ORGANOFUNCTIONALIZED MESOPOROUS SILICA CARBON PASTE ELECTRODE FOR VOLTAMMETRIC DETERMINATION OF Pb(II)

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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 Pb(II). Square wave anodic stripping voltammetry was used, the best results being obtained under the following conditions: - 1.1 V vs. SCE accumulation potential, 120 s accumulation time in Britton-Robinson buffer (pH 4.35). Linear response to Pb(II) was found between 0.05 and 1.7 ppm.

INTRODUCTION

Lead has various uses (in accumulators, ammunitions, piping, paints, as additive for gasoline, can appear from mining activities and industrial processing of some metals like silver and gold), but many of them are backed off because of lead toxicity and damage already caused by the uncontrolled dispersion in the environment.[1]

Lead poisoning is a medical condition caused by increased level of lead in blood. Lead can cause irreversible neurological damage, renal diseases and cardiovascular effects.[2]

The importance of controlling lead levels from biological and environmental samples generated a special interest in the development of new sensors for lead quantitative determination.

As for the used techniques, the electrochemical ones are attractive for quantitative determination of heavy metal ions at trace levels because they are not expensive and present good sensitivity. Among these, anodic stripping voltammetry is the most used and proved to be adequate, its advantage

being the preconcentration step taking place prior to voltametric measurement and quantification.[3, 4]

Recently, free-mercury chemically modified electrodes are developed and used in stripping voltammetry, considering mercury toxicity and the new regulation related to this aspect.[5] The modifier is employed to preconcentrate the analit before its electrochemical detection.

Chemically modified electrodes are characterized by intentionally altering their surface characteristics to present new properties that can be exploited for analytical purposes. For lead quantitative determination, sometimes together with other metal ions, chemically modified electrodes, using various modifiers, were developed and used.[6-12]

Carbon paste electrode represents a convenient conductive matrix to prepare chemically modified electrodes by simple mixing of graphite-binder paste with the modifier. [13] This type of electrodes is inexpensive and presents low background currents, wide range of used potential, easy fabrication and rapid regeneration by simple mechanical polishing.[14, 15]

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Analytical performances of these electrodes are directly related to the selectivity of the recognition event and to the effectiveness of the accumulation process, defining the selectivity and the sensibility of the entire detection procedure. [16, 17]

Different types of materials were used as modifiers: zeolites, [12, 18] clays, [19, 20] organic polymers and ligands, [16, 21] sol-gel-derived silica materials, [18, 22-26] because of their mechanical and thermal stability and interesting chemical properties.

There are numerous articles that report carbon paste electrodes modified with organically modified silica applied for lead and other heavy metals determination from different samples. [27-32]

When associated to an electrode, these materials allow tuning their recognition properties via a judicious choice of functional groups and ensure fast mass transport to the active sites, as a consequence of their highly porous texture. [22, 25]

Silica based materials are of interest because they are robust inorganic solids, with high specific surface area (200-1500 $m^2 \cdot g^{-1}$) and 3D structure made of highly open spaces interconnected to each other. This leads to high diffusion rates of target analytes towards a large number of accessible binding sites, which represents a very important factor in designing devices with high sensitivity. Silica based organic-inorganic hybrids combine the robustness of the silica with the chemical activity of the organo-functional groups attached to the solid surface. [1, 23]

Previously, Cu(II), respectively Cd(II) quantitative determination from water samples using carbon paste electrodes modified with acetyl-acetone functionalized mesoporous silica (AcAcNH$_2$-HMS) were reported. [27, 28]

In the present study a carbon paste electrode modified with acetyl-acetone functionalized mesoporous silica (AcAcNH$_2$-HMS) was developed, characterized and applied for Pb(II) quantitative determination from residual water samples. In order to define the optimal conditions leading to the best analytical performances several experimental parameters were varied.

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 HMS silica functionalized with AcAc 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. Square wave anodic stripping voltammetry was used for the stripping step.

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 Britton-Robinson buffer solution (pH 4.35). A "Certipur" (Merck) stock solution containing 1000 $\mu g \cdot L^{-1}$ Pb(II) was used for daily preparation of working standard solutions by appropriate dilution.

Graphite powder (with particles diameter < 20 μm) (Fluka) and paraffin oil (Merck) were used for the preparation of carbon paste electrodes. Dodecylamine (Aldrich), tetraethoxysilane (TEOS) (Fluka), 3-aminopropyl-triethoxysilane (APTES) (Aldrich) and 3-bromo-2,4-pentandione were used to functionalize the HMS silica.

