CARBON PASTE ELECTRODE MODIFIED WITH ORGANOFUNCTIONALIZED MESOPOROUS SILICA FOR ELECTROCHEMICAL DETECTION AND DETERMINATION OF COPPER(II) USING CYCLIC VOLTAMMETRY AND ANODIC STRIPPING VOLTAMMETRY

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A carbon paste electrode modified with hexagonal mesoporous silica functionalized with acetyl-acetone (AcAcNH$_2$-HMS) was prepared and used as a sensor for copper(II). The advantage of mesoporous HMS silica is that it is not necessary a pre-treatment before modifying the surface, compared to silica gel typically used in these methods. In order to characterize the electrochemical behaviour of carbon paste - functionalized HMS silica mixture, to detect and to determine copper(II) in aqueous medium, cyclic voltammetry and anodic stripping voltammetry were used. The best results were obtained under the following conditions: 100 mV·s^{-1} scan rate, - 0.65 V vs. SCE deposition potential, 210 s accumulation time in Britton-Robinson buffer (pH 2.56). Linear response to copper(II) was found between $0.4 \cdot 10^{-6}$ and $8 \cdot 10^{-5}$ mol·L^{-1}, with a detection limit of $3.02 \cdot 10^{-7}$ mol·L^{-1}.

INTRODUCTION

The sensitivity of electrochemical sensors can be enhanced by modifying the electrode surface with a suitable chemical reagent liable to accumulate the target analyte.[1-4] This accumulation process induces a local increase of the analyte concentration at the electrode surface, which becomes considerably higher than in solution and enables various chemical species detection at trace levels using anodic stripping voltammetry. The general analytical procedure involves two main steps: a chemical accumulation performed at open circuit in the analyte solution, followed by voltammetric quantification of the analyte. Various electrode modifiers were used for this purpose, including ion exchange materials, chelating agents or selective adsorbent.[1-7]

The discovery of MCM-41, MCM-48 and SBA-15 first reported in 1990's, led to a whole new class of materials with high thermal and mechanical stability.[4,8] The continuing development of mesoporous silica led to numerous studies in this field. Due to their uniform pore size, hexagonal array of one-dimensional cylindrical channels and large surface area, mesoporous silica are important for applications in emergent areas as energy storage in double layer supercapacitors, catalytic support in fuel cell electrodes, adsorption of bulky molecules in liquid phase, improvement of selectivity and sensitivity in the preparation of electrodes for electroanalysis. Walcarius,[6,7,9] Cesarino[10,11] and B.J. Melde et al.[8] presented extensive reviews about the preparation and application of silica modified electrodes showing their importance as electroanalytical sensors. Mesoporous silica can be

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modified and functionalized by incorporation of organic groups in the silica structure either during the synthesis or by immobilization of organic moieties that can be attached to the silanol groups on the silica surface.

The new electrochemical sensors based on electrochemical stripping appear to be a promising tool for determining aqueous heavy metal concentrations, being sensitive, compact, low cost and easily integrated into portable analysis systems.[11] Carbon paste electrodes modified with functional ligands have been widely used to pre-concentrate and quantify trace metal ions,[12-24] especially from environmental samples.

In the present work the preparation, characterization and the use of organofunctionalised HMS silica with acetyl-acetone (AcAcNH$_2$-HMS) in the preparation of carbon paste modified electrodes are described. HMS silica has the advantage that a pre-treatment it is not necessary before modifying the surface. The aims were to prove the ability of AcAcNH$_2$-HMS to be a carbon paste electrode modifier, to obtain an electrochemical sensor for copper(II) ions, as well as to emphasize the analytical characteristics and performances of this sensor.

EXPERIMENTAL

Apparatus

All the voltametric measurements were carried out with an voltametric analyzer Voltalab PST 050 Radiometer, controlled by VoltaMaster 4.0 software, in a 20 mL capacity thermostated glass cell at 25°C, using a carbon paste modified with AcAcNH$_2$-HMS as working electrode, a saturated calomel as reference electrode (SCE) and a platinum wire as auxiliary electrode. High purity argon (Linde Gas 5.0) was used for solutions deaeration. For the stripping step linear sweep anodic stripping voltammetry was used.

FTIR spectra were performed on a Bruker Vector 22 spectrometer after heating the samples at 50°C, in vacuum, to eliminate the adsorbed water at pores surface.

The atomic absorption measurements were carried out with an M Series AA Spectrometer (Thermo Fisher Scientific).

