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Self-assembled monolayer modified gold electrodes for traces Cu(II) determination

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Abstract

D,L-Penicillamine and thiodimethylglyoxime (TDMG) self-assembled monolayers (SAMs) on gold electrode were prepared and characterized by electrochemical measurements. The two sensors exhibit sensitive and selective response to Cu(II), both forming 2:1 complexes, the first one in acetic buffer and the second one in ammonia buffer.

Copper determination at trace level (LOQ 0.2 and 0.3 μg/L for D,L-penicillamine and TDMG, respectively) is possible with both the electrodes as verified in tap, spring and sea water. The influence on copper determination of most common ions present in natural waters and of organic matter has been investigated. Accuracy was checked by recovery test on spiked samples.

Keywords: Self-assembled monolayers; D,L-Penicillamine SAM; Thiodimethylglyoxime SAM; Cu determination; Adsorptive stripping analysis

In recent years, a great interest was given to SAM (self-assembled monolayer) electrodes as tools for voltammetric determination of organic and inorganic compounds, in view of their advantages over ordinary electrodes: good reproducibility, easy preparation, exclusion of toxic component such as mercury, possibility of introducing on the electrode selective functional groups able to bind specific compounds [1–3]. Moreover, limitations that are often encountered in electrochemical determinations at thin polymeric films electrodes, typically slow diffusion across the film, are minimized in SAMs [4]. In particular, the development of SAMs based on chemisorption of thiols or disulfide on gold electrode surface, has greatly increased in the last years also for their stability [5,6].

Such films are formed simply by dipping the cleaned gold electrode in ethanolic solution of the thio-compound of interest. The chemisorption of the –SH onto the gold surface is followed by an ordering step in which the chains of the molecules co-align to form a highly ordered surface film; the entire process requires generally 10–12 h.

Due to the environmental and biological importance of Cu(II) many chemosensors for the determination of this ion have been developed [7–9]. Considering a series of compounds of general formula R–CH_2–SH, sensitivity to Cu(II) greatly increases from R=CH_3 to R=CH_2OH to R=COOH to R=CH_2NH_2. Among these molecules, cysteamine (HS–CH_2–CH_2–NH_2) exhibits the best results with detection limit less than 5 μg/L [7].

Other substrates which exhibit great affinity for Cu are amino acids: their complexation constant with Cu(II) is four orders of magnitude larger than with any other metal ion [10]; surfaces containing such functional groups are expected to be selective for Cu(II) determination. In view of this consideration and with the aim to lower the detection limit, a SAM electrode has been developed using a similar amino acidic complexing compound, D,L-penicillamine, which is readily available and can easily form a monolayer on gold surface through chemical adsorption.

Starting from the consideration that dimethylglyoxime (DMG) can form strong complexes with Cu and other metals in alkaline medium (pH > 8, where oximes are partially deprotonated), a second SAM electrode was prepared with its thioderivative (thiodimethylglyoxime, TDMG). It exhibited good affinity for copper in ammonia buffer. Both SAMs have been electrochemically characterized and best working

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conditions for each SAM have been carefully studied and optimized.

1. Experimental

1.1. Materials and methods

Measurements were carried out with an Amel 433/W polarographic analyser equipped with a standard three-electrode cell with an Amel gold electrode as working electrode (2.0 mm diameter), a platinum wire as auxiliary electrode and an Ag/AgCl/KCl (4 M KCl saturated with AgCl) reference electrode. Reagents were of the purest grade available purchased from Fluka or C. Erba and used as received; acetic buffer was purified before use on Chelex 100 (batch procedure: 30 mL acetic buffer are stirred overnight with 500 mg Chelex 100, purified as previously described [11]). Copper diluted solutions were daily prepared in ultrapure grade water (Milli-Q, Millipore) from a standard 1000 μg/mL atomic adsorption Cu(II) solution. All glassware was carefully cleaned with concentrated nitric acid and Milli-Q water to avoid contamination. D,L-Penicillamine was used as received, TDMG was synthesized in our laboratory, as described below.

UV digestions were made on an apparatus equipped with 4 × 125 W Hg lamps (λ_{max} 254 nm). Samples were UV digested for 4 h, when necessary. FTIR spectra were acquired on Perkin Elmer Spectrum RX I. NMR spectra were registered on 300 MHz Bruker Spectrometer. Inductively coupled plasma-mass spectrometer measurements were carried out on a Perkin Elmer Mod. ELAN DRC-e Instrument, following the standard procedures suggested from manufacturer. Sea water was analyzed by ICP-MS after copper preconcentration on Chelex-100 resin [11].

