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Determination of Se(IV) by anodic stripping voltammetry using gold electrodes made from recordable CDs

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Abstract

This work presents a simple, reproducible and low cost method, employing differential pulse anodic stripping voltammetry, for determination of selenium(IV). A gold electrode obtained from recordable compact disks (CD-R) was used to evaluate the voltammetric behavior of the metallic ion in 0.1 mol L^{-1} $HClO_4$. To evaluate the voltammetric behavior of Se(IV), parameters such as deposition potential and deposition time were optimized. A wide linear response range, from 0.5 to 291 ng mL^{-1}, was obtained using a 5.0 mm diameter gold electrode. Recovery tests for Se(IV) utilizing standard reference solutions provided values between 94 and 96%.

Keywords: Selenium; Gold electrode; Recordable CDs

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1. Introduction

Selenium is a trace element present in almost all environmental and biological materials, rarely found in concentrations above 100 $\mu g\,g^{-1}$. It is an essential element for animals and human beings in concentrations between 0.04 and 0.1 g mL^{-1} but it shows toxic effects above 4 g mL^{-1} [1]. Previously, only the toxic effects of Se have attracted the interest of the scientific community. Nowadays, the interest in selenium has increased considerably due to its presence in the active centers of some enzymes named selenoproteins. These enzymes, in general, participate in antioxidant reactions whose main functions are to eliminate free radicals derived from oxygen. Efficient removal of these free radicals maintains the integrity of the membranes, reduces the risk of cancer, slows the aging processes and, therefore, degenerative diseases [2,3]. Another feature of the Se ion that has attracted the interest of scientists is its possibility to interact with toxic metals (e.g., Hg, Cd and Pb). This interaction is important because it changes the toxicity of those metals as well as inherent selenium toxicity [1].

The determination of selenium in different matrices is very important in environmental, biochemical and chemical analyses. Instrumental methods commonly used for analysis of Se include atomic absorption spectrometry [4–6] and voltammetry [7–9]. Stripping voltammetry has been widely applied due to its high sensitivity, inexpensive instrumentation and the easy maintenance of the equipment. However, anodic stripping voltammetry (ASV), usually carried out with gold electrodes, is not so often applied to determination of Se because the stripping of this metalloid is accompanied by multiple peaks, which impair the reproducibility of the curves to be obtained. In addition, the pretreatment of the electrode is inconvenient, demanding a long time. Usually, this pretreatment involves electrode surface polish and an electrochemical conditioning step, which consists of applying a cathodic potential on the electrode for a few minutes.

Film gold electrodes are a cheaper alternative for voltammetric selenium determination. Frequently, these films are deposited on a substrate (for example, glassy carbon electrodes), by electrochemical or sputtered processes. However, before gold film deposition, a pretreatment of almost substrates is still necessary. In order to overcome this pretreatment, the use of the gold layer from recordable compact disks (CD-R) is a promise possibility.

All compact disks (CDs) have a nanometric metal layer (e.g., gold, silver, copper or aluminum) which contains very thin lines

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to be tracked during the recording process. The use of gold layer from CDs as electrodes was described in details by Richter et al. in 2000 [10,11]. This new source of electrodes (gold-sputtered type), named CDtrode, was applied for mercury determination in a flow injection analysis (FIA). The main advantage of CDtrodes is their low cost, allowing their replacement without exhaustive treatment of their surfaces. This is possible because almost 30 electrodes with only one CD (approximately \$1.00) (it is less than \$0.05 per electrode) with 5.0 mm diameter working surface can be done. By the way, this price will change with the electrode size. In spite of their low cost, these electrodes show good results, which are in agreement with that obtained utilizing commercial gold electrodes [10,11]. Besides, it is important to point out that these electrodes are versatile and easy to obtain. Our laboratory was encouraged to investigate the Se electrochemical behavior in batch and flow system because there are few works about the voltammetric behavior of selenium at gold electrodes and these electrodes can be easily obtained from recordable CDs. Recently, we proposed an automatic electrochemical system for differential pulse amperometry (DPA) with electrochemical deposition and its application for Se(IV) determination in doped fish samples using FIA [12].

In this work, we introduce a simple, reproducible and low cost method, using differential pulse anodic stripping voltammetry for the determination of selenium(IV) in batch system.

2. Experimental

2.1. Instrumentation

For anodic stripping voltammetric determination of Se(IV), a Metrohm E-506 polarographic analyzer was employed. The three-electrode system consisted of a gold working electrode (CDtrode), a saturated calomel reference electrode (SCE) and a platinum wire auxiliary electrode.

