution and the non-spiked harbour water samples by the GHPSAM

analyte	*volume water (mL)*	$c_{extract}$ *GHPSAM (mg* L^{-1}*)*	c_{sample} *GHPSAM (mg* L^{-1}*)*
phenol	100	−0.35 ± 0.17	−0.0105 ± 0.005
	250	−0.38 ± 0.15	−0.0046 ± 0.0018
	500	1.2 ± 0.2	0.0072 ± 0.0012
	1000	0.9 ± 0.5	0.0027 ± 0.0015
	1000	1.8 ± 0.4	0.0054 ± 0.0012
o-cresol	250	−0.6 ± 0.07	−0.0072 ± 0.0008
	1000	−1.4 ± 0.2	−0.0042 ± 0.0006
m-cresol	250	−0.1 ± 0.11	−0.0012 ± 0.0013
	1000	−0.7 ± 0.4	−0.0021 ± 0.0012
p-cresol	250	−0.08 ± 0.07	−0.0010 ± 0.0008
	1000	0.6 ± 0.2	0.0018 ± 0.0006
4-chloro-3-	250	−0.06 ± 0.19	−0.001 ± 0.002
methylphenol	1000	1.1 ± 0.6	0.0033 ± 0.0018
4-chlorophenol	250	0.15 ± 0.1	0.0018 ± 0.0012
	1000	0.9 ± 0.5	0.0027 ± 0.0015

These estimations agree with the absence of chromatography peaks when these samples were chromatographed according to the optimised conditions. The chromatography signal is inferior to 3 times the noise signal. An example of a chromatogram of harbour sample non-spiked and spiked with 0.3 mg L^{-1} of each phenolic compound is presented in Figure 4. It can be seen that the chromatographic signals of water samples, at the retention times of each analyte, are similar to the limit of detection, even for the two different processed volumes.

CONCLUSIONS

Our study demonstrates that the GHPSAM provides the concentration of an analyte, phenolic compounds, in water samples with unknown interferences.

The preconcentration step in BondElut PPL cartridges presents an acceptable reproducibility for a wide range of processed water volume and a wide interval of analyte concentrations. Moreover, the use of pre-treatment procedures, such as distillation or extraction, with expensive and environmentally harmful organic

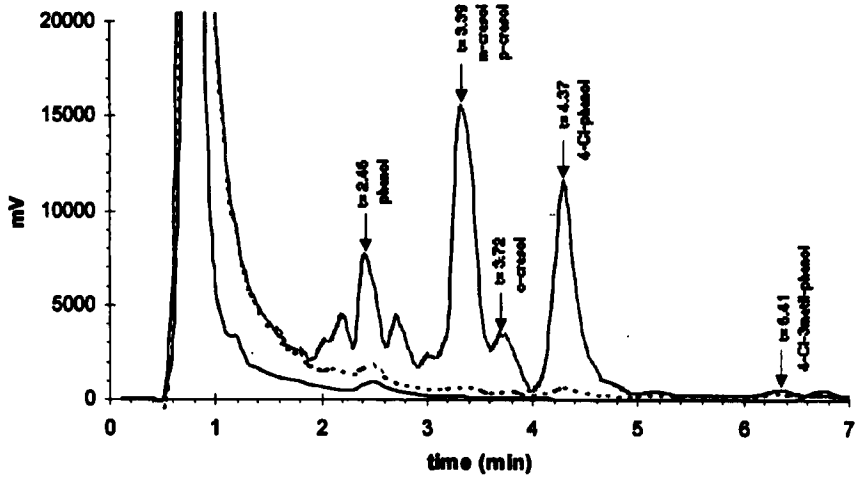

FIGURE 4 Chromatograms obtained for water sample with different processed volumes: 500 mL (solid line) and 1000 mL (dashed line) and for a sample spiked with 0.3 mg L^{-1} of each phenolic compound with a concentration factor equal to 333 (dotted line). The retention times of each analyte are included. For experimental details, see text

solvents is avoided. The combination of this preconcentration step and the treatment of the analyte signal by the GHPSAM allows good limits of detection and removes and cancels out the unknown interferent signals. The proposed method is not attended to replace the powerful and definitive GC-MS method, it can be an alternative for screening samples or for laboratories where this technique is not present. The proposed method is cheaper, fast and does not requiere qualified personnel.

The principal advantage of this method is that no reaction is required for the determination since the particular absorbance characteristics of the phenols are used. There are no restrictions for analysis of para-substituted phenols, as there are with methods based on reaction with 4-aminoantipyrine (4-AAP), so the determination of p-cresol, 4chlorophenol or 4-chloro-3-methylphenol is possible.

With regard to the analytical parameters, limit of detection and the dynamic range of concentrations, the method proposed is similar to the other proposed methods.

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APPENDIX A: GHPSAM THEORETICAL BACKGROUND

The GHPSAM[15,16] makes it possible to estimate the concentration of an analyte in the presence of an unknown interferent. The first step to apply the GHPSAM is the location of linear intervals in the interferent spectrum.

Let us assume that X is the analyte or the selected form of it to be determined and Z is the unknown global interference. If the spectral behaviour of the interferent Z ($A_{Z,j}$) in the range of wavelengths λ_l-λ_m, can be described as a straight line with an a intercept and a b slope then it can be written:

$$A_{Z,j} = a + b\lambda_j \quad \lambda_j \in [\lambda_l, \lambda_m] \qquad [A.1]$$

The absorbance of the sample S at each wavelength in the interval selected will be the sum of the absorbances of X at a concentration $c_X$and of Z:

$$A_{S,j} = A_{X,j} + A_{Z,j} = M_{X,j}c_X + a + b\lambda_j \qquad [A.2]$$

where $A_{X,j}$ is the absorbance at λ_j of X and M_j is the molar absorption coefficient and the optical path product (or related measure) at λ_j of the analyte X.

