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Head space voltammetry: A novel voltammetric method for volatile organics and a case study for phenol

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ABSTRACT

Present paper describes the results of a novel method which combines the Head space (HS) preconcentration of the analyte on the electrode prior to the voltammetric analysis. Thereafter, the method was called HS-Voltammetry. The performance of the method was tested upon using an electroactive and volatile molecule, phenol molecule, which gives an oxidation peak at conventional electrodes. In this study, a glassy carbon electrode was modified with polypyrrole by electropolymerization and then, the electrode was placed over the solution in a sealed vial heated gently on a hotplate with a stirrer for phenol determination. By controlling the thickness of the polymeric coating and optimizing preconcentration parameters such as vial pH and temperature, stirring rate and exposure time, a very consistent (5.2% at 5.0×10^{-7} M) fraction of the analyte can be extracted during a predetermined time. The oxidation peak current at 0.8 V depended linearly on the phenol concentration over a wide range (3 orders of magnitude). The detection limit was estimated as 7.0×10^{-8} M at 60 °C ($S/N=3$) which is well below the limit set by the European Community for phenols in wastewaters (ca. 5×10^{-6} M). The effect of other phenolic compounds was also examined and it was shown that head space preconcentration eliminated the interference of non-volatile phenolic acids studied. For volatile phenolic compounds, the selectivity can be maintained in cases when isolated peaks are obtained for each component. The proposed method has been applied successfully for the determination of phenol in artificial wastewater and recovery percentage was calculated as 93%.

1. Introduction

In trace analyses, the preconcentration of the analyte plays a vital role in terms of sensitivity, and in some cases, the selectivity. In stripping techniques, this step usually includes an electrochemical deposition process on the electrode surface at a controlled potential under stirred conditions [1]. Despite the wide application of electroanalytical techniques, the selectivity of the methods suffers from the interference of electroactive impurities in the matrices and the electrode performance is usually impaired by the presence of surface active materials [2].

Head Space (HS) techniques, on the other hand, provide a practical tool for determination of volatile organic compounds by simply eliminating any interference from non-volatile components of the sample [3]. In HS sampling, the sample is heated in a sealed vial until the volatile compounds reach the equilibrium with the gas phase above the liquid. The analytes can be selectively preconcentrated on a solid [4] or liquid phase [5] and subsequent detection of target analyte is generally performed by chromatographic techniques. When it is combined with a solid phase micro extraction (SPME) fiber, this solventless technique endow with analyte/matrix separation and preconcentration for volatile organic compounds [3]. The technique is particularly practical for complex matrixes such as wastewaters and clinical samples as many interference problems are eliminated since the fiber is not in contact with the sample [6,7].

Present study includes the earliest results of a novel method which combines the HS preconcentration of the analyte in the polymeric coating on a glassy carbon electrode (GCE) prior to the voltammetric analysis. Thereafter, the method was called HS-Voltammetry. Phenol being a semi-volatile and electroactive molecule was chosen to test the effectiveness of the method.

Phenol and a considerable number of its derivatives are important toxic compounds and are extensively used in several industrial processes such as plastics, dyes, pesticides, papers, and petrochemical products [8]. As a result, phenols are often detected in water, soil and sediment samples [9–14]. Owing to their poor biodegradability, high toxicity and ecological aspects, phenolic compounds have been included in the US Environmental Protection Agency (EPA) list of priority pollutants that should be monitored in the environment [15].

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A number of analytical techniques have been used for analysis of phenols, mostly employing chromatographic based instrumentations such as gas chromatography (GC) [16,17], high performance liquid chromatography (HPLC) [18,19] and also capillary electrophoresis (CE) [20,21] in combination with different detectors. Since their concentration in water is rather low, various methods for preconcentration from water, including liquid–liquid extraction (LLE) [22] and solid phase extraction (SPE) [23,24] have been utilized. In SPME studies, polypyrrole coated fibers were used as HS sorbent for phenolic compound determination by GC [4].

