Assay of Trace Gold Ion in a Skin Cell Using a Stripping Voltammetry

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Abstract : Threelectrodes systems were used in stripping voltammetry (SW) and cyclic voltammetry (CV) instead of the expensive platinum and Ag/AgCl reference electrodes. Moreover, the electrolyte solution was used with deep seawater, which can reduce water pollution, is more eco-friendly, and has a lower cost. The analytical optimum parameters measured via CV and SW and with working ranges were obtained from 10 to 80 ug/L using fluorine immobilized on a graphite pencil electrode (FE). Under the optimum conditions, the analytical detection limit of 6.30 ug/LAu was obtained. The results of the study can be applied to diagnostic assay for natural minerals and human finger tissue.

Keywords : pencil electrode, seawater, gold assay, voltammetry

1. Introduction

Gold is used extensively in the petroleum/chemical industry as well as in agriculture and medicine[1], and its nanosphere compounds have long been used in anticancer[2] biological treatments of immunocytochemistric cell systems[3] and others. Here diagnostic in vivo or vitro assays are requires in cell biological systems with low analytical detection limits. Several analytical methods have been developed of late, such as the gamma absorption technique[4], graphite furnace atomic-absorption spectrometry[5], neutron activation analysis[6], inductively coupled plasma mass spectrometry[7], multipulse-laser-induced breakdown spectroscopy[8], PIXE[9], effusion mass spectrometry[10], ED-XRF spectrometry [11], UV-vis spectrophotometry[1], neutron activation analysis[12], kinetic spectrophotometric method[13], and electrothermal atomic-absorption spectrometry [14]. These methods are complicated and time-consuming, however, and they cannot be used for in-vivo or in-vitrodirect assay. Recently, the voltammetric method was proven to be easy and usable for modified working sensors such as carbon paste modified with montmorillonite[15], graphite expoxy composite electrode[16], and modified carbon paste electrode[17]. Even though they are difficult to make and need a long preparation time. Here pencil graphite electrodes were used in this study as working, counter, and

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reference electrodes because not only are they affordable; they are also effective for detecting materials. Moreover, seawater electrolyte has been used to detect other ions, such as nitrate[18], bromide ions[19], and alkylbenzene sulfonate[20], instead of acid or base electrolyte solutions. Seawater is inexpensive, ecological, and helps yield good results for the detection of trace assay. The developed device was applied to a trace metal and a human finger cell for the detection of gold ion in human cells.

2. EXPERIMENT

The experiment systems were carried out using a Bioelectronics-2 circuit constructed by the authors'institution. Its second version was a computerized handheld voltammetric system with a 2.4 V potential window, a 2 mA current range, a 10 pico A measuring current, and a 5″4″1″ compact size. It makes use of a rechargeable battery or external power supply, has a USB interface with a PC, and is as small as a typical cellular phone. Three nontreated pencils served as the working, reference, and auxiliary electrodes, respectively. The supporting electrolyte was prepared with clean seawater. All the other reagents were of analytical grade. Electrolyte voltammetry was carried out at an open circuit. A gold standard was obtained from Merck.purified water was prepared via three-time distillation, using 18-Mcm-1Milli -Q Ultra-Pure Water System (Millipore, Bedford, USA). Fluorine immobilized FE was prepared using on a 10-mL-conc HF electrolyte solution by 10-cycle scan with a 1.0 V initial potential, a 1.0 V switching potential, and a 0.5 V/s scan rate. The stripping voltammetric parameters were used for the SW: 0.06 V amplitude, 25 Hz, 170 sec deposition time, and -1.3 V initial potential. All the experiments were performed at room temperature and without oxygen removal.