2.2. Reagents

A 0.1 mol L^{-1} perchloric acid (Reagen) solution, concentrated nitric acid (Vetec), and Se(IV) stock solution [1000 mg L^{-1} atomic absorption standard solution, Merck] were used in this work. All chemicals were of analytical grade. All the solutions were prepared with sub-boiling bi-distilled water.

2.3. Composition of recordable compact disk and preparation of the gold electrodes

Recordable CDs are generally constructed on a polycarbonate base, which provides the mechanical support for the unit. A very thin layer of photodegradable polymer (e.g., having phthalocyanine, azo groups or metal-stabilized cyanine), which is sensitized during the recording process, is cast on that base. On this layer, a nanometric gold, silver, copper or aluminum film is fixed. This film contains very thin lines to be tracked during the recording process and the thickness of this film ranges between 50 and 100 nm. This gold layer is usually covered by two polymeric protecting films, the first consisting of a lacquer that protects the reflective film and the second that is designed for accepting the ink from printers [10,12].

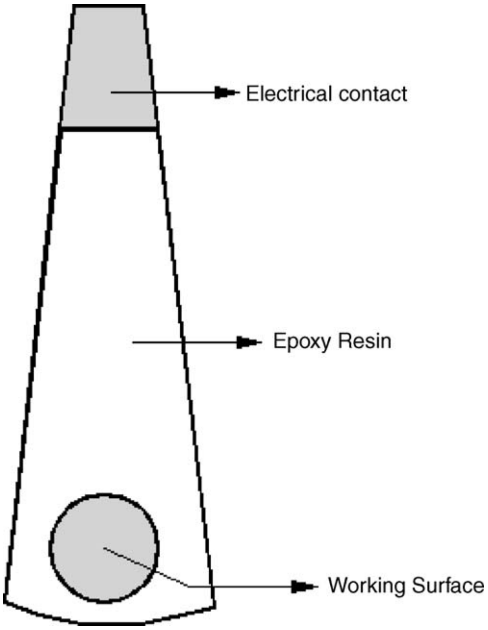

Fig. 1. Gold electrode scheme.

The gold electrode was prepared cutting a slice of the recordable CD. The gold layer of the CD was exposed by chemical attack (concentrated HNO_3) on the protective films. Two areas were exposed for obtaining the electric contact and the working surface (Fig. 1), as previously described [10]. The working surface was delineated using a pipette tip (internal diameter = 5.0 mm) and epoxy resin.

2.4. Experimental procedure for evaluation of the voltammetric behavior of Se(IV)

Voltamograms for Se(IV) were obtained by proper dilution of a stock solution of 10 g mL^{-1} (Merck) in the electrochemical cell containing 20 mL of 0.1 mol L^{-1} $HClO_4$ supporting electrolyte solution. After a deposition time of 60 s, at a potential of −0.2 V, the anodic scanning of the working electrode potential up to +1.4 V was performed with differential pulses, at a scan rate of 10 mV s^{-1}, and pulse height of 50 mV. Effects of the deposition potential and deposition time on the oxidation of selenium on the gold electrode were studied, employing the above experimental conditions.

3. Results and discussion

3.1. Evaluation of the Se(IV) voltammetric behavior on gold electrodes from recordable CDs

The reduction of Se(IV) on gold electrodes is a process that involves six electrons, generating the species Se(−II) [13]. The anodic stripping process in 0.1 mol L^{-1} $HClO_4$ solution of the selenium deposited on the surface of the gold electrode showed three different peaks, indicating the existence of several

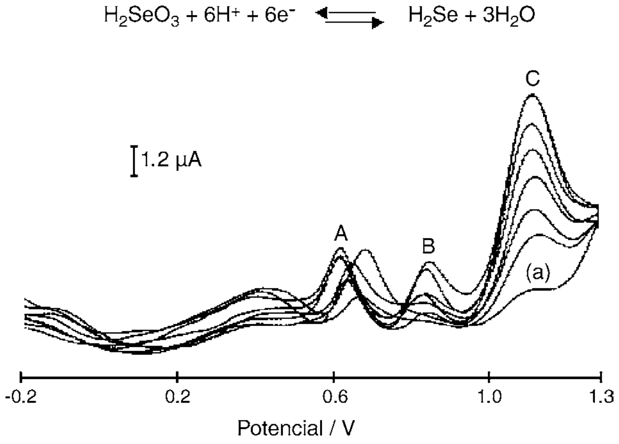

Fig. 2. Anodic stripping voltammograms for successive additions of 10 μg mL^{-1} Se(IV) stock solution utilizing gold electrodes obtained from CDs. (a) Supporting electrolyte (0.1 mol L^{-1} $HClO_4$).

