

## Disposable carbon electrodes as an alternative for the direct voltammetric determination of alkyl phenols from water samples

Iulia Gabriela DAVID<sup>1,\*</sup>, Irinel Adriana BADEA<sup>1</sup>, Gabriel Lucian RADU<sup>2</sup>

<sup>1</sup>Department of Analytical Chemistry, Faculty of Chemistry, University of Bucharest, Bucharest, Romania

<sup>2</sup>Department of Analytical Chemistry and Environmental Engineering, Faculty of Applied Chemistry and Material Science, University "Politehnica" Bucharest, Bucharest, Romania

Received: 21.03.2012 • Accepted: 04.12.2012 • Published Online: 24.01.2013 • Printed: 25.02.2013

**Abstract:** Disposable sensors based on a pencil graphite electrode were described for detection of alkyl phenols. The performances of the disposable bare pencil graphite electrode (PGE) and PGE modified with carbon nanotubes, regarding the cyclic and differential pulse voltammetric determination of 4-nonylphenol, 4-octylphenol, and 4-tert-octylphenol, were compared. Some experimental variables of the electrode surface pretreatment and measurement parameters were optimized. Using a phosphate buffer solution (pH 7.40) as the supporting electrolyte, alkyl phenols gave a well-defined oxidation peak at about 700 mV vs. Ag/AgCl. The detection limits established for each alkyl phenol were: 0.25  $\mu\text{M}$  for 4-octylphenol, 0.42  $\mu\text{M}$  for 4-nonylphenol, and 0.77  $\mu\text{M}$  for 4-tert-octylphenol. This method is suitable for the direct determination of the total content of these pollutants found at micromolar levels in water samples. The results obtained applying this method are in good agreement with those obtained by high-performance liquid chromatography.

The developed sensor has shown some advantages such as low cost, sensitivity, and capability to generate reproducible results using a simple and direct electrochemical protocol. By using this type of commonly available disposable working electrode and a portable electrochemical analysis system, the developed method can be applied to the determination of alkyl phenols directly at the sampling point.

**Key words:** 4-Nonylphenol, 4-octylphenol, 4-tert-octylphenol, pencil graphite electrode, voltammetry

### 1. Introduction

Phenols and substituted phenols are toxic and persistent pollutants resulting from different industrial processes such as petroleum, paper, plastic, pharmaceutical, and pesticide manufacturing. Thus, the determination of these compounds from water samples is of major concern in environmental monitoring.<sup>1–3</sup>

Alkyl phenols (APs) are degradation products of alkyl phenol polyethoxylates (APnEOs), which are used as major compounds in the fabrication of detergents. The APs appear in the environmental matrices as the results of anthropogenic activities related to all kind of industries, agriculture, or domestic waste. Due to their estrogenic activities and persistency in surface waters, APnEOs and APs represent pollutants with a major risk for humans and animals and have been included in the list of 33 priority substances.<sup>4,5</sup> For these reasons, the monitoring of those compounds in various water matrices requires selective and sensitive methods. A critical survey of the literature reveals that chromatographic methods represent the major choice in determination of

\*Correspondence: i\_g\_david@yahoo.com

APs and APnEOs in environmental samples.<sup>6,7</sup> Even if the chromatographic methods comply with the aim of environmental survey, the need for a rapid and reliable method for determination of APs gives rise to the development of a new, simple, sensitive, and reliable voltammetric method for the routine determination of APs. Thus, electrochemical studies of APs at different working electrodes have been also reported.<sup>8–12</sup> Due to their unique characteristics like high surface area, special conducting properties, and electrocatalytic effect, carbon nanotubes are often used to modify the electrode surface in order to develop more sensitive voltammetric detection methods for different species, phenols<sup>13–17</sup> being some of these.

In this study, cyclic and differential pulse voltammetry on disposable pencil graphite electrodes (PGEs), bare or modified with carbon nanotubes (CNTs), were used for direct electrochemical quantification of the APs (4-nonylphenol [NP], 4-octylphenol [OP], and 4-tert-octylphenol [TOP]) content in water samples. Pencil graphite was chosen as the electrode material because it is cheap and easy available while the electrode is thin, can be easily replaced with a new one, and has an adjustable active surface area so that it can be used to detect low analyte concentrations and analyze small sample volumes. Moreover, disposable PGEs have good mechanical rigidity and can be easily modified and miniaturized. The PGE is a suitable electrode for trace analysis when it is used in combination with a sensitive voltammetric technique like differential pulse voltammetry or stripping voltammetry.

Bare or modified PGEs were employed previously in electroanalytical studies<sup>18–22</sup> for the determination of different classes of analytes, e.g., trace metals,<sup>23,24</sup> organic compounds,<sup>25–34</sup> and especially nucleic acids.<sup>35–37</sup>

## 2. Experimental

### 2.1. Apparatus

All experimental measurements were carried out using a portable potentiostat–galvanostat PG 581 electrochemical analysis system from Uniscan Instruments and the UiEChem<sup>TM</sup> software package.