For modifying the carbon paste electrode, hexagonal mesoporous silica (HMS) was synthesised using dodecylamine (CH$_3$(CH$_2$)$_{11}$NH$_2$) as a template and TEOS as a silica precursor and ethanol as co-solvent by a procedure reported in a previous work. [27] For the acetyl-acetone functionalized HMS silica, the HMS silica was firstly silanized with APTES. Thereafter, the NH$_2$-HMS solid was reacted with 3-bromo, 2,4-pentandione in order to obtain the AcAcNH$_2$-HMS mesoporous silica by a procedure already reported. [27]

Preparation of the modified carbon paste electrodes. Modified carbon paste electrodes were prepared by thoroughly mixing of graphite powder with AcAcNH$_2$-HMS, (1:6 ratio of AcAcNH$_2$-HMS : graphite powder) and a few drops of paraffin oil, until a homogenous paste was obtained.

To establish the optimum ratio between AcAcNH$_2$-HMS and graphite powder, electrodes with different percent of modifier were prepared and their voltammetric signals were examined and compared. The maximum peak current intensity and a well defined peak were obtained for an organofunctionalized silica: graphite powder ratio of 1:6.

The carbon paste electrode was finally obtained by packing the paste into a plastic tube (2 mm interior diameter) equipped with a piston. 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

Voltametric behaviour of Pb(II) on organofunctionalized silica modified carbon paste electrode

Square wave anodic stripping voltammetric experiments were carried out on unmodified and

modified electrodes with AcAcNH$_2$ functionalized HMS silica, in Britton-Robinson buffer (pH 4.35).

Figure 1 presents square wave anodic stripping voltammograms of Pb(II) on: HMS modified carbon paste electrode (a) and AcAcNH$_2$-HMS modified carbon paste electrode (b). Anodic stripping voltammetric signals were obtained: (a) -

0.617 V; (b) -0.614 V; vs. SCE. Comparing the peak current intensity it can be seen that the one obtained in case (b) is almost 1.5 times bigger than in case (a). The peak from (b) voltammogram is much better defined than that from (a) voltammogram.
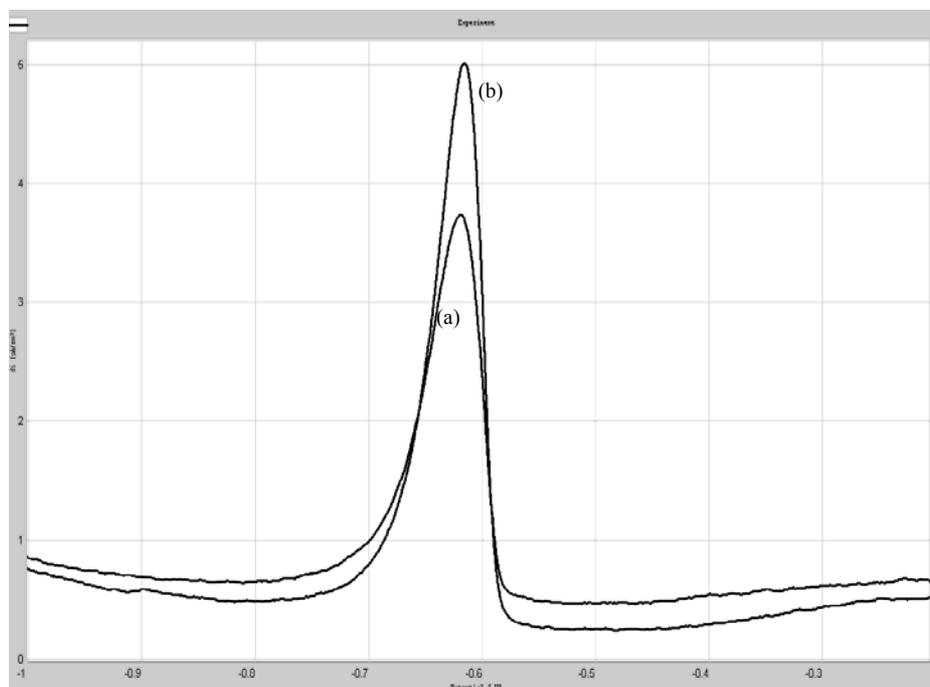

Fig. 1 – Square wave anodic stripping voltammograms obtained for 0.5 ppm Pb(II), in Britton-Robinson solution (pH 4.35): (a) HMS silica modified carbon paste electrode; (b) AcAcNH$_2$-HMS modified carbon paste electrode; accumulation potential, -1.1 V vs. ESC; accumulation time, 120 s.

Supporting electrolyte nature and pH influence

Voltammetric behaviour of Pb (II) was investigated in different supporting electrolytes of various concentrations (0.01 – 0.4 mol$\cdot$L^{-1}): HCl, HNO$_3$, H$_2$SO$_4$, HClO$_4$ and in Britton-Robinson buffers at different pH values (2.09-7.00). Although voltammetric peaks were obtained in all supporting electrolytes, the best defined and intense were those in pH 4.35 Britton-Robinson buffer. These Britton-Robinson buffers also offer the advantage of maintaining constant the composition of the buffer when the pH effect is studied.

