

ASSESSMENT OF NON-AQUEOUS SOLVENTS IN THE ELECTROOXIDATION OF RESORCINOL, PHLOROGLUCINOL, PYROGALLOL, AND ROLE OF CO-SOLVENT IN DETERMINATION OF PYROGALLOL WITH MICROELECTRODE VOLTAMMETRY

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ABSTRACT. This study reveals the behavior of resorcinol, phloroglucinol and pyrogallol in several non-aqueous solvents (acetonitrile, acetone, dimethyl sulphoxide, dimethyl formamide, nitrobenzene, nitromethane, dichloromethane, methanol). The voltammetric curves showed that the results obtained with the outlined compounds depend strongly on the solvent used. Resorcinol and phloroglucinol undergo some fouling during their electrooxidation while pyrogallol gave reproducible voltammograms in many solvents. The optimal solvent was chosen then for the determination of pyrogallol in cooking oil taking into consideration the antifouling, miscibility, permittivity and viscosity effects with steady-state voltammetry by using microelectrode.

Keywords: Resorcinol; Phloroglucinol; Pyrogallol; Co-solvent; Microelectrode

INTRODUCTION

Polyhydroxy phenols are investigated due to several applications mainly in aqueous solvents considerably due to their antioxidant properties. Hydroquinone, resorcinol and catechol can be determined simultaneously so numerous works are based on their quantification in lower concentrations [1-5]. The low oxidation potential is utilized by using pyrogallol as antioxidant also in apolar environments such as biodiesel and cooking oil so some works aimed at measuring it by using special electrochemical detection techniques [6-8].

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In several electroanalytical procedures a co-solvent is used due to different reasons, for example improving the transport properties, solution permittivity and altering favourably the molecular environment. The higher diffusion coefficient enhances the sensitivity towards the analytes and the higher permittivity contributes to the reduction of the ohmic distortion. In the viewpoint of reproducibility of current signals the solvent has essential role as deactivation processes can take place and moreover, the rapid fouling already diminishes remarkably the magnitude of the peak currents of the subsequent scans after the first one. This process is difficult to describe quantitatively as porosity of film and the nature of solvent highly affects electrode deactivation as it was shown in earlier works [9-11]. Therefore, these requirements should be taken into consideration when choosing the appropriate co-solvent for analysis of compounds prone to fouling and on the other hand the solvent is miscible with the sample. So, the electrochemical behavior of widely used polihidroxi benzenes was the aim of this work in different non-aqueous solvents and the introduction of an analytical procedure.

RESULTS AND DISCUSSION

In the first part of studies the examination of electrochemistry of the three polyhydroxy phenols was carried out in different non-aqueous solvents dissolved in 50 mM concentration scanning in the potential range between 0 and 2 V with 0.1 V/s scan rate. It is clearly seen from Fig. 1 that resorcinol and phloroglucinol deactivates the working electrode (1 mm in diameter platinum) in all solvents. The low values of the first current peaks in nitrobenzene, nitromethane and dichloromethane are due to the limited solubility of solutes well below 50 mM. The curves obtained in methanol displayed in Fig. 2 show the usual fouling behavior for resorcinol and phloroglucinol but after the second scan a slight increase of peak currents appears indicating that there is only a weak adherence of formed deposit on the electrode surface. It also suggests that porosity of film varies during the experiment.

Dimethyl sulphoxide highlights the importance of solvent in the behavior of a compound namely resorcinol and phloroglucinol (Fig. 3a and b) as the peak currents of curves show that no tendency can be observed in the subsequent scans which is a sign of formation of weakly bound organic layer. Its thickness was high enough to see with naked eye as a brownish deposit and it was easy to remove mechanically.

The position of hydroxyl groups determines significantly the ability to fouling as resorcinol and phloroglucinol showed previously as these groups are in 1,3 position relative to each other. On the other hand, this is also indicated by pyrogallol (Fig. 1c). The magnitude and reproducibility of peak currents in majority of solvents suggest that pyrogallol undergoes also non-fouling processes reinforced also by the curves in Fig. 3c. The part of molecule

where neighbouring hydroxyl groups can be found oxidizes similarly to catechol (1,2-position). In parallel to this process polymerization reaction can take place but the removal of the products depend significantly on the solvent. Nitrobenzene has an identical effect on its electrochemistry. However, the solute dissolved completely in 50 mM concentration the peak height of the first voltammogram is unprecedently low compared with the other solvents. The reason is the very low polymer solubility and on the other hand it deposits as a compact layer.