The 3-electrode system consisted of a PGE or a CNT-modified PGE (CNT-PGE), respectively, as the working electrode; an Ag/AgCl/3 M KCl (BAS, USA, Cat. No. MF-2079) reference electrode; and a platinum wire (2.5 cm length, 0.5 mm diameter) as the auxiliary electrode.

The holder of the pencil lead was a Rotring pencil. Electrical contact with the lead was achieved by soldering a metallic wire to the metallic part fixing the lead inside the pencil. HB pencil leads with a length of 60 mm and a diameter of 0.5 mm were employed. The pencil lead can be extruded to different lengths to yield different active surface areas (exposed to the sample). Leads were cut into half. The cut edge was introduced in the pencil holder so that 15 mm of the lead remained outside. The pencil was held vertically so that 10 mm of the pencil lead was immersed in the solution to be analyzed. The pencil leads were used as received or after electrochemical pretreatment. Each measurement was performed on a new pencil lead. Measurements were carried out in a glass cell containing 5 mL of solution.

For electrochemical measurements, cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were used.

The ULTRA CLEAR system (Siemens, Germany) was used for producing the ultrapure water used in this study.

The pH was measured using a pH/mV-meter Consort P901 (Consort, Belgium), provided with a combined pH electrode.

## 2.2. Chemicals

All chemicals used were of analytical grade. NP (98.5%), TOP (99.4%), and OP (99.9%) were purchased from Supelco. Phenol (~99%), polycyclic aromatic hydrocarbons (PAH), methanol, N,N-dimethylformamide (DMF), dichloromethane, acetic acid, sodium hydroxide, magnesium sulfate, disodium hydrogen phosphate, and potassium dihydrogen phosphate were obtained from Sigma-Aldrich.

The stock solutions of the corresponding alkyl phenols were of  $0.216 \text{ mg} \times \text{mL}^{-1}$  NP,  $0.147 \text{ mg} \times \text{mL}^{-1}$  TOP, and  $0.164 \text{ mg} \times \text{mL}^{-1}$  OP, respectively, in 50:50 (w/w) water-methanol mixture.

Working solutions of the corresponding APs were prepared by diluting stock solutions with phosphate buffer solution (PBS), pH 7.40, or with the other used supporting electrolytes (acetate buffer solution [ABS], pH 4.80, or  $0.1 \text{ mol} \times \text{L}^{-1}$  NaOH solution).

Stock solution of PAH calibration mix ( $10 \text{ } \mu\text{g}/\text{mL}$  of each component in acetonitrile) was purchased from Sigma-Aldrich. This solution contains the following PAHs: acenaphthene, acenaphthylene, anthracene, benz[*a*]anthracene, benzo[*b*]fluoranthene, benzo[*k*]fluoranthene, benzo[*ghi*]perylene, benzo[*a*]pyrene, chrysene, dibenz[*a,h*]anthracene, fluoranthene, fluorine, indeno[1,2,3-*cd*]pyrene, naphthalene, phenanthrene, and pyrene. An intermediate stock solution containing  $1 \text{ } \mu\text{g}/\text{mL}$  of each PAH in acetonitrile was used to prepare the working solutions by dilution with PBS, pH 7.40

Multiwall carbon nanotubes (diameter 4–5 nm; length 500–1500 nm bundles) were purchased from Aldrich.

## 2.3. Procedure

Each measurement was performed using a new 10-mm-long graphite lead surface exposed to the analysis solution and involved the electrode surface pretreatment, the CNT immobilization on the electrode surface, and the voltammetric detection steps. All experiments were performed at room temperature ( $25.0 \pm 0.2 \text{ } ^\circ\text{C}$ ).

## 2.4. Preparation of CNT solution

The required amounts of multiwall CNTs were suspended in the organic solvent DMF in order to obtain the following dispersions:  $0.4 \text{ mg} \times \text{mL}^{-1}$  (A) and  $2.5 \text{ mg} \times \text{mL}^{-1}$  (B) CNT in DMF, respectively. These mixtures were then sonicated for 30 min at room temperature.

## 2.5. Electrode surface preparation

The surface of the pencil graphite electrode was electrochemically activated in ABS, pH 4.80, by means of 2 methods, namely by maintaining the electrode for 60 s at 1400 V or by performing 10 voltammetric cycles in the potential range from  $-500 \text{ mV}$  to  $2000 \text{ mV}$  with a scan rate of  $500 \text{ mV} \times \text{s}^{-1}$ .

## 2.6. Preparation of CNT-PGEs

Each unpretreated or pretreated (activated) bare pencil lead was immersed into a 0.2-mL Eppendorf tube filled to a height of 10 mm with 0.1 mL of previously prepared CNT dispersion for 2 h or even overnight in order to form a thin CNT layer on the electrodes' surface. Each of the electrodes was rinsed with double distilled water for 10 s, and then CNT-PGEs were allowed to dry in air for 15 min in an upside-down position.

