Voltammetric Behaviour of Cu-NTA and Pb-NTA on a Mercury Iridiun Microelectrode Coated with Agarose

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Abstract

The complexation of nitriloacetic acid (NTA) with copper and lead was studied by square wave stripping voltammetry (SWSV) using a mercury iridium microelectrode as the working electrode. The results show that NTA interfere with the measurements, but if the mercury iridium microelectrode is coated with different concentrations of agarose (0.75%, 1.5% and 15% w/v) this interference is greatly minimized. The best results were obtained with 1.5% agarose.

Keywords: NTA, iridium microelectrodes, copper, lead, agarose, PLM.

Introduction

Permeation Liquid Membrane techniques (PLM) are newly emerging processes for separation and pre-concentration of target elements or species. The PLM system contains a permeation liquid membrane that separates source solution from strip (or acceptor) solution. The liquid membrane consists of a porous plastic hydrophobic membrane filled with a water-immiscible organic fluid and a carrier selective for the species of interest. Transport over the membrane is based on liquid-liquid extraction coupled with diffusion, the chemical potential

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difference (concentration gradient) between the source and the strip phase being the driving force for the transport. A very strong complexing agent is added to the strip phase thus keeping the free metal concentration negligible, hence keeping a large concentration gradient and therefore a large driving force [1].

One of the most interesting applications is the use of a PLM system as an *in situ* sensor, with online detection. The online detection might be accomplished by inserting a microelectrode in the strip solution and using a suitable voltammetric technique to quantify the evolution of total metal with time.

It is a fundamental issue to find a suitable stripping agent that allows us to perform flux determinations and whose metal complex is voltametrically quantificable as well.

Voltammetric techniques coupled to small microsensors are well designed for real-time continuous measurements (*in situ*) and speciation of trace elements in natural waters. However, their applications for direct measurements in complex media are frequently limited by the well-known fouling problem. To overcome this, studies have been done using different types of thin protective membranes based on size exclusion or electric charge repulsion, or both [2-4].

Microelectrode properties can be exploited to develop a form of electrode protection. Here, the spherical diffusion occurs at the microelectrode surface, enabling trace metal measurements by stripping techniques in quiescent solution. This characteristic, together with low *iR* drop, makes it possible to cover the Hg-plated microsensor with a gel layer, in order to overcome the fouling problem [3,4].

Mercury remains a material of choice for the detection of metals because of its large hydrogen overvoltage. Electroplating mercury on microelectrodes is an attractive means of producing mercury microelectrodes with size ≤ 10 μm. Iridium, which exhibits low solubility in mercury and good wettability, has been found to be a good substrate for the formation of a mercury film. Furthermore, in contrast to the macroelectrodes mercury-plated iridium-based microelectrodes can be left in open circuits, without coalescence of the Hg film [5,6].

Previous work indicated that a $5x10^{-4}$M nitriloacetic acid (NTA) solution at pH 6.0 is a suitable stripping agent for the lead and copper PLM system under study [7]. The aim of the present work was to determine if total metal quantification is possible, in a strip solution containing NTA, using a mercury iridium microelectrode and square wave stripping voltammetry (SW-SV) [1,8,9].

Experimental

All compounds were reagent grade, and all solutions were freshly prepared with Milli-Q water 5 µS/m (Millipore) before use. Agarose and nitric acid were suprapure grade. Standard stock solutions of 1000 mg/L of copper and of lead were used, and dilutions prepared almost daily with Milli-Q water 5 µS/m. Experiments were done at room temperature (22 ºC).

Electrochemical measurements were made using an Ecochimie Autolab PGSTAT 12 potentiostat, controlled by PC using GPES software, with three-electrode configuration. The signal was amplified by an ECD module.

The reference electrode was a Methrom Ag/AgCl/3M KCl/1M $NaNO_3$ electrode, the counter electrode was a vitreous carbon rod and the working electrode an iridium microelectrode with a mercury film. After mercury deposition the microelectrode was covered with a gel layer of 15%, 1.5% or 0.75% w/v agarose.

