

Stripping Chronopotentiometry: An Alternative Method for the Determination of Gold in Geological Samples

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Abstract

A stripping chronopotentiometric method was developed for reliable determination of gold in geological samples. Gold in gold ore and steam sediment samples was determined by constant current film stripping chronopotentiometry at a bare glassy carbon working electrode. The following optimum conditions were obtained: 0.5 M hydrochloric acid as a supporting electrolyte, an electrolysis potential of -0.6 V vs. saturated calomel electrode (SCE), an electrolysis time of 2 min and a constant oxidative current of $+4$ μ A. A linear concentration range was obtained from 1.0 to 20 mg/l. The detection limit was 0.27 mg/l ($n = 10$) and the relative standard deviations of 1.0 mg/l Au(III) was 2.8 % ($n = 10$). In order to check the analytical accuracy, standard solution was spiked in a sample and the recoveries were found at 100.1 to 105.8 %. The results revealed that the quantity of gold in gold ore and sediment were 0.6 to 3.3 % and 0.9 to 1.2 %, respectively.

Keywords: Gold, geological, stripping chronopotentiometry

Introduction

Traditional analytical methods such as neutron activation analysis (NAA), flame or graphite furnace atomic absorption spectrophotometry (FAAS or GFAAS) and inductively coupled plasma mass spectrometry (ICP-MS) are currently employed for determination of gold at low concentrations [1]. However, these methods required sophisticated instruments with high purchase and operating costs, while electroanalytical methods are much cheaper. Surprisingly, electroanalytical methods are not commonly used as a routine technique for gold determination at trace levels. Some analytical procedures involving anodic stripping voltammetry (ASV) and potentiometric stripping analysis (PSA) can also be found in the previous works [2-4]. Unacceptable values for detection limits and poor precision have discouraged the use of these methods for gold analysis, although the

equipment acquisition and maintenance costs present compensating advantages. The drawback of electroanalytical methods for gold analysis is mainly due to the high positive oxidation potential exhibited by this element that prevents its electrodeposition at a glassy carbon electrode. In addition, electroactive species encountered with gold such as Cu, Hg, Ag and Fe seriously interfere with the analytical determination and thus limiting the applicability of the technique. Stripping chronopotentiometry is an alternative method for determination of many metal ions at trace levels. The advantages of this method are that it is rapid, simple, simultaneous, portable, and it gives high sensitivity. Stripping chronopotentiometry (SCP) consists of 2 steps, a deposition step and a stripping step. First, the deposition of gold (III) on the working electrode occurs according to the following equation:



Next, the stripping of gold allows quantification of the accumulated metal on the electrode:



During the stripping step, the electrode potential is monitored against time, the time needed the complete re-oxidation of the gold atom being proportional to the concentration of Au^{3+} in the sample.

In this study, we have used constant current stripping chronopotentiometry (CCSCP) with a bare glassy carbon electrode to determine the content of gold in gold ore and stream sediment samples.

Materials and methods

Chemicals and Reagents

All the chemicals were of analytical reagent grade. The solutions used were all prepared with deionized water (Millipore, Bedford, USA). Standard stock solutions containing 1,000 mg/l Au(III) in 1.3 M HNO_3 were purchased from Fluka and diluted as required. Aqua regia was prepared by mixing three parts concentrated HCl with one part concentrated HNO_3 . A 0.5 M HCl was used as a supporting electrolyte.

Apparatus

Potentiometric measurements were performed with an Autolab PGSTAT 100 (Eco Chemie B.V., Netherlands). The GPES 4.9 software package was used to develop and optimize the experimental and analytical conditions. The electrochemical cell was a standard 50 mL glass vessel (Metrohm, Switzerland) equipped with a Ag/AgCl reference electrode, a Pt counter electrode and a glassy carbon (GC) working electrode (3 mm in diameter). All glassware and plasticware were soaked with 10 % HNO_3 for 12 h and rinsed several times with deionized water prior to use.

Sample Preparation

The gold ore and stream sediment samples were ground to pass through a 400 mesh sieve. Then, a 2.0 g portion of the sample was accurately weighed into a beaker and 40 ml of aqua regia was added. The solution was heated on a hot-plate nearly to dryness and dissolved with 1 ml of aqua regia. The final volume was made up to 100 ml with deionized water.

Stripping Chronopotentiometric Determination

Gold was determined by constant current stripping chronopotentiometry (CCSCP) on a bare GCE. Prior to its use, the glassy carbon disk electrode was polished with a 0.05 mm alumina slurry on a felt pad. The 3 electrodes were immersed in a 50 ml electrochemical cell, containing 0.2 ml of the sample solution and 2.5 ml of 6 M HCl, and made up to 30 ml with deionized water. An electrochemical reduction at -0.6 V for 120 s was performed prior to oxidative stripping with a constant current of $+4$ μA .