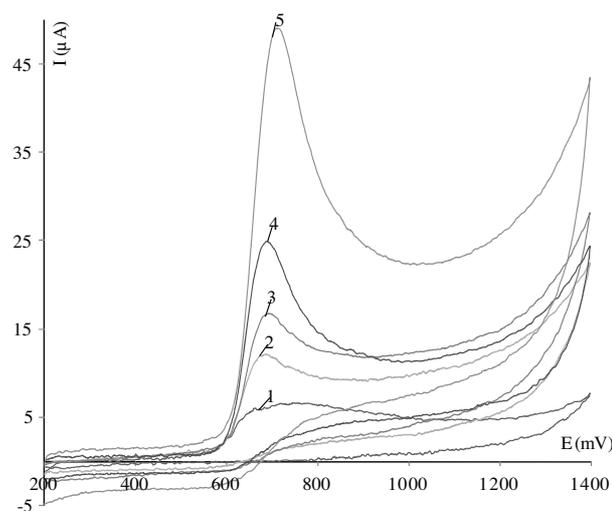
## 2.7. Analysis of water samples collected from various industrial plants

Water samples were collected from various industrial plants according to the standardized procedure<sup>38</sup> and were treated as described in a previous paper:<sup>39</sup> a volume of 500 mL of water sample was extracted 3 times with fractions of 15 mL of dichloromethane. The organic phases were collected and dried on a magnesium sulfate bed. After filtration (using Whatman grade no. 50) the organic solvent was evaporated in vacuum. The residue was quantitatively transferred into a 5-mL volumetric flask with methanol:water (50:50). The flask was filled up to the mark with the same mixture of solvents and the resulting solution was analyzed using the proposed method.

## 3. Results and discussion

### 3.1. Optimization of electrode surface preparation procedure

The electrochemical behavior of TOP, using PBS (pH 7.40) as the supporting electrolyte, was investigated on a disposable PGE and also on CNT-PGE, which have an advantage over glassy carbon electrodes in that the surface is easily renewed by a simple mechanical replacement of the lead. Such surface renewal is actually the closest solid-electrode analog of mercury drop electrodes.<sup>35</sup> The voltammograms recorded at different scan rates ( $v$ ) in the range of  $5 \text{ mV} \times \text{s}^{-1}$  to  $500 \text{ mV} \times \text{s}^{-1}$  (Figure 1) present a single anodic oxidation peak whose potential is shifted in the range of  $\sim 675 \text{ mV}$  to  $\sim 740 \text{ mV}$  when the scan rate increases, indicating an irreversible electrode oxidation process.

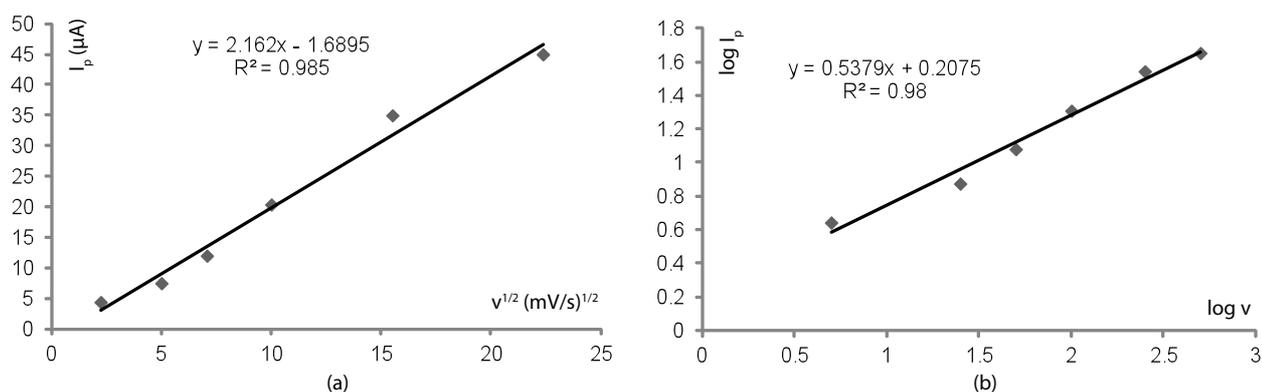


**Figure 1.** Influence of the scan rate on cyclic voltammograms recorded on chronopotentiostatically activated PGE for a concentration of  $4.85 \times 10^{-4} \text{ mol} \times \text{L}^{-1}$  TOP solution in PBS (pH 7.40): 1 -  $5 \text{ mV} \times \text{s}^{-1}$ ; 2 -  $25 \text{ mV} \times \text{s}^{-1}$ ; 3 -  $50 \text{ mV} \times \text{s}^{-1}$ ; 4 -  $100 \text{ mV} \times \text{s}^{-1}$ ; 5 -  $250 \text{ mV} \times \text{s}^{-1}$ . CV recorded for  $500 \text{ mV} \times \text{s}^{-1}$  is not shown.

