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Individual and Simultaneous Voltammetric Determination of Ultra-Trace Environmental Contaminant Dihydroxybenzene Isomers Based on a Composite Electrode Sandwich-like Structure

Ziad Khalifa,* Khalid Hassan, Mohamed Fathi Abo Oura, Abla Hathoot, and Magdi Abdel Azzem

ABSTRACT: An advanced electroanalytical technique for the simultaneous assessment of environmental contaminant dihydroxybenzene isomers, catechol (CC), hydroquinone (HQ), and resorcinol (RC), has been investigated using palladium nanoparticles (PdNPs) incorporated onto a poly(1,5-diaminonaphthalene) (DAN) matrix over a glassy carbon electrode (GCE). Concurrently, these types of phenols can be assessed by the PdDAN/GCE modified electrode employing square wave voltammetry and cyclic voltammetry (CV) techniques under optimal conditions. This modified electrode has demonstrated linear responses for CC, HQ, and RC from 50.0 to 1000.0 mM; concomitantly, low detection limits of 0.22, 0.22, and 0.47 nM and low quantification limits of 0.740, 0.758, and 1.590 nM, have been, respectively, shown. Successfully, the simultaneous assessment of the three isomers in river stream water, tap water, and underground water has been implemented via the modified electrode under investigation. In comparison to reported studies, the PdDAN catalytic electrode has shown an effective sensitivity, leverage reproducibility, long-term stability, and excellent anti-interference capability for the determination of dihydroxybenzene isomers.

1. INTRODUCTION

Dihydroxybenzene isomers such as catechol (CC), hydroquinone (HQ), and resorcinol (RC) have been widely used in tanning, dye, pesticides, cosmetics, antioxidant, flavoring agents, medicines, and photography chemicals. International bodies such as the United Nations Environment Program, European Union (EU), and the US Environmental Protection Agency (EPA) have considered these chemicals as environmentally hazardous materials because of their great toxicity, limited degradability, and long-term negative effects on human health and the environment. Some of these compounds could be inadvertently released into the environment polluting ground waters and rivers during the production and usage processes, which might lead to major human and animal health problems. Hence, it has become essential to develop an easy and fast analytical method for the determination of dihydroxybenzene isomers. Moreover, these three isomers often coexist and have similar chemical structures, which make its simultaneous analysis more difficult. Hence, constructing and designing a highly sensitive and selective sensor for CC, HQ, and RC detection and discrimination are a challenging point of research.

These phenols have been determined via many chemical analysis methods and techniques, such as capillary electrophoresis, chemiluminescence, fluorescence, gas chromatography/mass spectrometry, and high-performance liquid chromatography. High cost, time consuming, sophisticated sample preparation procedures, and using hazard solvents are some of the major drawbacks of these techniques. However, electroanalytical techniques have attracted further attention because of its superior advantages of low cost, real-time results, high accuracy and stability, small sample size, and environmentally friendliness. It has been reported that the bare electrode surface modified by a thin coat of the organic polymer has got much attention because of its versatile characteristics of enhancing the electrode performance and utilization of the electrocatalytic methods on different unique applications. Our research group has recently reported the individual and simultaneous determination of CC, HQ, and RS on poly(1,5-diaminonaphthalene) (DAN)/glassy carbon electrode (GCE)-modified electrode.
Dispersion of noble metal nanoparticles on conducting polymer films and in its porous matrix can effectively enhance the electrocatalytic properties, sensitivity, selectivity of such modified electrodes. Palladium metal (Pd) has been relatively abundant and inexpensive.\textsuperscript{14,15} Nevertheless, bulk palladium materials still demonstrate unsatisfactory electrocatalyst activity.\textsuperscript{16} However, such noble metal catalytic activity could be enhanced effectively by controlling its size and way of distribution on the matrix of the support material producing a modified electrode with effective stability, selectivity, and superior catalytic performance. Typical support materials have been characterized by important parameters, which are directly related to catalyst activity, such as porosity, high specific surface area, and active sites, which exert an influence on the morphology of the metal crystallites. The excellent catalytic effect of palladium nanoparticle (PdNPs) incorporated in the conducting polymer matrix returns to the hollow polymer nanospheres that act as a solid support to stabilize PdNPs.\textsuperscript{17} This leads to formation of a highly efficient and stable nanocatalyst in electro-oxidation reactions with great enhancement in the electrochemical performances.\textsuperscript{18}

In this study, Pd nanoparticles have been incorporated into the DAN polymer thin film by a convenient deposition method to examine the synergetic effect and the role of PdNPs on the sensitive simultaneous determination of CC, HQ, and RC in real samples of freshwater, groundwater, and tap water.