Electrochemical techniques appear to be very promising since they ensure reasonably good analytical performance characteristics with essentially no need for expensive and sophisticated instrumentation [1]. Furthermore, these techniques exhibit a potential for miniaturization and automation that could enable obtaining portable analytical devices. Despite the vast number of publication on voltammetric determination of pollutants in water matrices, only a few are encountered in the literature that utilizes HS preconcentration. A recent study deals with direct voltammetric detection of phenols in wastewaters with an ionic-liquid based probe after preconcentration from HS [25]. The electrode assembly was exposed to the HS in equilibrium with wastewater samples for controlled times, until a convenient preconcentration of volatile phenols was achieved.

Here, we present a simpler method that utilizes a voltammetric electrode modified with a conducting polymer as a head space preconcentration tool for volatile compounds and a transducer as well which allows monitoring the responses. The GCE surface was modified with polypyrrole by electropolymerization to serve as a porous layer for phenol adsorption. Then, the modified electrode was placed over the solution in a sealed vial heated gently on a hotplate with a stirrer for phenol determination. By controlling the thickness of polymeric coating and optimizing preconcentration parameters, a very consistent fraction of the analyte can be extracted during a predetermined time. Therefore, the parameters related to the preconcentration (polymerization cycle number, vial pH, stirring rate, exposure time, salt amount, vial temperature, and sample volume) and measuring cell (cell pH and composition) were optimized. A similar study was published very recently dealing with a head space adsorptive accumulation of nitrobenzene and nitrotoluene on the surface of a multi-walled carbon nanotube modified glassy carbon electrode [26]. The method was applied to the water and wastewater samples with satisfactory recoveries.

2. Experimental

2.1. Reagents

All reagents were analytical reagent grade. Pyrrole (Py) was obtained from Alfa-Aeser and was distilled before the use. Other analytical reagents (sodium dodecylsulfate (SDS), sulfuric acid, sodium hydroxide, glacial acetic acid, o-phosphoric acid, boric acid, sodium chloride, phenol and 2,4-dichlorophenol) were obtained from Merck used without any purification. Britton Robinson (BR) buffer systems were prepared by using 0.04 M glacial acetic acid, o-phosphoric acid and boric acid mixture. Ultrapure water was supplied from Millipore Q. Artificial wastewater sample was prepared by mixing 0.50 g of $(NH_4)_2SO_4$, 1.00 g of $MgSO_4$, 0.1 g of $MnSO_4$, 0.005 g of $FeSO_4$ and known amounts of phenol in 1.0 L of tap water. The pH of this solution was made 2.0 by simply adding H_2SO_4 solution [27].

2.2. Instrumentation

Electrochemical polymerization of Py and voltammetric detection of phenol were performed by using an Autolab PGSTAT 101 potentiostat driven by the corresponding software installed on a computer. The three-electrode system used in this study contained a glassy carbon electrode (id. 3 mm) as the working electrode, a platinum wire as the counter electrode, and a Ag/AgCl as the reference electrode (saturated KCl). Orion 4 star pH meter was used for the pH adjustment. The HS studies were carried out on an IKRA hotplate.

2.3. Electrode preparation

PPy-DS film was directly electrodeposited on the glassy carbon electrode from an aqueous solution containing 0.1 M Py and 7.0×10^{-3} M SDS by using cyclic voltammetry (CV) as described elsewhere [4]. The CV technique was operated using a scan rate of 20 mV s^{-1} at a potential range of 0.5–1.2 V. The number of scans was optimized between 1 and 10 cycles. To remove non polymeric Py from the electrode surface, the electrode was rinsed with ultrapure water and then, the electrode was scanned between 0.0 and 1.2 V in 0.01 M H_2SO_4 supporting electrolyte until a steady state current–voltage profile was obtained.

2.4. Analytical procedure

5 mL of phenol standard or sample solution is pipetted and placed into a 20 mL glass vial. After a certain amount of salt (0.75 g NaCl) is added, the modified electrode is carefully slotted in the silicone septum. The vial is placed on a hot plate and the stirrer is switched on. The electrode is exposed to the HS of the sample for a predetermined time at various temperatures which is controlled by using a thermocouple inserted in a control vial placed next to the real sample vial. At the end of the preconcentration time, the electrode is carefully removed from the vial and transferred to the measuring cell containing BR buffer for subsequent measurement. Stripping voltammograms are recorded in a differential pulse (dp) mode in a potential range of 0–1.2 V at a scan rate of 50 mV s^{-1} with a 25 mV pulse amplitude. All results were obtained in three replicates to ensure reproducibility.