The dependence of the anodic peak current ( $I_p$ ) on the square root of the scan rate ( $v^{1/2}$ ) obeying the Sevcik relation, as well as the slope of about 0.5 of the linear  $\log(I_p) = f(\log v)$  dependence (Figure 2), indicate that the electrode process is diffusion-controlled and no adsorption is involved.

Previous electrochemical studies on PGE have shown that electrochemical pretreatment of the graphite electrode surface results in enhanced voltammetric performances.<sup>32,35,40</sup> Thus, electrochemical activation of the

PGE surface was tested in ABS (pH 4.80) by means of 2 methods, namely by maintaining the electrode for 60 s at 1400 mV or by performing 10 voltammetric cycles in the potential range from  $-500$  mV to  $2000$  mV with a scan rate of  $500 \text{ mV} \times \text{s}^{-1}$ . The results obtained for DPV determination of TOP and OP in PBS (pH = 7.40) using nonactivated or electrochemical activated PGE are given in Table 1. These data emphasize that chronopotentiostatic activation of the PGE surface results in increased voltammetric peak currents of the investigated APs. Thus, further measurements were carried out only on PGE treated at  $1400$  mV for  $60$  s in ABS (pH = 4.80).



**Figure 2.** Dependence of the anodic peak current on the square root of the scan rate (a) and the  $\log(I_p) = f(\log v)$  dependence (b) for the voltammograms from Figure 1.

**Table 1.** Influence of PGE surface electroactivation on the differential pulse voltammetric determination of alkyl phenols in PBS (pH 7.40).

Alkyl phenol (concentration)	$I_p$ ( $\mu\text{A}$ )*		
	Unactivated PGE	PGE activated by	
		1400 mV; 60 s	CV (n = 10; $-500$ to $2000$ mV; $v = 500 \text{ mV} \times \text{s}^{-1}$ )
TOP ( $9.51 \times 10^{-6} \text{ mol} \times \text{L}^{-1}$ )	$0.566 \pm 0.021$	$0.916 \pm 0.027$	$0.642 \pm 0.036$
OP ( $1.79 \times 10^{-6} \text{ mol} \times \text{L}^{-1}$ )	$0.826 \pm 0.030$	$1.222 \pm 0.032$	$1.003 \pm 0.023$

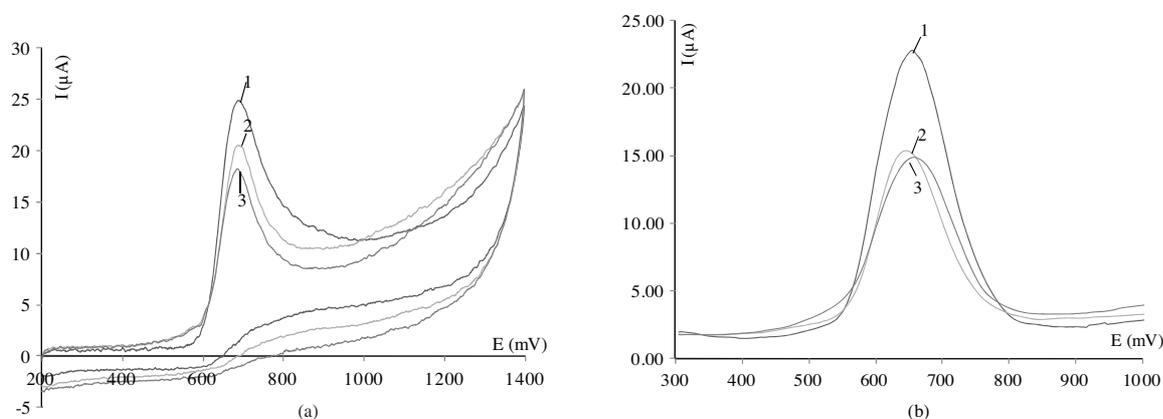
\*Average of 5 determinations.

Cyclic voltammograms recorded for TOP on both activated PGE and CNT-PGE respectively present a single irreversible oxidation peak at a potential of about  $700$  mV (Figure 3a).

In order to determine lower concentrations of APs for further quantitative analysis, DPV at chronopotentiostatic activated PGE and CNT-PGE (Figure 3b) was employed using the oxidation peak of TOP.

The influence of CNT concentration and of the PGE surface modification time by CNT deposition was studied on the DPV signal recorded for a TOP solution. Despite the fact that we expected an enhancement of the electrochemical oxidation response due to the known electrocatalytic effect of CNT,<sup>13–15</sup> from the voltammograms shown in Figure 3 it can be observed that the modification of the PGE surface with CNT does not lead to any improvement of the TOP oxidation signal, and moreover, the DPV signal of TOP decreased. A similar effect was indicated by Vega et al.<sup>11</sup> for NP oxidation using a CNT-modified glassy carbon electrode. Considering some data reported in the literature<sup>41–45</sup> indicating that phenoxy radicals produced during phenol

electrooxidation lead to the formation of nonconducting polymeric films passivating the electrode surfaces, it is possible that this unexpected behavior observed in our study may also be due to a “passivation” of the CNT-covered electrode surface, but this aspect constitutes the topic of another study.