The iridium microelectrode (Idronaut) was polished with diamond paste 1 µm on a polishing cloth using an automatic polisher [6], for 45 min., and cleaned in lubricant blue (Struers). The diameter of the iridium microelectrode was determined experimentally as indicated elsewhere [10] and it was of 5.22 µm.

Mercury films were deposited before each set of experiments by electroplating mercury on the iridium surface. This was achieved by maintaining the Ir potential at – 400 mV vs. Ag/AgCl, in a deoxygenated solution of 5.10^{-3} M $Hg(CH_3COO)_2$ in 10^{-2} M HNO_3, until a total charge of –20 µC was deposited (ca. 500-600 seconds). Because the deposition was followed in time by chronoamperometry, the exact size of the mercury is known. After each day of measurements, the mercury was removed from their iridium substrate by reoxidation in KSCN 1 M. Linear potential scans from –0.3 V to 0.3 V were performed at a scan rate of 5

mV/s until no redissolution signal was left. For agarose layer, the mercury was removed with a wet tissue paper, and a scan was done after this, indicating no mercury in iridium surface. The iridium surface was controlled regularly with an optical inverted microscope (Leica).

Agarose layer preparation.

Milli-Q water was heated to about 80 ºC in a water bath. An appropriate volume of the hot water was added to a known quantity of agarose placed in a test tube to obtain a gel with the desired percentage of agarose (15%, 1.5% or 0.75% w/v). The test tube was vigourously agitated until all the agarose dissolves and the gel becomes transparent. The gel was left to cool and the microelectrode was submerged into the gel.

Square Wave Voltammetry (SWV) was used under the following conditions: first purging time: 900 s (to equilibrate the gel); conditioning: 60 s at -100 mV; deposition: 20 s; potential scan from –0.3 V to +0.075 V (for copper) and potential scan from –1.1 V to -0.1 V (for lead) at 25Hz; step potential 4 mV; amplitude 25 mV; current range 100 nA.

Experiments were performed in 25 mL electrolyte solution of $NaNO_3$ 0.1 M. The same mercury iridium microelectrode was used for calibration curve (metal without NTA) and for titration curve (addition of metal from 10^{-9} until 10^{-7} M to a constant concentration of NTA of 5.10^{-4} M). For calibration curves pH was maintained at 3.5 (with HNO_3 adjust) and for titration curves pH was maintained at 6.0 (with NaOH adjust). Before measurements all solutions were deoxygenated for 15 minutes, and between measurements were deoxygenated during 3 min. for calibration curves and during 10 min. for titration curves (i.e., in order to achieve equilibrium). Experimental conditions (pH, equilibrium time, NTA concentration) were defined according to a previous work [7].

Results and Discussion

To determine the detection limit for copper and lead in the PLM stripping solution ($5x10^{-4}$M NTA, pH 6.0), we performed additions of metal ion in the
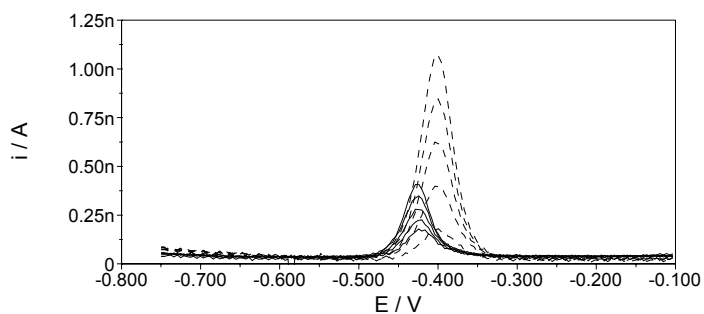
presence of NTA (titration curves). Calibration curves for the metal ions in absence of NTA were also performed for comparison. Metal concentrations varied between 10^{-9} until 10^{-7} M.

We observed just one peak with or without the presence of NTA, for both metals (copper and lead). The current values were smaller in the presence of NTA when comparing with the peak obtained for the same metal concentration, and this was also applied for both metals.