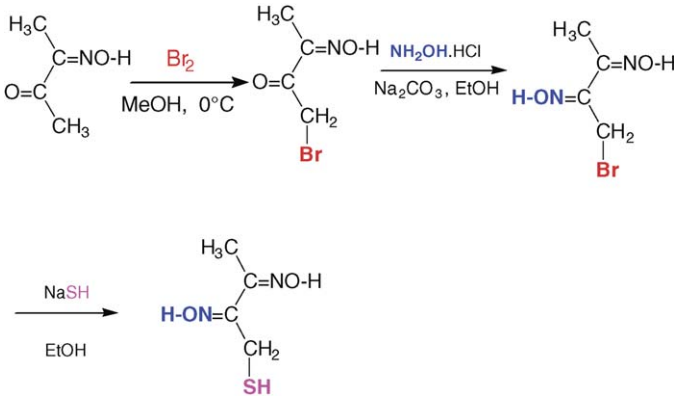
1.2. Electrodes preparation

The gold disk cross-section exposed (diameter 2.0 mm) was abraded with successively finer grades of alumina (from 1 to 0.05 μm) and then rinsed with water and briefly cleaned in an ultrasonic bath to remove trace alumina from the surface.

SAMs were prepared by dipping the cleaned gold electrode in 5 mM ethanolic solution of D,L-penicillamine or TDMG for 12 h: the electrode is then rinsed with ethanol and water before use.

1.3. Synthesis of thiodimethylglyoxime

This compound was synthesized as described below. Intermediates and final products were characterized by MS, NMR and chromatographic techniques. The reaction scheme is the subsequent:



1.3.1. Bromo-monomethyl glyoxime(*1*)

This compound was synthesized according to a slightly modified procedure [12]. Anhydrous bromine (10.5 mL) is added in one time under stirring to a diacetyl monoxime (20 g) solution in methyl alcohol (25 ml) cooled in an ice bath. The reaction takes place immediately and it is vigorous: it must be done in a wide crucible because foam is formed. When the reaction is finished (bromine colour disappears), ice water is added and the precipitate is filtered and washed with ice water. Dichloromethane is added to the mixture to dissolve all the solid. The organic phase is washed with water and dried over magnesium sulphate. The solvent is evaporated and the product is recrystallize from 300 mL boiling hexane (cooling with ice). Yield: 46%, mp 83–84 °C, MW 179. ^{1}H NMR (CD_3OD), δ: 4.9 (s, 1H, –OH); 4.5 (s, 2H, $–CH_2–$Br); 1.9 (s, 3H, $–CH_3$). IR (thin film, KBr), ν: (cm^{-1}) 3383, 1684 1405, 1219, 1019, 944, 869, 752. EI-MS, m/z: 177–179 (M^+) caution! The compound is lachrymatory and strongly irritant!

1.3.2. Bromo-dimethylglyoxime (II)

This compound was synthesized according to a slightly modified procedure [13]. To an ethanolic solution of (**1**) (0.2 mol in 120 ml EtOH 95% (v/v)), 20.7 g hydroxylamine hydrochloride are added. When all the solid is dissolved, 16 g of finely pulverized anhydrous sodium carbonate are gradually added. CO_2 is evolved.

After 24 h standing under magnetical stirring, EtOH is evaporated at reduced pressure and the residue is dissolved in 200 ml boiling water: in this way if diacetyl monoxime was still present in (I), dimethylglyoxime formed during this step will separate on standing (NMR done on separated solid showed the identity of the compound). The solution is filtered and water is eliminated at reduced pressure. The solid obtained is dissolved in 250 mL boiling toluene, the solution filtered and cooled with ice. Bromo-dimethylglyoxime separates as needles that are collected over Buchner and washed with cold toluene. Yield: 47%, mp 142–143 °C, MW 195. ^{1}H NMR (CD_3OD), δ: 4.9 (s, 2H, –OH); 4.3 (s, 2H, $–CH_2–$Br); 2.0 (s, 3H, $–CH_3$). IR (thin film, KBr), ν: (cm^{-1}) 3434, 1640, 983, 920, 910. EI-MS, m/z: 193–195 (M^+).

