# Differential Pulse Voltammetric Method for 4-Nonylphenol Determination in Water Samples

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*A novel assay for the electrochemical detection of 4-nonylphenol (4-NP) based on carbon nanotubes modified screen-printed carbon electrodes (CNTs-SPCEs) has been investigated. The electrochemical behavior of the modified SPCEs and the mechanism of the oxidation of NP were investigated using cyclic voltammetry. The differential pulse voltammetry parameters were optimized for quantitative determination of 4-nonylphenol. A detection limit of $9.95 \cdot 10^{-6}$ mol·L$^{-1}$ was obtained for 4-nonylphenol using its oxidation signal at +0.25 V. The disposable sensor showed good performance and was applied for the determination of 4-nonylphenol in tap water with satisfactory results.*

*Keywords: 4-nonylphenol, CNTs screen-printed carbon electrode, voltammetry*

The alkylphenols (APs) 4-nonylphenol (4-NP) and 4-tertoctylphenol (4-t-OP) exist mainly as intermediates in the manufacturing industry; they are also degradation products of non-ionic surfactants alkylphenols ethoxylates used in industrial formulations. Alkylphenols have been shown to exist in the environment such as river water, sewage sludge and in fish tissue [1-4]. In addition, the estrogenic activity of APs (4-NP and 4-t-OP) has been extensively evaluated in a variety of assays [4,5]. 4-Nonylphenol it is also an endocrine disruptor, having the similar effect of hormone 17-oestradiol [6]. Thus, it can interfere with the reproduction of fish, reptiles and mammals [7]. Hence its monitoring in the environment is of great significance. Leaching and contamination of 4-nonylphenol from food wrapping films, food-contacting plastics, toys and foods have been reported [8]. Therefore, it is possible that healthy humans are exposed to 4-nonylphenol via a variety of daily activities [1].

Different analytical techniques have been used for the determination of alkylphenols in environmental and water samples. The reliable methods for 4-nonylphenol analysis are direct solid-phase microextraction-gas chromatography-mass spectrometry [2,9,10] and liquid chromatography (LC) with coulometric-array detection [11]. In addition, there are reports on the use of LC with mass spectrometry (LC–MS) for the determination of alkylphenols in environmental samples [1,12-14]. LC–MS is very useful for the determination of trace levels of alkylphenols because the MS detector has higher sensitivity, selectivity and reliability than other commonly used detectors.

Electrochemical methods were well exploited for NP determination using enzymatic [15, 16] or non-enzymatic electrodes [17-30]. Thus, the 4-nonylphenol oxidation peak was used to estimate the content of this compound using different kinds of modified electrodes such as glassy carbon electrode [17-23], bare carbon electrode [24], carbon paste electrode [25], pencil graphite electrode [26], screen-printed carbon electrode [27], platinum electrode [28], gold electrode [29] or boron-doped diamond [30].

In the present study, we report an electrochemical method for determining 4-nonylphenol based on carbon nanotubes modified screen-printed carbon electrodes (CNTs-SPCE). Electro-analytical performances of the disposable sensor are presented. A differential pulse voltammetric method was developed and successfully applied for the determination of 4-nonylphenol in tap water samples.

## Experimental part

### *Materials and methods*

4-Nonylphenol was obtained from Merck and all other used reagents were analytical grade and used as received. Stock standard solution ($1 \cdot 10^{-2}$ M) of 4-nonylphenol was daily prepared by dissolution in ethanol. The working solutions under voltammetric investigation were prepared by diluting stock standard solution with supporting electrolyte just before the measurements. *p*H studies were done in 0.04 M Britton-Robinson buffer (BRB) solutions of *p*H 2.21 – 11.58 or in a 0.1 M solution of NaOH for *p*H values higher than 12.00.

Cyclic voltammetry (CV) and differential pulse voltammetry (DPV) were performed with an AUTOLAB electrochemical analyzer (PGSTAT 128N Ecochemie B.V., Netherlands). The terminals of the working (WE), reference (RE) and counter electrodes (CE) of the AUTOLAB electrochemical analyzer were connected to the respective terminals of the disposable SPE system via standard connectors and all data processing and experimental controls were driven through the Nova 1.8 software installed on a computer interfaced with the electrochemical analyzer. Commercially available screen-printed carbon electrodes (ref. 110) and multi-walled carbon nanotubes modified screen-printed carbon electrodes (ref. 110CNT) obtained from Dropsens were used. The diameter of the working electrodes was 4 mm, which resulted in an apparent geometric area of 0.125 cm$^2$. Disposable SPE systems had a carbon paste WE, carbon CE and silver RE. Their dimensions are: 3.31.0 x 0.05 cm (Length x Width x Height).