For lead the peak potential (E_{pPb}) change with the presence of NTA (E_{pPb} = -0.400 $\pm$ 0.004 V and E_{pPbNTA} = -0.428 $\pm$ 0.004 V), and the half-peak width ($W_{p/2}$) is a little larger in the presence of NTA comparing with the value obtained with the metal alone ($W_{p/2Pb}$ = 0.047 $\pm$ 0.004 V and $W_{p/2PbNTA}$ = 0.054 $\pm$ 0.004 V), but both are maintained constant during the addition of lead (Fig. 1).

For copper, E_p also varies with the addition of metal ion in the presence of NTA. It is more negative at the beginning of the experience (E_{pCu} – E_{pCuNTA} = 0.030 V) and with the addition of metal ion it becomes less negative until reaches a constant value (E_{pCu} – E_{pCuNTA} = 0.025 V), that is still negative comparing with the E_{pCu} (+0.003 $\pm$ 0.004 V). The half-peak width ($W_{p/2}$) is a little larger in the presence of NTA comparing with the value obtained with the metal alone at the beginning of the experiment ($W_{p/2Cu}$ = 0.041 $\pm$ 0.004 V and $W_{p/2CuNTA}$ = 0.045 $\pm$ 0.004 V), but with the addition of copper $W_{p/2CuNTA}$ approximates that of $W_{p/2Cu}$ (Fig.2).

However, problems arised with the functioning of iridium microelectrodes when in the presence of NTA, and therefore the polishing of the microelectrode was done more frequently than recommended. These problems were confirmed by the anomalous aspect of the iridium surface upon direct observation using an inverted microscope.

Figure 1. An example of the voltammograms obtained for calibration (---) and titration (−) curves for lead in the absence and presence of 5.10^{-4} M NTA, respectively (calibration curve: 2, 5, 7, 10 and 12 nM; titration curve: 14, 19, 24, 29 and 34 nM). The mercury iridium microelectrode was not coated with agarose.

These observations were also confirmed by the fact that the mercury removed (Q_{ox}) was significantly less than the deposited at the beginning of the experiments (Q_{red}) for values obtained when the microelectrode was in the presence of NTA (Table 1).
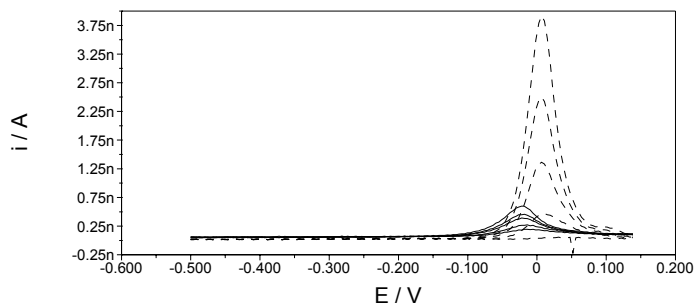

Figure 2. An example of the voltammograms obtained for calibration (---) and titration (−) curves for copper in the absence and presence of 5.10^{-4} M NTA, respectively (calibration curve: 8, 1.6, 2.4, 3.1 and 3.9 nM; titration curve: 4.7, 6.3, 7.9, 9.4 and 11.0 nM). The mercury iridium microelectrode was not coated with agarose.

Due to problems with the mercury iridium microelectrode in the presence of NTA, an attempt was made to protect the mercury iridium microelectrode with a gel agarose layer of different concentrations (15 %, 1.5% and 0.75% w/v).