interactions of Se with the electrode material (Fig. 2). Peak B, at +0.8 V, is due to the oxidation of the superficial Se monolayer that is strongly adsorbed on the electrode surface. Peak A, at +0.6 V, is attributed to the oxidation of bulk Se deposited on the electrode surface. The peak C, at +1.1 V, results from the stripping of the Se of an intermetallic Au–Se compound of unknown stoichiometry that is formed due to Se diffusion into the Au electrode from the bulk deposit. Such a difusional process is promoted by the large Se activity gradient at the Au–Se interface produced by deposition of bulk Se [14]. Therefore, if peak C is observed, necessarily peak A will also be observed because these two peaks are interdependent.

It is reported [13,14] that in commercial gold macroelectrodes and microelectrodes the deposition of trace amounts of Se by short deposition times produce only peak B, i.e., the Se adsorbed on the electrode surface does not exceed the amount equivalent to the superficial monolayer. However, in gold electrodes obtained from CDs (Ø = 5.0 mm) the peak referring to the bulk deposit (the peak at +0.6 V) and to the intermetallic Au–Se compound (the peak at +1.1 V) are observed even for concentrations of Se(IV) as low as 0.5 ng mL^{-1}. This fact indicates that Se should be strongly adsorbed on the gold electrode surface, which is an extremely thin layer (50–100 nm). An irreversible difusional transport takes place, indicating that the formation of the bulk deposit and, subsequently, of the intermetallic Au–Se compound, are interdependent processes, as previously mentioned [14].

According to Hrehocik et al. [15], in both gold microelectrodes (Ø = 10 μm) and macroelectrodes (Ø = 1.7 mm), only the peak at +0.8 V presents linear behavior and can be applied to the analysis of Se(IV). The peak at +1.0 V is not very well resolved due the background current and the peak at +0.6 V is irreproducible, showing a poor correlation between concentration and peak current. For gold electrodes obtained from CDs, the same behavior was observed for the peak at +0.6 V (Fig. 2). However, for the peaks at +0.8 and +1.0 V, different results were obtained. The peak at +0.8 V was irreproducible while the peak at +1.1 V showed a linear and reproducible behavior over the concentration ranges studied (0.5–2.0 ng mL^{-1} and 17.7–291 ng mL^{-1}).

Posey and Andrews in 1981 [16], observed only the stripping peak at +1.1 V for Se(IV) deposited on gold-plated glassy carbon disk electrodes. However, it was verified that the peak regarding the monolayer of Se deposited on the electrode surface, due to the quantity of charge consumed in the oxidation of the deposited selenium in the peak at +1.1 V, never exceeds a monolayer equivalent. On the other hand, for CD gold electrodes, the peak of Se(IV) observed at +1.1 V is probably due to the Au–Se intermetallic compound, as it always appears accompanied by the peak at +0.6 V, which seem to be interdependent (Fig. 2).

The reproducibility observed for the peak regarding the oxidation of the Au–Se intermetallic compound deposited on the CD gold electrode surface (peak at +1.1 V) required the optimization of the voltammetric parameters, such as deposition potential and deposition time, in order to evaluate the effects of these parameters on the analytical sensitivity of the method. These two voltammetric parameters are the most important and are responsible for the extremely low detection limits achieved by techniques based on preconcentration and stripping of metallic ions. The results obtained due to the variation of such analytical parameters are shown in the following items.

3.2. Effect of the deposition potential on the selenium stripping peak currents

The effect of the deposition potential on the selenium anodic stripping voltammetric response was investigated with a reference solution of 338 ng mL^{-1} Se(IV) and a deposition time of 60 s. The deposition potential was changed from −0.4 to +0.4 V. The stripping currents as a function of the deposition potentials for peaks A–C are shown in Fig. 3.

