

*Full Paper*

## **Sensitive Determination of Copper on New Modified Glassy Carbon Paste Electrode**

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**Abstract-** This paper describes determination of trace level of copper ions on a new type of modified glassy carbon paste electrode based on addition of different amount of Co-ferrites in glassy carbon paste (CoFeMGCPe). Co-ferrite nanoparticles with different amount of cobalt were synthesized and characterized using scanning electron microscopy (SEM) and X-ray powder diffraction (XRPD). A significant increase in current was achieved by introducing modifier in composition of the electrode in comparison with the bare glassy carbon paste electrode. Electrochemical parameters such as percentage of modifier, accumulation time and potential, pH and the optimized amount of cobalt in the ferrites were determined. The best voltammetric response was observed for  $\text{Co}_{0.5}\text{Fe}_{0.5}\text{Fe}_2\text{O}_4$  when percentage of modifier was 3%. In acetate buffer solution, pH 4.5, thus prepared electrode displays selective detection toward copper ions, detection limit of 96 nM and it was successfully applied for the determination of copper ions in natural water samples, with satisfactory recovery.

**Keywords-** Co-ferrite, Modified electrode, Glassy carbon paste, Copper

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## 1. INTRODUCTION

Differential pulse anodic stripping voltammetry (DPASV) because of its relatively low cost instrumentation, capability for simultaneous multi-element determination, sensitivity and remarkably low detection limit is one of the most used methods for determination of numerous ions besides other methods for analysis, like ion-selective electrode (ISE), atomic absorption spectrometry (AAS), inductively coupled plasma (ICP) and emission spectrometry. Other methods require sophisticated instruments, consuming manipulation step and special training. [1-7]. Methods employing DPASV technique can be successfully used for the determination of metal ions in water [8,9].

Copper is an essential micronutrient present in more than thirty enzymes, but in certain concentration it is toxic. Because the European Water Quality Directive and World Health Organization recommends that concentration of copper in drinking water should not to exceed 2 mg/L, a sensitive and low cost method for determination of copper is of the great interest [10,11].

Co-ferrite ( $\text{CoFe}_2\text{O}_4$ ) is a well-known hard magnetic material with high coercitivity and moderate magnetization. These properties, along with their great chemical and physical stability, make  $\text{CoFe}_2\text{O}_4$  nanoparticles suitable for wide fields of applications, such as electronic and biomedical [12-15].

A great variety of techniques has been used to obtain ferrite nanoparticles. The relationship between synthesis and applications is based on the fact that synthesis procedure determines structural and microstructural characteristics of materials. These characteristics further have favourable influence in physical (magnetic, electrical, optical) properties of the applied materials.

The mechanochemical route [16] has been recognized as a powerful method for the production of high-performance and low-cost materials. Stoichiometric and chemically pure nanoscale Co-ferrite was prepared by this way [17].

Recent years ferrites and its modifications, also and different modifiers, were used for modification of glassy carbon electrode and its application for the determination of different toxic metals [15,18,19-21].

All described above was the main reason why we decided to develop a new modified glassy carbon paste electrode for sensitive determination of copper ions. Preparation of Co-ferrite modified glassy carbon paste electrode, mechanochemical synthesis and characterisation of different Co-ferrite using scanning electron microscopy and X-ray diffraction, was done. The influence of some metal ions, selected as the most common companions of copper in water, were investigated. Thus prepared electrode was successfully applied for copper ions determination by using differential pulse anodic stripping voltammetry in water samples without any pre-treatment.

## 2. EXPERIMENTAL

### 2.1. Reagents

Copper ions stock solution ( $1 \times 10^{-3}$  mol/L) was prepared from  $\text{CuSO}_4 \times 5 \text{H}_2\text{O}$  (Sigma Aldich), and standardized complexometrically. Working solutions for DPASV investigations were prepared by diluting the appropriate amount of the stock solution in supporting electrolyte. Acetate buffer solutions 0.1 mol/L (different pH) was used to investigate optimal pH. The buffer solutions were prepared from sodium acetate and acetic acid, different ratio. All reagents were of analytical grade. Ultrapure water (Milli-Q plus 185, system Millipore) was used in all experiments.