Various CV optimization studies, such as *p*H and scan rate, were performed to study the electrochemical behaviour of 4-nonylphenol. DPV was used for the quantitative determination of 4-nonylphenol. The optimized instrumental parameters of DPV were as follows: v (mV s$^{-1}$) = 10; sample width (ms) = 17; pulse amplitude (mV) = 50; pulse width (ms) = 50; pulse period (ms) = 200; deposit time (s) = 100; quiet time (s) = 2.

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A single disposable SPE system is for one-time use only. In all electrochemical experiments 50 μL drop of analyte in electrolyte solution was dispensed on the used SPE system. All experiments were carried out at room temperature (22±2°C) and all the applied potentials mentioned in the paper are referred to the internal Ag pseudo-reference electrode of the SPE system.

## Results and discussions

Cyclic voltammetry experiments were performed in order to examine the electrochemical behaviour of 4-nonylphenol at the CNTs-SPCEs. Figure 1 shows the CVs obtained for a $5 \cdot 10^{-4}$ M 4-nonylphenol in NaOH 0.1 M solution at both SPCE and CNTs-SPCE. As can be seen, only a single ireversible anodic peak at +0.25 V was obtained corresponding to the 4-nonylphenol oxidation. Compared with SPCE, the peak current of 4-nonylphenol on CNTs-SPCE is enhanced, which indicates that modified electrode presents increased active surface area and electrical conductivity and can be used for sensor development to detect 4-nonylphenol.

Inset of figure 1 there are presented five consecutive cyclic voltamograms for a $5 \cdot 10^{-4}$ M 4-nonylphenol in 0.1 M NaOH solution at CNTs-SPCE. As can be seen, the anodic peak current intensity decreased after the first scan and remain practical constant indicating that after the initial oxidation of 4-nonylphenol a polymeric film is supposed to be formed which blocked the access of 4-nonylphenol at the electrode surface. A similar electrochemical behavior for phenolic compounds was reported by others as well [31-34].

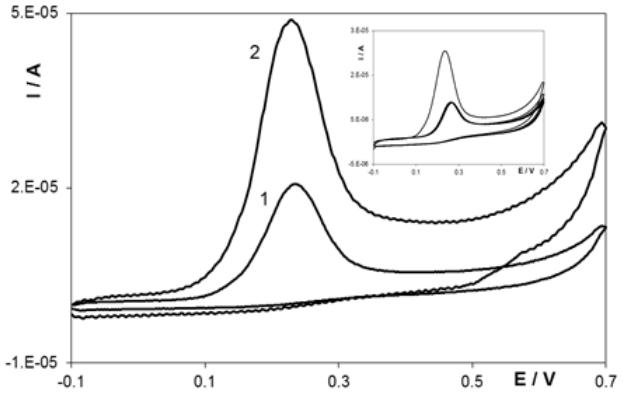



Fig. 1. Cyclic voltammograms of $5 \cdot 10^{-4}$ M 4-nonylphenol in NaOH 0.1 M solution obtained at SPCE (1) and CNTs-SPCE (2); scan rate 100 mV·s$^{-1}$. Inset: five consecutive cyclic voltammograms at CNTs-SPCE; scan rate 50·mV s$^{-1}$

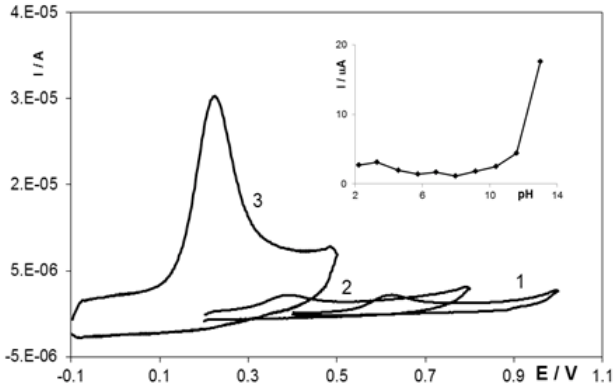



Fig. 2. Cyclic voltammograms of $5 \cdot 10^{-4}$ M 4-nonylphenol in Britton Robinson buffer *p*H 2.21 (1) and 6.80 (2) and 0.1 M NaOH solution (3) obtained at CNTs-SPCE for different *p*Hs values. The inset graph is $I_{pa}$ = f(*p*H) dependence; scan rate 50 mV·s$^{-1}$