3. RESULTS AND DISCUSSION

3.1. Cyclic Voltammetry and SW Stripping Potential
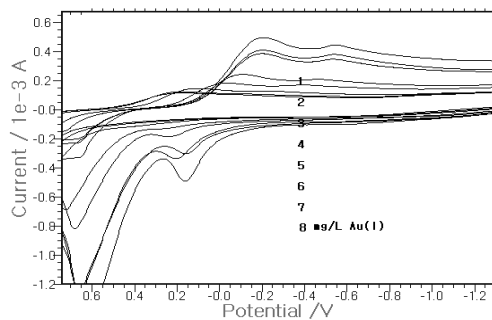
(A)
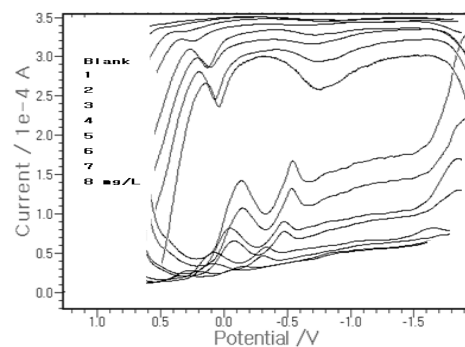
(B)

Fig. 1. (A): Cyclic voltammetric scan using a 1- to 8-mgL^{-1}-Au-spike FE. (B): Stripping voltammetric working anodic and cathodic range of 1-8 mgL^{-1} Au with FE in the seawater electrolyte, optimum parameters.

First, the cyclic and stripping voltammetric peak potentials were examined using FE. In this study, three graphite pencil sensors were used as reference, auxiliary, and working electrodes, respectively. Moreover, clean deep seawater was used as electrolyte solutions. Fig. 1(A) shows the CV results range of blank, 1-, 2-, 3-, 4-, 5-, 6-, 7-, and 8-mgL^{-1} Au add. The first curve shows the blank solution, where no current was obtained, then the Au concentrations were

spiked in the order mentioned earlier. In the oxidation scan, the peak currents were not obtained at the 1, 2, and 3 mgL^{-1} Au concentrations, but after the 4 mgL^{-1}Au concentration, the peak current appeared from -0.1015×10^{-4} A to -2.085×10^{-4} A at 0.1 V.the reduction scan, it increased from 0.8458×10^{-4} A to 3.283×10^{-4} A at -0.2 V. After that, SW was examined using FE, and Fig. 1(B) shows the result. No signal was obtained at the blank sea water solution, then the 1, 2, 3, 4, 5, 6, 7, and 8 mgL^{-1} Au concentrations were spiked in that order. At the 1 mgL^{-1}Au concentration, the curve did not obtain any signal; otherwise, it increased continually from 0.08904×10^{-5} A to 7.6×10^{-5} A as the 2-8 mgL^{-1}Au concentrations were spiked. The two peak potentials of $-0.2, -0.6$ V anodic and $0.0, -0.8$ V cathodic were obtained sensitively for the detection of gold. They can be used under the optimized conditions.

3.2. Square-Wave Optimizations

The stripping voltammetric optimizations were examined using FE. First, the various SW amplitude values were examined. Fig. 2(A) shows the results at 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4, 0.5, and 0.6 V. The peak current increased slowly from 0.05 to 0.15 V (12.49×10^{-6} A), and continually at 0.2 V amp, but it dropped to 10.9×10^{-6} A at 0.25 V amp. It increased again after a decline, until it reached 41.32×10^{-6} A at 0.4 V, which was the maximum current, after which it decreased again to 32.68×10^{-6} A. Then Fig. 2(B) shows the SW frequency variations of 5, 10, 15, 20, 25, 30, 35, and 40 Hz. The peak current of 1.412×10^{-5} A was obtained at 5 Hz. It increased to 5.374×10^{-5}A, but it dropped at 15 Hz. It increased again to 5.559×10^{-5}A at 20 Hz, which was the maximum, after which it decreased again. Here, 20 Hz was chosen as the optimum condition. Fig. 2(C) shows the SW increment potential variation range of 0.001, 0.002, 0.003,
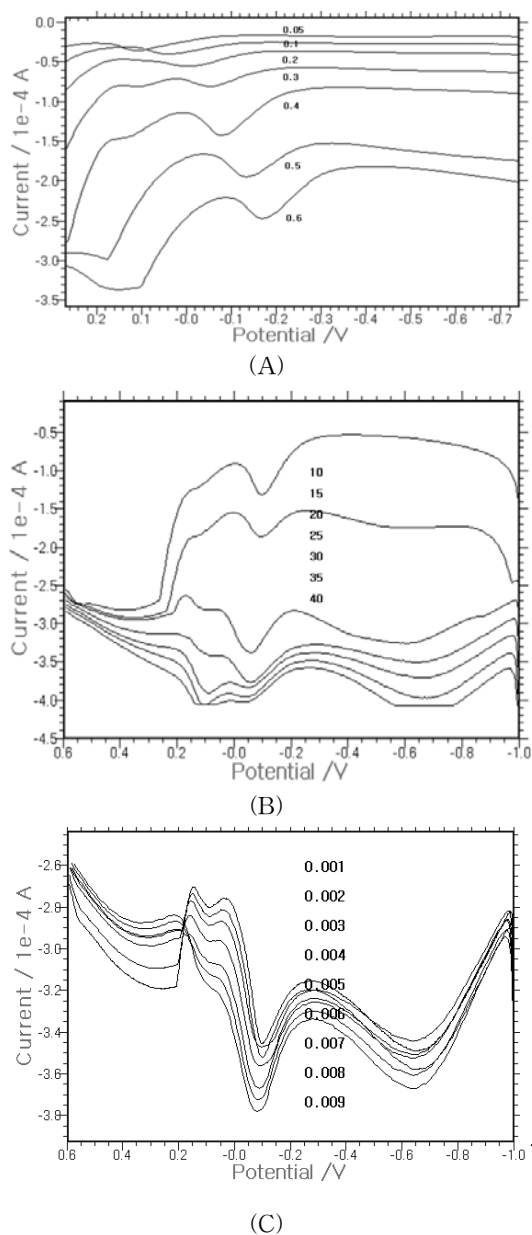

