

VOLTAMMETRIC DETERMINATION OF  
DIPYRONE USING GRAPHITE PASTE ELECTRODE  
MODIFIED WITH NANOPARTICLES OF NICKEL  
HEXACYANOFERRATE

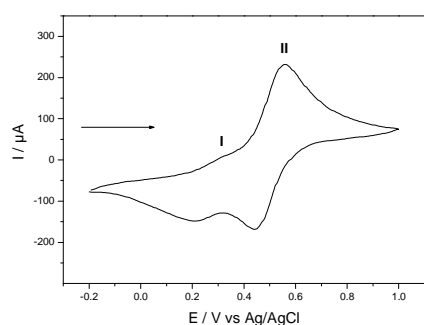
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Nanomaterials are materials that have dimensions on the scale of a few tens of nanometers. Among nanomaterials, nanoparticles are materials that have received great attention due to their potential applications in areas that include chemistry, physics, biology and engineering since, many magnetic properties, electrical, optical and chemical properties that are dependent on particle size [1]. The hexacyanoferrate ion, a Prussian Blue analogue, has been subject of major investigations because of its excellent chemical and electrochemical stability [2] and have an ability to form stable binuclear complexes of transition metals with different oxidation states that can be studied by various spectroscopic and electrochemical techniques, these insoluble binuclear complexes provide a wide range of analytical applications [2]. This paper proposes an alternative synthesis route to obtaining nanoparticles of nickel hexacyanoferrate (NNiHF), using formamide as solvent. The material was characterized by different spectroscopic techniques: by Infrared (FT-IR), X-Ray diffraction (XRD) and Ultraviolet-Visible (UV-Vis) Spectroscopy.

The cyclic voltammogram of the NNiHF modified electrode exhibits two redox couples (Fig. 1), as illustrated in Figure 1. The obtained formal potentials:  $(E^{\theta'})_1 = 0.25$  V and  $(E^{\theta'})_2 = 0.50$  V vs Ag/AgCl (KCl = 1.0 mol L<sup>-1</sup>;  $\nu = 20$  mV s<sup>-1</sup>) were attributed to the redox processes formamide oxidation and [Fe<sup>II</sup>(CN)<sub>6</sub>/Fe<sup>III</sup>(CN)<sub>6</sub>], respectively.

Studies on various supporting electrolytes (KCl, NaCl, LiCl, KNO<sub>3</sub>, NaNO<sub>3</sub> and NH<sub>4</sub>NO<sub>3</sub>) for studies of cations. It was observed that the nature of the cations affected the average potential ( $E^{\theta'}$ ) and the current intensities, but was not verified any interference of anions with exception of chloride (Cl<sup>-</sup>, NO<sub>3</sub><sup>-</sup>).

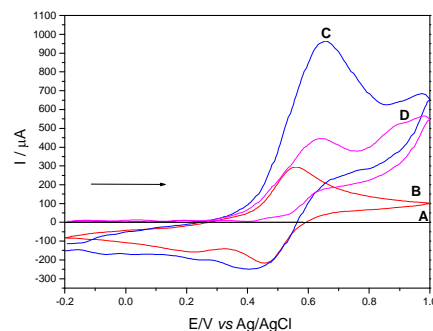


**Figure 1.** Cyclic voltammograms of graphite electrode modified with NNiHF (KCl, 1.0 mol L<sup>-1</sup>;  $\nu = 20$  mV s<sup>-1</sup>; 20% (w/w)).

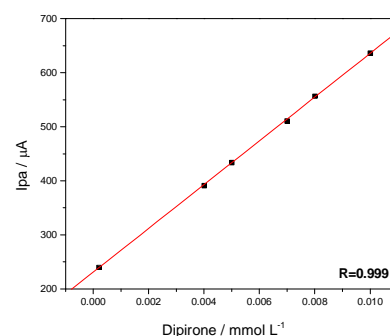
Fig. 2 illustrates the voltammetric behavior of the graphite paste electrode modified with NNiHF for the electro-oxidation of sodium dipyrone.

The modified electrode showed a linear response from  $4.0 \times 10^{-3}$  to  $1.0 \times 10^{-2}$  mol L<sup>-1</sup> with the corresponding

equation  $Y(\mu A) = 230.965 + 40.478 \times 10^3$  [dipyrone], and a correlation coefficient of  $r=0.999$  (Fig. 3). The method showed a detection limit of  $1.63 \times 10^{-4}$  mol L<sup>-1</sup> with a relative standard deviation of  $\pm 2\%$  ( $n = 3$ ) and amperometric sensitivity of  $40.478 \times 10^3$  A mol L<sup>-1</sup>.



**Figure 2.** Cyclic voltammograms: (A) of the graphite paste electrode; (B) graphite paste electrode modified with NNiHF; (C) graphite paste electrode modified with NNiHF and  $1.0 \times 10^{-2}$  mol L<sup>-1</sup> of dipyrone; (D) graphite paste electrode and  $1.0 \times 10^{-2}$  mol L<sup>-1</sup> of dipyrone (KCl 1.0 mol L<sup>-1</sup>; 20 mV s<sup>-1</sup>; 20% (w/w)).



**Figure 3.** Analytical curve for the determination of dipyrone using the graphite paste electrode modified with NNiHF (KCl 1.0 mol L<sup>-1</sup>; 20 mV s<sup>-1</sup>; 20% (w/w)).

The electrocatalytic oxidation of dipyrone occurs as follows: Fe<sup>3+</sup> produced during anodic scan, chemically oxidize the molecule dipyrone when it is reduced to Fe<sup>2+</sup>, which will again be electrochemically oxidized to Fe<sup>3+</sup>.

## Conclusion

The use of electrodes modified with NNiHF presented themselves susceptible to being employed for the determination of dipyrone, is advantageous because dispense any prior chemical treatment, it is easily confection, allowing the surface to be quickly renewed thereby decreasing the time for its quantification.

## Acknowledgements

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## References

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