2. EXPERIMENTAL SECTION

2.1. Instrumentation and Chemicals. All electrochemical analyses have been performed on a PST 006 electrochemical work station from Voltalab-Radiometer Analytical equipped with Volta Master 4 software. Traditional three electrode 5.0 mL cells have been used for all measurements: silver/silver chloride (Ag/AgCl) as a reference electrode, platinum wire (Pt) as an auxiliary electrode, and 3.0 mm GCE as the working electrode. Before each preparation the working electrode surface has been rinsed with water followed by methanol to flush away any encrusted material on the surface. Wet the disk with triple-distilled water and apply a few drops of the 2.0 mm diamond polish slurry.

All chemicals used were of analytical grade and have been used as received without any further purification: 1,5-diaminonaphthalene (97%, Merck), catechol (99%, Sigma-Aldrich), HQ (99%, Merck), RC (99%, Merck), palladium (II) chloride (59%, Merck), hydrochloric acid (37%, Sigma-Aldrich), perchloric acid (70%, Sigma-Aldrich), and sodium hydroxide (Pellets, Merck). Triple distilled water has been used for all chemical preparations.

2.2. Syntheses of the PdDAN/GCE Modified Electrode. We have reported the electrochemical preparation of DAN/GCE using a cyclic voltammetry (CV) technique from a well mixed solution of 1.5 mM 1,5-diaminonaphthalene and 1.0 M HClO\textsubscript{4} in the potential range 0.0−800 mV at a scan rate scan rate of 20 mV/s for 15 consecutive cycles.\textsuperscript{17} Modification of DAN/GCE with PdNPs has been attained electrochemically using a CV technique by placing a freshly prepared DAN/GCE with PdNPs has been attained electrochemically in a supporting electrolyte of 5.0 mM HClO\textsubscript{4} electrodes. Wet the disk with triple-distilled water and apply a few drops of the 2.0 mm diamond polish slurry.

Besides, the in-lab water samples used for calibration and testing have been prepared by adding known quantities of the analytes to 5.0 mM HClO\textsubscript{4}. Real water samples have been collected from the local water stream of Al-Shohdaa city, Menoufia governorate, Egypt, and tested without any further processing.

3. RESULTS AND DISCUSSION

3.1. Surface Area Measurement (A) and Kinetic Studies. The effective surface area of bare GCE, DAN/GCE, and PdDAN/GCE has been measured by applying the effect of the scan rate on the standard substance,\textsuperscript{20} as shown in Figure 1. The effect of the scan rate has provided a linear relation between the peak current ($I_p$) values and the square root of the scan rate ($v^{1/2}$) at PdDAN/GCE that indicates a diffusion-controlled electrode reaction,\textsuperscript{20,21} as presented in Figure 2c. The surface area (A) has been calculated from the regression analysis of the linear relation, as presented in Figure 2b, and slope value of the linear line applied in a Randles-sevcik equation.\textsuperscript{22} The surface area value has been calculated for bare GCE, DAN/GCE, and PdDAN/GCE to be 0.072, 0.113, and 0.561 cm\textsuperscript{2}, respectively. In a previous article, we have measured a Pd nanoparticle size (between 114.6 and 179.9).\textsuperscript{23} The correlation factor between the nanometal particle size and the obtained surface area is a negative correlation.

The peak current of both segments of 1.0 mM K\textsubscript{4}Fe(CN)\textsubscript{6} in 0.1 mM KCl at PdDAN/GCE have been increased linearly with a scan rate increase and slightly shifted to positive (anodic) and negative (cathodic) potentials, where $E_p$ = 288 mV, $E_{pc}$ = 109 mV, and $\Delta E_p$ = 179 mV (Figure 2a). From eq 1, we could apply for $I_p/v$ as the slope of the graph, as shown in Figure 2a, “$n$” is the number of electrons transferred, “A” (calculated surface area); “$F$” (Faraday constant); “$R$” (universal gas constant); and “$T$” (absolute temperature) have their normal values. From the calculation, surface coverage “$\Gamma$” value of PdDAN/GCE was 9.4 x 10\textsuperscript{-9} mol/cm\textsuperscript{2}. The moles of K\textsubscript{4}Fe(CN)\textsubscript{6} redox site per unit surface area of the electrode were represented by “$I$”.\textsuperscript{21,23,24}
The electrochemical response of the modified electrode has been greatly enhanced by the presence of the Pd nanoparticles in the polymer matrix that contributes to the enhancement in the anodic current response for the catalytic oxidation processes. This superior feature has been returned to the redox activity of the compiled Pd-polymer matrix that mediates the charge transfer and boosts both selectivity and sensitivity to a much lower detection limits other than the DAN/GCE itself. 28, 29

The analyte concentration effect on the PdDAN/GCE detection performance has been investigated by varying the concentration in the range of 0.1–10 mM for each one of the di-hydroxybenzene isomers, CC, HQ, and RC. All electrochemical responses have been recorded using SWV techniques at room temperature under optimum conditions with a scan rate of 50 mV/s and 5.0 mM perchloric acid as the supporting electrolyte.