3. Results and discussion

Most of the efforts were dedicated to the optimization of the parameters related to the preconcentration and the measuring step. By controlling the thickness of polymeric coating and preconcentration conditions, a very consistent fraction of the analyte can be extracted.

3.1. The cell pH

Initial studies were conducted to see the effect of pH on the electrochemical signal of phenol at a PPy modified GCE surface. BR buffer systems were used in the pH range of 3.0–11.0. The oxidation peak current of phenol has shown a dependence on the medium pH and the peak current has increased up to 7.0 and then, decreased as the pH increases to 11.0 (Fig. 1). The results were found in good agreement with a previous study [28] and further experiments were performed at pH 7.0. The peak current at this pH was built upon addition of standard phenol solution and a calibration curve was found linear in the concentration range of 1.5×10^{-6}–1×10^{-4} M ($R^2 = 0.9997$) by direct measurement without any preconcentration step.

3.2. The vial pH and the composition

In extraction studies of organic compounds those display weak acidic character, the pH < p*K*a 2 media is recommended to

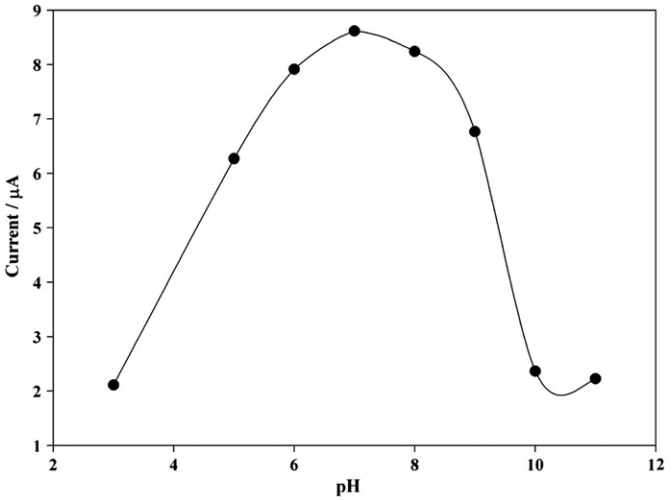

Fig. 1. Dependence of the dp voltammetric response of 2×10^{-4} M phenol prepared in Britton Robinson buffer systems on the medium pH at a PPy modified GCE.

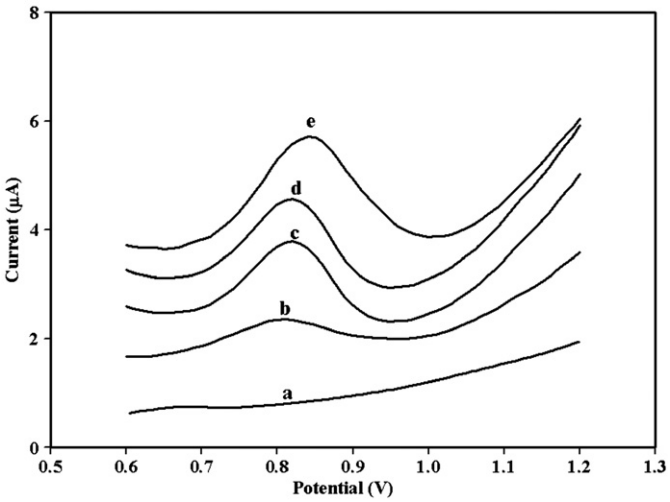

Fig. 2. The effect of PPy film thickness on the voltammetric signal of phenol in pH 7.0 BR buffer after head space preconcentration from 0.01 M H_2SO_4 solution for 15 min at 70 °C where (a) bare GCE, after cycling the potential (b) 1, (c) 3, (d) 4 and (e) 5 subsequent cycles.

Table 1
The effect of vial pH on the characteristics of the voltammetric signal recorded at pH 7.0 BR buffer after 15 min exposure to 2×10^{-5} M phenol at 70 °C.