**Figure 3.** Cyclic voltammograms ( $v = 100 \text{ mV} \times \text{s}^{-1}$ ) of  $4.85 \times 10^{-4} \text{ mol} \times \text{L}^{-1}$  TOP (a) and differential pulse voltammograms of  $2.43 \times 10^{-4} \text{ mol} \times \text{L}^{-1}$  TOP (b) in PBS (pH 7.40) recorded at chronopotentiostatic activated bare PGE (1) and CNT-PGE modified by immersion of the PGE for 2 h in a 0.4 mg CNT/mL DMF suspension (2) and in a 2.5 mg CNT/mL DMF suspension (3), respectively.

The possibility of analyte accumulation by simple physical adsorption on the electrode surface before the DPV measurement was also investigated. The accumulation time was varied between 0 and 30 s by maintaining the PGE in the measurement solution at 0.0 mV. No significant peak current change was observed, suggesting that no accumulation takes place. These results confirmed that there is no adsorption of APs on the electrode surface, as was previously concluded by cyclic voltammetry.

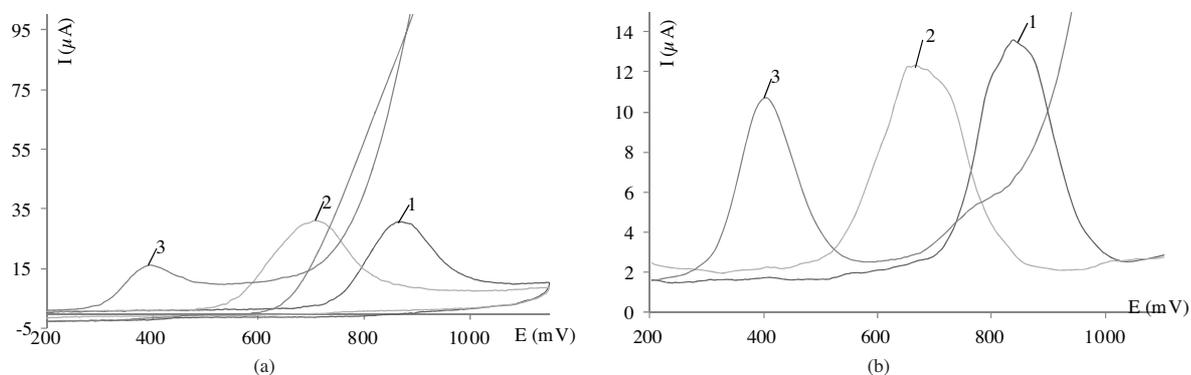
### 3.2. Influence of pH

The influence of pH on both the cyclic and differential pulse voltammetric responses of OP, TOP, and NP, investigated in 3 different media, namely ABS (pH 4.80), PBS (pH 7.40), and  $0.1 \text{ mol} \times \text{L}^{-1}$  NaOH (pH = 13), indicates a similar behavior for the 3 APs. It was observed that the peak potential shifts towards more positive potentials when the pH of the analyzed AP solution decreases (from  $\sim 400 \text{ mV}$  in NaOH  $0.1 \text{ mol} \times \text{L}^{-1}$  to  $\sim 850 \text{ mV}$  in ABS of pH 4.80) (Figure 4). The height of the AP oxidation peak does not vary significantly in ABS (pH 4.80) and PBS (pH 7.40), and therefore, for further investigations, the almost neutral pH solution was selected due to the fact that the peak potential is situated at less positive values. In PBS at pH 7.40, the 3 APs give an oxidation peak at almost the same potential ( $\sim 700 \text{ mV}$ ). Thus, if all of these APs are present together in a mixture, only their sum can be detected by this new developed method.

### 3.3. Validation of the method

**Linearity:** The influence of AP concentration on the intensity of the maximum peak current ( $I_p$ ) was studied in the range of  $0.5\text{--}500 \mu\text{mol} \times \text{L}^{-1}$  for each AP. The intensity of the anodic peak current corresponding to TOP oxidation at chronopotentiostatic activated PGE in PBS (pH 7.40) varies linearly with the analyte concentration in the range of  $2.38\text{--}243 \mu\text{mol} \times \text{L}^{-1}$  TOP (Figure 5). In the same conditions, the linear ranges

for OP and NP were  $0.6\text{--}78 \mu\text{mol} \times \text{L}^{-1}$  ( $I_p = 0.2617 \times C_{OP} + 0.8059$ ;  $R^2 = 0.9992$ ) and  $1.20\text{--}94.0 \mu\text{mol} \times \text{L}^{-1}$  ( $I_p = 0.1542 \times C_{NP} + 0.05$ ;  $R^2 = 0.9978$ ), respectively.