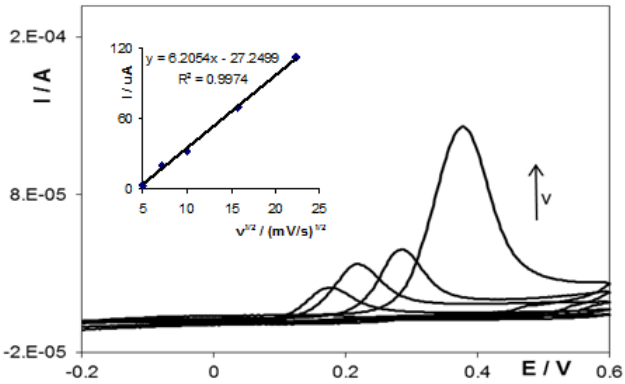



Fig. 3. Cyclic voltammograms of $5 \cdot 10^{-4}$ M 4-nonylphenol in 0.1 M NaOH solution at CNTs-SPCE for different scan rates (25, 50, 100, 250 and 500 mV/s). The inset graph is the plot for the dependence of oxidation peak current vs. square root of the scan rate

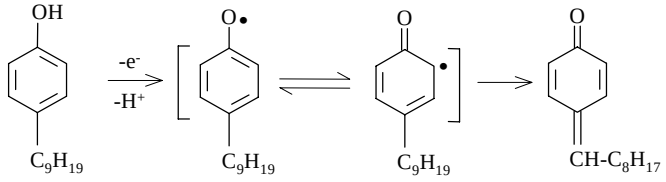
The electrochemical behavior of 4-nonylphenol was investigated at CNTs-SPCE at various pHs of the solution. As shown in figure 2, the anodic wave associated with 4-nonylphenol oxidation occurred at positive potentials at all ***p***H values and shifted to less positive potentials with *p*H increasing. This is an indication that protons are involved in the electrochemical redox process. The negative shift of the anodic peak potential ($E_{pa}$) with *p*H varies linearly by the equation: $E_{pa}$ (V) = 0.7366 – 0.048 *p*H ($R^2$ = 0.9947). The slope of the regression is close to theoretical value (0.059) as usual for a process in which the number of protons equals the electron number. The oxidation peak current of 4-nonylphenol in all Britton-Robinson solutions varied slightly but increased drastically in magnitude in 0.1 M NaOH solution (fig. 2) and this solution was selected for the future experiments to obtain a better sensibility.

Useful information involving electrochemical mechanism usually can be acquired from the relationship between the peak current and scan rate. Figure 3 shows the cyclic voltammograms of $5 \cdot 10^{-4}$ M 4-nonylphenol in 0.1 M NaOH solution recorded at CNTs-SPCE with different scan rates from 25 to 500 mV·s$^{-1}$. By increasing of the scan rate, the oxidation peak currents increased gradually. The anodic peak current varied linearly with the square root of the scan rate and the linear regression equation was $I_{pa}$ (μA) = 6.2054 $v^{1/2}$ (mV·s$^{-1}$) - 27.2499 (fig. 3). As it is well known, the linear relationship between voltammetric peak currents and square root of the scan rate indicates diffusion-controlled process on the surface of CNTs-SPCE.

Also, the peak potential shifted toward more positive values with the increasing of the scan rate confirming the irreversible electrode reaction. The relationship between the oxidation peak potential and decimal logarithm of the scan rate was $E_{pa}$ (V) = 0.1578 log v - 0.0934 ($R^2$ = 0.9914). The $\alpha n$ value (n - the number of the electrons involved in the charge transfer step, a - charge transfer coefficient) was calculated from the slope of $E_p$ *vs.* log v, which is equal with (2.303 RT/$\alpha$nF) [35]. The calculated value of $\alpha$n was 0.33. Considering the charge transfer coefficient, $\alpha$ = 0.5 for an irreversible electrode process [36], the number of the transferred was estimated as 1.

Previously it was shown that the number of electrons and protons involved in the electrochemical oxidation of 4-nonylphenol is the same, and so electrochemical oxidation of 4-nonylphenol at CNTs-SPCEs is one electron/proton process. Hydroxyl radicals play an important role in alkylphenol electrochemical oxidation; in general, it is considered that initially 4-nonylphenol oxidation start with an electron transfer which generates phenoxy radicals [37]. Radicals reactions lead to quinone formation which seems

to be an importantant intermediate of 4-nonylphenol oxidation. The mechanism of reaction proposed for the 4-nonylphenol electrochemical oxidation is:




DPV behaviour of 4-nonylphenol at CNTs-SPCE was examined in order to develop an electro-analytical method for its determination. Under the optimized experimental conditions, a linear relationship between the oxidation peak current of 4-nonylphenol and its concentration at the CNT-SPCEs was observed in the range of $10 \cdot 10^{-6} - 300 \cdot 10^{-6}$ mol·L$^{-1}$ (fig. 4).