1.3.3. Thiodimethylglyoxime (III)

1.5 g of (II) are dissolved in 40 ml water and 20 ml EtOH. 2.4 g of sodium hydrosulphide hydrate (containing 70% NaSH)

are added. The solution is let stand for 1 day in a closed container at room temperature. The white-cream solid separated is collected over Buckner and washed with cold EtOH:water 1:3. The compound is recrystallized from EtOH:water 1:3 (40 ml for each gram of compound). The compound slowly oxidizes to disulphide on exposing to air. Yield: 0.9 g, 80%. mp 203 °C (decomposition), MW 148.17. ^{1}H NMR (d_6-DMSO), δ: 11.8 (s, 1H, –OH); 11.5(s, 1H, –OH); 3.9 (s, 2H, –CH_2–S); 1.9 (s, 3H, –CH_3). IR (thin film, KBr), ν: (cm^{-1}) 3433, 1650, 988, 915. EI-MS, m/z: 147 (M^+).

2. Results and discussion

2.1. SAMs electrode characterization

Effective gold electrode area was determined electrochemically using cyclic voltammetry (CV), E_i = +200 mV, E_f = +800 mV, scan rate from 20 to 200 mV/s, in a solution containing 1 mM ferrocene and 0.1 M tetrabutylammonium perchlorate in acetonitrile. The electrode area was calculated according to the Randles–Sevcik equation: $I_p = (2.69 \times 10^5) n^{3/2} A D^{1/2} C_\infty \nu^{1/2}$, where C_∞ is the concentration of ferrocene in the bulk solution (mol/cm^3), n the electron stoichiometry (n = 1), I_p the peak current (A), A the electrode area (cm^2), D the diffusion coefficient (2×10^{-5} cm^2/s at T = 298 K) and ν is the scan rate (V/s). The area was estimated to be 0.0309(7) cm^2.

The adsorption process for both the substrates (here simplified as R–SH) is supposed to be [14,15]:

$$RSH \rightarrow RS_{(ads)}^{\bullet} + H^+ + e^-$$

The chemisorption of thiols was studied by open circuit potential measurements [14] and the results suggest a donation of charge to the gold surface by sulphur. This interpretation is consistent with the thiol being adsorbed in a predominantly neutral radical state, donating its charge to the gold surface.

The presence of SAM on the electrode surface was confirmed by double layer capacitance measurements using cyclic voltammetry, before and after electrode modification [16]. Bare gold electrode double layer capacitance was 75 ± 3 μF/cm^2, while TDMG SAM and D,L-penicillamine SAM capacitance were 35 ± 2 and 40 ± 1 μF/cm^2, respectively (mean values and standard deviations are calculated from three independent measurements on the same electrode).

The formation kinetics and the adsorption mechanism of thiols from solution can be described by a two-step mechanism. The first one in which more than 80% of the monolayer is formed, is completed in a few minutes. The second step extends over several hours, it is independent of the concentration of the thiol and could be identified in an ordering process [17].

The thiols adsorption behaviour was evaluated using the Langmuir rate law [18,19]: the rate surface coverage is expressed by the relationship: $\vartheta(t) = [1 - \exp(-Kt)]$, where $\vartheta(t)$ is the coverage at any instant of time "t" and "k" is the rate constant of the adsorption. Surface coverage ϑ can be obtained using the expression: $\vartheta = (C_0 - C_t)/(C_0 - C_f)$, C_0 being the bare electrode capacitance, C_t the capacitance at any time "t" and C_f the capacitance of fully covered monolayer [20]. The interfacial capacitance of SAMs electrodes was determined by CV (calculated from the current values read at 150 mV versus Ag/AgCl in 0.1 M phosphate buffer pH 8.0 [16]). Surface coverage versus time curves for 5 mM concentration of D,L-penicillamine and TDMG are shown in Figs. 1 and 2.

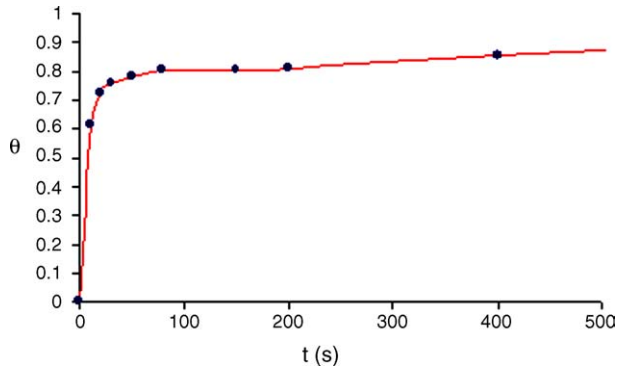


Fig. 1. Electrode surface coverage vs. time curve for 5 mM D,L-penicillamine.