The voltammetric responses of the chemically modified electrode (CME) were measured with the Metrohm 797 VA Computance instrument (Herisau, Switzerland). The triple-electrode system consisted of a working electrode, our modified glassy carbon (GC) paste electrode, home-made Teflon body, with working diameter 2 mm, a reference Ag/AgCl, KCl (3 M) (Model 6.0728.010) and an auxiliary platinum rod electrode (Model 6.0340.000). All measurements were taken at ambient temperature. During the accumulation step the sample was stirred. To remove oxygen, nitrogen was purged for 60 s.

All measurements were carried out in acetate buffer pH solution 4.5 (after optimization of pH). The potential range, where DP stripping steps were performed was set from -0.2 to 0.05 V vs. Ag/AgCl electrode with scan in anodic direction (reoxidation of metal to metal ions) at following optimized conditions: deposition potential -0.3 V and deposition time 4 min (pulse amplitude 50 mV, pulse time 40 ms). A series of standard solutions of copper ions for calibration curves and the recovery studies were measured by DPASV under the optimized working parameters describe above. The influence of possible interference was investigated under the same experimental conditions.

The morphology of the powders and the sizes of mechanochemically synthesized ferrite crystals were examined by SEM Jeol JSM-6610LV. The X-ray powder diffraction (XRPD) analysis of the synthesized products was conducted using Philips PW-1710 automated diffractometer (equipped with a diffracted beam curved graphite monochromator and a Xe-filled proportional counter) using a Cu-tube operated at 40 kV and 30 mA. Data were collected in the  $2\theta$ -range between  $15\text{--}60^\circ$  with a counting time of 2.5 s per step and a step size of  $0.05^\circ 2\theta$ . A fixed  $2^\circ$  divergences and 0.2 mm receiving slits were used.

### 2.2. Reagents

#### 2.2.1. Preparation of river water samples

The water samples (1,2) were obtained from the two rivers, Danube and Sava, Belgrade, Serbia. After taking samples water was acidified with nitric acid (final concentration  $\sim 1\%$ ). Each water samples was filtered through a filter paper to obtain a clear filtrate and then

quantitatively transferred into 50 mL volumetric flask and stored in a fridge at 4 °C. The determination of copper was performed as follows: the calculated amount of standard addition of copper ions was added to the volumetric flask containing 2 mL of river water and 8 mL of supporting electrolyte solution. The solution was stirred and ultrapure nitrogen was bubbled to remove dissolved oxygen. Every sample was analysed by standard addition method.

### 2.2.2. Synthesis of Co-ferrite

Mechanochemical synthesis of Co-ferrite was performed in planetary ball mill, Retsch PM 100 CM. Co-ferrite samples ( $\text{CoFe}_2\text{O}_4$ ,  $\text{Co}_{0.75}\text{Fe}_{0.25}\text{Fe}_2\text{O}_4$ ,  $\text{Co}_{0.50}\text{Fe}_{0.50}\text{Fe}_2\text{O}_4$ ,  $\text{Co}_{0.25}\text{Fe}_{0.75}\text{Fe}_2\text{O}_4$  and  $\text{Fe}_3\text{O}_4$ ) were obtained by the mechanochemical reaction of Co(II), Fe(II) and Fe(III) carbonates mixed in stoichiometric ratios. Mechanochemical treatment was performed in a planetary ball mill. A hardened steel vial of 150 cm<sup>3</sup> volume, filled with 10 hardened steel balls with a diameter of 8 mm, was used as the milling medium. The mass of powder mixtures was 5 g and the balls to powder mass ratio was 20:1. The milling was carried out in air atmosphere without any additives. Milling time was 10 h, at 500 rpm.