Reagents and solutions

All the necessary solutions were prepared with water purified in a Millipore Mili-Q system. All the chemicals were of analytical grade. The supporting electrolyte for voltammetric experiments was a pH 2.56 Britton-Robinson buffer solution. Stock solutions of $1 \cdot 10^{-3}$ mol L^{-1} copper(II) were prepared daily by dissolving an appropriate amount of copper sulphate (Merck) in 100 mL volumetric flask, in Britton-Robinson buffer solution (pH 2.56).

Dodecylamine (Aldrich), tetraethoxysilane (TEOS) (Fluka), 3-aminopropyl-triethoxysilane (APTES) (Aldrich) and 3-

bromo-2,4-pentandione (synthesised according to[25]) were used to functionalize the HMS silica. Graphite powder (with particles diameter < 20 μm) (Fluka) and paraffin oil (Merck) were used for the preparation of carbon paste electrodes.

Preparation of acetyl-acetone functionalized HMS silica

For the acetyl-acetone functionalized HMS silica, dodecylamine (CH$_3$(CH$_2$)$_{11}$NH$_2$) was used as a template and TEOS was used as a silica precursor and ethanol as co-solvent.

In order to obtain HMS silica, dodecylamine (3.7072 g) was dissolved in a mixture of ethanol (46 g) and H$_2$O (72 g) and stirred for 30 min. TEOS (16.66 g) was thereafter added dropwise, under vigorous stirring. The mixture was stirred for 20 h at room temperature. The resulting precipitate was filtered and air dried. The product was then washed for the surfactant removal by Soxhlet extraction with ethanol for 24 h, and then dried for 24 h at room temperature and for 1 h at 373 K.

Firstly, the HMS silica was silanized with APTES according to a previously described procedure.[28] Thereafter, the NH$_2$-HMS solid (1 g), activated under vacuum at 403 K for 1 h, was dispersed in a mixture of dry toluene (15 mL) and dry tetrahydrofurane (15 mL) before adding 1 mL of 3-bromo, 2,4-pentandione. The mixture was refluxed at 403 K for 8 h under N$_2$ flux and the obtained solids (AcAcNH$_2$-HMS) were collected by filtration and washed successively with toluene, ethylic alcohol and diethyl ether. The obtained samples were dried under vacuum at room temperature.

Preparation of the modified carbon paste electrodes

Organofunctionalized HMS modified carbon paste electrodes (MCPE) were prepared by homogenous mixing HMS-NH$_2$AcAc with graphite powder at typical ratio (1:6). Subsequently, paraffin oil was added, mixing thoroughly to obtain a homogenous paste. The carbon paste electrode was finally obtained by packing the paste into a plastic tube (2 mm interior diameter). A copper wire served as an external electric contact. The surface was smoothed on a bond paper. When necessary, a new surface was obtained by pushing an excess of paste out of the tube, removing this excess, and again mechanically polishing the electrode surface.

RESULTS AND DISCUSSION

## Characterization of HMS and modified HMS

The advantage of mesoporous silica compared to amorphous silica gels is that the surface nature (especially the number and distribution of silanol groups that participate to functionalization) could be more easily controlled. Despite of the hexagonal mesoporous silica (HMS) being less ordered than the MCM-41 and SBA-15 materials, they are much easier and straightforward to synthesize due to the use of a cheap and neutral template, i.e. long chain amines, which does not require the need of strongly acidic conditions.[29]

For the HMS silica synthesis a fixed DDA:TEOS:H$_2$O:EtOH ratio of 1:4:200:50 was

used knowing that this ratio is important for the control of the morphology and of the silica pore structure.[26, 27]

