

## Detecting gold by voltammetric handhold systems

Nack-Joo Kim<sup>†</sup> · Dal-Woong Choi<sup>\*</sup> · Hai-Soo Yoo<sup>\*\*</sup> · Kyung Lee<sup>\*\*\*</sup>  
Chang-Hyun Lee<sup>\*\*\*\*</sup> · Suw-Young Ly<sup>\*\*\*\*\*</sup> · Tae-Yun Kim<sup>\*\*\*\*\*</sup>

<sup>†</sup>*Dept. of Fine Chemistry, Seoul National Univ. of Science & Technology, Seoul, Korea*

<sup>\*</sup>*Department of Public Health Sciences, Graduate School, Korea University, Seoul 136-703, Korea*

<sup>\*\*</sup>*Korea Institute Ocean Science Technology, 787 Haean ro(st),*

*Sangnok gu, Ansan si, 425-744, KOREA*

<sup>\*\*\*</sup>*Excavation Literature and Ancient Scripts Research Institute, Fudan University,*

*Shanghai, 400223, China*

<sup>\*\*\*\*</sup>*Division of General Education, Pyeongtaek University, Gyeonggi do 405-701, Korea*

<sup>\*\*\*\*\*</sup>*Biosensor Research Institute, 139-743, Seoul, Korea*

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**Abstract** : A voltammetric investigation of Au assay was conducted at a low cost, using Nafion and DNA immobilized on a graphite Pencil working electrode (NDP) with a black lead counter and reference. The following optimal parameters were found: 0.4 V amplitude, 500 Hz frequency, -0.7 V initial potential, and 0.015 V increment potential. These optimal conditions were also applied to sand obtained from the river site. The aforementioned technique is simpler and less costly compared to the common voltammetry and spectrophotometric methods.

*Keywords* : gold, graphite nafion, voltammetry, alluvial gold

### 1. Introduction

Au is useful and necessary for the manufacture of electronic goods, especially in the composition of circuits. Au is expensive and rare, and is scattered in soil, sand, and planet rocks. Therefore, a convenient and inexpensive method of detecting Au is needed. Current methods used to detect Au, such as ICP spectrometry and kinetic photometric method [1], electrothermal atomic absorption spectrometry [2], and the ion exchange resin

method [3], are complicated. The equipment required by such methods are large and expensive. The electrochemical method, however, is easy to execute, is inexpensive, and uses minute equipment. More recently, electrochemical methods were used for detecting Au, such as the graphite-epoxy composite electrode [4] and the modified carbon paste electrode with the ethylenediamine-fixed humic-acid [5]. The problem with electrochemistry, however, is that it needs an Ag/AgCl electrode (as a reference electrode), which is difficult to make, as well as platinum wire (as an auxiliary electrode), which is expensive. In this paper, inexpensive graphite was used as a reference Ag/AgCl

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<sup>†</sup>Corresponding author  
(E-mail: suwyong@snut.ac.kr)

electrode and an auxiliary platinum electrode. Renewable graphite pencil writing devices have been available for many years [6]. These include pencil-lead bismuth-film electrodes for detecting trace metals [7], pencil graphite electrodes for detecting trepibutone [8], low-cost flow-through cells for detection of acetaminophen in pharmaceutical formulations [9], a disposable electrochemical biosensor for the detection of the interaction between DNA and lycorine based on guanine and adenine signals [10], an electrochemical biosensor for the detection of the interaction between arsenic trioxide and DNA based on the guanine signal [11], and carbon electrodes for the detection of osmium-labeled target DNA [12]. The disadvantage was compensated for by using graphite, which can be used by anyone as it is convenient to use, renewable, and inexpensive. Moreover, DNA was used because its surface area is large and it has numerous bond electrons with metal gold. It can also produce reactants fast, and this is why it is often used in antigen-antibody sensors. In the experiment that was performed in this study, DNA was melted with nafion and then fixed onto graphite to detect Au.