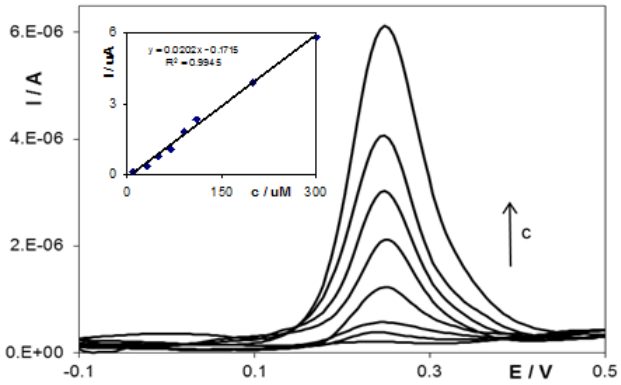



Fig. 4. Differential pulse voltammograms obtained at CNTs-SPCE for different 4-nonylphenol concentrations (10, 30, 50, 70, 90, 110, 200, 300μM) in 0.1 M NaOH solution. The inset graph is the plot for the dependence of the peak current on the 4-nonylphenol concentration

| 4-NP added [μM] | Intra-day | | | Inter-day | | |
|---|---|---|---|---|---|---|
| | NP found ± SD [μM] | Precision (RSD%) | Accuracy (%) | NP found ± SD [μM] | Precision (RSD%) | Accuracy (%) |
| 25 | 25.38 ± 1.04 | 4.10 | 101.51 ± 4.16 | 25.29 ± 1.09 | 4.33 | 101.17 ± 4.38 |
| 100 | 99.80 ± 0.84 | 0.84 | 99.80 ± 0.84 | 99.83 ± 1.11 | 1.11 | 99.83 ± 1.11 |
| 300 | 299.92 ± 0.93 | 0.23 | 99.97 ± 0.31 | 299.79 ± 0.97 | 0.32 | 99.93 ± 0.32 |

**Table 1**
RESULTS OBTAINED FOR THE EVALUATION OF THE INTRA-DAY AND INTER-DAY PRECISION AND ACCURACY OF 4-NONYLPHENOL DETERMINATION BY DPV

The detection and quantification limits were calculated as $3.3s_y/b$ and $10s_y/b$, respectively, where b is the slope of the calibration curve and $s_y$ is the standard deviation of the y-residuals of regression equation [38]. The obtained values were $9.95 \cdot 10^{-6}$ mol·L$^{-1}$ and $30.18 \cdot 10^{-6}$ mol·L$^{-1}$ for the detection limit and quantification limit, respectively.

The precision of the DPV method was evaluated by repeatability (intra-day) and intermediate precision (inter-day). The repeatability was evaluated by analysing standard solutions at three different concentrations six times per day and the intermediate precision was evaluated comparing the results obtained in three different days. The intra-day and inter-day precision were given as relative standard deviation (RSD%) and the obtained results are showed in the table 1. The accuracy was expressed as the percentage of the added concentration.

Interferences of some cations ($Cd^{2+}$, $Cu^{2+}$, $Pb^{2+}$) and anions ($Cl^-$, $NO_3^-$) which could exist in water samples in electrode response were studied and none of them modified the electrode response for 4-nonylphenol. The presence of n-octylphenol or of t-octyphenol could interfere in quantitative determination of 4-nonylphenol but this inconvenient could be over passed by using the well-known standard addition method used for elimination of matrix effect.

In order to evaluate the applicability of the proposed method, the concentration of 4-nonylphenol in tap water samples was determined. No 4-nonylphenol was detected in the tap water with the CNTs-SPCE, which means that the analyte content was below the detection limit. Thus, the DPV method was applied for spiked tap water samples. The quantitative determination of 4-nonylphenol was performed by standard addition method in order to minimize the matrix effect. To calculate the recovery, a known amount (50 μM) of 4-nonylphenol was added to the sample (10 mL). The average recovery was 98.69% ± 1.20% (RSD 1.22%) for four determinations.

## Conclusions

The differential pulse voltammetric method using a disposable pencil graphite electrode proved to be a rapid and sensitive method for the quantification of the 4-nonylphenol. The linear range was $10 \times 10^{-6} - 300 \times 10^{-6}$ mol·L$^{-1}$ 4-NP and the detection limit was estimated to be $9.95 \times 10^{-6}$ mol·L$^{-1}$. The presented method was successfully applied for the 4-NP quantitative determination from spiked tap water samples.

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