**Figure 4.** Cyclic voltammograms ( $v = 100 \text{ mV} \times \text{s}^{-1}$ ) of  $7.27 \times 10^{-5} \text{ mol} \times \text{L}^{-1}$  OP (a) and differential pulse voltammograms of  $4.11 \times 10^{-5} \text{ mol} \times \text{L}^{-1}$  OP (b) in 1 - ABS (pH 4.80); 2 - PBS (pH 7.40); and 3 - NaOH  $0.1 \text{ mol} \times \text{L}^{-1}$  solution, respectively, recorded at chronopotentiostatic activated bare PGE.

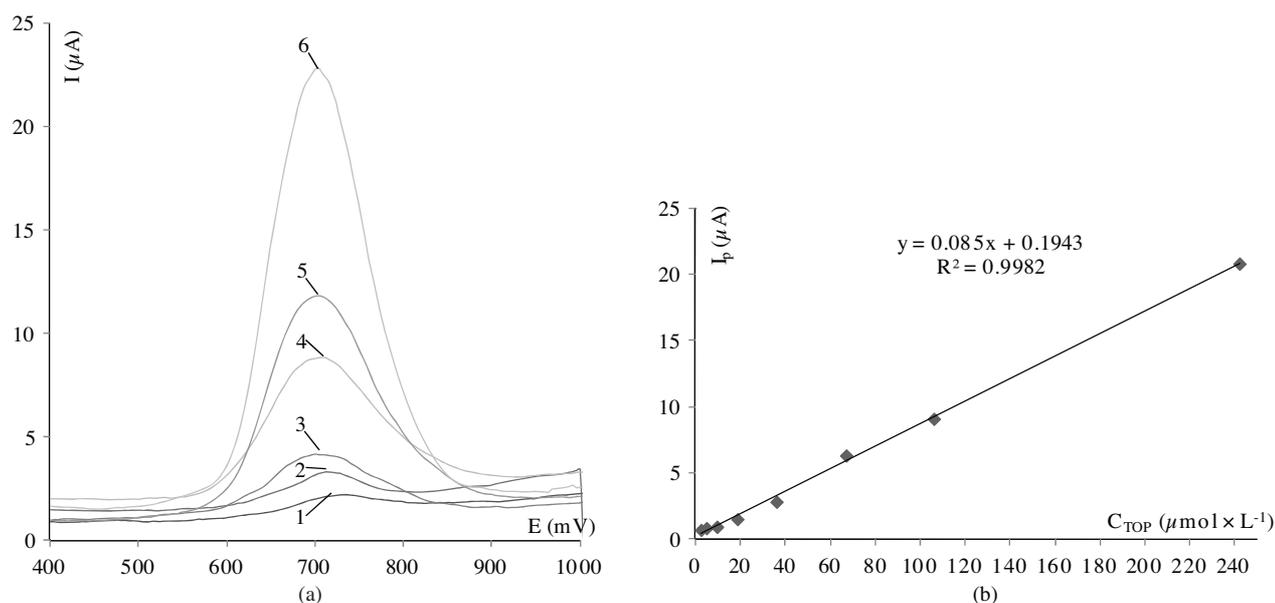
The detection limits (LOD) for each AP were established based on the calibration curve according to international rules.<sup>46</sup> The obtained LODs were  $0.25 \mu\text{mol} \times \text{L}^{-1}$  for OP,  $0.42 \mu\text{mol} \times \text{L}^{-1}$  for NP, and  $0.77 \mu\text{mol} \times \text{L}^{-1}$  for TOP.

These results are similar to or even better than (e.g., for TOP) those reported in the literature for the electrochemical detection of different APs using various working electrodes.<sup>10,12,16,17</sup>

**Selectivity:** Common metallic ions like  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ , and  $\text{Cd}^{2+}$ , which can exist in water samples, do not interfere in the voltammetric determination of APs because as cations they are not oxidized voltammetrically. DPV studies performed in PBS (pH 7.40) at activated PGE on a mixture of common PAHs did not show any voltammetric signal in the potential range of 0.0 to 1000 mV, such that neither of these compounds interfere in AP voltammetric determination on PGE. Unlike PAHs, in the above-mentioned experimental conditions, phenol gives a well-defined oxidation at a potential of about 850 mV, which is about 150 mV more positive than the APs' oxidation peak. If the phenol is present at almost the same concentration as AP, then the AP oxidation peak presents a shoulder. At a phenol:AP molar ratio of 20:1, one can observe 2 peaks corresponding to the oxidation of the 2 compounds, but these peaks are not totally resolved, such that the presence of the 2 phenols can be detected but a reliable determination of their concentration is not possible.