Results and discussion

Effect of HCl Concentration

Hydrochloric acid was used as a supporting electrolyte for determination of gold. The influence of the concentration of 0.01 - 1 M HCl on peak area for a gold concentration of 200 $\mu\text{g/l}$ Au(III) signal is shown in **Figure 1**. A concentration of 0.5 M HCl was chosen for subsequent measurements as this concentration provides good sensitivity.

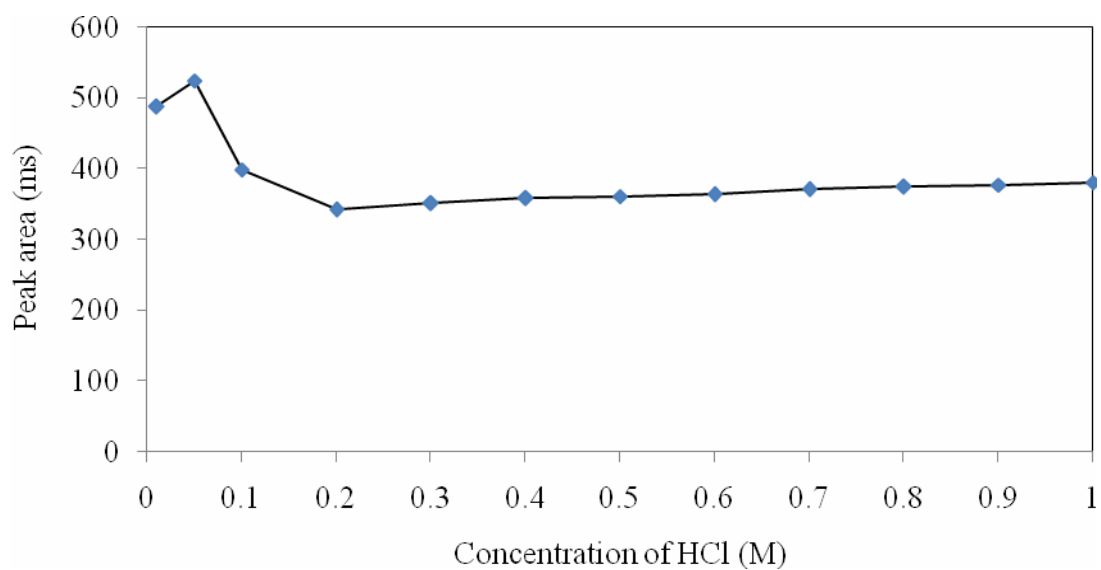


Figure 1 Influence of HCl concentration on gold measurement. A solution containing 200 $\mu\text{g/l}$ of Au(III). Deposition potential, -0.7 V; deposition time, 90 s; constant current, $+3$ μA .

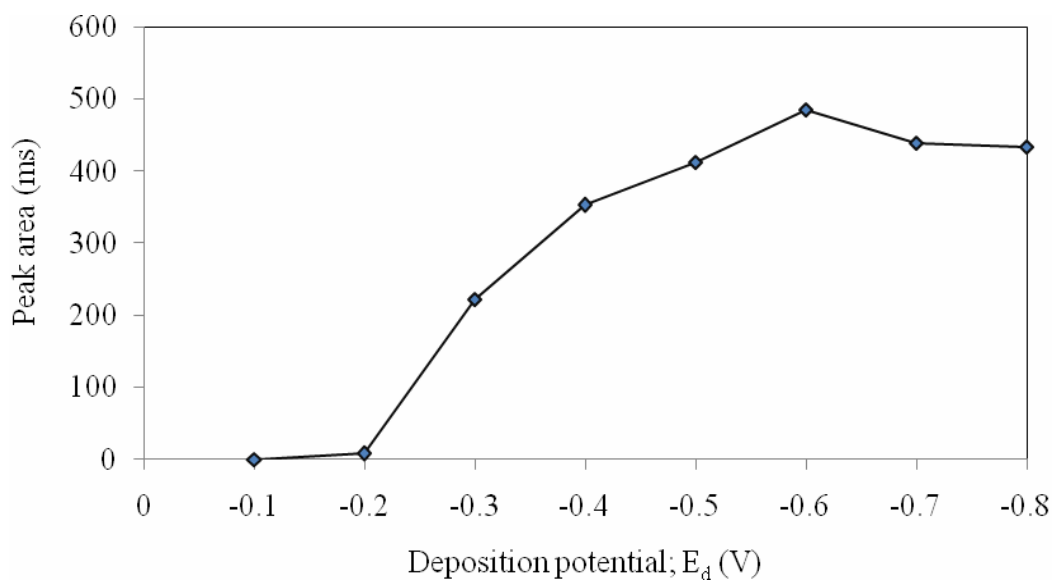


Figure 2 Influence of deposition potential (E_d) on gold measurement. A solution containing 200 $\mu\text{g/l}$ of Au(III). Supporting electrolyte, 0.5 M HCl; deposition time, 90 s; constant current, $+3$ μA .