Surface coverage was measured from the oxidative desorption of the thiols. The electrochemical oxidation of adsorbed thiol on gold surface is believed to occur by the reaction [15]:

$$RS_{(ads)}^{\bullet} + 3H_2O \rightarrow RSO_3^- + 6H^+ + 5e^-$$

concomitantly with the formation of surface gold oxide and the desorption of the sulphonic acid produced. During the oxidation the current due to the second reaction can be measured and used to estimate the surface coverage of thiol on gold.

Cyclic voltammograms (E_i = 500 mV, E_f = 1800 mV) for the oxidation of the two thiols adsorbed on a gold electrode were recorded in 0.05 M nitric acid free of added thiol at different scan speeds; from these data surface coverage (Γ) was estimated by the following equation [21]:

$$I_{p,c} = n^2 F^2 V A \Gamma_{o,i} / 4RT$$

where $\Gamma_{o,i}$ is the surface concentration (mol/cm^2) of the adsorbed species before desorption takes place, F the Faraday constant, I the peak current (A), ν the scan rate (V/s), A the effective gold electrode area (cm^2), R the gas constant (J/mol K) and n is the number of electrons (n = 5). The anodic

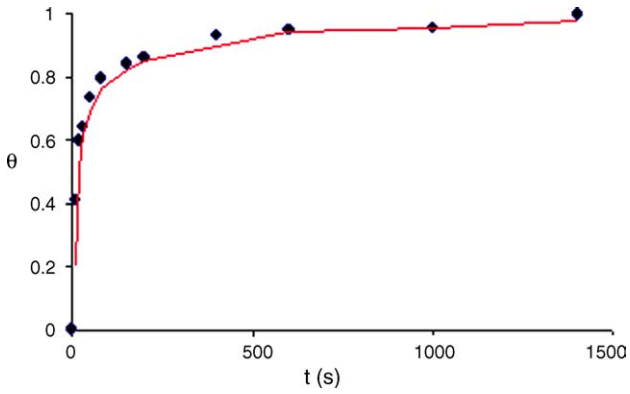


Fig. 2. Electrode surface coverage vs. time curve for 5 mM TDMG.

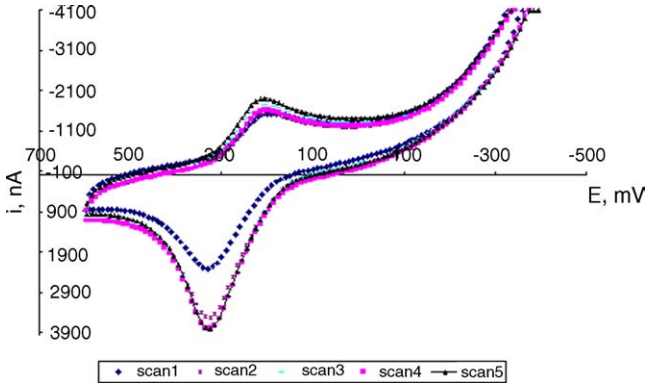


Fig. 3. CV of 5 mg L^{-1} Cu(II) in acetic buffer 0.1 M, pH 4.0, at D,L-penicillamine SAM electrode. Scan rate 100 mV s^{-1}, $E_i = -400$ mV, $E_f = 600$ mV.

peak obtained (+1300 mV in the case of D,L-penicillamine and +1450 mV for TDMG) is due to the oxidation of the adsorbed compound and to the formation of gold oxide. Experiments were conduced also on bare gold electrode and the difference in current obtained with and without SAM can be attributed to the oxidation of the adsorbed thiol [15]. $\Gamma_{o,i}$ was calculated to be $1.6(3) \times 10^{-10}$ mol/cm^2 for DL penicillamine and $1.2(2) \times 10^{-10}$ mol/cm^2 for TDMG.

The copper accumulation process was investigated by repetitive CV in 5 ppm Cu^{2+} solution in nitric acid, pH 4.0 (DL penicillamine) or NH_3/NH_4Cl 0.1 M, pH 9.0 (TDMG). Cyclic voltammograms obtained when each SAM electrode is immersed into a solution containing copper, show two waves (see Figs. 3 and 4) whose peak currents increase from a cycle to another, reaching a constant profile after 3–4 cycles, when the complexation reaches equilibrium [15].

The degree of copper coverage, Γ_{Cu}, was evaluated by chronocoulometry. Γ_{Cu} was calculated [22] assuming one electron process (as below discussed). $\Gamma_{Cu} = 8.7(2) \times 10^{-11}$ and $6.2(2) \times 10^{-11}$ mol/cm^2 were obtained for DL penicillamine and TDMG SAMs, respectively. Being the thiols coverage about twice as much copper, we can assume that two neighboured thiols complex one copper ion.