The organic–inorganic hybrid materials were obtained by a two-step post-grafting procedure with 3-aminopropyl-triethoxysilane (APTES) and 3-bromo-2,4-pentandione, respectively. In the first step the –SiOH groups on the silica surface were silanised with APTS. The amino groups then reacted with 3-bromo-2,4-pentandione molecules to form bidentate ligand containing oxygen chelating groups supported on the HMS surface:
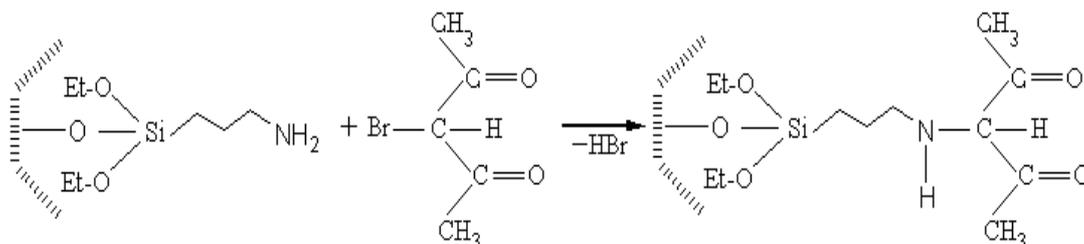
FTIR spectra of the HMS precursor and of the organic-inorganic hybrid HMS materials are illustrated in Figure 1 and confirm the organic functionalities grafting on the HMS mesoporous silica surface. The infrared spectrum of the calcinated HMS showed the typical Si–O lattice vibration: two broad bands between 2000-1750 cm^{-1}, with medium intensity, a strong and broad band with two peaks in the 1450-900 cm^{-1} region and two strong bands between 900-450 cm^{-1}. Furthermore, a very broad band centred at 3450 cm^{-1}, due to the O–H stretching vibrations. A band at 1618 cm^{-1} was also observed in the spectrum and was attributed to the H–O–H bending vibration of physisorbed water.
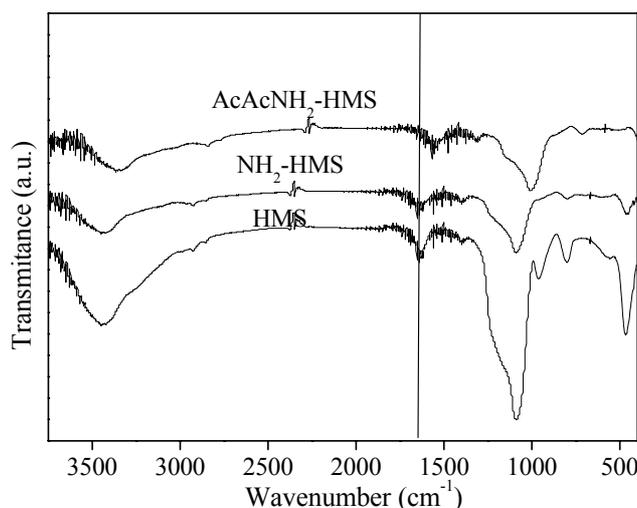

Fig. 1 – FTIR spectra for unmodified HMS and functionalized HMS silica.

Upon amine functionalisation, a decrease of the intensity of the bands at 3450 cm^{-1} and at 800 cm^{-1} was observed. The band at 960 cm^{-1} disappeared indicating that the reaction between the isolated silanol groups of the surface of HMS with the ethoxy groups of the silane derivative took place. The N–H and C–H stretching vibrations of APTES were observed around 3400-3000 cm^{-1} and 3000 cm^{-1}, respectively, and the corresponding H–N–H and H–C–H bending vibrations can also be observed in the 1700-1500 cm^{-1} and 1500-1300 cm^{-1} regions.

The FTIR spectra of the AcAcNH$_2$-HMS showed, with respect to the parent material, some changes in the regions where vibration from APTES occurred: 3500-3000 cm^{-1} region, due to N–H stretching vibrations and 1700-1300 cm^{-1}, weak absorptions due to the H–N–H and H–C–H bending vibrations, that suggesting some molecular changes in the spacer. On the other hand, a new broad band was observed at about 1560 cm^{-1} which may be attributed to the acetylacetonate ring vibration.

The voltammetric behaviour of carbon paste AcAcNH$_2$-HMS modified electrode in presence of Cu^{2+} in Britton-Robinson buffer solution (pH 2.56) was studied. From the cyclic voltammogram obtained in absence of Cu^{2+} (figure 2, curve a) it can be seen that it is not present any signal between +0.400 V and -0.650 V vs. SCE. Voltametric curves obtained for increasing concentrations of Cu^{2+} (figure 2, curve (b1-b3)) showed measurable signals, in cathodic, as well as in anodic scan.
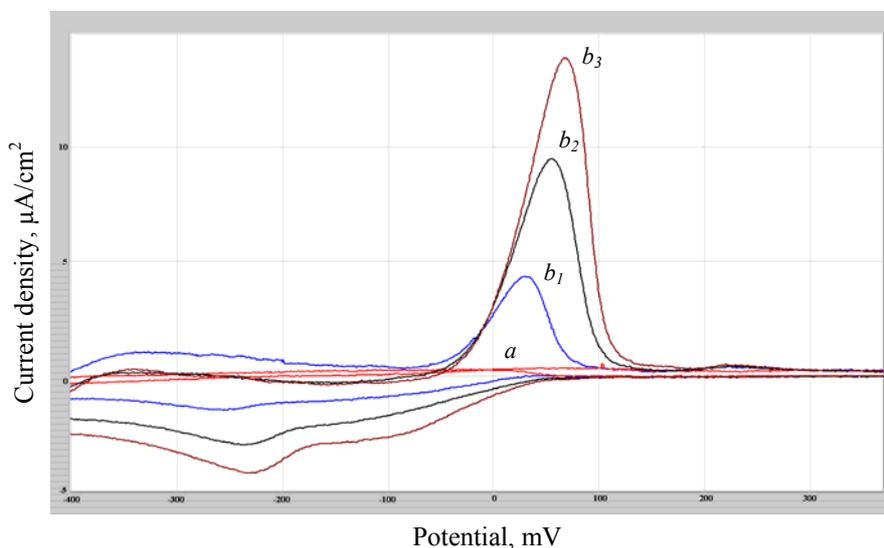