The linear relation between the modified electrode oxidation current responses for various concentrations of each isomer has clearly been depicted in Figure 4a–c. Calibration curves have been plotted for each isomer individually, as shown in Figure 4 (a, b and c insets). In all, the oxidation peak current values have been increased linearly by increasing the CC, HQ, and RC concentrations. Table 1 presents the calculated calibration parameters of low detection limits (LODs), linear detection ranges (LDRs), low quantification limits (LOQs), and correlation coefficients (R). It is obvious that the modified electrode has been highly sensitive for the very limited quantification of CC, HQ, and RC in acidic medium.

3.3. Simultaneous Assessment of CC and HQ in Binary Solutions. It has been clear that CC and HQ are electro-oxidized at the close anodic potentials of 220 and 120 mV, respectively. Therefore, the sensitivity and selectivity of PdDAN/GCE for the simultaneous determination of each isomer have been investigated to determine its redox interference performance among each isomer in binary solutions.

Figure 2. Kinetic relations at PdDAN/GCE for (a) dependence of the peak current ($I_p$) on the scan rate ($v$), (b) plot of $I_p$ vs square root of scan rate ($v^{1/2}$), and (c) variation of peak potential ($E_{pp}$) vs logarithm of the scan rate ($log v$).

$\log k_f = \alpha \log (1 - \alpha) + (1 - \alpha) \log \alpha - A + B \quad (3)$

where; $A = \log RT/nF \nu, B = (1 - \alpha) nF \Delta E_p/2.303RT \quad (3)$

Figure 2c shows the volt variation for both redox peak potentials ($E_{pa}$ & $E_{pc}$) with a logarithmic function of scan rate (log $v$) in V/s. According to Laviron theory, a linear relation is gained with a value of 2.3RT/($1 - \alpha$)nF and 2.3RT/anF for anodic and cathodic slopes, respectively. From eq 2, the charge transfer coefficient ($\alpha$) has been calculated from the ratio of anodic and cathodic slopes and is equal a value of 0.152.25 Besides, the standard rate constant ($k_f$) —that helps to understand charge transfer at the interface—has been estimated using Laviron theory, as shown in eq 3. The $\Delta E_p$ value has been calculated by the change in peak to peak separation volts at the same range of scan rates.26,27 The value of $k_f$ at PdDAN/GCE was found to be $13.8 \times 10^{-3}$ cm/s.

3.2. Individual Assessment of CC, HQ, and RC at PdDAN/GCE. The electrochemical response of the modified electrode for each of CC, HQ, and RC has been investigated by the SWV technique. A freshly prepared 10.0 mM/5.0 mM HClO4 solution of each isomer has been examined at both DAN/GCE and PdDAN/GCE electrodes for comparison studies. By analyzing the current potential relations shown in Figure 3a–c, it is clear that the incorporation of Pd particles in the DAN/GCE matrix resulted in a great enhancement of the SWV current response. The oxidation current responses for CC, HQ, and RC at DAN/GCE are 56, 54, and 14 $\mu$A; however, at PdDAN/GCE they are 123, 87 and 38 $\mu$A, which have elucidated the superior enhancement in the range of 220, 160, and 270% for each one of them, respectively. On the other hand, a negative potential shift has been recorded for each isomer on PdDAN/GCE over DAN/GCE as follows; CC: 260 mV to 210 mV, HQ: 145–110 mV, and RC: 660–550 mV.

It is clear that both conductivity and electrocatalytic activity of the modified electrode have been greatly enhanced by the presence of the Pd nanoparticles in the polymer matrix that mediates the charge transfer and boosts both selectivity and sensitivity to a much lower detection limits other than the DAN/GCE itself.28, 29

The analyte concentration effect on the PdDAN/GCE detection performance has been investigated by varying the concentration in the range of 0.1–10 mM for each one of the di-hydroxybenzene isomers, CC, HQ, and RC. All electrochemical responses have been recorded using SWV techniques at room temperature under optimum conditions with a scan rate of 50 mV/s and 5.0 mM perchloric acid as the supporting electrolyte.