Table 1. Comparison between deposited (Q_{red}) and removed (Q_{ox}) mercury from the iridium microelectrode, at the beginning and ending of the experimental work, respectively.

|	Q_{ox} (μC)	Q_{red} (μC)	Q_{ox}/Q_{red}
Cu	-18.12	-20.0	0.9
	-19.10	-20.0	1.0
Cu with NTA	-16.67	-20.0	0.8
	-17.28	-20.0	0.9
	-17.72	-20.0	0.9
	-17.42	-20.0	0.9
Pb	-19.11	- 20.0	1.0
	-19.11	- 20.0	1.0
Pb with NTA	-17.25	- 20.0	0.9
	-17.49	- 20.0	0.9
	-16.25	- 20.0	0.8
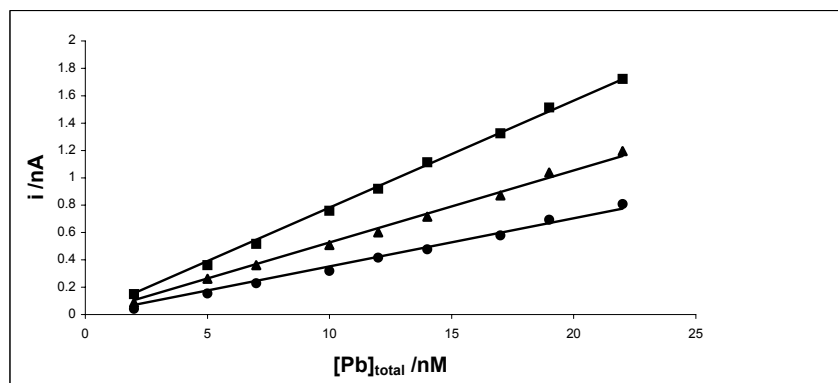
Figure 3. Lead calibration curves with the mercury iridium microelectrode: without agarose (■), with 15% agarose (●) and with 1.5% agarose (▲).

For 15% agarose the mercury iridium microelectrode became less sensitive to the concentration of metal, but it protected the microelectrode. The calibration curves obtained had a smaller slope (Fig. 3). For 0.75% agarose similar results were obtained as for 1.5% of agarose. However, it is still less sensitive and was more difficult to prepare because the agarose layer took longer to dry (higher quantity of water) (Fig. 4). The mercury iridium microelectrode coated with