## 2. Experiment Method

### 2.1. System, preparation of the electrode

Analytical measurement systems were used with the new Bioelectronics-2 system, which was constructed at the authors' institute. The second version is a computerized handheld voltammetric system with a  $\pm 2.4$  V potential range, a 2 mA current range, a 10-pico A measuring current, and a 5" x 4" x 1" instrument size, and which uses a rechargeable battery or external power and has a USB port interface with a PC. Before the experiment, a working electrode was made with paste. The DNA was mixed with calf thymus sigma 70 % and 30 % mineral oil. A mixture of 5 g was homogenized in a mortar for 30 min. The

mixed paste (0.1 g) was coated on a 1.5-mm diameter graphite pencil lead, using a 0.5-mm diameter copper wire that was connected to the measurement system. Moreover, 1.5 mm diameter graphite pencils are used as the reference Ag/AgCl electrode and the platinum counter electrode.

### 2.2. Reagents

All the experiment solutions were prepared from 18 M-ohm/cm<sup>-1</sup> double-distilled water. A 0.1M electrolyte solution with a pH level of 4.75 was used as a supporting electrolyte. All the systems were carried out in dissolved oxygen, and electrode cleaning was not necessary for every measurement. The phosphoric-acid solution was found to be the most suitable medium, 1000 ppm Au was used with atomic standard absorption solution.

### 2.3. Experiment procedure

The common parameter that was used for Cyclic voltammetry (CV) was a scan rate of 100 mVs<sup>-1</sup>, and the common parameters for Square Wave Stripping Voltammetry (SWSV) were set at the optimized conditions. DNA immobilization was performed through a cyclic scan with an initial potential of +1.6 V, a switching potential of 0.6 V, and a scan rate of 0.5 mVs<sup>-1</sup>, with a tan cyclic repeat to stabilize the electrode surface. Since the voltammetric response of Au is dependent on the electrolyte solutions and the hydrogen ionic strength, various types of electrolyte solutions were tested. The phosphate solution was found to yield the best results.

## 3. Results and Discussion

### 3.1. Cyclic voltammetry

Cyclic voltammetry was performed using graphite working, counter and reference electrode. The first voltammograms were obtained to sensitive oxidation and reduction peak currents. Fig. 1(A) shows the results of

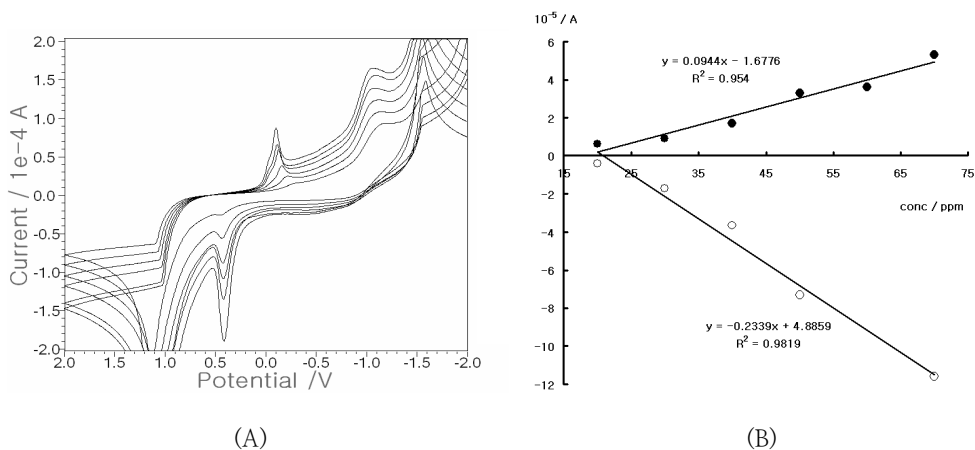


Fig. 1. (A): Various cyclic voltammetric concentration effects of the 20–70–mgL<sup>-1</sup> Au spike at the 100 mVs<sup>-1</sup> scan rate when three graphite electrode systems were used. (B): Results of the linear regression showing of anodic and cathodic, the 0.5–M phosphate electrolyte solutions.