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Figure 3. SWVs of (b) 10 mM HQ, (a) 10 mM CC, and (c) 10 mM RC in 0.05 M HClO4 at a-PDAN/GCE and b-PdDAN/GCE at a scan rate of 50 mV s$^{-1}$, duration of 1.0 s, amplitude of 50 mV, and pulse of 25 mV.
Binary solutions have been prepared from various equal concentrations of both CC and HQ in the range 0.1−10.0 mM using 50 mM HClO₄ as the supporting electrolyte, and they have been subjected to the SWV analysis at a scan rate of 50 mV/s, as shown in Figure 5. Effectively, the modified electrode has demonstrated a magnificent independent performance in detecting each isomer in the binary mixture. Besides, the current peak intensity response varies linearly with the increase in CC and HQ concentrations with well-defined oxidation peak current intensities and uninterfered peak potential values. Table 2 presents the calibration parameters for the binary mixture of CC and HQ, such as LOD, LDR, and R.

Table 2. Determination of Calibration Parameters for CC and HQ in Binary Solutions at PdDAN/GCE

| analyte | CC  | HQ  |
|---------|-----|-----|
| $E_p$ (V) | 0.233 | 0.120 |
| LOD (nM)  | 0.141 | 0.138 |
| LDR (nM)  | 0.1−10 | 0.1−10 |
| R         | 0.99  | 0.99  |

On the other hand, sequential contrariwise binary solutions have been prepared with one isomer at a fixed concentration and the other at varying concentrations in 5.0 mM HClO₄. SWV analysis was performed at 50 mV/s for solution mixtures put together from a fixed concentration of CC of 5.0 mM and HQ at variable concentrations in the range 0.1−8.0 mM. Figure 6a illustrates the good sensitivity of PdDAN/GCE in detecting the increase in HQ concentration with stability in the CC-fixed concentration response. The HQ oxidation current peak values increased linearly with the increasing concentrations, while the CC response was stable, which demonstrated the modified electrode independent performance of both of them in various mixed concentrations.

Moreover, by fixing the HQ concentration at 5.0 mM and varying the CC concentration in the range 0.1−8.0 mM, a linear increase in the SWV response for the CC oxidation at PdDAN/GCE has been recorded while steady ones have been displayed for the fixed concentration of HQ in all preparations, as shown in Figure 6b. Detection sensitivities, LOD, LDR, and R for quantifications of both CC and HQ in various binary solutions have been displayed in Table 3.
3.4. Simultaneous Assessment of CC, HQ, and RC in a Ternary Solution. Sensor selectivity and sensitivity in multicomponent solutions is an important performance of a reliable one that should be verified. Tertiary solutions from CC, HQ, and RC prepared from a range of concentrations 0.1–10.0 mM in 5.0 mM HClO₄ have been simultaneously detected at PdDAN/GC via the SWV technique at a scan rate of 50 mV/s, duration of 1.0 s, amplitude of 50 mV, and pulse of 25 mV. Figure 7 demonstrates the modified electrode sound effectiveness in selecting each isomer in the tertiary solution distinctly, in addition to its corresponding sensitivity for concentration variation from the very limited to the high levels of mixed analyte intensity. The oxidation current peak values for each isomer vary linearly with the increase in each isomer’s concentration in a pretty relationship. It has been clear that PdDAN/GCE proves its feasibility in the simultaneous determination and sensing of each isomer in mixed solutions at various concentrations with an enhancement in the oxidation current peak values with an adequate catalytic separation for each isomer in the mixture.

By analyzing the peak-to-peak potential separations between each of CC–HQ and RC–CC, they have been found to be 110 and 382 mV, respectively. This reasonable potential separation has demonstrated PdDAN/GCEs’ capabilities to recognize each of CC, HQ, and RC simultaneously in tertiary solutions. Such profound performance could be due to the presence of Pd in the polymer matrix that provides more surface area and more active sites for catalytic redox reactions, which has enhanced the sensor’s conductivity, electroactivity, selectivity, and sensitivity. Calibration parameters such as LODs, LDRs, and R for the simultaneous detection of dihydroxybenzene isomers in ternary mixtures values have been calculated and presented in Table 4.

Furthermore, the electrochemical behavior of the fixed concentrations of both CC and RC of 0.05 mM in the presence of variable concentrations of HQ in the range of 0.2–8.0 mM in 5.0 mM HClO₄ have been determined at PdDAN/GC using the SWV technique under optimum conditions, as has been presented in Figure 8. The voltammetric oxidation peak current intensities of HQ have been linearly increased by increasing its bulk concentration with a correlation coefficient of 0.98, whereas the oxidation peak currents of CC and RC remain constant. For ternary mixtures of variable CC concentrations in the range of 0.2–2.0 mM and fixed HQ and RC concentrations of 0.05 mM, a direct proportionality has been detected between the CC oxidation peak current values and its concentration with a correlation coefficient of 0.97, at constant currents for both HQ and RC, as shown in Figure 8b.