(A)

(B)

(C)

Fig. 2. (A): Variations of the 0.05-0.6 V SW amplitude. (B): 5-40 Hz frequency range. (C): Variations of the 0.001-0.009 V increment potential of 10-mgL^{-1}gold in the seawater electrolyte. The other parameters were also examined and used under the optimum conditions.

0.004, 0.005, 0.006, 0.007, 0.008, and 0.009 V, under this condition. The peak current of 5.208x10-5Awas attained when the 0.001 V increment was given. It increased little by little and reached 2.229x10-5A at the 0.004 V. It then decreased quickly at the 0.005-0.006 V. The maximum current was obtained at 0.004 V, which was chosen as an optimum condition. The other parameters that were obtained were -1.4 V initial potential and 60 sec accumulation time (not shown here). These conditions were used for examining the working ranges, detection limit, and application.

3.3. Statistics and Diagnosis

Under the optimum conditions, the working range was examined using FE. Fig. 3(A) shows the CV effect of the various concentrations of 10, 20, 30, 40, 50, 60, 70, and 80 ug/L using CV. A higher current was obtained by spiking more Au concentrations with 1.203x10-5A at 0.1-mg/L Au, and it increased continuously to 89.49x10-5A, with the linear equation y=1.157x-22.901, with a precision of R2=0.8694, at the 1.1 and 1.3 V peak potentials. Fig. 3(B) shows the SW results within the range of 10, 20, 30, 40, 50,

60, 70, and 80 ug/L variations under these conditions. A 1.006x10-5A peak current was attained when 10-ug/L Au was spiked. It increased to 38.28x10-5A at the 80 ug/L variations. The peak current also appeared at 1.1-1.3 V, and the linear equation was y=0.5007x-8.3752, with a precision of R2=0.9147. The peak current was sharp and sensitive, and it can be used for in-vivo or in-vitrodiagnostics assay.

3.4. Statistics and Application

As shown in Fig. 4(A), based on the optimum conditions, the developed sensor was used to measure the Au content of a mineral from a near by city. First, a 0.1-ml-solution-dissolved mineral was spiked