2.2. Copper electrochemistry at SAMs electrodes

Cyclic voltammetry (CV) in different media and conditions, shows that Cu is complexed at both SAMs electrodes as Cu(II) and immediately reduced to Cu(I) at the applied potential ($E_i = -400$ mV); Cu(I) is than oxidized in the anodic scan to Cu(II).

The proposed mechanism (here detailed for D,L-penicillamine) derives from the following observations:

- After copper accumulation for a few minutes (3–5 min) at opened circuit in 5 ppm Cu(II) 0.1 M acetic buffer solution pH 4, the SAM electrode is washed (with distilled water or acetic buffer, as well) and immersed in acetic buffer not containing copper, for the anodic scan (LSSV, $E_i = -400$ mV, $E_f = 600$ mV, scan rate 50 mV/s): no peak appears.
- Copper accumulation (3–5 min) at opened circuit in 5 ppm Cu(II) acetic buffer solution was followed by washing and medium exchange in a Cu(II) free 0.1 M acetic buffer solution: the electrode is hold at −400 mV for 60 s before the anodic scan, in the electrochemical conditions described above (i.e. LSSV, $E_i = -400$ mV, $E_f = 600$ mV, scan rate 50 mV/s): a peak at 250 mV is obtained. This behaviour is consistent with the proposed mechanism: at −400 mV Cu(II) complexed at the SAM surface is reduced to Cu(I), which is then re-oxidized in the anodic scan.
- If the electrode is kept in an acetonitrile solution of Cu(I) acetonitrile perchlorate (0.05 MTBAP as supporting electrolyte), no accumulation occurs; by adding Cu(II) to this solution, the behaviour of the electrode is similar to that observed in aqueous medium. That means that only Cu(II) can be strongly complexed at the SAM electrode, which is then reduced to Cu(I) at the applied potential.

Similar results were obtained with TDMG SAM (in this case all the measurements and accumulation processes were done in NH_3/NH_4Cl buffer 0.1 M, pH 9, LSSV, $E_i = -700$ mV, $E_f = 500$ mV, $E_{dep} = -700$ mV, scan rate 50 mV/s).

In both cases the oxidation of Cu(I) is accomplished by the stripping of Cu(II) from the electrode surface, stabilized by acetate or ammonia, respectively.

Copper accumulation and redox processes for both the SAMs occur by the reaction [8]:

$$(Au)_n^+ \cdot {}^-SRH + \tfrac{1}{2}Cu^{2+} \rightleftarrows (Au)_n^+ \cdot {}^-SR^- \cdot \tfrac{1}{2}Cu^{2+}$$

$$+ H^+ \overset{e^-}{\rightleftharpoons} (Au)_n^+ \cdot {}^-SR^- \cdot \tfrac{1}{2}Cu^+ + H^+$$

The pH dependence of the Cu(II) complexation was investigated in both cases. With D,L-penicillamine SAM, maximum binding of copper occurs at pH close to the isoelectric point (4.85) of the compound, so that the zwitterionic form of the substance is involved in the complexation of Cu(II). At pH > 6, the signal decreases due to the interaction of the deprotonated amino group with the gold surface and, as well in non-complexing media, $Cu(OH)_2$ will begin to form (K_{ps} 1.6×10^{-19}) [15]. At pH < 2 the carboxylate becomes protonated and Cu(II) complexation does not take place. The signal of copper can therefore be expected to decrease at these lower pH values: from these considerations it ensues the necessity to work in a buffered environment, such as that provided by acetic buffer.

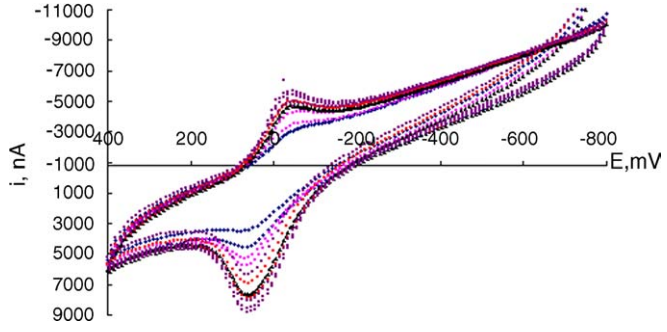


Fig. 4. CV of 5 mg L^{-1} Cu(II) in NH_3/NH_4Cl buffer 0.1 M, pH 9.0 at TDMG SAM electrode. Scan rate 100 mV s^{-1}, $E_i = -800$ mV, $E_f = 400$ mV.