different concentrations of agarose (0.75%, 1.5% and 15% w/v) showed calibration curves with smaller slopes when comparing with calibration curves without agarose protection (Figs. 3 and 4).
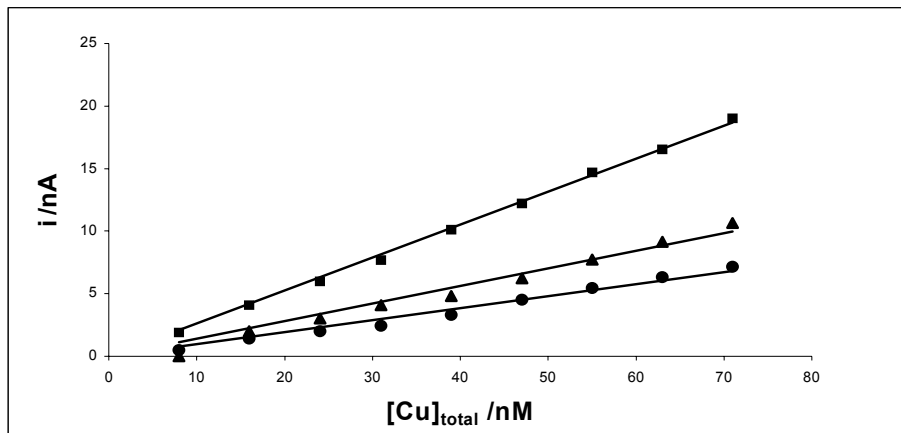
Figure 4. Copper calibration curves with the mercury iridium microelectrode: without agarose (■), with 1.5 % agarose (▲) and with 0.75% agarose (●).
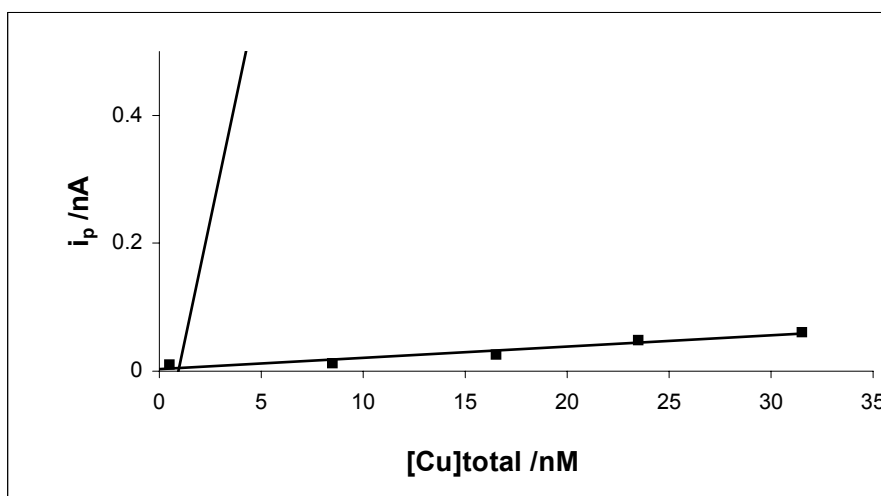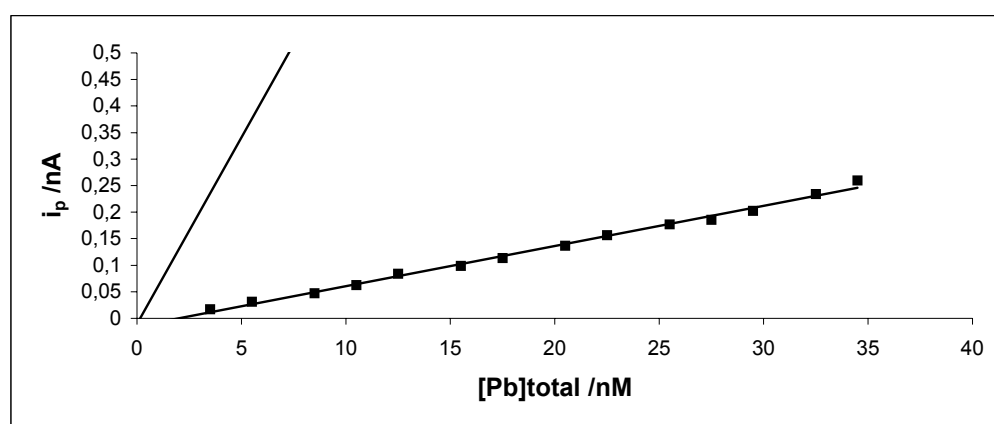

Figure 5. Calibration (−) and titration (■) curves for copper in the absence and presence of 5.10^{-4} M NTA, respectively. The mercury iridium microelectrode was coated with 1.5% agarose.

The best results were obtained with 1.5 % of agarose. The values obtained for the calibration curves were reproducible and linear, and the functioning problems did not exist. An example of all the titration curves obtained is presented in Figs. 5 and 6, i.e., a titration curve and a calibration curve for copper and lead,

respectively. For copper the $E_{pCu} = +0.003 \pm 0.004$ V and $E_{pCuNTA} = -0.020 \pm 0.004$ V, and $W_{p/2Cu} = 0.041 \pm 0.004$ V and $W_{p/2CuNTA} = 0.045 \pm 0.004$ V. For lead $E_{pPb} = -0.429 \pm 0.004$ V and $E_{pPbNTA} = -0.466 \pm 0.004$ V, and $W_{p/2Pb} = 0.047 \pm 0.004$ V and $W_{p/2PbNTA} = 0.045 \pm 0.004$ V. An example of the voltammograms obtained in Figs. 5 and 6 is presented in Figs. 7 and 8, respectively.