Effect of Deposition Potential (E_d)

The influence of a deposition potential (E_d) on the stripping signals was investigated in the range of 0.0 V to -0.8 V, in a standard solution containing $200 \mu\text{g/l}$ of Au(III) ($n = 10$). It should be noted from **Figure 2**, that the peak area increased as the deposition potential changes from -0.2 V to -0.6 V. A value of -0.6 V was selected as the lowest negative potential necessary to obtain maximum sensitivity.

Effect of Deposition Time (t_d)

The influence of the deposition time on the signal area was also studied in the range of 30 to 180 s for a solution containing $200 \mu\text{g/l}$ of Au(III) in 0.5 M HCl as illustrated in **Figure 3**. A deposition time of 120 s was used for the analysis of the gold ore and stream sediment samples.

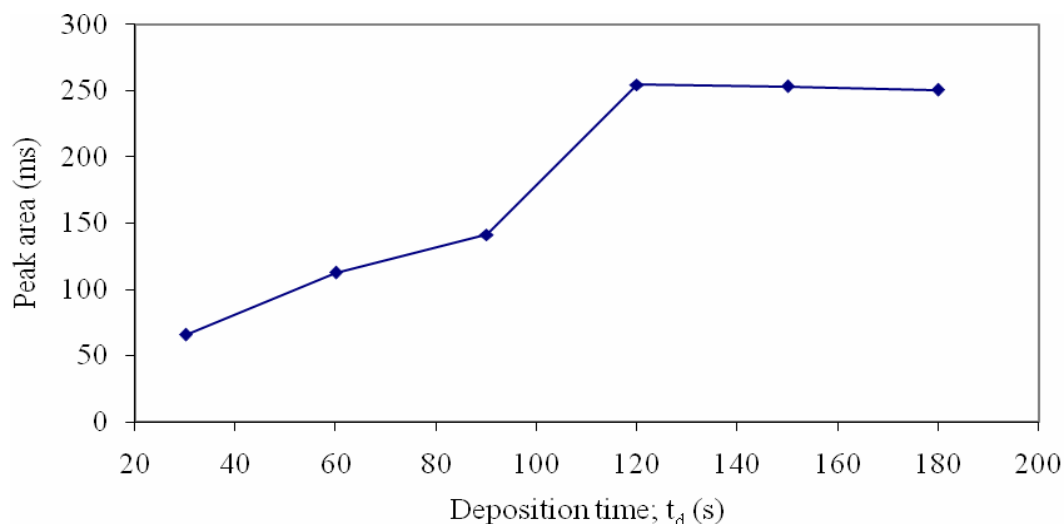


Figure 3 Influence of deposition time (t_d) on gold measurement. A solution containing $200 \mu\text{g/l}$ of Au(III). Supporting electrolyte, 0.5 M HCl; deposition potential, -0.6 V; constant current, $+3 \mu\text{A}$.