**Accuracy:** Accuracy was determined by calculating the recovery of each AP from synthetic samples according to international rules.<sup>46</sup> The concentration of each AP was  $20 \mu\text{mol} \times \text{L}^{-1}$ . The recoveries obtained were between 96.87% and 105.4%.

**Precision:** The precision was estimated by both repeatability and intermediate precision.<sup>46</sup> Three levels of concentration (80%, 100%, and 120%) ranging around the main concentration, which was  $20 \mu\text{mol} \times \text{L}^{-1}$ , were studied. Precision was evaluated by calculating the relative standard deviation (RSD). For all studied samples the calculated RSDs do not exceed 2.46%, which represents a good value for a voltammetric method.



**Figure 5.** Selected differential pulse voltammograms recorded at chronopotentiostatic activated bare PGE for different TOP concentrations in the range of 2.38–243  $\mu\text{mol} \times \text{L}^{-1}$  in PBS (pH 7.40) (1 - 2.38; 2 - 9.51 ; 3 - 35.9; 4 - 66.9; 5 - 10.6; and 6 - 243  $\mu\text{mol} \times \text{L}^{-1}$ ) (a) and the corresponding calibration curve (b).

### 3.4. Application on water samples collected from various industrial plants

By using the standard addition method (3 additions of 50  $\mu\text{L}$  of 0.216  $\text{mg} \times \text{mL}^{-1}$  NP), the developed differential pulse voltammetric method on disposable, low-cost PGE was applied to the determination of the sum of the AP concentration in water samples collected from a detergent plant and an electricity and heat industrial plant. The obtained results are presented in Table 2 and are in agreement with those obtained by high-performance liquid chromatography.<sup>39</sup>

**Table 2.** Comparative results obtained by the developed DPV on PGE and a HPLC method for the determination of the total content of alkyl phenols in water samples collected from 2 different plants.

Profile of plant	Total alkyl phenol content obtained (mean $\pm$ SD $\times 10^3$ ), $\mu\text{g} \times \text{L}^{-1}$	
	by DPV on PGE	HPLC <sup>39</sup>
Detergents	0.224 $\pm$ 5.16	0.212 $\pm$ 3.32
Electricity and heat	0.354 $\pm$ 4.05	0.361 $\pm$ 4.71

## 4. Conclusions

The present paper describes the performance of cheap and commonly available disposable PGEs for the determination of total content of APs in water samples at micromolar levels. The linear ranges and detection limits obtained for TOP, OP, and NP determination by DPV on PGE are similar to or even better than (e.g., TOP) some others presented in the literature.<sup>10,12,16,17</sup> The described PGE has the main advantage of a cheap, simple, and fast electrode surface “regeneration”, which enhances its applicability to routine analysis and offers the possibility of direct on-field testing by using a portable potentiostat. The PGE constitutes, thus, a less expensive alternative to commercially available disposable screen-printed electrodes.

## Acknowledgments

The authors acknowledge the Romanian Ministry of Education, Research, and Innovation for grants PN II 82102/2008 and PN II 32111/2008.