	H_2SO_4 conc (M)				pH of BR buffer systems				
	1.000	**0.100**	**0.010**	**0.005**	**2.0**	**4.0**	**6.0**	**8.0**	**10.0**
Ep (V)	0.79	0.80	0.75	0.75	0.79	0.80	0.80	0.80	0.80
Ip (µA)	0.425	0.946	2.267	2.107	1.902	1.597	1.587	1.603	0.439

maintain the molecular form in the solution [3]. Considering the weak acidic character of phenol (p*K*a 9.90), the electrode was exposed for 15 min to 10 mL of different concentrations of sulfuric acid (0.005–1.0 M) and BR buffer (2–10) solutions each spiked with phenol standard to be 2×10^{-4} M in the vial. The solution was stirred at 400 rpm throughout the preconcentration step. As follows from Table 1, best results were obtained with 0.01 M H_2SO_4 solution.

3.3. Electropolymerization

The polymeric film thickness, along with the porosity and active surface area, has a major influence on the extraction capacity. In addition, the polymeric film on the electrode should exhibit a conductive character necessary to function as a transducer. The thickness of the film can simply be adjusted by increasing the number of potential scan used in electropolymerization step. The GCE surfaces were coated by cycling the potential between 0.5 and 1.2 V at a scan rate of 20 mV s^{-1} for several times (1–10) in 0.1 M Py solution containing 7.0 $\times 10^{-3}$ M SDS as the dopant as described earlier. As shown in Fig. 2, no peak was observed for 2.0×10^{-4} M phenol at the bare electrode. The anodic peak current of 2.0 $\times 10^{-4}$ M phenol at 0.8 V ascended with the scan number from 1 to 5. After 7th cycle, the oxidation peak was badly affected by the high capacitive current which designates a decrease in the film conductivity. Further experiments were carried out with 5 subsequent scans in polymerization step.

3.4. Salt amount

The addition of an inert salt is known to enhance the evaporation of volatile components from aqueous solutions. In this work, the effect of salt addition on the extraction efficiency has been studied by addition of NaCl in a concentration range of 0–200 g L^{-1} and resulting peak currents were plotted as the average of three replicates against the salt amount (Fig. 3A). Best results were obtained with 150 g L^{-1} NaCl.

3.5. Vial temperature

Preconcentration temperature plays a key role in the HS micro extraction technique. The volatile analytes can effectively dissociate from the matrix at elevated temperatures and move into the HS for rapid extraction by the polymeric coating on the electrode surface. However, the coating/HS distribution coefficient also decreases with an increase of temperature resulting in a decline in the amount of the analyte extracted. Therefore, HS temperature should compromise between the two opposite effects.

A temperature range of 30–75 °C was used to study the extraction temperature on the extraction efficiency of phenol. As shown in Fig. 3B, the extraction effiency increases at elevated temperature. However, a significant decrease in adsorption capacity was observed at 75 °C. It should be noted that adsorption is generally an exothermic process and therefore, the partition coefficient of analytes between HS and fiber decreases at high temperatures. Best results were obtained at 60 °C and this finding was found in agreement with a former study carried out with a PPy coated SPME [4]. Therefore, the vial temperature was set to 60 °C for further studies.

3.6. Exposure time

The time that the electrode was exposed to the head space of the solution was studied in the range of 5–60 min at 60 °C and the stirring rate constant at 400 rpm. A series of 2.0×10^{-4} M standard phenol solutions were prepared and resulting signal was plotted as a function of exposure time (Fig. 3C). A significant rise in the oxidation peak was observed in the first 15 min and then, a sharp decrease was observed for preconcentration times longer than 30 min, probably due to the desorption of adsorbed phenol molecules. Therefore, 20 min was selected as a reasonable compromise between preconcentration and analysis time.