The only solvent where pyrogallol could not be dissolved in 50 mM concentration was dichloromethane but reproducibility of currents show the lack of deactivation and therefore appropriateness for analytical purposes.

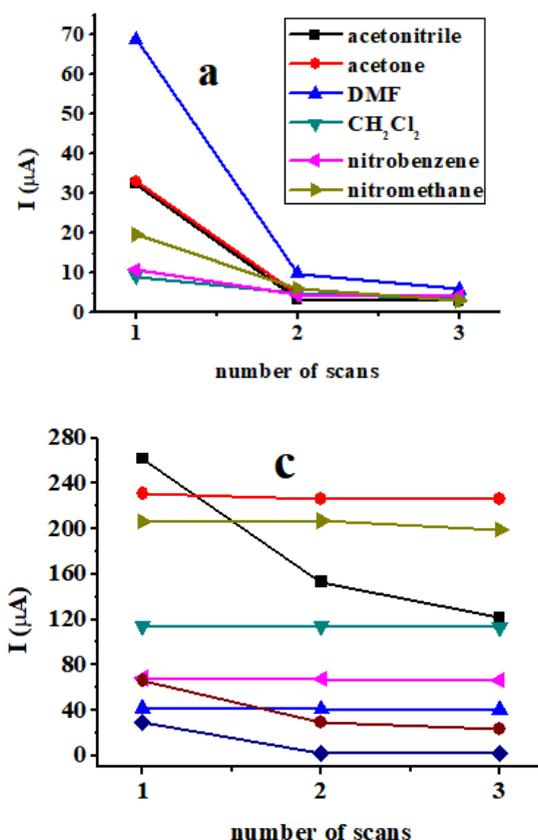


Figure 1. Voltammetric peak currents of 50 mM resorcinol (a), phloroglucinol (b) and pyrogallol (c) in the different non-aqueous solvents (scan rate 0.1 V/s, supporting electrolyte 70 mM TBAP). In part c: ■: acetonitrile, ●: acetone, ▲: CH₂Cl₂ (saturated solution), ▼: dimethyl formamide, ►: methanol, ◆: dimethyl sulphoxide, ●: nitromethane, ◆: nitrobenzene.