Peak current intensity and peak potential dependences on pH variation are presented in Figure 2.

It can be observed that at pH range of 2.09 to 4.35 the peak current intensity increased with

increasing pH; after that pH value, the peak current intensity decreased. Peak potential shifts linear towards more cathodic values with increasing pH. The optimal pH value found and used for further studies was 4.35.

Accumulation potential and time influences

The influence of accumulation potential on the peak current intensity of 1 ppm Pb(II) was studied over the potential range between -0.3 and -1.4 V vs. SCE. The highest anodic peak current intensity was obtained for the accumulation potential value of -1.1 V vs. SCE (Figure 3 ($\bullet$)), this value being chosen as accumulation potential in further studies.

The influence of accumulation time on the anodic peak current intensity for 1 ppm Pb(II) was also examined. Peak current intensity increased

almost linearly with increasing accumulation time from 0 to 240 s and then remains almost constant (Figure 3 (▲)), due to electrode surface saturation. For all subsequent measurements for the accumulation time a value of 120 s was used, as a compromise between measurements sensitivity and analysis time.
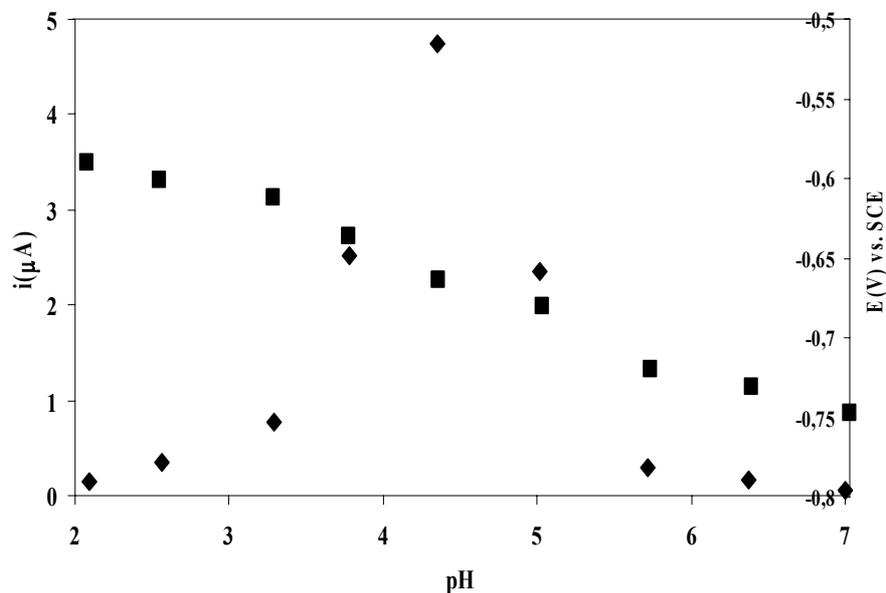

Fig. 2 – Anodic peak current intensity (♦) and potential (■) dependencies on pH value
for 0.5 ppm Pb^{2+}, in Britton-Robinson buffer, -1.1 V vs. SCE accumulation potential and 120 s accumulation time.
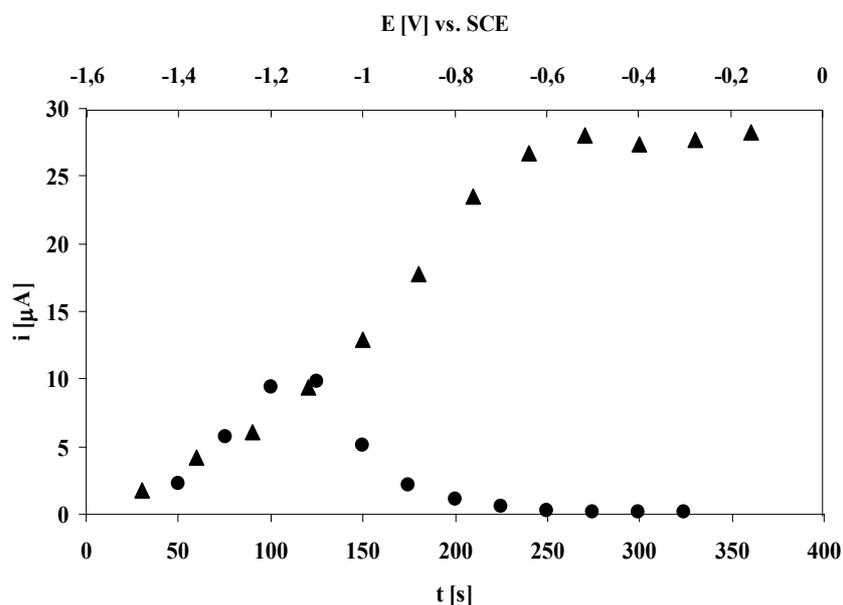

Fig. 3 – Influence of accumulation potential (●) and accumulation time (▲) on stripping
peak current intensity for 1 ppm Pb^{2+}, pH 4.35 Britton-Robinson buffer.