Fig. 2 – Cyclic voltammograms obtained with AcAcNH$_2$-HMS modified electrode in: Britton-Robinson buffer solution (pH 2.56) (a); Britton-Robinson solution (pH 2.56) in presence of $1\cdot10^{-4}$ mol·L^{-1} Cu^{2+} (b1); $2\cdot10^{-4}$ mol·L^{-1} Cu^{2+} (b2); $3\cdot10^{-4}$ mol·L^{-1} Cu^{2+} (b3); 100 mV·s^{-1} scan rate.
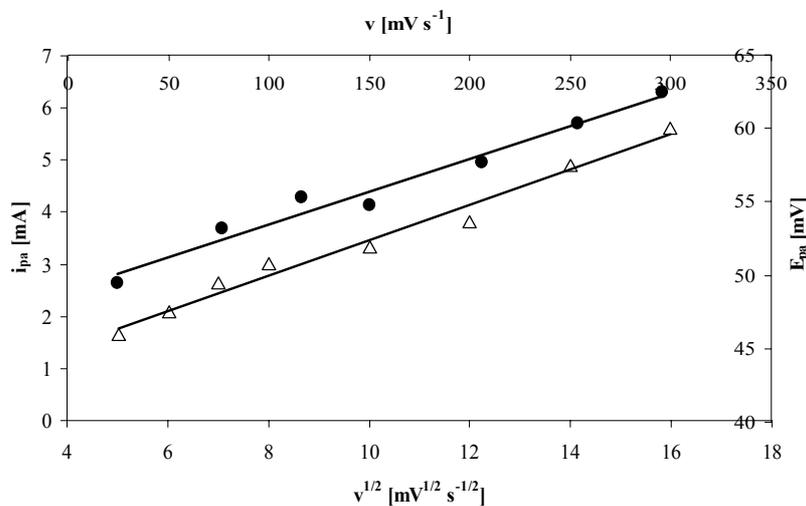

Fig. 3 – Current anodic peak variation vs. square root of scan rate (•) and peak potential variation vs. scan rate (Δ) for $1\cdot10^{-4}$ mol·L^{-1} Cu^{2+} solution, Britton-Robinson buffer (pH 2.56).

On direct scan and for higher scan rates, two reduction peaks are present, poorly defined and wide, whose potentials varied with the concentration increase, from -0.015 V to -0.087 V vs. SCE for the first peak and from -0.209 V to -0.295 V for the second one. These peaks can be attributed to irreversible reduction of Cu^{2+} to Cu$^+$ and Cu$^+$ to Cu^0, respectively. On the reverse scan, a well defined, symmetrical and intense anodic peak appears which slightly modifies, with the concentration increase, from +0.046 V to +0.060 V vs. SCE and which corresponds to Cu^0 deposits oxidation formed during the cathodic scan.

The current variation of the two cathodic peaks vs. scan rate was linear and the peak potentials shifted towards more negative values, fact that corresponds to irreversible reductions.

Linear dependencies of current vs. square root of scan rate for anodic peak and of peak potential vs. scan rate (figure 3) indicate an irreversible oxidation, the irreversibility degree being lower (well defined and intense peaks). Owing to ill defined cathodic signals, the quantitative determination of copper (II) species was realized using the anodic stripping peaks corresponding to copper oxidation.

Parameters optimization for copper(II) determination by linear sweep anodic stripping voltammetry (LSASV)

LSASV of $1 \cdot 10^{-5}$ mol·L^{-1} Cu^{2+} solution in Britton-Robinson buffer (pH 2.56) showed one anodic peak around 0.16 V vs. SCE. Parameters that affect the voltammetric peak current, such as deposition potential, accumulation time, scan rate and pH, were optimized as it follows.