## References

1. Frenzel, W.; Frenzel, J. O.; Moeler, J. *Anal. Chim. Acta* **1992**, *261*, 253–259.
2. Yi, H.; Wu, K.; Hu, S.; Cui, D. *Talanta* **2001**, *55*, 1205–1210.
3. Cruz Moraes, F.; Tanimoto, S. T.; Salazar-Banda, G. R.; Spinola Machado, S. A.; Mascaroa, L. H. *Electroanal.* **2009**, *21*, 1091–1098.
4. European Directive **2003/53/EC**.
5. US EPA Priority Pollutant List on EPA Website (<http://water.epa.gov/scitech/methods/cwa/pollutants.cfm>). US Environmental Protection Agency (EPA), 2006
6. ISO 18857-1, *Water Quality - Determination of Selected Alkylphenols - Part 1*, 2005.
7. Zgoła-Grzeškowiak, A.; Grzeškowiak, T.; Rydlichowski, R.; Łukaszewski, Z. *Chemosphere* **2009**, *75*, 513–518.
8. Brugnera, M. F.; Gonçalves Trindade, M. A.; Boldrin Zanoni, M. V. *Anal. Lett.* **2010**, *43*, 2823–2836.
9. Ngundi, M. M.; Sadik, O. A.; Yamagushi, T.; Suye, S. I. *Electrochem. Commun.* **2003**, *5*, 61–67.
10. Evtugyn, G. A.; Eremin, S.A.; Shaljamova, R. P.; Ismagilova, A.R.; Budnikov, H. C. *Biosens. & Bioelectron.* **2006**, *22*, 56–62.
11. Vega, D.; Agui, L.; Gonzalez-Cortes, A.; Yanez-Sedeno, P.; Pingarron, J. M. *Talanta* **2007**, *71*, 1031–1038.
12. Huang, J.; Zhang, X.; Liu, S.; Lin, Q.; He, X.; Xing, X.; Lian, W.; Tang, D. *Sens. & Actuat. B: Chemical* **2011**, *152*, 292–298.
13. Yang, C. H. *Microchim. Acta* **2004**, *148*, 87–92.
14. Huang, W.; Yang, C. H.; Zhang, S. *Anal. Bioanal. Chem.* **2003**, *375*, 703–707.
15. Stuart, E. J. E.; Pumera, M. *J. Phys. Chem. C* **2011**, *115*, 5530–5534.
16. Gurban, A. M.; Rotariu, L.; Baibarac, M.; Baltog, I.; Bala, C. *Talanta*, **2011**, *85*, 2007–2013.
17. Yang, P.; Li, L.; Cai, H.; Song, H.; Wan, Q. *Conference on Environmental Pollution and Public Health*, **2010**, 1–2, 908–911.
18. Aoki, K.; Okamoto, T.; Kaneko, H.; Nozaki, K.; Negishi, A. *J. Electroanal. Chem.* **1989**, *263*, 323–333.
19. Blum, D.; Leyffer, W.; Holze, R. *Electroanal.* **1996**, *8*, 296–297.
20. Bond, A. M.; Mahon, P. J.; Schiewe, J.; Beckett, V. V. *Anal. Chim. Acta* **1997**, *345*, 67–74.
21. Majidi, M. R.; Asadpour-Zeynali, K.; Hafezi, B. *Electrochim. Acta* **2009**, *54*, 1119–1126.
22. Reza Majidi, M.; Asadpour-Zeynali, K.; Hafezi, B. *Int. J. Electrochem. Sci.* **2011**, *6*, 162–170
23. Kakizaki, T.; Hasebe, K. *Fresenius J. Anal. Chem.* **1998**, *360*, 175–178.
24. Demetriades, D.; Economou, A.; Voulgaropoulos, A. *Anal. Chim. Acta* **2004**, *519*, 167–172.
25. Rashmi, B. B. P.; Tiwari, M. P.; Sharma, P. S. *Sens. & Actuat. B: Chemical* **2010**, *146*, 321–330.
26. Gao, W.; Song, J.; Naiying, W. *J. Electroanal. Chem.* **2005**, *576*, 1–7.
27. Özcan, L.; Şahin, Y. *Sens. & Actuat. B: Chemical*, **2007**, *127*, 362–369.

28. Levent, A.; Yardim, Y.; Senturk, Z. *Electrochim. Acta* **2009**, *55*, 190–195.
29. Aladag, N.; Trnkova, L.; Kourilova, A.; Ozsoz, M.; Jelen, F. *Electroanal.* **2010**, *22*, 1675–1681.
30. Keskin, E.; Yardim, Y.; Şentürk, Z. *Electroanal.* **2010**, *22*, 1191–1199.
31. Özcan, A.; Şahin, Y. *Biosens. & Bioelectron.* **2010**, *25*, 2497–2502.
32. Özcan, A.; Şahin, Y. *Electroanal.* **2009**, *21*, 2363–2370.
33. Buratti, S.; Scampicchio, M.; Giovanelli, G.; Mannino, S. *Talanta* **2008**, *75* 312–316.
34. King, D.; Friend, J.; Kariuki, J. *J. Chem. Educ.* **2010**, *87*, 507–509.
35. Wang, J.; Kawde, A.; Sahlin, E. *Analyst* **2000**, *125*, 5–7.
36. Yardim, Y.; Keskin, E.; Levent, A.; Özsöz, M.; Sentürk, Z. *Talanta* **2010**, *80*, 1347–1355.
37. Ozkan-Ariksoysal, D.; Tezcanli, B.; Kosova, B.; Ozsoz, M. *Anal. Chem.* **2008**, *80*, 588–596.
38. ISO 5667–10. *Water quality—sampling—part 10. Guidance on sampling of waste waters*. International Standards for Business, Government and Society, 1992.
39. Cruceru, I.; Florescu, A.; Badea, I. A.; Vladescu, L. *Environ. Monit. Assess.* DOI 10.1007/s10661-011-2403-1.
40. Allen, B. W.; Piantadosi, C. A. *Nitric Oxide* **2003**, *8*, 243–252.
41. Iotov, P. I.; Kalcheva, S. V. *J. Electroanal. Chem.* **1998**, *442*, 19–26.
42. Andreescu, S.; Andreescu, D.; Sadik, O. A. *Electrochem. Commun.* **2003**, *5*, 681–688.
43. de Carvalho, R. M.; Kubota, L. T.; Rath, S. *J. Electroanal. Chem.* **2003**, *548*, 19–26.
44. Ferreira, M.; Varela, H.; Torresi, R. M.; Tremiliosi-Filho, G. *Electrochim. Acta* **2006**, *52*, 434–442.
45. Kuramitz, H.; Saitoh, J.; Hattori, T.; Tanaka, S. *Water Res.* **2002**, *36*, 3323–3329.
46. Green, J. M. *Analytical Chemistry News & Features* **1996**, *1*, 305A–309A.