### 2.2.3. Preparation of unmodified glassy carbon paste electrode (GCPE) and Co-ferrite nanoparticles modified glassy carbon paste electrode (CoFeMGCPE)

Unmodified carbon paste electrode was prepared by mixing of 80% of glassy carbon powder (Sigma Aldrich) and 20% of paraffin oil. The glassy carbon powder was taken because of its advantages in comparison with carbon powder. The modified glassy carbon paste electrode (CoFeMGCPE) was prepared by hand-mixing of glassy carbon powder with different percentage of Co-ferrite (from 1 to 5%, to get 80% of paste) followed by mixing with 20% of paraffin oil in a mortar for approximately 10 min to form the homogeneous modified glassy carbon paste. After the homogenization of the mixture the paste was placed into the inner hole of the working electrode body, the electrode surface was polished with a weight paper until the surface had a shiny appearance and it was used directly for voltammetric measurements without preconditioning.

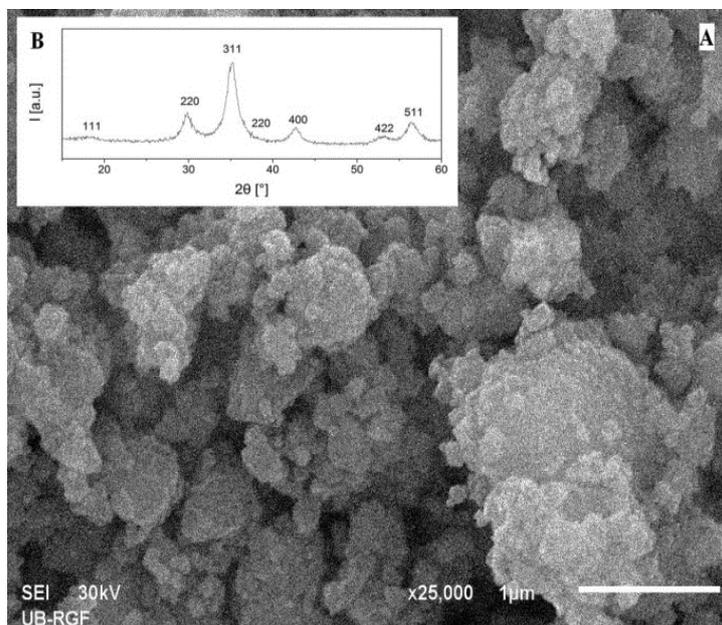
## 3. RESULTS AND DISCUSSION

### 3.1. Characterisation of ferrites

Figure 1 A) SEM image of the modifier; B) Characteristic spinel XRPD pattern of the modifier ( $\text{Co}_{0.5}\text{Fe}_{0.5}\text{Fe}_2\text{O}_4$ )

SEM picture (Fig. 1) shows that all obtained ferrite materials are ultrafine, with particle size mostly between 10-50 nm and well agglomerated structure.

From representative XRPD pattern of mechanochemically synthesized ferrite (Inset of Fig. 1) it is obvious that obtained material crystallizes in spinel type structure. On the other hand very broad peaks lead to the conclusion that crystallites are nanosized.



**Fig. 1.** A) SEM image of the modifier; B) Characteristic spinel XRPD pattern of the modifier ( $\text{Co}_{0.5}\text{Fe}_{0.5}\text{Fe}_2\text{O}_4$ )

### 3.2. Optimization of different ferrites depending of amount of cobalt and percentage of modifier

Before starting optimization these two parameters, the best conditions for determination of copper at the bare glassy carbon electrode using DPASV were determined. The highest value for peak current at bare glassy carbon electrode was at pH 4.5 (acetic buffer), deposition potential -0.4 V and deposition time 3 min for 5  $\mu\text{M}$  concentration of copper (data not shown). After that, the best percentage of the modifier was investigated when the modifier was 3%  $\text{CoFe}_2\text{O}_4$ . At the same condition as for the bare glassy carbon electrode the percentage of 3%  $\text{CoFe}_2\text{O}_4$  has the highest peak current for the determination of copper ions, approximately the peak current was 20% higher than those obtained for bare glassy carbon paste electrode (data not shown). For the experiments for optimization of amount of cobalt in the ferrite, was used 3% of modifier. As can be seen from the Table 1, when amount of cobalt increased and amount of iron decreased in the ferrite structure, the peak current become higher, to the value of 0.5 of amount of cobalt and 0.5 amount of iron. When the ferrite was 1 Co/1 Fe ( $\text{Co}_{0.5}\text{Fe}_{0.5}\text{Fe}_2\text{O}_4$ ) the current has maximum value. For further increase the amount of cobalt and decrease the amount of iron the current is decreased in comparison to the maximal value. From Table 1 it can be concluded that the highest peak current for the copper ions