Deposition potential and accumulation time influences

From stripping current variation vs. deposition potential (figure 4) between -0.500 and -0.900 V vs. SCE, came out that the optimal value of this potential is -0.650 V vs. SCE. This value chosen was deposition potential in further studies.

The dependence of anodic peak current with the accumulation time for $1 \cdot 10^{-5}$ mol·L^{-1} Cu^{2+} was also studied (figure 4). The anodic peak current increased with the increase of accumulation time between 30 and 210 s, after that remaining nearly constant due to the electrode surface saturation. Thus, for all subsequent measurements the accumulation time of 210 s was used.
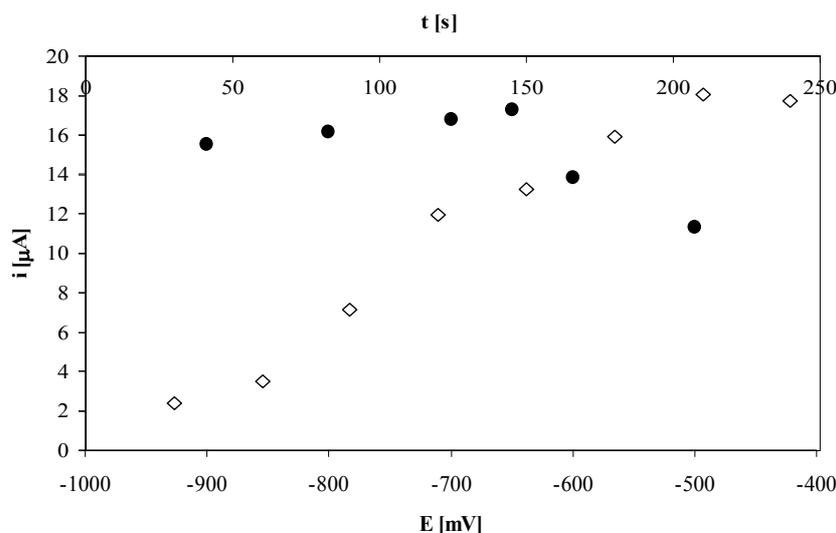

Fig. 4 – Influence of deposition potential (•) and accumulation time (◊) on stripping peak current for $1 \cdot 10^{-5}$ mol·L^{-1} Cu^{2+} solution, Britton-Robinson buffer (pH 2.56), 100 mV/s scan rate.

Supporting electrolyte and pH influence

Voltammetric behaviour of Cu^{2+} was investigated in different supporting electrolytes: HNO$_3$, H$_2$SO$_4$, HCl, HClO$_4$ and Britton-Robinson buffer. Voltammetric peaks were obtained in all investigated supporting electrolyte, but in Britton-Robinson buffer the anodic peak currents were higher and the peaks were better defined, this supporting electrolyte being used in the further experiments. The effect of pH on voltammetric peaks was studied in the range from 2.09 to 7.00, for a $1 \cdot 10^{-5}$ mol·L^{-1} Cu^{2+} solution, in Britton-Robinson buffer (figure 5).

The anodic peak current increased, reaching a maximum at pH 2.56, after that decreasing almost linear. The anodic peak potentials are also pH dependent, shifting towards more anodic values with pH increasing.
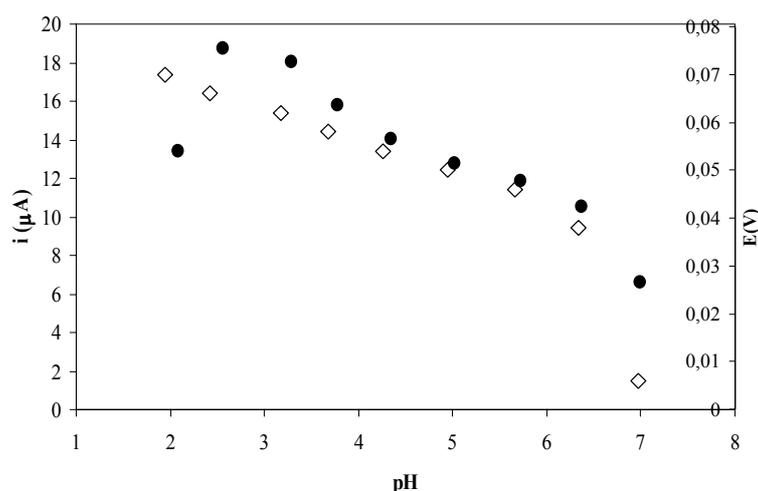
Fig. 5 – Influence of pH on anodic peak current (•) and potential (◊) of $1 \cdot 10^{-5}$ mol$\cdot$L^{-1} Cu^{2+}, in Britton-Robinson buffer (pH 2.56), 100 mV/s scan rate, -0,650 V vs. SCE deposition potential and 210 s accumulation time.