Table 3. Determination of Calibration Parameters for CC and HQ in Variant Binary Solutions at PdDAN/GCE

| analyte | CC   | HQ   |
|---------|------|------|
| Eₚₐ (V) | 0.213| 0.110|
| LOD (nM) | 0.788| 0.688|
| LOQ (nM) | 2.629| 2.395|
| LDR (nM) | 100–800| 100–800|
| R       | 0.98 | 0.99 |

Table 4. Determination of Calibration Parameters for the Simultaneous Detection of Dihydroxybenzene Isomers in Ternary Mixtures at PdDAN/GCE in 5.0 mM HClO₄

| analyte | CC   | HQ   | RC   |
|---------|------|------|------|
| Eₚₐ (V) | 0.190| 0.083| 0.572|
| LOD (nM) | 0.272| 0.233| 0.52 |
| LOQ (nM) | 0.908| 0.778| 1.74 |
| LDR (nM) | 100–1000| 100–1000| 100–1000|
| R       | 0.99 | 0.99 | 0.99 |

Table 5. Determination of Calibration Parameters for Single CC and HQ in Ternary Isomer Mixtures at PdDAN/GCE in 5.0 mM HClO₄

| analyte | CC   | HQ   |
|---------|------|------|
| Eₚₐ (V) | 0.210| 0.110|
| LOD (nM) | 0.227| 0.222|
| LOQ (nM) | 0.758| 0.740|
| R       | 98   | 97   |

Conclusively, the characteristic electrocatalytic responses for the detection of CC, HQ, and RC at PdDAN/GCE and other modified electrodes, as reported in the literature, have been listed in Table 6. It has been observed that PdDAN/GCE has manifested a superior catalytic performance compared with the mentioned electrodes.
3.5. Dihydroxybenzene Electrooxidation Mechanism.

The imino groups (−NH) of the polymer film (PdDAN) have constructed hydrogen bonds leading to a decrease in the hydroxyl bond energy through an O−H···NH bond.13 Moreover, PdNPs have created more O−H···PdNPs bonds helping the electron transfer,41 as shown in the following scheme (Scheme 1).

Scheme 1. Dihydroxybenzene Electrooxidation Mechanism

![Scheme 1](image)

3.6. Application in Real Samples. The PdDAN/GCE sensitivity and selectivity for CC, HQ, and RC detection in real natural water samples from various sources; river stream water, tap water, and underground water have been studied. Because naturally occurring concentrations of dihydroxybenzene isomers are very low and under the current detection limit, the standard addition method has been employed in all real natural water samples tests. Equal concentrations of 50 μM from each isomer have been spiked to each sample under analysis. The results have demonstrated the effective sensitivity and selectivity of the sensor under investigation with acceptable recovery results, as listed in Table 7. It is obvious that river stream water samples got ~100% recovery for all isomers, the tap water samples displayed ~100% recovery for both HQ and RC while 97.8% for CC, however, the underground water samples recovery have 95, 98, and 100% for CC, HQ, and RC, respectively. This has proven both high selectivity and sensitivity of PdDAN/GCE and its applicability as an effective sensor for the determination of CC, HQ, and RC simultaneously.

Moreover, the long-term stability of PdDAN/GCE performance in detecting the three isomers in real natural water samples has been also studied using SWV under several ranges of prolonged conditions such as a scan rate 50−500 mV/s, duration of a single potential pulse 0.25−100 ms, amplitude 20−100 mV, and various time intervals of analysis range 1 h to 3 days. The three isomers have been simultaneously detected in the three water samples under investigation using the same standard addition method used before. All results have demonstrated both reproducibility and stability of the sensor oxidation current peak intensity and the oxidation potential values. The isomers CC, HQ, and RC testing results have displayed acceptable RSD values in the three samples; river stream water: 1.15, 1.03, and 1.01%; tap water: 1.18, 1.06, and 1.02%; and underground water: 1.22, 1.08, and 1.02% for each isomer, respectively. It has been obvious that the modified electrode exhibited long-term stability, high precision, and tenuous fatigue factor.