determination was achieved when the modifier was  $\text{Co}_{0.5}\text{Fe}_{0.5}\text{Fe}_2\text{O}_4$  and the percentage of added modifier was 3%.

**Table 1.** Obtained current for copper ions with different modified electrodes, percentage of modifier 3%, supporting electrolyte acetate buffer pH 4.5, accumulation time 3 min, accumulation potential -0.4 V, concentration of Cu (II) 5  $\mu\text{M}$

Ferrites	Current obtained for copper (nA)
$\text{CoFe}_2\text{O}_4$	71
$\text{Co}_{0.25}\text{Fe}_{0.75}\text{Fe}_2\text{O}_4$	120
$\text{Co}_{0.5}\text{Fe}_{0.5}\text{Fe}_2\text{O}_4$	365
$\text{Co}_{0.75}\text{Fe}_{0.25}\text{Fe}_2\text{O}_4$	36
$\text{FeFe}_2\text{O}_4$	Non detectable

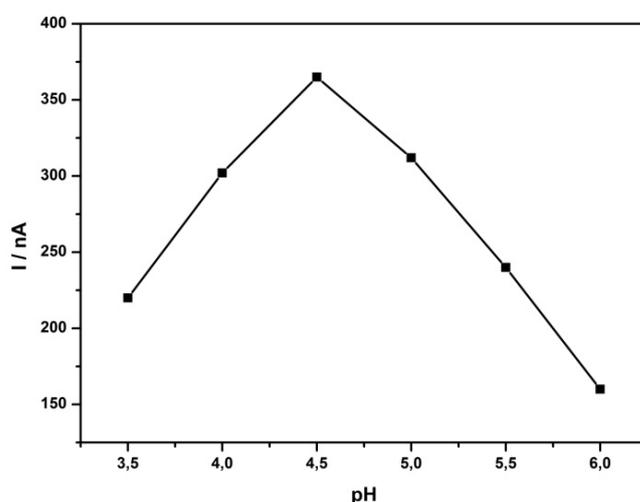
### 3.3. Effect of pH of the supporting electrolyte on the response of the modified electrode

Based on previously study at the bare glassy carbon paste electrode, the influence of pH was investigated in range of 3.5-6. As well as for the bare glassy carbon paste electrode (Fig. 2) the peak current is increased by changing pH from 3.5 to 4.5, after which a further increase of the pH value coming to a reduction in the intensity of the peak current. These results confirm our hypothesis that the pH value has a big influence on specific adsorption towards Cu (II) and that weak peak current obtained at low pH (3.5 and 4) is probably due to this modifier (oxide) being less stable at low pH, and thus, less sorption will occur. From these results, the best pH of supporting electrolyte for the copper ions determination with proposed modified glassy carbon paste electrode was pH 4.5, and for all further experiments pH 4.5 was used for determination.

### 3.4. Effect of accumulation potential and accumulation time

In stripping analysis preconcentration of target analyte onto a certain substrate is significant. Thus, the voltammetric signal was controlled by how well the electrode materials can adsorb analyte, which are subsequently accumulated on the electrode surface. In order to confirm the preconcentration mechanism of the modified electrode in compared with bare GCPE (bare GCPE, GCPE modified with  $\text{Fe}_3\text{O}_4$  and GCPE modified with  $\text{Co}_{0.5}\text{Fe}_{0.5}\text{Fe}_2\text{O}_4$ ) the 5  $\mu\text{M}$  of copper ions was determined with all three electrodes. The lowest peak current after experiments is measured at sample with bare GCPE, then  $\text{Fe}_3\text{O}_4$  modified electrode and on the end in the sample with  $\text{Co}_{0.5}\text{Fe}_{0.5}\text{Fe}_2\text{O}_4$  modified GCP electrode. Compared with bare GCPE, the  $\text{Fe}_3\text{O}_4$  modified electrode showed higher peak current for copper ions confirm the role of ferrites for accumulating metal ions and consequently enhances the sensitivity. Aim of