Comparison of voltammetric behaviour of copper(II) on carbon paste and silica modified electrodes

Figure 6 presents anodic stripping voltammograms for a $3 \cdot 10^{-5}$ mol$\cdot$L^{-1} Cu^{2+} solution in Britton-Robinson buffer (pH 2.56) for an unmodified carbon paste electrode (curve a), HMS (curve b) and AcAcNH$_2$-HMS modified carbon paste electrode (curve c).
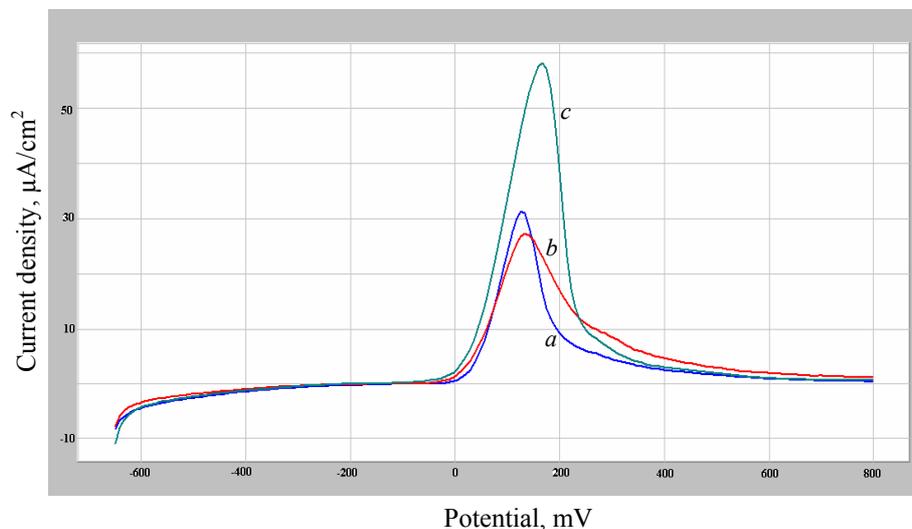

Fig. 6 – Linear sweep anodic stripping voltammograms obtained for $3 \cdot 10^{-5}$ mol$\cdot$L^{-1} Cu^{2+}, at a scan rate of 100 mV/s, in Britton-Robinson buffer (pH 2.56): a) unmodified carbon paste electrode; b) HMS silica modified and c) AcAcNH$_2$-HMS modified carbon paste electrode (deposition potential -0.650 V vs. SCE, accumulation time 210 s).

When the accumulation process was carried out for 210 s at -0.650 V vs. SCE using the unmodified carbon paste electrode, the Cu^{2+} oxidation peak appears at 0.126 V vs. SCE. When was used the HMS modified electrode the peak potential became 0.134 V vs. SCE, the peak widened and the peak current decreased with approximately 15%. For AcAcNH$_2$-HMS modified electrode, the peak potential became 0.158 V vs. SCE and the value of peak current doubled compared to that corresponding to the unmodified electrode. The anodic peak current increase for the functionalized HMS electrode emphasized the important role of the organic functionality grafted on the mesoporous silica in the accumulation process of copper(II) on electrode surface, leading also to a sensitivity growth.

Calibration curve, linearity, precision, accuracy and detection limit

The homogeneity test was carried out to establish the working concentrations range, test that verifies if there are significant differences at working concencentration range limits.[30,31] A preliminary working range was established ($0.4\cdot10^{-6}$ – $8\cdot10^{-5}$ mol·L^{-1} Cu^{2+}) and measurements of copper(II) current peak were done using 10 replicates for minimum concentration level and 10 for the maximum one. Testing value (PG) was calculated (4.97) and was compared with the tabled value of F function (5.35). PG < F, subsequently the concentration range was correctly chosen.

The linearity statistical test was carried out to decide whether the method presents linearity or not. The current peak values for 10 standard solutions, whose concentrations were equidistant dispersed on the whole working range, were measured. After calculating the residual standard deviations for linear ($y = a + bx$) and nonlinear ($y = a + bx + cx^2$) functions, the testing value (PG = 2.21) was calculated and compared with tabled F value (6.99), resulting that nonlinear function does not provide an adjustment (table 1).