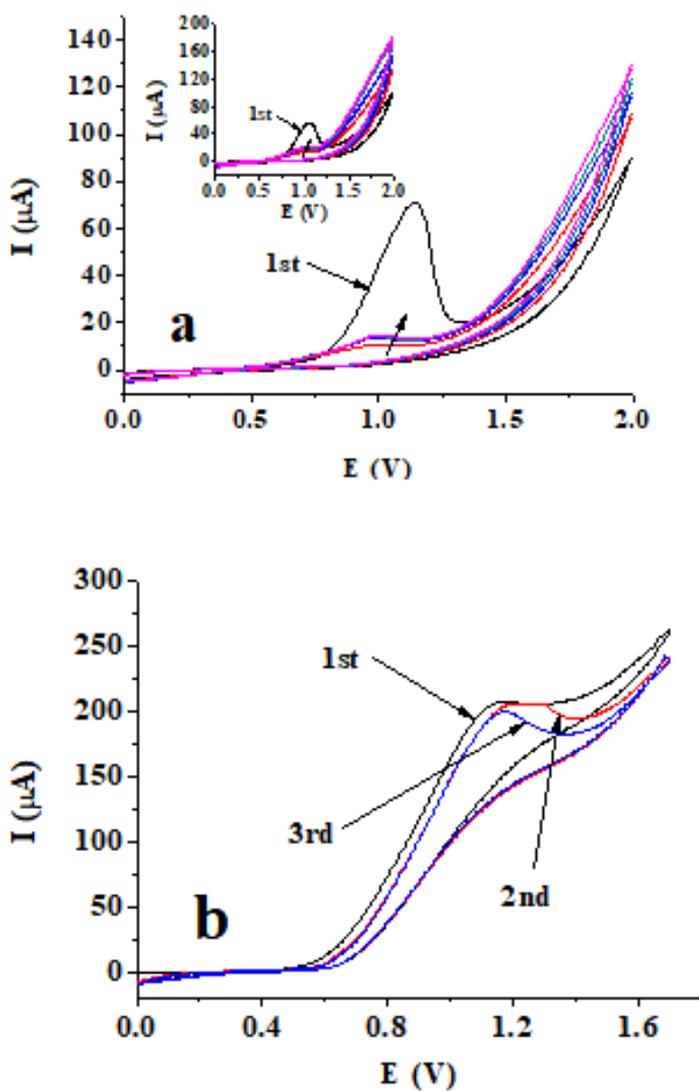


Figure 2. Subsequent cyclic voltammetric curves of 50 mM resorcinol (a), phloroglucinol (inset graph in part a) and pyrogallol (b) in methanol (scan rate 0.1 V/s, supporting electrolyte 70 mM TBAP)

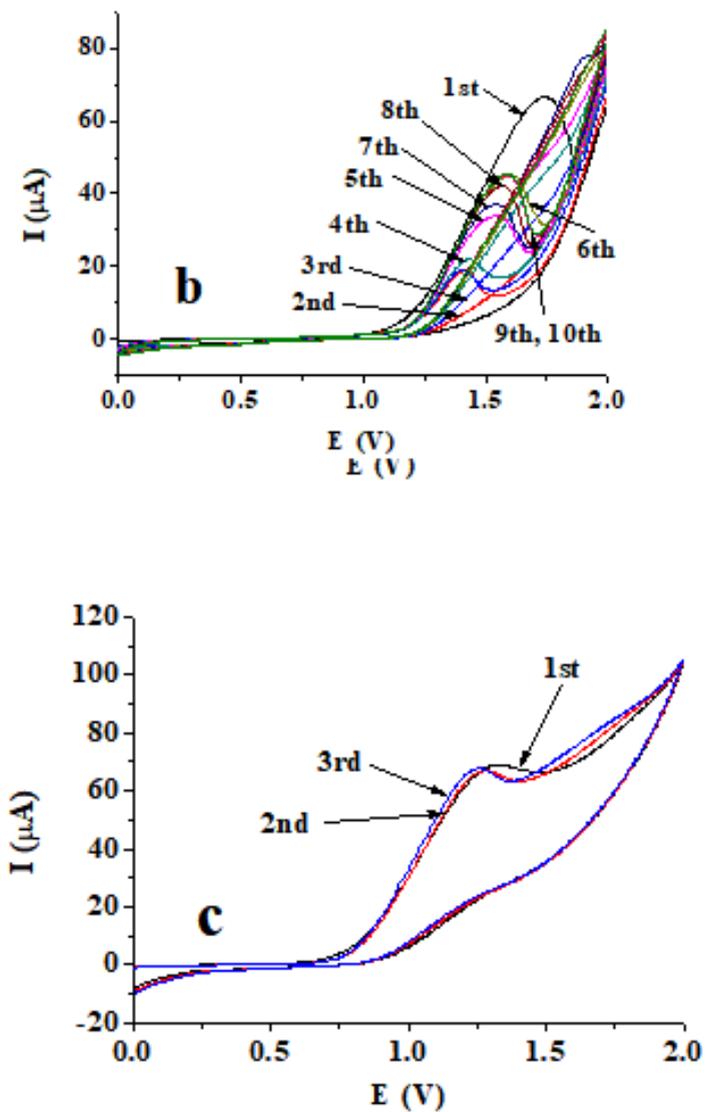


Figure 3. Subsequent cyclic voltammetric curves of 50 mM resorcinol (a), phloroglucinol (b) and pyrogallol (c) in dimethyl sulphoxide (scan rate 0.1 V/s, supporting electrolyte 70 mM TBAP)