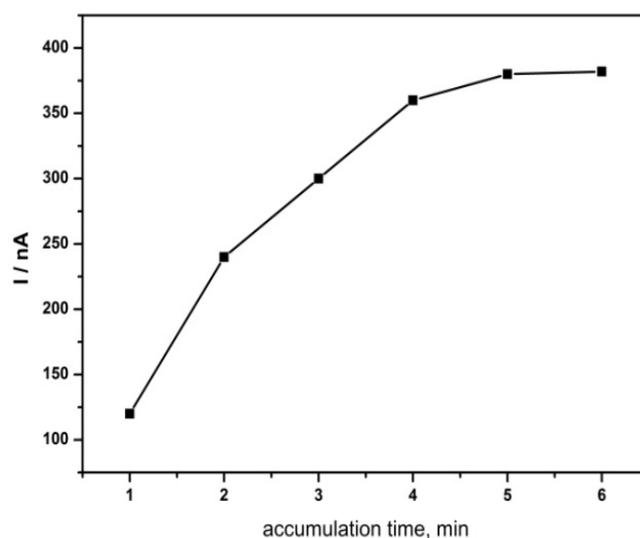
this work was to further enhanced adsorption of copper ions by introducing different modified ferrites (e.g. Co-ferrites). These electrodes can serve as basis for preparation of screen printed electrodes, and as basis for further modification and preparation of biosensors. To the best of our knowledge, this paper for the first time dealing with introducing this kind of modified ferrites in carbon paste electrodes. Peak current, for this further modified electrode, become higher than for unmodified and carbon paste electrode modified with  $\text{Fe}_3\text{O}_4$ . This hypothesis may well explain the phenomenon because there are differences between different ferrites in affecting analysis of copper ions (see Table 1.). However, to clarify this effect, more studies are necessary.



**Fig. 2.** Effect of different pH of supporting electrolyte on peak current of copper ions, working electrode 3% modified  $\text{Co}_{0.5}\text{Fe}_{0.5}\text{Fe}_2\text{O}_4$ , accumulation potential  $-0.4$  V, accumulation time 3 min, concentration of Cu (II)  $5 \mu\text{M}$ , supporting electrolyte acetate buffer different pH

As expected for voltammetry with increasing accumulation time the peak current for the copper determination obtained by DPASV increased proportional to the accumulation time up to 4 min (Figure 3). Further increase of the preconcentration step the observed current becomes almost constant, changes in intensity becomes negligible. Taking into account the time required for the analysis of a sample, optimal accumulation time for thus prepared electrode was 4 min.

From Table 2 it can be concluded that the accumulation potential that gives the highest value of the peak current with the proposed electrode was  $-0.3$  V. At the  $E_{\text{acc}}$  values more positive than those the peak currents were lower. At the more negative potential values ( $-0.4$  and  $-0.5$  V) the current decreased, because there was probably reduction of some amount of iron which was in the structure of the modifier.



**Fig. 3.** Effect of accumulation time on peak current of copper ions, working electrode 3% modified  $\text{Co}_{0.5}\text{Fe}_{0.5}\text{Fe}_2\text{O}_4$ , accumulation potential  $-0.4$  V, concentration of Cu (II)  $5 \mu\text{M}$ , supporting electrolyte acetate buffer pH 4.5