CV using graphite at 0.4 V oxidation, current ranges from  $0.2 \times 10^{-4}$  A to  $1.9 \times 10^{-4}$  A,  $-0.2$  V reduction, ranges from  $0.1 \times 10^{-4}$  A to  $0.8 \times 10^{-4}$  A, Fig. 1(B) shows the results of the linear regression with wide working ranges by 5 points reduction and 6 points oxidation, depicting the electrolyte solutions. The concentrations of 20, 30, 40, 50, and 70 mgL<sup>-1</sup> spiked, and the peak's shape and width symmetrically narrowed. Peak current gradually increased. The more the Au spiked, the higher the peak current was. When the  $y=0.0944x-1.6776$  equation ( $y$ : reduction peak current in A;  $x$ : concentration in mg/L) was obtained and the  $R^2=0.945$  correlation was sensitive. When the  $y=-0.2339x+4.8859$ , cathodic linear equation and the  $R^2=0.9819$  correlation was obtained. Here, the anodic results were sensitive and were found to be applicable for any field, but better sensitive stripping voltammetry was examined.

### 3.2. Optimizations of NDP for the square-wave anodic stripping voltammetry, electrolyte pH effect and statistics

Fig. 2(A) shows the results of the SW amplitude variations in a fixed concentration. The voltammetric peak current gradually increased, and the peak current reached  $14.36 \times 10^{-1}$ , where 0.4 V was found to be sensitive. Under this condition, Fig. 2(B) shows the variation results in electrolyte pH ionic strength. The peak current increased to  $12.96 \times 10^{-1}$  at the range of 2.97 to 6.13 pH but dropped to  $7.572 \times 10^{-1}$  at 7.18 pH. 6.13 pH was chosen as the optimum SW ionic strength. Under this solution, other influencing parameters in the SW increment potential (0.015 V), initial potential ( $-0.7$  V), SW frequency (500 Hz), SW stripping accumulation time (500 s), and 0.1M electrolyte ionic strength were obtained (not shown here). In this condition, Fig. 2(C) shows the electrode statistic results when these parameters were used. Measurements were made 15 times, using SW, and the statistics were obtained. The anodic peak current reached  $3.602 \times 10^{-1}$  in the first measurement, then decreased to  $2.066 \times 10^{-1}$  A but went up again to  $2.835 \times 10^{-1}$  in the fourth measurement. Thereafter, similar values were