Table 7. Determination of CC, HQ, and RC Simultaneously in Real Water Samples at PdDAN/GCE

| sample            | added μM | found recovery μM (%) | SD | RSD | found recovery μM (%) | SD | RSD | found recovery μM (%) | SD | RSD |
|-------------------|----------|-----------------------|----|-----|------------------------|----|-----|------------------------|----|-----|
| river stream water| 50       | 50                    | 100| 0.52| 1.03                   | 50 | 0.57| 1.15                   | 50 | 0.57| 1.01|
| tap water         | 50       | 48.9                  | 97.8| 0.53| 1.06                   | 50 | 0.58| 1.18                   | 50 | 0.52| 1.02|
| underground water | 50       | 47.5                  | 95 | 0.53| 1.08                   | 49 | 0.58| 1.22                   | 50 | 0.52| 1.02|

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3.7. Interference Effect and Stability Studies. The interfering effect of very high concentrations of various cations and anions existing in natural water samples on the simultaneous assessment of CC, HQ, and RC has been investigated. Accordingly, various mixtures of CC, HQ, and RC containing 1.0 mM of each isomer have been tested in the presence of variable very high concentrations of interfering ions. In laboratory, anion and cation solutions have been prepared in triple-distilled water containing 1000-fold of K⁺, 1000-fold Cl⁻, 500-fold SO₄²⁻, 500-fold Cu²⁺, 500-fold urea, 250-fold Na⁺, and 250-fold F⁻ have been spiked with 1-fold concentration of CC, HQ, and RC and tested at Pd/DAN/GCE by SWV under optimum conditions. By comparing the gained results in the presence of interfering ions with the previous ones in its absence, no significant variations have been observed in both oxidation peak currents and potential value for the determination of isomers, just a signal change ≤5%. This has confirmed the modified electrode anti-interference capability toward the simultaneous assessment of CC, HQ, and RC.

4. CONCLUSIONS

According to this study, a simple and sensitive electroanalytical system for the simultaneous assessment of CC, HQ, and RC has been developed employing a new modified electrode, namely, PdDAN/GCE. Combining the advantageous features of DAN and PdNPs, a composite film has been constructed on the surface of GCE forming a unique thin polymer film. Under the optimum conditions, the PdDAN/GC electrode has shown excellent selectivity and sensitivity properties and is capable of separating the three isomers’ oxidation peaks. The invented electroanalytical sensor has exhibited resplendent electrocatalytic responses toward dihydroxybenzene isomer oxidation at very small concentrations. PdDAN/GCE could be further used for the multicomponent analysis in environmentally hazardous pollutant control and chemical industry. LOD of CC, HQ, and RC have been as low as 0.22, 0.22, and 0.47 nM, respectively.

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Notes
The authors declare no competing financial interest.

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REFERENCES

(1) Wang, J.; Park, J.-N.; Wei, X.-Y.; Lee, C. W. Room-temperature heterogeneous hydroxylation of phenol with hydrogen peroxide over Fe₃O₄-N₂ ion-exchanged NaI zeolite. Chem. Commun. 2003, 628–629.
(2) Xie, T.; Liu, Q.; Shi, Y.; Liu, Q. Simultaneous determination of positional isomers of benzenediols by capillary zone electrophoresis with square wave amperometric detection. J. Chromatogr. A 2006, 1109, 317–321.
(3) Lee, B. L.; Ong, H. Y.; Shi, C. Y.; Ong, C. N. Simultaneous determination of hydroquinone, catechol and phenol in urine using high-performance liquid chromatography with fluorimetric detection. J. Chromatogr. A 1993, 619, 259–266.
(4) Cui, H.; Zhang, Q.; Myint, A.; Ge, X.; Liu, L. Chemiluminescence of cerium(IV)-rhodamine 6G-phenolic compound system. J. Photochem. Photobiol., A 2006, 181, 238–245.
(5) Pistonesi, M. F.; Di Neezio, M. S.; Centurion, M. E.; Palomeque, M. E.; Lista, A. G.; Fernandez Band, B. S. Determination of phenol, resorcinol and hydroquinone in air samples by synchronous fluorimetry using partial least-squares (PLS). Talanta 2006, 69, 1265–1268.
(6) Nagaraja, P.; Vasantha, R. A.; Sunitha, K. R. A new sensitive and selective spectrophotometric method for the determination of catechol derivatives and its pharmaceutical preparations. J. Pharm. Biomed. Anal. 2001, 25, 417–424.
(7) Nagaraja, P.; Vasantha, R.; Sunitha, K. A sensitive and selective spectrophotometric estimation of catechol derivatives in pharmaceutical preparations. Talanta 2001, 55, 1039–1046.
(8) Deceuninck, Y.; Bichon, E.; Durand, S.; Bemrah, N.; Zendong, Z.; Morvan, M. L.; Marchand, P.; Dervilly-Pinell, G.; Antignac, J. P.; Leblanc, J. C.; Le Bizec, B. Development and validation of a specific and sensitive gas chromatography tandem mass spectrometry method for the determination of bisphenol A residues in a large set of food items. J. Chromatogr., A 2014, 1362, 241–249.
(9) Guan, N.; Zeng, Z.; Wang, Y.; Fu, E.; Cheng, J. Open tubular capillary electrochromatography in fused-silica capillaries chemically bonded with macrocyclic dioxypolyamine. Anal. Chim. Acta 2000, 418, 145–151.
(10) Cui, H.; He, C.; Zhao, G. Determination of polyphenols by high-performance liquid chromatography with inhibited chemiluminescence detection. J. Chromatogr., A 1999, 855, 171–179.
(11) Ahammad, A. J. S.; Nath, N. C. D.; Xu, G.-R.; Kim, S.; Lee, J.-J. Interference-Free Determination of Dopamine at the Poly(thionine-)Modified Glassy Carbon Electrode. J. Electrochem. Soc. 2011, 158, F106–F110.
(12) Maduravveeran, G.; Jin, W. Nanomaterials based electrochemical sensor and biosensor platforms for environmental applications. Trends Environ. Anal. Chem. 2017, 13, 10–23.
(13) Hassan, K. M.; Hathoot, A. A.; Abo oura, M. F.; Azzem, M. A. Simultaneous and selective electrochemical determination of hydroquinone, catechol and resorcinol at poly(1,5-diaminophthalene)/glassy carbon-modified electrode in different media. RSC Adv. 2018, 8, 6346–6355.
(14) Liang, Z.; X.; Zhao, T. S.; Xu, J. B.; Zhu, L. D. Mechanism study of the ethanol oxidation reaction on palladium in alkaline media. Electrochim. Acta 2009, 54, 2203–2208.
(15) Zhang, L.; Lu, T.; Bao, J.; Tang, Y.; Li, C. Preparation method of an ultrafine carbon supported Pd catalyst as an anodic catalyst in a direct formic acid fuel cell. Electrochim. Commun. 2006, 8, 1625–1627.
(16) Jana, N. R.; Wang, Z. L.; Pal, T. Redox Catalytic Properties of Palladium Nanoparticles: Surfactant and Electron Donor-Acceptor Effects. Langmuir 2000, 16, 2457−2463.