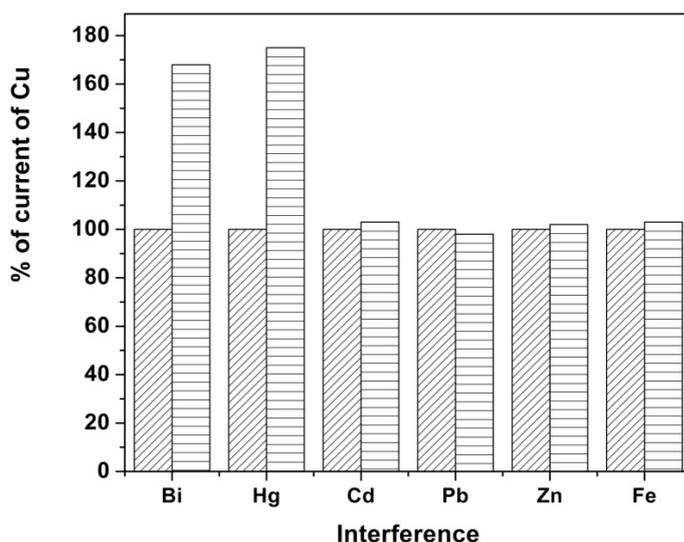
**Table 2.** Effect of different accumulation potential on peak current of copper ions, working electrode 3% modified  $\text{Co}_{0.5}\text{Fe}_{0.5}\text{Fe}_2\text{O}_4$ , accumulation time 4 min, concentration of Cu (II)  $5 \mu\text{M}$ , supporting electrolyte acetate buffer pH 4.5

Accumulation potential	Peak current (nA)
-0.1	84
-0.2	1550
-0.3	1750
-0.4	1310
-0.5	1120

### 3.5. Effect of possible interfering cations on the response of the sensor

Selectivity of electroanalytical methodology presented important parameter of its applicability in real sample analysis. As could be concluded from the Figure 4. the peak shape obtained from DPASV was regular and the most of the cations presented in natural water which are likely to be present together with copper do not has influence on the determination of copper ions with the proposed modified electrode and the proposed method. Concentration of copper ions in these experiments was  $1 \mu\text{M}$ . The interfering agent was considered to interfere if it gives a signal change more than 3%. No alteration of the

voltametric signals of copper was experienced in excess of following ions:  $\text{Li}^+$ ,  $\text{Na}^+$ ,  $\text{K}^+$ ,  $\text{Cs}^+$ ,  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$ ,  $\text{Ba}^{2+}$ ,  $\text{Mn}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Fe}^{2+}$ ,  $\text{Fe}^{3+}$  and  $\text{Cd}^{2+}$ , when they were presented in molar ration 1:1, 10:1 and 50:1 relative to copper. Concerning Hg and Bi as interference, the high effect was register already in presence of these cations in ratio 1:1, because if their close peak potentials under these optimized experimental conditions, and overlapping with copper peak (Fig. 4).

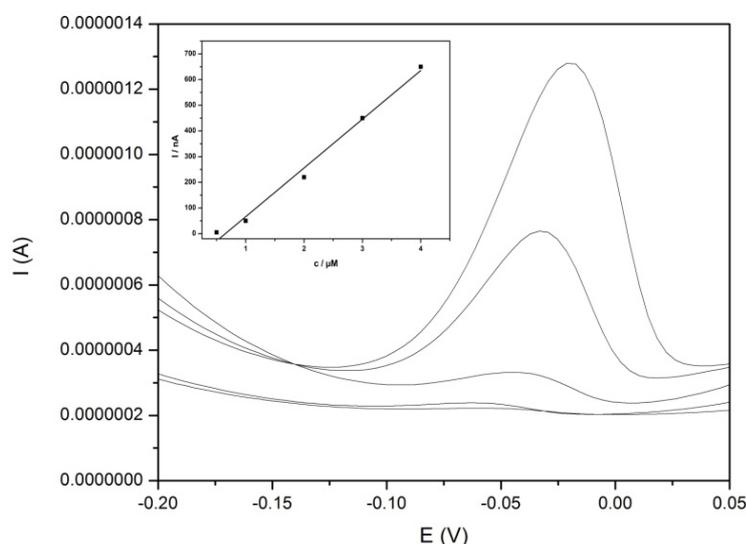


**Fig. 4.** Effect of most common interferences on peak current obtained for copper without presence of interferences under optimized experimental parameters