The second derivative absorbance of the sample with regard to the wavelength in this interval is:

$$A''_{S,j} = \frac{d^2A_{X,j}}{d\lambda^2} + \frac{d^2A_{Y,j}}{d\lambda^2} = M''_j\ c_X \qquad [A.3]$$

Equation [A.3] can be re-written as:

$$\frac{A''_{S,j}}{M''_j} = c_X \qquad [A.4]$$

Thus, when plotting the values of the ratio $A''_{S,j}/M''_j$ vs. λ_j constant values equal to the analyte concentration will be obtained in those intervals where the interferent spectrum presents a linear behaviour.

Three wavelengths λ_j, λ_k and λ_l within the interferent linear interval [λ_l, λ_m] must be selected to calculate the concentration of the analyte. The absorbance of the sample at those wavelengths, considering that the standard addition method has been followed, can be written as:

$$\begin{aligned} A_{S,j} &= M_{X,j}\ c^0_X + M_{X,j}\ c^i_X + a + b\lambda_j \\ A_{S,k} &= M_{X,k}\ c^0_X + M_{X,k}\ c^i_X + a + b\lambda_k \\ A_{S,l} &= M_{X,l}\ c^0_X + M_{X,l}\ c^i_X + a + b\lambda_l \end{aligned} \qquad [A.5]$$

where c^0_X is the analyte concentration in the sample, c^i_X is the analyte added concentration (the i superscript denotes the different standard additions) and $M_{X,j}$, $M_{X,k}$ and $M_{X,l}$ are the slopes of the calibration lines (or the molar absorption coefficients or related measure) at λ_j, $\lambda_k$and λ_l of the analyte X.

Two parameters, p and q, can be defined as:

$$p = \frac{\lambda_k - \lambda_j}{\lambda_l - \lambda_j} \quad q = \frac{\lambda_l - \lambda_k}{\lambda_l - \lambda_j} \qquad [A.6]$$

and also two lines can be defined as the weighted differences between $A_{S,j}$ and $A_{S,l}$ and between $A_{S,j}$ and $A_{S,k}$

$$q\Delta A_{S,j,l} = q(A_{S,j} - A_{S,l}) = q\Delta M_{j,l}\ c_X^0 + q(A_{Z,j} - A_{Z,l}) + q\Delta M_{j,l}\ c_X^i$$
$$p\Delta A_{S,j,k} = p(A_{S,j} - A_{S,k}) = p\Delta M_{j,k}\ c_X^0 + p(A_{Z,j} - A_{Z,k}) + p\Delta M_{j,k}\ c_X^i \qquad [A.7]$$

These two lines allow the calculation of the concentration of the analyte from the abscissa of their intersection point, the so-called H point ($-c_H$, ΔA_H), where c_H is equal to c_X^0, the analyte concentration in the sample:

$$-c_H = \frac{q\Delta A_{S,j,l} - p\Delta A_{S,j,k}}{q\Delta M_{j,l} - p\Delta M_{j,k}} = \frac{A_{X,k}^0 - qA_{X,j}^0 - pA_{X,l}^0}{qM_j + pM_l - M_k} \qquad [A.8]$$

From this expression we can optimise the wavelengths (λ_j, λ_k and λ_l) to be those that make bigger the denominator in equation [A.8], in order to obtain the most accurate results.

APPENDIX B: STUDY OF THE FIRST DERIVATIVE VALUE AT THE ANALYTE ABSORPTION MAXIMUM FOR THE INTERFERENCE LINEAR INTERVAL LOCATION

We previously[17] reported a complementary procedure for the location of linear intervals in the interferent spectrum. The linearity of the interferent, Z, was located by considering the value of the sample first derivative spectrum equal to the value of the first derivative of the interferent at the wavelength of the maximum absorbance (λ_m) of the analyte, X.

$$\left(\frac{dA}{d\lambda}\right)^{S}_{\lambda_m} = \left(\frac{dA}{d\lambda}\right)^{Z}_{\lambda_m} \qquad [B.1]$$

Selecting a couple of wavelengths λ_j and λ_k where the analyte presents the same absorbance ($A_{X,j} = A_{X,k}$), the absorbance increment $\Delta A_{S,j,k}$can be written as:

$$\Delta A_{S,j,k} = A_{Z,k} + A_{X,k} - A_{Z,j} - A_{X,j} = A_{Z,k} - A_{Z,j} \qquad [B.2]$$

Dividing $\Delta A_{S,j,k}$ by the corresponding $\Delta\lambda_{j,k}$, a value equal to the sample first derivative at λ_m will be obtained if the interferent is linear in this wavelength interval.

$$\frac{\Delta A_{S,j,k}}{\Delta\lambda_{j,k}} = \frac{A_{i,j} - A_{l,k}}{\lambda_j - \lambda_k} = \left(\frac{dA}{d\lambda}\right)^{S}_{\lambda_m} \qquad [B.3]$$

The value of $\Delta A_{S,j,k}/\Delta\lambda_{j,k}$ must be included in the interval $(dA/d\lambda)^{S}_{\lambda_m} \pm 3 \times s((dA/d\lambda)^{S}_{\lambda_m})$ in order to consider the absorbance of the interferent as linear in that range of wavelengths.