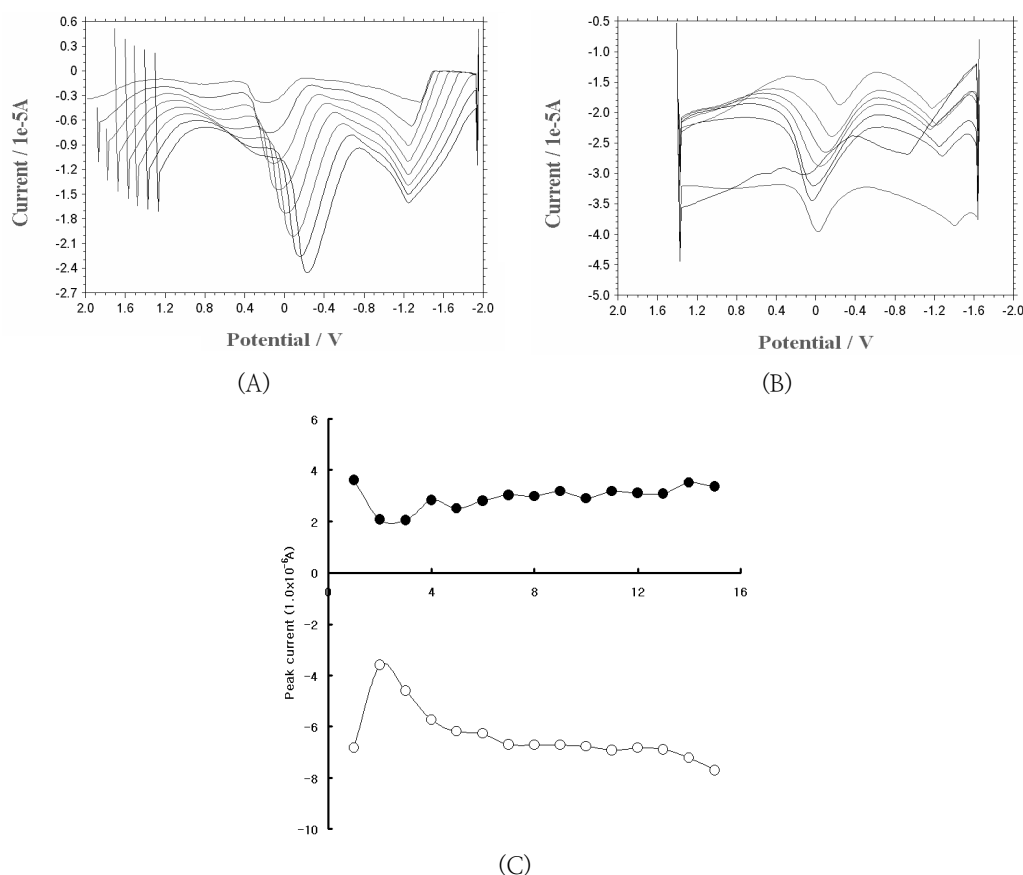


Fig. 2. Optimization of the SW stripping voltammetric parameters for (A): the 0.05, 0.1, 0.15, 0.2, 0.25, 0.3, 0.35, and 0.4 V amplitudes variations; (B): the 2.97, 3.3, 3.89, 4.89, 5.43, 5.81, 6.13, and 7.18 pH variation; and (C): the statistics of the SW anodic and cathodic peak currents in the 10.0-mg/L Au spike using the conditions in Fig. 3(A).

recorded. The cathodic peak was obtained from  $-6.828 \times 10^{-1}$  to  $-7.704 \times 10^{-1}$  and then stabilized. Under this condition, low working ranges and analytical application was performed.

### 3.3. Analytical application

Fig. 3(A) shows the results of CV when NDP was used. The results ranged from 1 to 9 mg/L variation. The reduction peak current reached  $47.57 \times 10^{-6}$ , with the linear equation of  $y=4.284x-1.53$ , statistics of  $R^2=0.714$  and oxidation scan of  $-51.41 \times 10^{-6}$ A,  $y=-9.57x+4.07$ ,  $R^2=0.619$ . It can be used in

field analysis. Stripping voltammogram was also obtained for sensitive working ranges. Fig. 3(B) shows the anodic results when SW was used. At 2–9 mg/L, the peak current reached to  $-94.59 \times 10^{-6}$ , and  $y=-12.496+10.548$ ,  $R^2=0.9383$ . In this range, the cathodic SW manifested and the spikes ranged from 2 to 9 mg/L. Here, the linear working curves were obtained for the ppm levels of  $y=2.5821x-1.236$ ,  $R^2=0.796$ . Both peaks can be applicable for soil fields and water resources. The developed techniques were examined on liver sand. Fig. 3(C) shows the SW anodic results of the application to sand