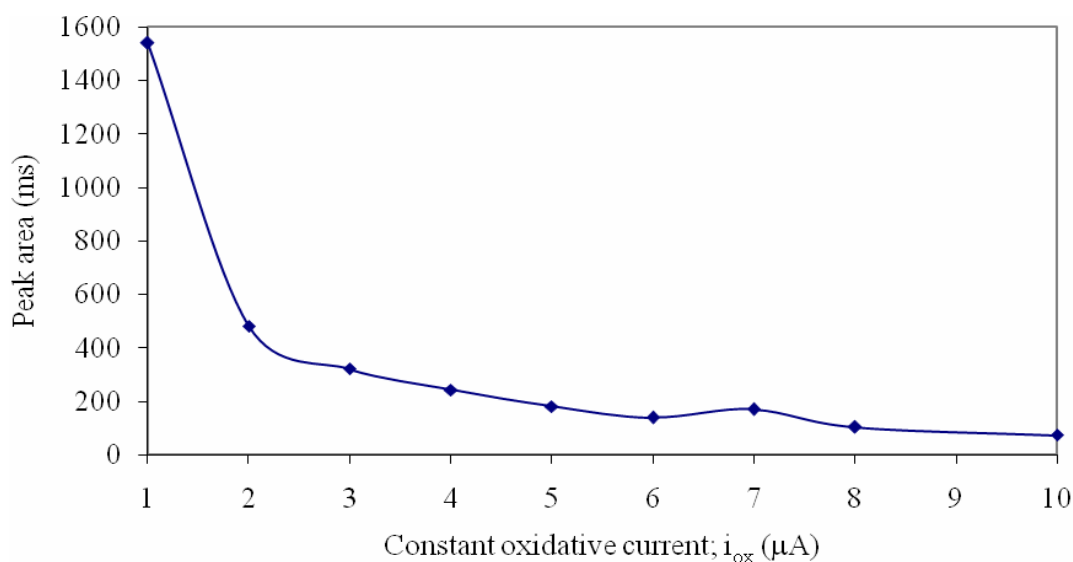


Figure 4 Influence of constant current (i_{ox}) on gold measurement. A solution containing $200 \mu\text{g/l}$ of Au(III). Supporting electrolyte, 0.5 M HCl; deposition potential, -0.6 V; deposition time, 90 s.

Effect of Constant Oxidative Current (i_{ox})

Figure 4 shows that the sensitivity increased when the applied current was varied from +10 to +0.1 μA . The optimum sensitivity and resolution for the gold response was obtained with the application of a stripping current of +4 μA . Although higher sensitivity was obtained with the application of +1 to +3 μA but the gold peak resolution under these condition were not precise whereas +5 to +10 μA were less sensitive. Thus, an oxidative current of +4 μA was selected for Au(III) quantification.

Effect of Interference Ions

Possible interference by other metal ions, such as Hg, Cu, As and Ag, with the constant current film stripping chronopotentiometry of gold were examined by the addition of the interfering ions to a solution containing 1.0 mg/l Au(III) using optimized conditions. The following ions were

added: Hg(II), Cu(II), As(III), As(IV) and Ag(I). Hg(II) did not interfere with the gold ion when the ratio of Hg:Au was less than 2:1. Whereas, Cu(II) suppresses the peak area down to 50 % at a 100-fold excess. However, it was found that As(III), As(IV) and Ag(I) did not affect the peak area of 1.0 mg/l Au(III) in the concentration range from 0.1 to 2 mg/l of the added ions.

Calibration Curve and Detection Limit

Figure 5 shows the stripping chronopotentiogram and a calibration curve of gold in a concentration range of 1.0 - 20.0 mg/l Au(III). A detection limit of 1.0 mg/l Au(III) after a deposition time of 120 s, calculated from the (3σ) standard deviation [5] was found to be 0.27 mg/l. The relative standard deviation ($n = 10$) was 2.8 % at 1.0 mg/l Au(III).