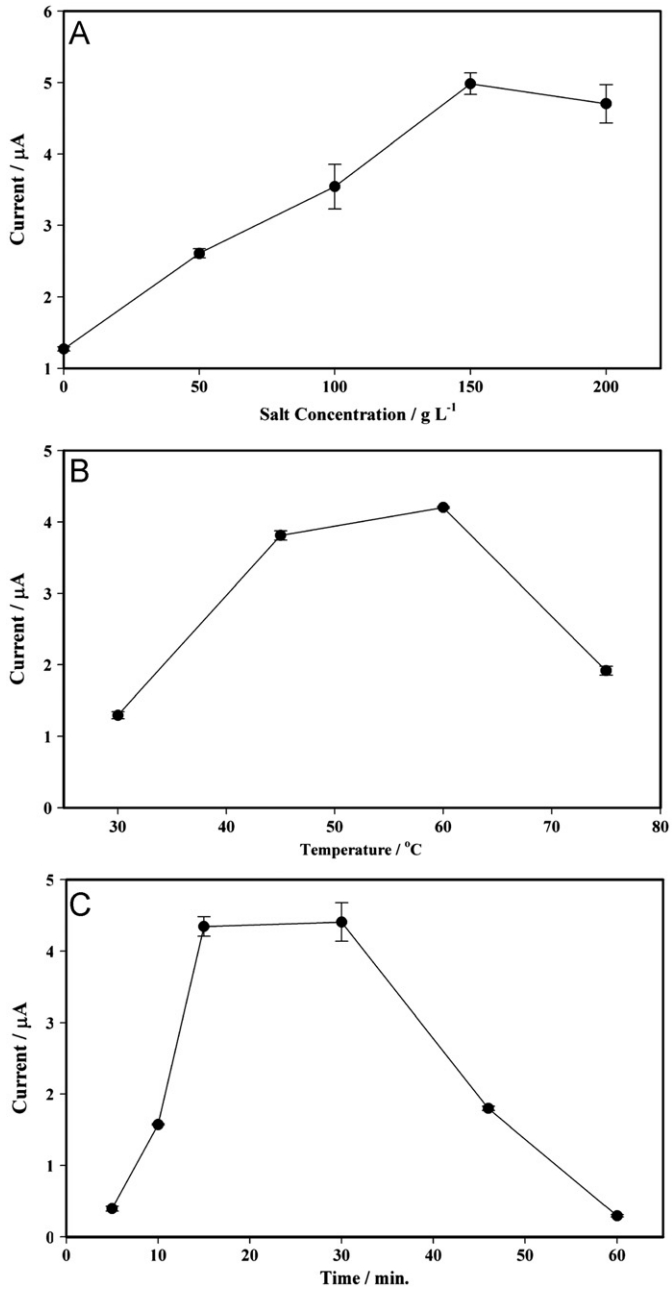

Fig. 3. The effect of (a) salt concentration, (b) HS exposure time and (c) preconcentration temperature on HS voltammetric signal of 2×10^{-4} M phenol in pH 7.0 BR buffer after preconcentration by volatilization from 0.01 M H_2SO_4 solution.

3.7. Agitation

Stirring the sample increases the mass transfer in the aqueous phase and induces the convection in the HS. Therefore, the equilibrium between the aqueous phase and HS can be achieved more rapidly. The effect of stirring rate on the voltammetric signal of phenol standard was examined in a range of 200–800 rpm during 20 min exposure time applied for 10 mL of the sample solutions containing 150 g L^{-1} NaCl. Subsequent recordings have revealed that preconcentration efficiency reaches a maximum and remains constant above 600 rpm. Thus, further experiments were carried out at a stirring rate of 600 rpm.

3.8. Sample volume

The effect of sample volume was studied in a range of 2–15 mL sample each containing 2.0×10^{-4} M phenol and resulting voltammograms were recorded in pH 7.0 BR buffer. The change in oxidation peak currents with the volume has revealed that more analyte evaporates to reach the equilibrium as the HS volume increases. Further experiments were carried out with 5 mL of sample volume.

3.9. Quantitative analysis

Under optimized conditions, analytical characteristics of the method were studied. Voltammetric responses characterized by good repeatability (5.2% at 5.0×10^{-7} M) were recorded, whose height depended linearly on the phenol concentration over a wide range (3 orders of magnitude). The detection limit was estimated as 7.0×10^{-8} M at 60 °C ($S/N=3$) which is well below the limit set by the European Community for phenols in wastewaters (ca. 5×10^{-6} M). For the higher concentration range the calibration curve was linear in 1.25×10^{-6}–2×10^{-4} M with a correlation coefficient of 0.9967.