in 10-ml seawater, and a 1.283x10-5A peak current was attained. After that, 0.2-, 0.3-, 0.4-, and 0.5-mL Au standards were spiked, in that order, and 1.801, 2.051, 2.366, and 2.734x10-5A peak currents were obtained, respectively. The curve was sharp, and the equation was y=3.114x+1.148 (not shown). These results obtained with 3.08 ug/mL Au concentrations indicate that gold exists in the minerals in soils. More advanced detection
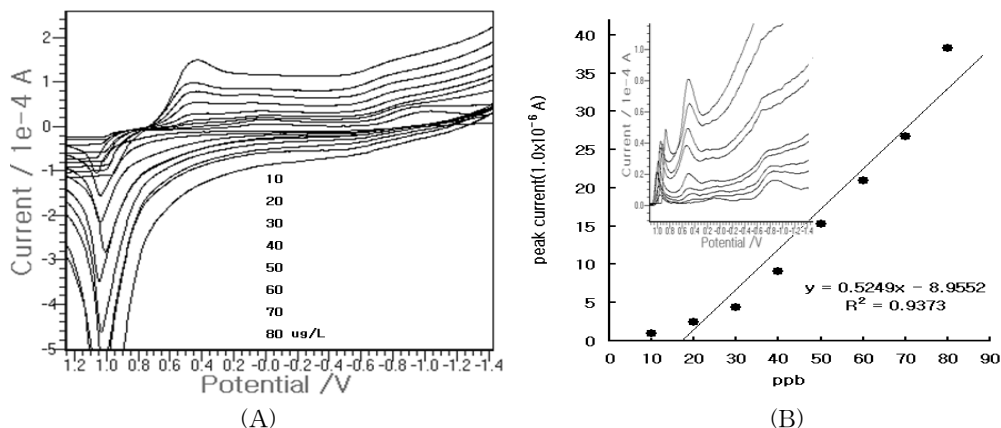

(A)   (B)

Fig. 3. (A): Examination of the analytical working range with CV using FEin the microgram
        ranges. (B): The SW effects for the 10-80 ugL-1variation at 0.4 V amplitude, 20 Hz
        frequency, 0.004 V increment, -1.4 V initial potential, and 60 sec accumulation time.

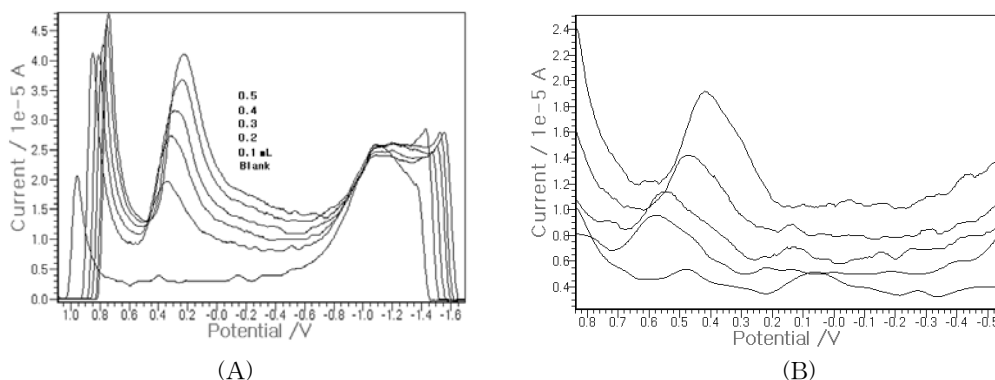(A)   (B)

Fig. 4. (A): Results of a mineral that includes gold found in SW using FE by conducting the standard addition method. (B): SW result of the application to a human finger cell using FE under the optimum conditions. The bottom curve was the result of the blank solution. After a 1-ml unknown solution was spiked, the standard solution was spiked three times.

was performed using human finger tissue for the standard addition method Fig. 4(B) shows the result of the application finger's washed solution. The cell was obtained from a person's finger with a gold ring on it. This 1-ml unknown solution was spiked in seawater electrolyte, and a 3.371×10^{-5}A peak current was attained. After the 2-, 3-, and 4-ml Au standards were spiked, the 3.822, 4.914, and 7.938×10^{-5}A peak currents were obtained. The linear equation was $y=0.3092x+1.325$, with a precision of $R2=0.9969$, and 3.58 ug/mL Au contents were obtained. Thus, Au was detected in the human finger cell, which can accumulate in the in vivo body systems.

4. Conclusion

Stripping voltammetry using FE was used in this study for determining the optimum conditions, and the results that were obtained were 0.4 V amplitude, 20 Hz frequency, 0.004 V increment, −1.4 V initial potential, and 60 sec accumulation time. Based on the optimum conditions, the detection limit of 10-ug/L Au

was attained. Due to the use of FE and seawater, the experiment could be performed easily and at low cost. The results were applied to a mineral and a human finger cell using the standard addition method. It was found that gold exists in the soils, rock and in the human cell systems. The results of the application of the developed sensor can be used in medicine, both in-vivo and ex-vivo.

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