The highest sensitivity is obtained for peak B at a cathodic deposition potential of −0.2 V. Similar results have been obtained by Tan and Kounaves [17]. According to these authors, to improve the selectivity in the presence of other metallic ions and to provide a maximum mass transfer, deposition potentials between −0.2 and 0.0 V should be used. However, in the present study, for a deposition potential of 0.0 V, the sensitivity is less

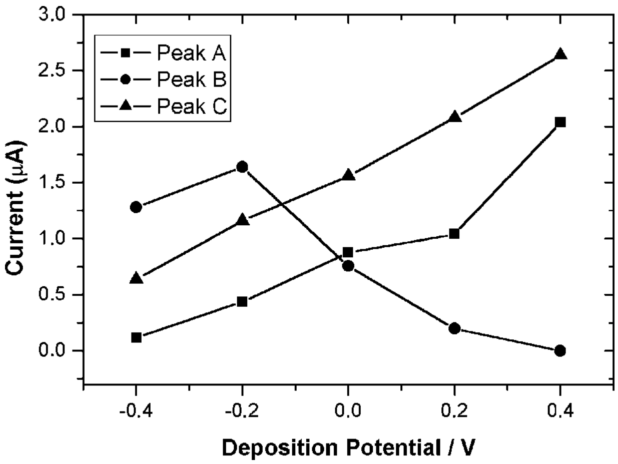

Fig. 3. Effect of the deposition potential on the selenium stripping peak currents in 0.1 mol L^{-1} perchloric acid, utilizing CD gold electrodes (CDtrodes).

effective, i.e., the mass transport at the electrode/solution interface seems to be lower.

Kazacos and Miller [19] demonstrated that, at negative deposition potentials such as −0.4 or −0,2 V, which reduces Se(IV) to Se(−II), the formed H_2Se may react with selenious acid yielding elemental selenium (1). The rate of this chemical reaction is dependent on the concentration of H_2SeO_3 and it is very fast at high H_2SeO_3 concentration so that the net process taking place at the surface of the electrode can be illustrated by Eq. (2).

$$2H_2Se + H_2SeO_3 \rightarrow 3Se + 3H_2O \tag{1}$$

According to McLaughlin et al. [18], there is an increase in the sensitivity of the selenium stripping peak (+0.8 V) as the cathodic deposition potential is increased, because the scan period becomes longer and, as a consequence, the stripping signal increases (a deposition potential of −1.0 V was used by these authors). For the gold electrode used in the present study, the opposite behavior was verified: using a more cathodic deposition potential, −0.4 V, the sensitivity of peak B decreases, in agreement with the results obtained by Tan and Kounaves [17]. For more anodic potentials, +0.2 and +0.4 V, the analytical sensitivity of peak B decreases to a value close to zero, results similar to those obtained by Hrehocik et al. [14], Tan and Kounaves [17] and McLaughlin et al. [18].

With respect to the peaks resulting from the oxidation of bulk deposit (peak A) and the Au–Se intermetallic compound (peak C), it can be verified that for gold electrodes they are only favoured at more anodic deposition potentials (0.0, +0.2 and +0.4 V). As described by Andrews and Johnson [14], at pH 1, Se(IV) exists as H_2SeO_3 in this noncomplexing media, and the standard reduction potential for the H_2SeO_3/Se couple in 0.1 H^+ is 0.43 V versus SCE. This behavior can be seen in Fig. 3. At positive deposition potentials such as +0.4 V, only peak A (+0.6 V) and peak C (+1.1 V) are observed. This result is in agreement with those described in the literature, once at this deposition potential Se(IV) is reduced to Se(0) and the chemical reaction taking place at the electrode surface is

$$H_2SeO_3 + 4H^+ + 4e \rightarrow Se + 3H_2O \tag{2}$$

Another factor that can explain the increase of the sensitivities of these two stripping peaks at these deposition potentials is that the effective deposition time increases, as seen in the following item. Therefore, the choice of more anodic deposition potentials, such as +0.4 V, optimise the analytical curves for the peak at +1.1 V.

3.3. Effect of the deposition time on the selenium anodic stripping peak at +1.1 V

The relationship between deposition time and the selenium stripping peak current at +1.1 V (Fig. 4) was investigated using a deposition potential of +0.4 V, a scan rate of 10 mV s^{-1}, and a solution containing 244 ng mL^{-1} of Se(IV), varying the preconcentration time between 60 and 840 s. As shown in Fig. 4, there is an increase in the current of peak C as the deposition time is increased. No saturation of the CD gold electrode surface was observed with the longest deposition time studied. The increase in the peak current is due to the irreversible difusional transport of Se into the gold electrode, as a consequence of the large concentration gradient formed at the Au–Se interface. Such irreversible difusional transport of Se is favored by the formation of the internal deposit (peak at +0.6 V) and Au–Se intermetallic compound (peak at +1.1 V).