### 3.6. Calibration data and analytical application

Application of the proposed method in real sample analysis was examined by construction of calibration curve by plotting peak current obtained under optimized experimental conditions against concentration of copper. DPAS voltammograms and calibration curve for different copper ions concentration were presented at Figure 5. From this observation it can be seen that with increasing concentration of copper ions the peak potential shifts to positive value. There are two theories about this phenomenon. According to the first theory the peak potential shifts with increasing metal ions concentrations are the consequence of the overlap diffusion layers produced from the stripping of the  $\text{M}^0$  to the  $\text{M}^{n+}$  in solution. Second theory, which dealing with ionic liquids, says that the presence of the ionic liquids, which some authors have used to improve characteristics if ferrite as a modifier, have an influence on the overlap of diffusion layers. In our work, we think that peak potential shifts occur according to the first theory, because as modifier we used solid ferrites, modified with different metals in their structure, without ionic liquids [15,18]. Correlation coefficient, corresponding equation, detection limit based on the three times background noise was

calculated, and also the one main advantage of each electrode, the reproducibility. For the proposed CoFeMGCPE electrode obtained linear range was 0.5-4  $\mu\text{M}$  corresponding equation was  $I \text{ (nA)} = -123.23 + 189.63 c \text{ (\mu M)}$ , the correlation coefficient was  $R^2 = 0.987$  and the detection limit was 0.096  $\mu\text{M}$  based on three times the background noise. LOQ obtained for proposed sensor under optimized parameters was 0.35  $\mu\text{M}$ . The linear range of proposed electrode under optimized electroanalytical parameters was from 0.5 to 4  $\mu\text{M}$ . Under the optimum condition the reproducibility from 8 repetitive measurements of concentration of 1  $\mu\text{M}$  copper ions was calculated to be 3.5% and for 3  $\mu\text{M}$  of copper ion 2.8%. From the results it can be concluded that this electrode could improve the sensitivity and selectivity of the modified electrode and can be applied for determination of copper ions in real samples of natural water.



**Fig. 5.** Differential pulse voltammograms and calibration curve obtained for different concentration of copper ions under optimized parameters

The determination of copper ions, from two natural waters samples without any pre-treatment, and the recovery, calculated for this determination, was presented in Table 3. Standard additions were added to made determination possible. The results are obtained after 3 measurements, as average value. For the method validation amount of copper ions in samples was measured with ICP-OES technique. After comparison of these two methods it is obvious that results obtained with proposed method are in good agreement with those obtained with standard ICP-OES method. Different oxide materials, such as  $\text{MnO}_2$ , are widely used to improve characteristics of carbon paste electrode. This study can serve as basis for its further modification and preparation of screen printed electrodes, for  $\text{H}_2\text{O}_2$  analysis, or as basis for preparation of biosensors. This electrode enabled direct determination

of copper ions in water had easily preparation procedure and the detection limit which is comparable to other electrodes proposed in the literature.

**Table 3.** Recovery tests for determination of copper ions in water samples

Sample	Cu in water before adding, ( $\mu\text{M}$ )	Added Cu ( $\mu\text{M}$ )	Found (average after 3 measurements), ( $\mu\text{M}$ )	Recovery%	Found by ICP-OES ( $\mu\text{M}$ )
1.	n. d.	1.00	1.02	102	1.0239
2.	n. d.	1.00	1.04	104	1.0403

n. d. non detectable

#### 4. CONCLUSION

For the first time introducing of Co-ferrites as modifiers in glassy carbon paste electrodes was presented in this paper. The cobalt ferrites, with different amount of cobalt were synthesized and characterized. The optimal electroanalytical parameters were selected. Preparation of new Co-ferrites modified glassy carbon paste electrode and its analytical application for determination of copper ions in water samples without any pre-treatment was developed. The modified electrode with low detection limit, high sensitivity and selectivity was successfully applied for determination of copper ions in natural waters.

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