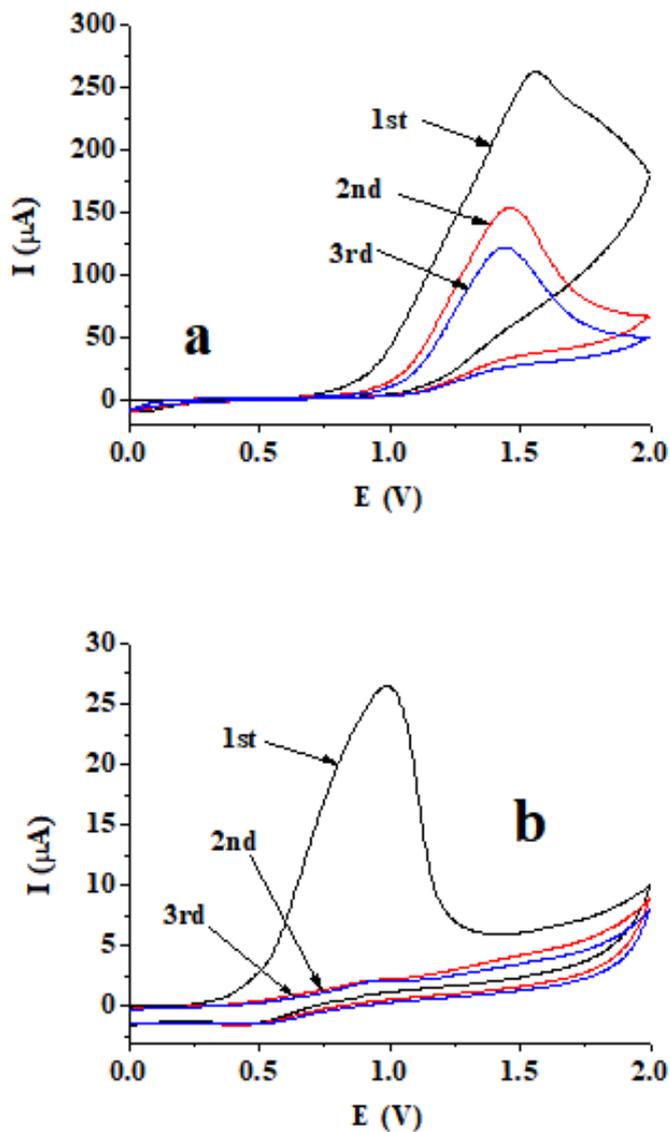


Figure 4. Cyclic voltammograms of 50 mM pyrogallol in acetonitrile (a) and in nitrobenzene (b) (scan rate 0.1 V/s, supporting electrolyte 70 mM TBAP)

The results of the above experiments showed that pyrogallol differs significantly from the other polyhydroxy compounds especially in signal reproducibility which is essential in analytical purposes. On the other hand, pyrogallol has an outstanding role as antioxidant in many applications so its quantification has gained high importance. The real sample used here was a cooking oil purchased from a supermarket. Taking into consideration the anti-fouling properties and sensitivity (magnitude of current signal) acetone seemed to be the most appropriate co-solvent for further analytical purposes. Moreover acetone has high miscibility with the majority of apolar samples. During the procedure a 25 μm in diameter platinum microelectrode was used which is suitable in highly resistive environments. The permittivity of acetone will be drastically diminished by mixing with oily samples but being enough for electroanalysis in this way. On the other hand the mixing with oil the addition of acetone increases significantly viscosity highly affecting the current signals of electroactive materials. The real sample may contain additives being electrochemically active in the potential range where pyrogallol oxidation occurs. Therefore for taking these facts into account the standard addition method was applied in the analytical procedure.

The cooking oil and acetone were mixed in 50-50 v/v% and concentration of added pyrogallol was varied for carrying out the calibration experiments so the viscosities of all solution were uniform. All solutions contained 10 mM TBAP supporting electrolyte. The steady-state voltammograms were measured with the platinum microelectrode between 0 and 2 V with 0.1 V/s scan rate and the current values read at the beginning of the current plateaus were utilized for calibration. The electrodes were thoroughly washed with acetone after each measurement to avoid the contamination of calibration solutions with each other, and working electrode was polished.

By examining the microelectrode voltammograms of added pyrogallol (Fig. 5), some deviations can be observed from the regular steady-state voltammograms. The current plateaus are not parallel at all to the x-axis. This is attributable to pyrogallol not to the other components which was verified by studies of pyrogallol alone in acetone as the shapes of its voltammograms were very similar to that obtained in the mixture prepared with the chosen cooking oil sample. These results suggest a complicated process described in a previous paragraph but the voltammetric curves were reproducible after renewing the electrode surface.