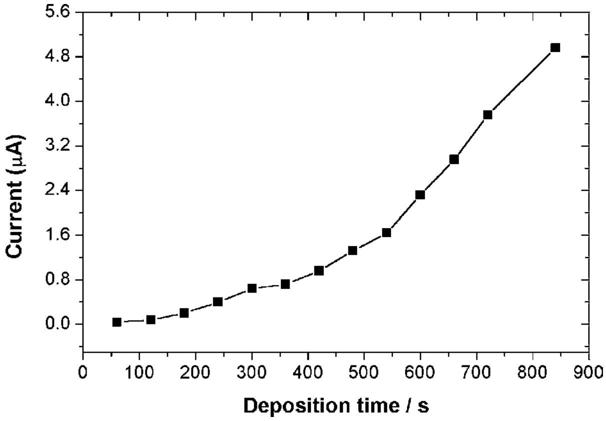

Fig. 4. Effect of the deposition time on the selenium stripping peak currents in 0.1 mol L^{-1} perchloric acid, utilizing CD gold electrodes (CDtrodes).

Andrews and Johnson [14], studying the effect of deposition time on stripping peaks of Se in gold electrodes, obtained similar results to those seen in the present work. They demonstrated that, for deposition times longer than 5 s, three anodic stripping peaks are observed for Se deposited on a gold electrode surface. Moreover, it was verified that longer deposition times decrease the sensitivity of the peak corresponding to the monolayer of Se deposited on the gold electrode (peak at +0.8 V). This fact was not observed in the study with CD gold electrodes because the applied deposition potential (+0.4 V) did not allow the anodic stripping peak at +0.8 V to emerge, as discussed in the previous item.

It can be concluded that, based on the results obtained, for longer deposition times, higher analytical sensitivities for peak C (at +1.1 V) will be achieved. However, for the determination of Se(IV), a deposition time of 180 s was used, in order to have shorter analysis times.

3.4. Determination of Se(IV) from Au–Se intermetallic compound

Once the optimisation had been completed the better voltammetric conditions (as given in Table 1) were used in this study. Analytical curves were obtained for Se(IV) by using standard

Table 1
Experimental parameters used in Se(IV) determination

Parameter	Value
Deposition potential (V)	+0.4
Pulse height (mV)	50
Scan rate (mV s^{-1})	10
Deposition time (s)	180
Equilibrium time (s)	30

Table 2
Determination of Se(IV) from the peak at +1.1 V

N	Se(IV) added (ng mL^{-1})	Se(IV) found (ng mL^{-1}), $X \pm$ S.D.	Average recovery (%)
3	50	48.2 ± 4.8	96.4
3	100	94.0 ± 11.3	94.0

X, average value; S.D., standard deviation.

solutions with concentrations between 0.5 and 291 ng mL^{-1}. Good reprodutibility and linearity along this concentration range (correlation coefficients above 0.996) were verified.

The proposed method was applied to the Se(IV) determination in the electrochemical cell. For this, the multiple standard addition method was utilized and the measurements were done in triplicate. Average recovery values above 94% (Table 2) show that the proposed procedure using CD gold electrodes (CDtrodes) can be applied to the determination of Se(IV). Similar recovery values were achieved by Richter et al. [10] for mercury determination by FIA, also employing the gold layer of recordable CD as working electrodes.

4. Conclusions

Selenium(IV) anodic stripping voltammetry in gold electrodes from recordable CDs was investigated for the first time. Such electrodes were shown to be versatile, reproducible and sensitive for determination of this chemical species. Moreover, CD gold electrodes are cheaper than commercial gold electrodes and easier to be prepared.

The working surface of CD gold electrode can vary with the procedure of preparation described in this work. However, for each analysis the same electrode has always been used. Besides, by comparing the performance of different electrodes, that were obtained in different days, the results are reproducible and comparable with those demonstrated in the literature.

The peak at +0.8 V, related to the oxidation of the monolayer of Se formed on the gold electrode surface, was not reproducible. However, the peak at +1.1 V was reproducible and provided a wide concentration linear range (0.5–291 ng mL^{-1}) with correlation coefficients above 0.996. The determination of Se(IV) using this anodic stripping peak was proved to be good, as average recoveries obtained for standard solutions of that metalloid were higher than 94%.

Finally, the CD gold electrodes showed a similar performance to the commercial gold electrodes without necessity of pretreatment of the electrode surface, which do not compromise their performance.

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