(17) Bai, Z.; Zhang, Q.; Lv, J.; Chao, S.; Yang, L. A Facile Preparation of Palladium Catalysts Supported on Hollow PolyPyrrrole Nanospheres for Ethanol Oxidation. Electrochim. Acta 2015, 177, 107−112.

(18) Qiao, M.; Sajjadi, M.; Shokouhimehr, M.; Varma, R. S. Recent developments in palladium (nano) catalysts supported on polymers for selective and sustainable oxidation processes. Coord. Chem. Rev. 2019, 397, 54−75.

(19) Hassan, K. M.; Hathoot, A. A.; Ashour, W. F. D.; Abdel-Aziz, M. Electrochemical and analytical applications for NADH detection at glassy carbon electrode modified with nickel nanoparticles dispersed on poly 1,5-diaminonaphthalene. J. Solid State Electrochem. 2015, 19, 1063−1072.

(20) Zahran, M.; Khalifa, Z.; Zahran, M. A.-H.; Abdel Aziz, M. Dissolved Organic Matter-Capped Silver Nanoparticles for Electrochemical Aggregation Sensing of Atrazine in Aquatic Systems. ACS Appl. Nano Mater. 2020, 3, 3868−3875.

(21) Sharp, M.; Petersson, M.; Edström, K. Preliminary Determination of electron transfer kinetics involving ferrocene covalently attached to a platinum electrode. J. Electroanal. Chem. 1979, 95, 123−130.

(22) Shatla, A. S.; Hassan, K. M.; Abd-El-Latif, A. A.; Hathoot, A. A.; Baltruschat, H.; Abdel-Aziz, M. Poly 1,5-diaminonaphthalene supported Pt, Pd, Pt/Pd and Pd/Pt nanoparticles for direct formic acid oxidation. J. Electroanal. Chem. 2019, 833, 231−241.

(23) Liu, T.; Li, M.; Li, Q. Electroanalysis of dopamine at a gold electrode modified electrode modified with N-acetylcysteine self-assembled monolayer. Talanta 2004, 63, 1053−1059.

(24) Prabhu, P.; Suresh Babu, R.; Narayanan, S. Amperometric determination of L-dopa by nickel hexacyanoferrate film modified gold nanoparticle graphite composite electrode. Sens. Actuators, B 2011, 156, 606−614.

(25) Laviron, E. General expression of the linear potential sweep voltammogram in the case of diffusionless electrochemical systems. J. Electroanal. Chem. 1979, 101, 19−28.