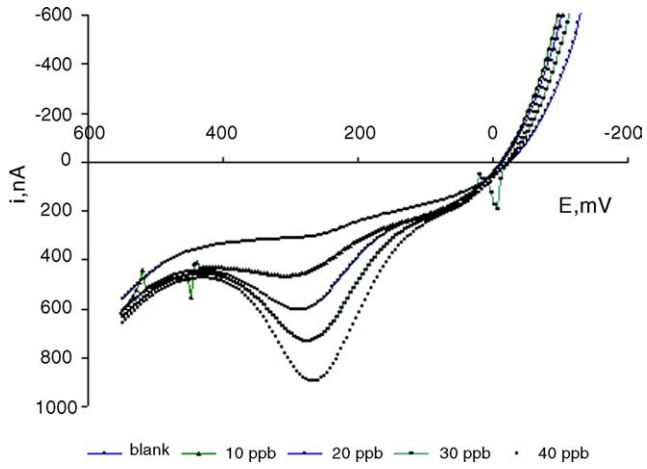


Fig. 5. LSV curves for Cu(II) in acetic buffer 0.1 M pH 4.0 at D,L-penicillamine SAM electrode. Experimental conditions described in the text.

In the case of TDMG, Cu is determined in basic environment (pH 9, in NH_3 buffer, to avoid $Cu(OH)_2$ precipitation) where the oxime, being deprotonated, can complex the metal ion. A decrease in Cu(II) signal is already observed at pH < 8.

2.3. Procedure for copper determination at D,L-penicillamine SAM electrode

Measurements are performed in acetic buffer solution (0.1 M) at pH 4.0 either by DPSV or LSSV (Fig. 5), even if the first technique is preferred for Cu concentration <1 μg/L. For higher concentrations LSSV gives lower residual currents and better reproducibility. Instrumental conditions are: deposition potential (E_{dep}) = −400 mV, deposition time (t_{dep}) = 60–120 s or more, depending on copper concentration in the sample, E_f = +600 mV, scan speed 50 mV/s in LSSV and 100 mV/s by DPSV. No interferences from chloride, citrate, tartrate, Ni, Cd, Pb, uranyl, Fe, Zn and other heavy metals generally present in natural waters have been evidenced, even at a concentration ratio ion to copper up to 10^3. These observations support the proposed mechanism: many of the investigated metal ions can form complexes in solutions with D,L-penicillamine or TDMG, but evidently complexation itself is not sufficient to give a signal. Iodide at concentration >10 ppm, masks copper signal. Bromide appears to increase Cu signal, reasonably stabilizing Cu^{2+}/Cu^{+} redox couple. In the described conditions and with t_{dep} = 240 s, current versus Cu(II) concentration is linear in the range 0.5–50 μg L^{-1}: E_p = 250 mV, i_p = 8.4(2)[Cu] − 2(3) for LSSV and 0.2–50 μg L^{-1}: E_p = 250 mV, i_p = 0.90(3)[Cu] − 0.06(8) for DPSV.

2.4. Procedure for copper determination at TDMG SAM electrode

Measurements are performed in NH_3/NH_4Cl solution (0.1 M) at pH 9.0. E_{dep} = −600 mV, t_{dep} = 60–120 s, or more depending on copper concentration in the sample. E_f = +500 mV, scan speed 100 mV/s, scan mode DPSV (Fig. 6). Also in this case no interference from common anions such as nitrate and sulphate or heavy metal ions (Ni, Cd, Pb, uranyl, Fe, Zn) have been found.

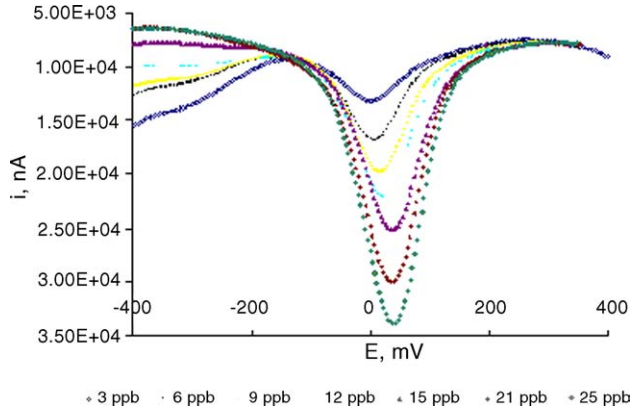


Fig. 6. DPSV curves for Cu(II) in NH_3/NH_4Cl 0.1 M pH 9.0 at TDMG SAM. Experimental conditions described in the text.