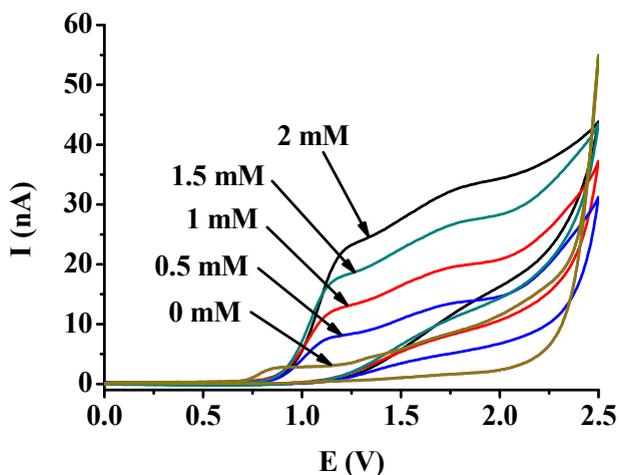


Figure 5 Steady-state voltammograms for the determination of pyrogallol in cooking oil

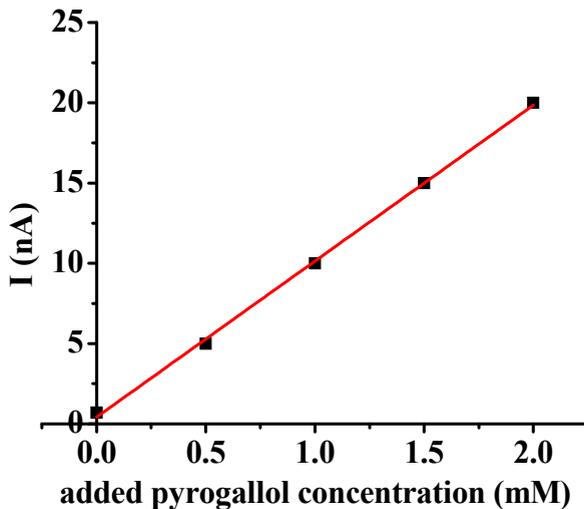


Figure 6. The calibration curve of the standard addition procedure for pyrogallol in 50-50 v/v% mixture of cooking oil and acetone (supporting electrolyte 10 mM TBAP, $v=0.1$ V/s, working electrode $25 \mu\text{m}$ platinum microdisc)

The calibration curve of standard addition method can be seen in Fig. 6 for added pyrogallol. It was linear and it enabled the determination of pyrogallol. Without added pyrogallol a current plateau appeared at a lower anodic potential than that characteristic of pyrogallol. It suggests that another additive more susceptible to oxidation is present in the cooking oil. Its plateau current was therefore subtracted from the other ones measured in presence of added pyrogallol and these corrected values served for making the calibration plot. By using the intercept at the x-axis 43.2 μM pyrogallol could be determined, but this measured concentration value is only the half of the true value due to addition of acetone so it should be taken into consideration. Finally, the concentration of pyrogallol in cooking oil was 86.4 μM .

The determined pyrogallol concentration is in the range of that usually found in non-aqueous real samples by using indirect electrochemical methods [12-14]. The method introduced in this work seems to be appropriate for the assessment of antioxidant content.

CONCLUSION

The obtained results showed that in non-aqueous solvents resorcinol and phloroglucinol has high susceptibility to electrode fouling while pyrogallol showed obviously larger and more reproducible current signals. Thanks to these facts determination of the latter compound is possible in apolar liquids with microelectrode voltammetry.

EXPERIMENTAL SECTION

High purity solvents and solid materials were used for the investigation of polyhydroxy phenols throughout the entire work which were products of Sigma Aldrich and Acros Organics. The solutions used for the studies were always freshly prepared particularly in case of pyrogallol which is very susceptible to the oxidation. The working electrode was a 1 mm in diameter platinum disc and a 25 μm in diameter platinum microdisc, a platinum wire served as counter and silver wire as quasi reference electrode. A potentiostat (Dropsens, Spain) was used for carrying out the measurements. Before all studies the surfaces of working electrodes were thoroughly polished on a polishing cloth with aqueous suspension of 1 μm average particle size alumina powder. The subsequent ultrasonication in deionized water and thorough washing with deionized water ensured the removal of physically adsorbed particles from the electrode surfaces. In all solutions tetrabutylammonium perchlorate (TBAP) was dissolved as supporting electrolyte.

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