(26) Sabzi, R.; Hasanzadeh, A.; Ghaseemlu, K.; Heravi, P. Preparation and characterization of carbon paste electrode modified with tin and hexacyanoferrate ions. J. Solid State Chem. Soc. 2007, 72, 993−1002.

(27) Si, W.; Lei, W.; Zhang, Y.; Xia, M.; Wang, F.; Hao, Q. Electrodeposition of graphene oxide doped poly(3,4-ethylenedioxythiophene) film and its electrochemical sensing of catechol and hydroquinone. Electrochim. Acta 2012, 85, 295−301.

(28) Zhang, W.; Zheng, J.; Lin, Z.; Zhong, L.; Shi, J.; Wei, C.; Zhang, H.; Hao, A.; Hu, S. Highly sensitive simultaneous electrochemical determination of hydroquinone, catechol and resorcinol based on carbon dot/reduced graphene oxide composite modified electrodes. Anal. Methods 2015, 7, 6089−6094.

(29) Tang, R.; Shi, Y.; Hou, Z.; Wei, L. Carbon Nanotube-Based Chemiresistive Sensors. Sensors 2017, 17, 882−897.

(30) Wang, L.; Zheng, Y.; Du, Y.; Lu, D.; Zhang, Y.; Wang, C. Simultaneous determination of catechol and hydroquinone based on poly (diallyldimethylammonium chloride) functionalized graphene-modified glassy carbon electrode. J. Solid State Electrochem. 2012, 16, 1323−1331.

(31) Song, D.; Xia, J.; Zhang, F.; Bi, S.; Xiang, W.; Wang, Z.; Xia, L.; Xia, Y.; Li, Y.; Xia, L. Multilayer carbon nanotubes-poly-(diallyldimethylammonium chloride)-graphene hybrid composite film for simultaneous determination of catechol and hydroquinone. Sens. Actuators, B 2015, 206, 111−118.

(32) He, K.; Wang, X.; Meng, X.; Zheng, H.; Suye, S.-i. Amperometric determination of hydroquinone and catechol on gold electrode modified by direct electrodeposition of poly(3,4-ethylenedioxythiophene). Sens. Actuators, B 2014, 193, 212−219.

(33) Ma, L.; Zhao, G.-C. Simultaneous Determination of Hydroquinone, Catechol and Resorcinol at Graphene Doped Carbon Ionic Liquid Electrode. Int. J. Electrochem. 2012, 2012, 1−8.

(34) Prathap, A.; Satpati, M.; Srivastava, B. Facile preparation of polyaline/MnO2 nanofibers and its electrochemical application in the simultaneous determination of catechol, hydroquinone, and resorcinol. Sens. Actuators, B 2013, 186, 67−77.

(35) Yin, H.; Zhang, Q.; Zhou, Y.; Ma, Q.; Liu, T.; Zhu, L.; Ai, S. Electrochemical behavior of catechol, resorcinol and hydroquinone at graphene−chitosan composite film modified glassy carbon electrode and their simultaneous determination in water samples. Electrochim. Acta 2011, 56, 2748−2753.

(36) Cheng, D.; Kan, X. Simultaneous determination of dihydroxybenzene isomers based on gold dendritic/pEDOT electrochemical sensor. J. Electroanal. Chem. 2020, 857, 113741−113749.

(37) Yang, S.; Yang, M.; Yao, X.; Fa, H.; Wang, Y.; Hou, C. A zeolitic imidazolate framework/carbon nanofiber nanocomposite based electrochemical sensor for simultaneous detection of co-existing dihydroxybenzene isomers. Sens. Actuators, B 2020, 320, 128294−128303.

(38) Chetankumar, K.; Kumara Swamy, B. E.; Sharma, S. C. Electrochemical preparation of poly (direct yellow 11) modified pencil graphite electrode sensor for catechol and hydroquinone in presence of resorcinol: A voltammetric study. Microchem. J. 2020, 156, 104979−104987.

(39) Huang, L.; Cao, Y.; Diao, D. Electrochemical activation of grapheme sheets embedded carbon films for high sensitivity simultaneous determination of hydroquinone, catechol and resorcinol. Sens. Actuators, B 2020, 305, 127495−127506.

(40) Zheng, X.; Fan, R.; Hu, Y.; Zhong, H.; Yang, X.; Lv, R.; Yang, X.; Huang, B. Selective and simultaneous determination of hydroquinone and catechol by using a nitrogen-doped bagasse activated carbon modified electrode. Mater. Chem. Phys. 2020, 242, 122525−122534.

(41) Besson, M.; Gallezot, P. Selective oxidation of alcohols and aldehydes on metal catalysts. Catal. Today 2000, 57, 127−141.

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