The gel membrane allows the diffusion of small metal ions and complexes but retains colloids and macromolecules [1-4]. However, in this case, it is likely that the gel layer gave mechanical stability to the mercury iridium microelectrode.
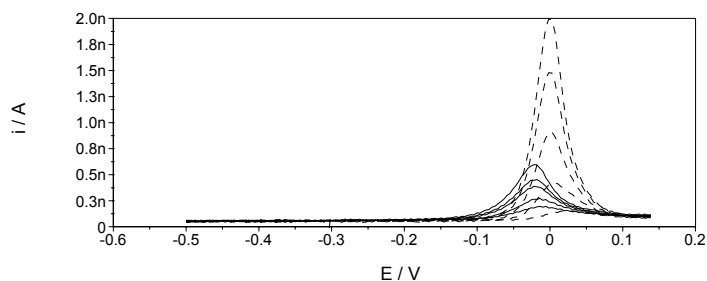

Figure 6. Calibration ($-$) and titration ($\blacksquare$) curves for lead in the absence and presence of 5×10^{-4} M NTA, respectively. The mercury iridium microelectrode was coated with 1.5% agarose.

The NTA systems have a linear response in the range studied with an estimated detection limit of 5 nM for lead and 8 nM for copper for the 20 s deposition time used.

The extremely short deposition time used is due to the interest in performing online measurements in the PLM cell, for which longer deposition time would create time average signals.

The short deposition time also takes into account the need of the stripped metal to diffuse away in the gel before the start of the new deposition step. According to Tercier et al. [4] this takes the same time as the deposition time, which in this case is sufficiently taken into account in the conditioning time (60 s).

Figure 7. An example of the voltammograms obtained for calibration (---) and titration (−) curves for copper in the absence and presence of 5.10^{-4} M NTA, respectively (calibration curve: 8, 1.6, 2.4, 3.1 and 3.9 nM; titration curve: 4.7, 6.3, 7.9, 9.4 and 11.0 nM). The mercury iridium microelectrode was coated with 1.5% agarose.
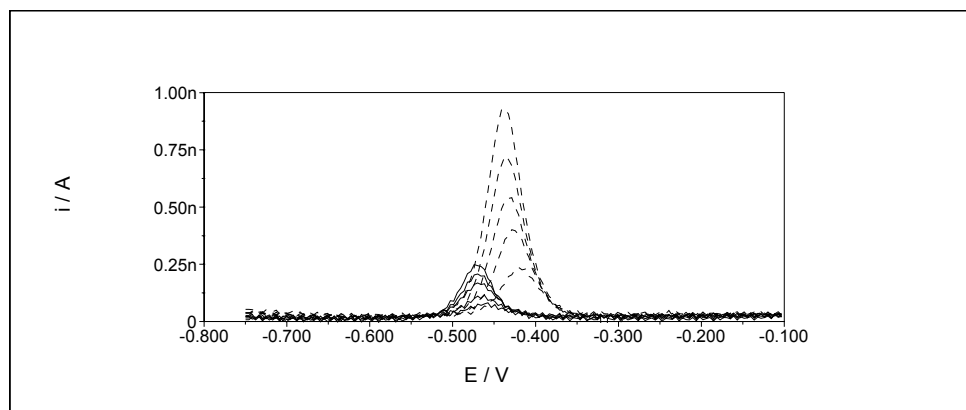
Figure 8. An example of the voltammograms obtained for calibration (---) and titration (−) curves for lead in the absence and presence of 5.10^{-4} M NTA, respectively (calibration curve: 2, 5, 7, 10 and 12 nM; titration curve: 14, 19, 24, 29 and 34 nM). The mercury iridium microelectrode was coated with 1.5% agarose.

In these conditions we obtain a minimum interval among measurements of 80 s with a detection limit on the nanomolar range. A better detection limit might be achieved increasing the deposition time but at the expense of a lower resolution in time for the flux analysis of the PLM, which is not desirable.

Conclusions

(1) The best results were obtained with 1.5 % of agarose, which also protects the mercury iridium microelectrode from NTA.

(2) The detection limit obtained, in the presence of NTA, was of the order of 5 nM for lead and 8 nM for copper, with a minimum time interval between measurements of 80 s, so the use of NTA as stripping agent is adequate for our future studies.

(3) These conclusions are valid taking into account the time scale of the voltammetric technique used, i.e., the experimental conditions of square wave stripping voltammetry.

Acknowledgements

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