The wave i_p versus Cu concentration is linear in the range 0.3–30 μg L^{-1}: t_{dep} = 240 s, E_p = 85 mV, i_p = 0.97(2)[Cu] − 0.3(4).

In both cases, Cu preconcentrated on the electrode surface is quantitatively stripped during the anodic scan, favoured by the complexation of Cu(I) with ammonia or acetate, respectively.

2.5. Influence of deposition potential and deposition time on copper signal at both the SAM electrodes

D,L-Penicillamine SAM: deposition potentials lower than 0 mV give a constant stripping peak height; at potentials more positive than 200 mV no signal appears (Fig. 7). For 5 μg L^{-1} copper concentration linear relationship i_p versus deposition time is obtained up to t_{dep} = 600 s (Fig. 8).

TDMG SAM: deposition potentials lower than −200 mV give a constant stripping peak height; at potentials more positive than 0 mV no signal is present (Fig. 9). For 5 μg L^{-1} copper concentration a linear relationship i_p versus deposition time is obtained up to t_{dep} = 400 s (Fig. 10).

In both cases longer deposition times cause deviation from linearity: saturation of the SAM complexing sites is reached, even if peak current still slightly increases, probably due to the deposition of copper onto the pinholes of the SAM [8].

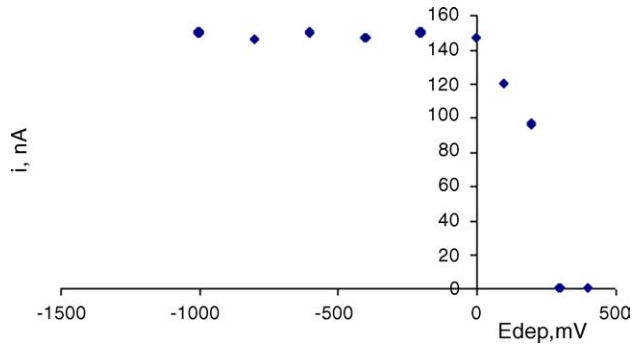


Fig. 7. Influence of deposition potential on 5 ppb Cu(II) peak height at D,L-penicillamine SAM electrode.

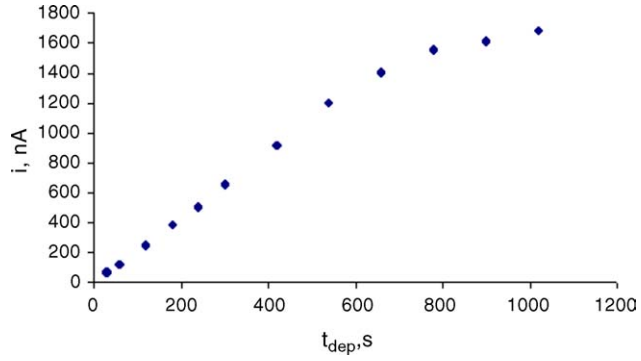


Fig. 8. Influence of deposition time on 5 ppb Cu(II) peak height at D,L-penicillamine SAM electrode.

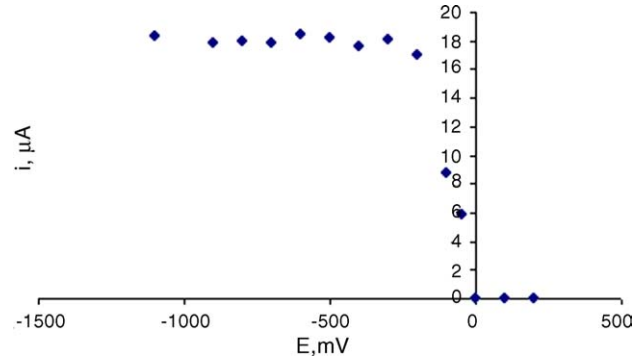


Fig. 9. Influence of deposition potential on 5 ppb Cu(II) peak height at TDMG SAM electrode.

2.6. Determination of copper concentration in high salinity samples

Ligurian sea water. The analysis was performed as described below, either on UV digested (see Section 1.1 for details) or not digested samples, using both the SAMs electrodes.

One milliliter of buffer (acetic buffer 1 M or NH_3/NH_4Cl 1 M) is added to a 10 mL sample aliquot, pipetted into the voltammetric cell. The solution is stirred at 300 rpm, at the suitable deposition potential, for 180 s deposition time. The results are reported below.