Calibration curve, detection and quantification limit, precision and accuracy

A calibration curve was realized, using the optimal parameters previously established. A linear relationship ($i = 9.53 \times c_{Pb(II)} - 0.51$, $R^2 = 0.997$) between peak current intensity and lead concentration was observed between 0.05 – 1.7 ppm Pb(II).

The detection limit (DL) and quantification limit (QL) were calculated as $DL = 3s_a/b = 0.04$ ppm and $QL = 10s_a/b = 0.138$ ppm, where s_a is standard deviation of the intercept ($s_a = 0.132$) and b is the calibration curve slope.

In this study, the method precision was evaluated only on repeatability level. Repeatability is expressed as percentage relative standard deviation (RSD%) and the value obtained after realizing the experiments and the calculations was 4.16%.

The method accuracy was evaluated from the recovery degree of the added analyte from spiked standard solutions. For recovery calculation 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 – total spike concentration) was used. Recovery values lied between 101.11% and 109.28%, with a average recovery of 104.79% and a standard deviation of 3.95% (3 additions of 0.3 ppm Pb(II) for each of the 3 identical standard solutions (I, II, III) of 0.3 ppm Pb(II)) (table 1).

Table 1

Recovery values of the added analyte from spiked standard solutions

	C_F-C_U (ppm) I	C_F-C_U (ppm) II	C_F-C_U (ppm) III	$\overline{C_F - C_U}$ (ppm)	C_A (ppm)	r%
1st addition	0.304	0.299	0.307	0.303	0.3	101.11
2nd addition	0.611	0.681	0.675	0.656	0.6	109.28
3rd addition	0.895	1.021	0.892	0.936	0.9	103.98

Interferences

Possible interferences from different metallic species (Cu(II), Cd(II), Mn(II), Ni(II), Zn(II)) on 1 ppm Pb(II) anodic peak current intensity were investigated. Potential interfering ions concentrations were equal, 10 and 100 times bigger than that of Pb(II).

The presence of Mn(II), Ni(II) and Zn(II) did not affect the Pb(II) signal, while Cu(II) and Cd(II) lead to Pb(II) signal increase. These effects should be related with the interactions of metallic ions with the silica modifier.

Although there are some influences, the standard addition procedure allows the accurate determination of Pb(II) in real samples, as follows.

Analysis of lead from residual water samples

The proposed modified electrode was applied for SWASV determination of Pb(II) in residual water samples in optimized conditions (table 2).

Table 2

The optimized parameters for Pb(II) quantitative determination using SWASV and AcAcNH$_2$-HMS modified carbon paste electrode

Parameter	Optimized value
Accumulation potential	-1.1 V vs. ESC
Accumulation time	120 s
Scan rate	50 mV/s
Pulse amplitude	50 mV
Ramp step amplitude	1 mV
Ramp step duration	0.02 s
Supporting electrolyte and pH	Britton-Robinson buffer, pH 4.35

The results obtained for Pb(II) quantitative determination in voltametric cell (5 mL residual water sample + 5 mL Britton-Robinson buffer, pH 4.35) are presented in table 3. Using standard addition method an average concentration value of

0.479 ppm (7.97% RSD) and an average recovery of 98.37 % (4.58 % RSD) were obtained.

The determined Pb(II) content in residual water sample (0.958 ppm) compared with the concentration obtained by flame atomic absorption spectrometry (0.96 ppm) proved that AcAcNH$_2$-

HMS modified electrode can be used for determination of Pb(II) in water samples, under optimised conditions and using the standard addition method (in order to eliminate the interferences and the matrix effect).

Table 3

Pb(II) quantitative determination from residual water samples by SWASV

Replicate	Addition number	C_{Pb}^{2+} (ppm)		R (%)
		Added	Found	
1	0	-	0.452	-
	1	0.476	0.849	91.45
	2	0.909	1.322	97.10
	3	1.304	1.813	103.22
2	0	-	0.506	-
	1	0.476	0.984	100.20
	2	0.909	1.354	95.69
	3	1.304	1.856	102.58

CONCLUSION

AcAcNH$_2$ functionalised silica can be used for the preparation of modified carbon paste electrodes and these electrodes can be used for Pb(II) determination in water samples using SWASV procedure. Various experimental parameters (supporting electrolyte, pH value, accumulation potential, accumulation time, interfering metallic ions) were studied and optimized. Pb(II) SWASV determination from residual water samples can be done using standard addition method.

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