The sensitivity of the proposed method was found comparable to other electroanalytical techniques developed for phenolic compounds. Table 2 shows the comparison of the performance of the developed method with other methods reported in the literature for the detection of phenol. It is clear that HS sampling provides more sensitive results than the direct measurement of phenol on PPy modified GCE and limit of detection improves nearly 20 times for 20 min exposure.

3.10. Interference study

The main objective of the method is to demonstrate that head space extraction can provide a practical tool for eliminating the interferences of non-volatile components of a complex matrix. Therefore, the effect of non-volatile phenolic compounds was

Table 2
Comparison of analytical characteristics of the methods for the detection of phenol.

Methods	Linear range (M)	LOD (M)	References
AdSV (Nafion modified GCE)	8.0×10^{-9}–1×10^{-5}	1.0×10^{-9}	[28]
SW (Pt/PPy–FeCN)	5.0×10^{-6}–1×10^{-4}	5.0×10^{-6}	[29]
Dp (CPE/polyamide)	1.0×10^{-5}–5×10^{-8}	8.5×10^{-9}	[30]
Amperometric enzyme sensor	1.2×10^{-7}–2.6×10^{-4}	1.0×10^{-7}	[31]
Amperometric enzyme gas sensor	1.0×10^{-5}–1×10^{-3}	0.89×10^{-6}	[32]
HS Probe with ionic liquid	2×10^{-2}–2×10^{-5}	2.0×10^{-7}	[25]
Ppy-GCE direct measuring	1.5×10^{-6}–1×10^{-4}	1.1×10^{-6}	This study
HS-Voltammetry	2.5×10^{-7}–1.25×10^{-6}	7.0×10^{-8}	Proposed method

AdSV: adsorptive stripping voltammetry, SW: square wave voltammetry, CPE: carbon paste electrode.

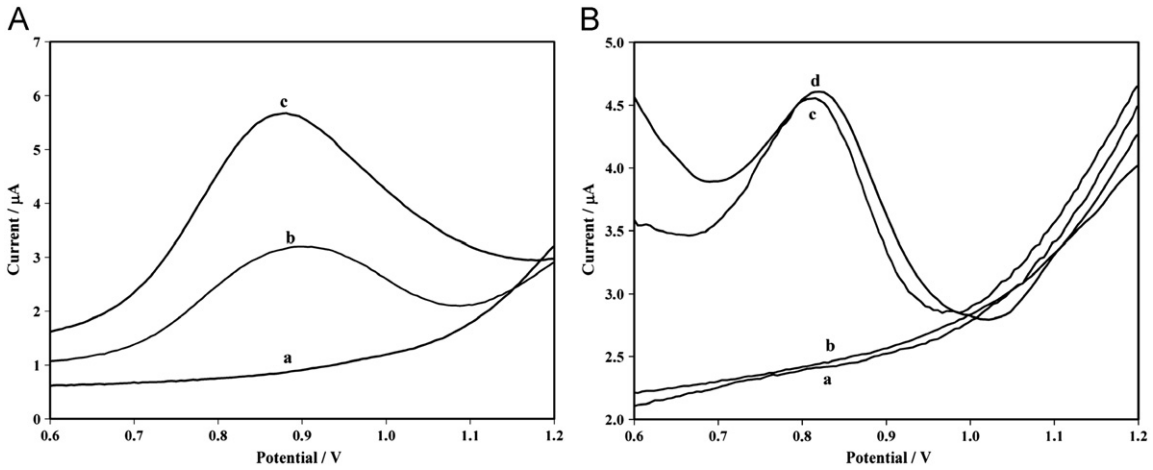

Fig. 4. The voltammograms obtained (a) without HS preconcentration, and (b) with HS preconcentration of 2×10^{-4} M phenol in pH 7.0 BR buffer containing equal concentrations of phenolic acids (p-coumaric, ferulic, caffeic, ellagic and 3,5-diethoxy-4-hyroxy cinnamic acid).

