



# Effect of cobalt doping level of ferrites in enhancing sensitivity of analytical performances of carbon paste electrode for simultaneous determination of catechol and hydroquinone



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## ABSTRACT

This work presents the simultaneous determination of catechol (CC) and hydroquinone (HQ), employing a modified carbon paste electrode (CPE) with ferrite nanomaterial. Ferrite nanomaterial was doped with different amount of cobalt and this was investigated toward simultaneous oxidation of CC and HQ. It was shown that this modification strongly increases electrochemical characteristics of the CPE. Also, electrocatalytic activity of such materials strongly depends on the level of substituted Co in the ferrite nanoparticles. The modified electrodes, labeled as CoFerrite/CPE, showed two pairs of well-defined redox peaks for the electrochemical processes of catechol and hydroquinone. Involving of ferrite material in the structure of CPE, cause increase in the potentials differences between redox couples of the investigated compounds, accompanied with increases in peaks currents. Several important parameters were optimized and calibration curves, with limits of detection (LOD) of 0.15 and 0.3  $\mu\text{M}$  for catechol and hydroquinone, respectively, were constructed by employing amperometric detection. Effect of possible interfering compounds was also studied, and proposed method was successfully applied for CC and HQ quantification in real samples.

## 1. Introduction

Catechol (CC) and hydroquinone (HQ) are two isomers of dihydroxybenzene with a similar structure and properties. CC and HQ are important environmental pollutants because of their high toxicity and low degradability [1,2] generally used in many fields, such as pharmaceuticals, fine chemicals, cosmetics and foods industries [3]. Usually they coexist and interfere with each other during their determination. The separation of the electrochemical response of HQ and CC with a high sensitivity has been one of the major goals of both the electroanalytical chemistry and biosensor research [4]. Therefore, it is important to establish a simple and fast analytical method for sensitive and selective determination of HQ and CC in different matrices. Several techniques are used to determine HQ and CC in environmental samples such as, high performance liquid chromatography [5], gas chromatography/mass spectrometry [6], chemiluminescence [7], capillary electrochromatography [8] spectrophotometry [9] and several electrochemical methods [10–14]. The electrochemical methods are more super-

ior for the simultaneous detection of HQ and CC, which provide advantages compared to other techniques including low cost, simple handling, fast response, high sensitivity, selectivity and stability. Nowadays, much effort has been devoted to the electrochemical determination of dihydroxybenzene isomers at new different electrodes. Carbon paste electrodes (CPE) have been widely used in electrochemistry because of their chemical inertness, wide potential window and suitability for different types of analysis and they can be simply modified [15–21]. Several carbon based electrodes, including carbon fiber electrode [22], carbon nanotubes (CNT)-modified electrode [23,24], and boron-doped diamond (BDD) electrode [25] and graphene based electrode [26,27] have been investigated for dihydroxybenzene sensor or to improve the electrochemical performances of these sensors.

Polycrystalline spinel ferrites have many unique properties, such as high electrical resistivity, high Curie temperature, large magnetocrystalline anisotropy, high coercivity, mechanical hardness, chemical stability, and temperature specific saturation magnetization, which

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make ferrites suitable for many applications. In the last years, their usability in electrochemical purposes has been widely investigated, as with decrease of the size of material (nanometer level) causes greatly increase in the surface area and this phenomena resulting with novel electrode characteristics such as increase in electrical conductivity, high adsorption ability and low mass transfer resistance [28–31].

Cobalt ferrites (Co/Ferrites) are a promising candidate for electrode material due to their similar electronic properties and mechanical strength which can be attributed to the anti-parallel spins  $\text{Fe}^{3+}$  and  $\text{Co}^{2+}$  ions from tetrahedral and octahedral sites respectively [32]. These nanoparticles increasing electrochemical performances and provides significant improvements of electrodes for the construction of sensors and biosensors for determination of important metals and biological active substances [33,34]. Also this material possesses low toxicity, easy preparation pathway, long term stability, low cost and safety.

In this work, cobalt ferrite (CoFerrite) composites were synthesized and the electrochemical properties were studied by fabricating a simple and sensitive electrochemical dihydroxybenzene sensor based on CoFerrite modified carbon paste electrode (CoFerrite/CPE). These electrodes exhibited highly sensitive performance for simultaneous determination of CC and HQ, fast voltammetric response, as well as good selectivity. It was shown that the electrocatalytic activity of such materials strongly depends on the level of substituted Co in the ferrite nanoparticles. The sensor was also applied to simultaneous determination of CC and HQ in tap water with satisfactory results.

## 2. Experimental

### 2.1. Chemicals

Deionized water was purified with a cartridge purification system (Milli-Q) to a resistivity of 18.2 M $\Omega$  cm and was used for all experiments. Catechol, hydroquinone, boric acid, sodium hydroxide, acetic acid, phosphoric acid and graphite powder (< 20  $\mu\text{m}$ ) were purchased from Sigma–Aldrich (Wien, Austria), paraffin oil (for IR spectroscopy) and used as received without any further purification. Calibration solutions were prepared from the stock solution (1 mM) by appropriate dilution with supporting electrolyte. Britton–Robinson buffer solution (BRBS) was prepared by mixing of 40 mM of all necessary components (phosphoric acid, acetic acid and boric acid). The pH of BRBS was adjusted with sodium hydroxide (0.2 M). Working solutions of CC and HQ were freshly prepared on the day of the experiment by appropriate dilution with the supporting electrolyte. All reagents used in this work were of analytical grade and were used without further purification.