Table 1

Linear and nonlinear regression data for copper(II) quantitative determination by LSASV

Linear function y = 2,3494x - 1,1529		
a = -1,1529; s_a = 0,2362	b = 2,3494; s_b = 0,0518	R = 0,9976; R^2 = 0,9952
S_{y1} = 0,4847	S_{x0} = 0,2063	V_{x0} = 5,61%
Nonlinear function y = 0,0356x^2 + 2,0599x - 0,8307		
a = -0,8307; s_a = 0,3110	b = 2,0599; s_b = 0,2007	c = 0,0356; s_c = 0,0240
E = 2,2322		R = 0,99805 ; R^2 = 0,9961
S_{y2} = 0,4578	S_{x0} = 0,1972	V_{x0} = 5,36 %

s_a, s_b, s_c - standard deviation of a, b, c coefficients, R - correlation coefficient, S_{y1} - residual standard deviation for the y estimate in the linear regression, S_{x0} - method standard deviation, V_{x0} - method variation coefficient, E - sensitivity at the center of the working range, S_{y2} - residual standard deviation for the y estimated in the nonlinear regression

In the literature there are several calculation methods for detection limit (DL) determination.[32] Data from the linearity study were used in this case when DL = $3s_a/b$ = $3.02\cdot10^{-7}$ mol·L^{-1}, where s_a is standard deviation of the intercept and b is the calibration curve slope.

The method accuracy was evaluated from the recovery degree of the added analyte from spiked samples. For recovery calculation was used the equation: $r\% = [(C_F–C_U)/C_A]*100$, ($C_F$ - analyte concentration in spiked sample, C_U - analyte concentration in unspiked sample and C_A - spike concentration). Recovery values lied between 93.15% and 103.48%, with an average recovery of 97.4% and a standard deviation of 1.48% (3 additions for each of the 3 identical standard solutions).

Precision can be evaluated on three different levels: repeatability, intermediate precision and reproducibility. In this study only repeatability was considered, being used the proposed method for identical samples, in one laboratory, in a short period of time. Repeatability, usually expressed as percentage relative standard deviation (RSD %), was 1.28 %.

Interferences

AcAcNH$_2$-HMS modified carbon paste electrodes sensitivity towards copper(II) was tested in presence of different metallic species (Pb^{2+}, Zn^{2+}, Cr^{3+}, Ni^{2+}, Mn^{2+}, Cd^{2+}) at different concentrations (the same, half and double compared to the Cu^{2+} concentration). The obtained results underlined that Cu^{2+} signal was influenced by interfering metallic species, namely the voltammetric Cu^{2+} response decreased, but these interferences could be diminished using standard addition method.

Analysis of copper in natural water

The proposed electrode was applied for Cu^{2+} determination by LSASV from natural water sample (5 mL water sample + 5 mL Britton-Robinson buffer, pH 2.56) in optimized conditions (scan rate of 100 mVs^{-1}, deposition potential of -0,650 V vs. SCE, accumulation time of 210 s). The determined copper(II) content in water sample was 0.056 mg·L^{-1} (n = 3) using three standard additions of Cu^{2+} solution. There were no significant differences compared with the concentrations

obtained by flame atomic absorption spectrometry (0.054 mg·L^{-1}), indicating that AcAcNH$_2$-HMS modified electrode can be used for determination of copper(II) in water samples, under optimised conditions and using the standard addition method. The relative error calculated as [(c_{ASV} − c_{AAS})/c_{AAS}]*100 was 3.7%, where c_{ASV} and c_{AAS} are concentration of copper(II) obtained for LSASV and AAS determination, respectively.

CONCLUSION

The use of functionalised silica with acetyl acetone in the preparation of modified paste electrodes is an alternative for copper(II) determination in natural water samples, although the signal was influenced by pH value, supporting electrolyte, deposition potential, accumulation time, scan rate, interfering metallic ions. All these parameters were studied and optimized so an accurate copper(II) determination procedure by linear sweep anodic stripping voltammetry was achieved.