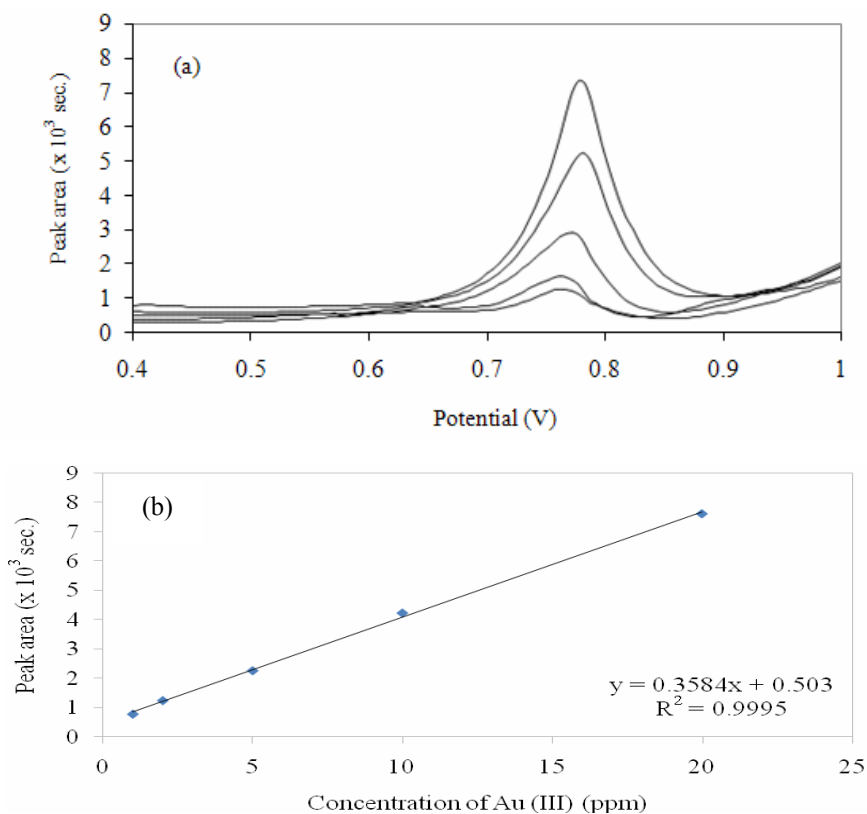


Figure 5 (a) Stripping chronopotentiograms of standard gold (1.0 - 20.0 mg/l Au(III)) and (b) corresponding calibration curve. Supporting electrolyte, 0.5 M HCl; deposition potential, -0.6 V; deposition time, 120 s; constant current, +4 μA .

Analysis of Geological Samples

Figure 6 shows the stripping chronopotentiogram from measurements of gold concentration in gold ore and stream sediment samples under the selected optimal conditions. The gold peak potential is approximately +0.8 V (vs. SCE). Under these optimized electrochemical conditions, standard calibration curve generated showed good linearity and precision ($R^2 = 0.9995$). In order to check the analytical accuracy, 1, 4, 7

and 10 mg/l of Au(III) were spiked into 200 μ l sample solutions and diluted to 30 ml with deionized water. The range of percentage recoveries were 100.1 to 112.3 %. The method has been successfully applied to the determination of gold in gold ore and stream sediment with contents ranging of 0.60 to 3.32 % and 0.99 to 1.17 % which are shown in **Table 1**.

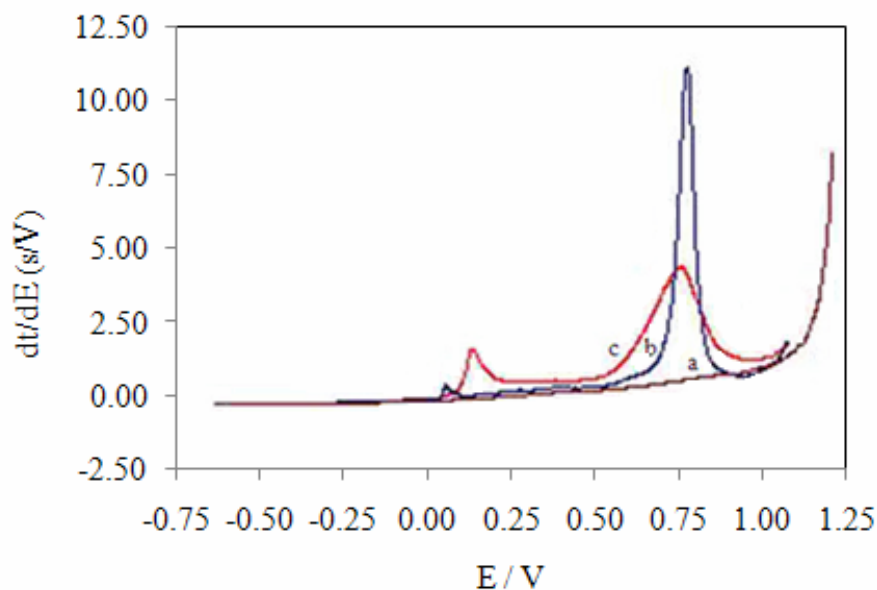


Figure 6 Stripping chronopotentiogram of standard gold and gold ore sample; blank (a), 1.0 ppm Au(III) (b) and gold ore sample (c) Supporting electrolyte, 0.5 M HCl; deposition potential, -0.6 V; deposition time, 90 s; constant current, $+4 \mu$ A.

Table 1 The result of the determination of gold in gold ores and stream sediment samples by CCSCP (n = 10).

Sample No.	Au(III) (%)
TF - 1	3.32 ± 0.22
TF - 2	1.85 ± 0.15
TF - 3	0.94 ± 0.07
TF - 4	1.85 ± 0.13
TF - 5	2.21 ± 0.48
TF - 6	0.60 ± 0.04
TF - 7	2.00 ± 0.30
MKSS - 1	1.17 ± 0.05
MKSS - 2	0.99 ± 0.30

Conclusions

A CCSCP using a bare electrode has been developed for the determination of gold in gold ores and stream sediment samples. The detection limit obtained of 1.0 mg/l Au(III) was 0.27 mg/l. It was confirmed that this routine method was applicable to examining gold in geological samples. The advantages of this method are known, such as short running times, low cost and easy operation. Furthermore, the mercury-free or film stripping chronopotentiometry is also an environmental friendly method.

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