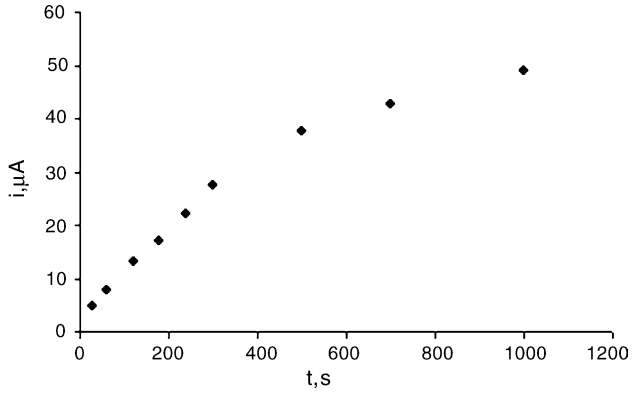


Fig. 10. Influence of deposition time on 5 ppb Cu(II) peak height at TDMG SAM electrode.

Original sample (S1) not UV digested. D,L-Penicillamine SAM: copper found 0.32(4) µg L^{-1} ($n = 4$). TDMG SAM: copper found 0.45(5) µg L^{-1} ($n = 4$). The labile metal is determined in both cases. TDMG SAM electrode competes more strongly with the Cu-ligands in solution, probably due to the working conditions.

Sample after UV digestion. D,L-Penicillamine SAM: copper found 0.65(4) µg L^{-1} ($n = 4$). TDMG SAM: copper found 0.5(1) µg L^{-1} ($n = 4$). The results are in good agreement with that obtained by ICP-MS 0.6(1) µg L^{-1}, ($n = 3$).

Spiked sample (S1 + 5 µg/L) not UV digested. D,L-Penicillamine SAM: copper found 1.76(5) µg L^{-1} ($n = 4$). TDMG SAM: copper found 3.0(1) µg L^{-1} ($n = 4$). The labile metal is determined in both cases. TDMG SAM electrode competes more strongly with the Cu-ligands in solution, probably due to the working conditions.

Spiked sample (S1 + 5 µg L^{-1}) after UV digestion. D,L-Penicillamine SAM: copper found 5.6(1) µg L^{-1} ($n = 4$). SAM: copper found 5.8(2) µg L^{-1} ($n = 4$). The results are in good agreement with that obtained by ICP-MS 6.0(3) µg L^{-1} ($n = 3$).

In order to verify the influence of organic complexing matter on Cu determination, samples of spring water (Cu concentration 0.5 µg L^{-1} by ICP-MS) were analyzed with the proposed procedure before and after UV digestion (30 min, 500 W) in presence of known amounts of humic acid (Aldrich) and the results compared with those obtained by ICP-MS. Results are reported in Table 1. Humic substances cause a depression of the

Table 1
Cu determination in natural water samples: results obtained by ICP-MS and SAMs electrodes

Samples	ICP-MS (µg L^{-1})	TDMG SAM (µg L^{-1})	D,L-Penilcillamine SAM (µg L^{-1})
Tap water	2.2(2)	2.0(2)	1.2(1)
Tap water UV digested		2.3(2)	2.4(2)
Spring water	0.5(1)	0.6(1)	0.6(1)
Spring water + 1 mg L^{-1} H.A.		−5% on peak current	−12% on peak current
Spring water + 3 mg L^{-1} H.A.		−8% on peak current	−27% on peak current
Spring water UV digested		0.5(1)	0.7(2)
Spring water + 10 µg L^{-11} Cu	13.0(2)	10.3(2)	11.0(3)
Spring water + 10 ppb Cu + 5 mg L^{-1} H.A.	11.6(1)	−13% on peak current	−40% on peak current
Spring water + 10 ppb Cu + 5 mg L^{-1} H.A. UV digested	10.5(2)	10.6(4)	10.1(3)

copper signal at both the SAMs electrodes. The UV irradiation releases quantitatively copper from the organic matter.

3. Conclusion

D,L-Penicillamine and TDMG SAMs electrodes show selective response to Cu^{2+} and can be used for routine analytical determinations in aqueous samples containing trace level of copper: the method is cheap, not time consuming, mercury-free and can be applied to samples with relatively high salt concentrations. LOQ for both SAMs are lower than those required by environmental laws and regulations.

Total copper concentration was determined in samples of natural waters with different salinity, after UV digestion. Accuracy of the method was verified comparing the results with those obtained by ICP-MS and from recovery test. The influence of common ions present in natural waters was investigated. The two SAMs show similar behaviour: D,L-penicillamine SAM works in acetic buffer while TDMG in ammonia buffer. Samples rich in metal ions that can form hydroxides in alkaline medium causing sample turbidity, such as Mg, are better analyzed with D,L-penicillamine SAM, otherwise TDMG SAM can be chosen for water samples with pH > 7.

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