REFERENCES

1. J. Wang, "Stripping Analysis", VCH, Deerfield Beach, Florida, 1985, p. 63.
2. Kh. Brainina, E. Neyman, "Electroanalytical Stripping Methods", Wiley, New York, 1993, p.55.
3. D.W.M. Arrigan, *Analyst*, **1994**, *119*, 1953-1966.
4. S. Sayen, C. Gérardin, L. Rodehüser, A. Walcarius, *Electroanalysis*, **2003**, *15*, 422-430.
5. K. Kalcher, J.-M. Kauffmann, J. Wang, I. Svancara, K. Vytras, C. Neuhold, Z. Yang, *Electroanalysis*, **1995**, *7*, 5-22.
6. A. Walcarius, *Chem. Mater*, **2001**, *13*, 3351-3372.
7. A. Walcarius, *Electroanalysis*, **2001**, *13*, 701-718.
8. B.J. Melde, B.J. Johnson, P.T. Charles, *Sensors*, **2008**, *8*, 5202-5228.
9. A. Walcarius, J. Bessiere, *Electroanalysis*, **1997**, *9*, 707-713.
10. I. Cesarino, G. Marino, J.R. Matos, É.T.G. Cavalheiro, *Ecletica Quimica*, **2007**, *32*, 29-34.
11. I. Cesarino, G. Marino, J.R. Matos, É.T.G. Cavalheiro, *Talanta*, **2008**, *75*, 15-21.
12. R.P. Baldwin, J.K. Christensen, L. Kryger, *Anal. Chem.*, **1986**, *58*, 1790-1798.
13. S.V. Prabhu, R.P. Baldwin, L. Kryger, *Anal. Chem.*, **1987**, *59*, 1074-1078.
14. B. Ogorevc, X.H. Cai, I. Grabec, *Anal. Chim. Acta*, **1995**, *305*, 176-182.
15. W. Yang, D. Jaramillo, J.J. Gooding, D.B. Hibbert, R. Zhang, G.D. Willett, K.J. Fisher, *Chem. Commun.*, **2001**, 1982-1983.
16. W. Yantasee, Y. Lin, G.E. Fryxell, B.J. Busche, *Anal. Chim. Acta*, **2004**, *502*, 207-212.
17. S.K. Alpat, U. Yuksel, H. Akcay, *Electrochem. Commun.*, **2005**, *7*, 130-134.
18. I. Jureviciute, A. Malinauskas, *Chem. Anal.* (Warsaw), **2004**, *49*, 339-350.
19. A. Yamaguchi, N. Teramae, *Anal. Sci.*, **2008**, *24*, 25-30.
20. M. Mazloum-Ardakani, Z. Akrami, H. Kazemian, H.R. Zare, *Int. J. Electrochem. Sci.*, **2009**, *4*, 308-319.
21. N.Yu. Stozhko, N.A. Malakhova, M.V. Fyodorov, K.Z. Brainina, *J. Solid State Electrochem.*, **2008**, *12*, 1219-1230.
22. A.M. Bond, W. Miao, T.D. Smith, J. Jamis, *Anal. Chim. Acta*, **1999**, *396*, 203-213.
23. C. A. Borgo, R.T. Ferrari, L.M.S. Colpini, C.M.M. Costa, M.L. Baesso, A.C. Bento, *Anal. Chim. Acta*, **1999**, *385*, 103-109.
24. M. Etienne, J. Bessiere, A. Walcarius, *Sensors and Actuators B*, **2001**, *76*, 531-538.
25. J.M. Caldwell, G.D.Meakins, *J.Chem.Soc.Perkin Trans.*, **1987**, *I*, 2305-2310.
26. H. Lee, J. Yi, *Separation Sci. Technol.*, **2001**, *36*, 2433-2448.
27. F. Di Renzo, F. Testa, J. D. Chen, H. Cambon, A. Galarneau, D. Plee, F. Fajula, *Micropor. Mesopor. Mater.*, **1999**, *28*, 437-446.
28. D. Brunel, A. Cauvel, F. Fajula, F. Di Renzo, *Stud. Surf. Sci. Catal.*, **1995**, *97*, 173-180.
29. P.T. Tanev, T.J. Pinnavaia, *Science*, **1995**, *267*, 865-867.
30. *** ISO 8466-1, "Water quality − Calibration and evaluation of analytical methods and estimation of performance characteristics. Part 1: Statistical evaluation of the linear calibration function", **1990**, ISO, Geneva.
31. *** ISO 8466-2, "Water quality − Calibration and evaluation of analytical methods and estimation of performance characteristics. Part 1: Statistical evaluation for nonlinear second calibration functions", **1993**, ISO, Geneva.
32. I.Gh. Tănase, G.L. Radu, A. Pană, M. Buleandră, "Validarea metodelor analitice. Principii teoretice şi studii de caz", Printech, Bucureşti, 2007.