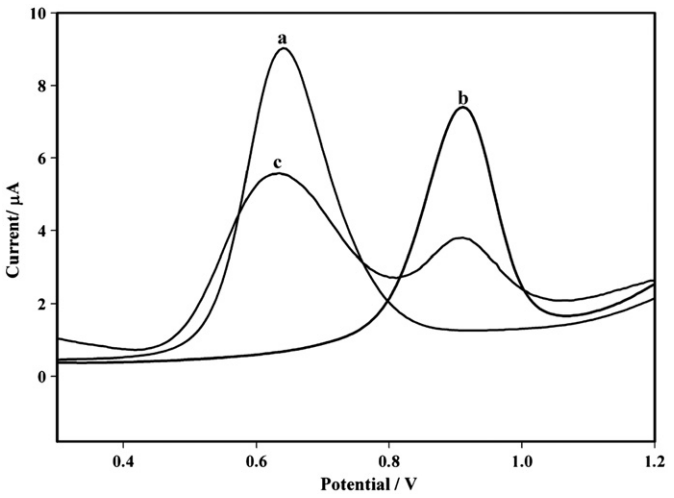

Fig. 5. Dp Voltammograms in pH 7.0 BR buffer of (a) 2×10^{-4} M 2,4-dichlorophenol, (b) 2×10^{-4} M phenol alone and (c) their mixture after head space preconcentration from 0.01 M H_2SO_4 solution.

examined by mixing equal (2.0×10^{-4} M) concentrations of p-coumaric, ferulic, caffeic, ellagic and 3,5-diethoxy-4-hydroxy cinnamic acid with phenol standard solution. Fig. 4 shows the dp voltammograms recorded at pH 7.0 BR buffer before and after HS preconcentration. Among the phenolic acids studied, coumaric acid severely interferes the oxidation peak of phenol giving a peak at 0.8 V (Fig. 4A). As can be seen from Fig. 4B, HS preconcentration not only increase the sensitivity, it also eliminates the interference of phenolic acids, particularly coumaric acid.

The real challenge emerges by the interference of other volatile phenols commonly occurring by the phenol. For this purpose, the effect of 2,4-dichlorophenol (DCP) on the phenol determination was examined. As can be followed in Fig. 5, well separated oxidation peaks were obtained for DCP and phenol. The signal decrease can be attributed to the limited capacity of the PPy film and competitive adsorption of phenol and DCP at relatively high concentration levels. It was also noticed that for equal concentrations of the DCP and phenol, the oxidation peak of DCP at 0.5 V was relatively high probably due to the higher volatility of this compound than phenol. Clearly, more sensitive results can be obtained for DCP by HS-Voltammetry; however, relatively higher toxicity of this compound over phenol necessitates more strict safety measures to be taken during the experiments.

3.11. Application of the method

The method developed was applied to the determination of phenol in artificial waste water samples described in section 2. The sample was spiked with 4.0×10^{-7} M phenol and standard addition method was applied to calculate the recovery values. Under optimized conditions, the voltammograms were recorded and resulting standard addition curve has an equation $y=1.89\times10^{8}x-70.5$ with a correlation coefficient of 0.9737. All results were obtained in three replicates to ensure reproducibility. The recovery values were calculated as 93% indicating the accuracy of the method.

4. Conclusion

Phenolic compounds have been proved to be toxic and therefore, monitoring of these compounds is important to evaluate the risk and the effectiveness of posterior water treatment. However, the selectivity of voltammetric methods is mostly impaired due to the matrix effect. The proposed method combined the advantages of HS sampling with voltammetric detection system and it was proven to be an efficient method for phenol determination as the analyte is evaporated from the solution and then, preconcentrated in a polymeric coating on the GCE slotted in the sample vial. Future studies will focus on other phenolic compounds and several other polymeric coatings will be tested for attaining more sensitive and selective results.

In conclusion, the main advantage of the proposed method is the selectivity inherited by the HS sampling. Although the scope of this method is limited to volatile and semi-volatile compounds, it can easily be applied for determination of volatile analytes in complex matrixes simply by eliminating the interference of non-volatile components. Moreover, the selectivity can be maintained for volatile compound mixtures in cases when isolated peaks are obtained for each component.

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