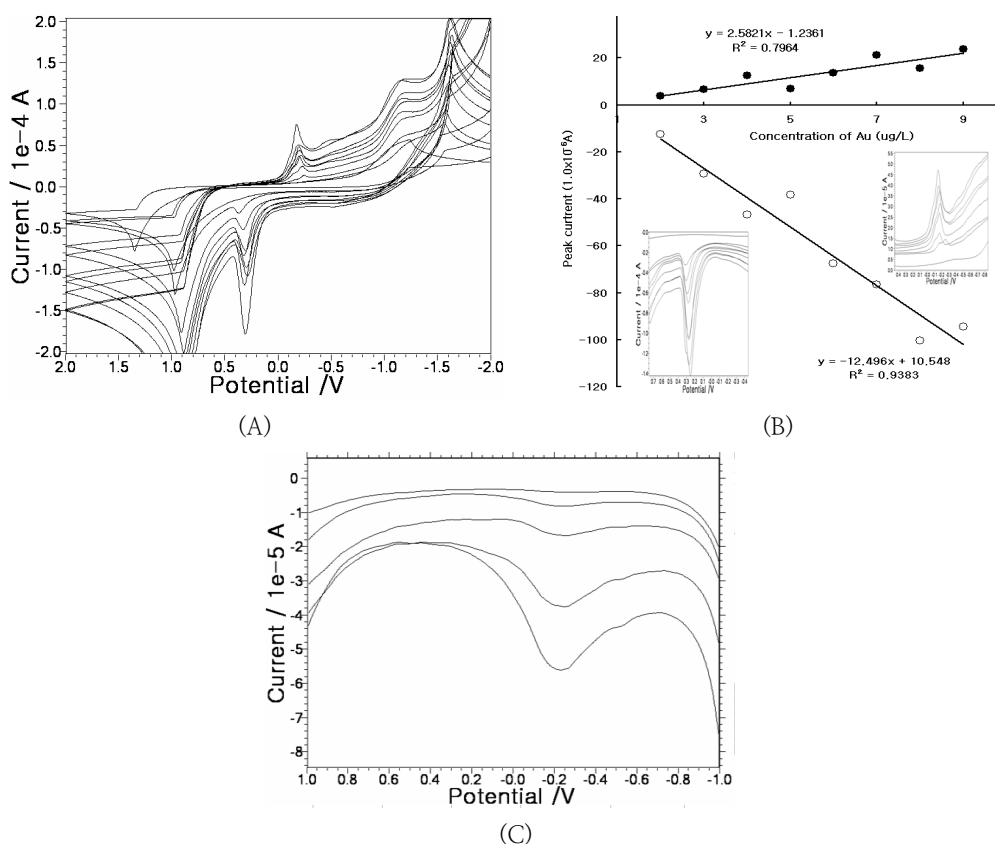


Fig. 3. (A): Results of CV when the 1- to 9-mgL<sup>-1</sup> Au variation, (B): Results of the anodic and cathodic SW when the 2- to 9-mgL<sup>-1</sup> Au variation, (C): SW anodic standard addition results for the liver sand.

in the liver site. Sand was brought from the city liver, and Au was detected there from using NDP. A 1-ml sand solution (1 gram sand + 10 ml conc HF) was first prepared, and an Au peak was detected using the standard addition method. The bottom line is the result of the blank electrolyte. After that, 0.1 mL solution spiked, then 0.5, 1, 1.5, and 2  $\mu\text{L}^{-1}$  AU standards (100 ppm) were added and were determined to have grown at the same slope. Its value was found to be  $2.192 \times 10^{-6}$  A peak current, after it reached 3.855, 14.24, 16.76. The final result was 0.4 mg/mL. Here, the developed methods are simple, inexpensive, and can be used in any field of investigation.

#### 4. Conclusions

A voltammetric analysis of Au was performed using nafion- and DNA-immobilized on a graphite pencil electrode. Graphite was used as an auxiliary electrode and a counter electrode instead of the Ag/AgCl and Pt electrodes. The Ag/AgCl electrode is difficult to produce outside a laboratory, but the defect of electrochemistry was overcome by using graphite as a reference electrode and as an auxiliary electrode. As such, it can be easily used by anyone. NDP is also easy to make, and the fabricated device is very small and handy. Therefore, it is expected that the developed method will be used not

only in the laboratory but also outside it.

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