### 2.2. Apparatus

Cyclic voltammetric (CV) measurements, electrochemical impedance spectroscopy (EIS) and hydrodynamic amperometric measurements were performed using an AUTOLAB PGSTAT 302N (Metrohm Autolab B.V., The Netherlands) potentiostat/galvanostat controlled by corresponding software (NOVA 1.10). The electrochemical cell (total volume of 10.0 mL) consisted of a glass vessel (Metrohm) equipped with the Ag/AgCl (3 M KCl, Metrohm 6.0733.100) as a reference electrode, platinum wire as an auxiliary electrode and CoFerrite/CPE as a working electrode. All of the pH values were measured using a pH meter (Orion, model 1230) with a combined electrode (glass-reference electrodes), which was calibrated every day with standard buffer solutions. All potentials given in the text are versus the Ag/AgCl reference electrode at room temperature.

The morphology of the ferrite powders were examined by SEM Jeol JSM-6610LV. The X-ray powder diffraction (XRPD) analysis was conducted using Philips PW-1710 automatized diffractometer with graphite monochromator and a Xe-filled proportional counter, using a Cu-tube operated at 40 kV and 30 mA. Data were collected in the range 15–60° with a counting time of 2.5 s/step and a step size of 0.05°. A

fixed 2° divergences and 0.2 mm receiving slits were used.

### 2.3. Preparation of the modified materials

#### 2.3.1. The preparation (Synthesis) of Co ferrites

Cobalt ferrites,  $\text{Fe}_{1-x}\text{Co}_x\text{Fe}_2\text{O}_4$  ( $x=0, 0.25, 0.50, 0.75$  and 1) were prepared by thermal decomposition of  $\text{Fe}(\text{AA})_2$ ,  $\text{Co}(\text{AA})_2$  and  $\text{Fe}(\text{AA})_3$  (where AA denotes acetylacetonate) in their stoichiometric ratios.

Mixtures of acetylacetonates were decomposed by heating up to 500 °C in air atmosphere in an electric furnace (heating rate was 20°/min). Obtained ferrite materials were washed, dried, and finally homogenized in agate mortar.

#### 2.3.2. The fabrication of the modified carbon paste electrodes

Bare carbon paste electrode was prepared by carefully hand mixing 380  $\mu\text{L}$  of paraffin oil with 1 g of graphite powder in a mortar with a pestle. After standing overnight a portion of the resulting paste was packed into the end of a Teflon tube (an inner diameter 5 mm, outer diameter 10.15 mm) and the surface was polished using a PTFE plate or wet filter paper. The carbon paste was modified by adding 5% (m/m) of CoFerrite. The amount of modifier was selected according to our experience and previously described articles, where it is found that modification with 5% of modifier gives best analytical response [35].

Whenever regeneration was required, a layer of the surface was removed and replaced by fresh paste. Electrical contact was made with a copper wire through the center of the tube.

### 2.4. Procedures

Cyclic voltammetry with a scan rate of 0.05 V/s (if not stated otherwise) was used for characterizing the electrochemical behavior of the analyte at the unmodified and modified electrode surface. The investigated solutions were transferred into the voltammetric cell and the voltammograms (usually 5 cycles) were recorded in a potential range between 0 V and +1.4 V. Amperometric measurements were taken at constant potentials of 0.40 and 0.55 V and were used for the quantification of CC and HQ. DPV measurements were done in the range of 0–1.4 V, at the modulation amplitude of 50 mV and modulation time of 40 ms. Electrochemical impedance spectroscopy (EIS) was performed in 5 mM  $\text{Fe}[(\text{CN})_6]^{3-/4-}$  (1:1) with 0.1 M KCl as supporting electrolyte, using an alternating current voltage of 10 mV within a frequency range of 0.01–10<sup>5</sup> Hz.

### 2.5. Interference studies

Electrochemical behavior of some possible interfering compounds such as caffeic acid, gallic acid, ascorbic acid, and some of the mainly present ions in tap water were tested in same concentrations, and for tested ions 20-fold excess, under optimized experimental conditions with proposed sensor. The changes of the peak current obtained for CC and HQ were compared in the absence and in the presence of selected interfering compounds. Also, amperometric response for these compounds was evaluated. It was considered that tested compounds strongly interfere with the determination of CC and HQ if gives signal changes more than  $\pm 10\%$ .

### 2.6. Sample analysis

Samples were taken from two different pipes. First sample was directly measured by adding 1 mL of sample in voltammetric cell. Second sample was artificially spiked with CC and HQ to increase its concentration in cell to the value of 2  $\mu\text{M}$  for HQ and 4  $\mu\text{M}$  for CC. All results are repeated three times, estimated from calibration curve and given as mean value of three measurements. In order to evaluate matrix effect recovery experiments were done.

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