*Journal of Chemical Health Risks 2(3): 33-40, 2012*
*ISSN:2251-6719*

# Determination of Trace Amounts of Gold in Environmental Samples by Adsorptive Stripping Voltammetry of Its Complex with Rhodamine Using Osc-Pls

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**Abstract:** The multivariate calibration method was applied for the determination of trace amounts of gold based on a hanging mercury drop electrode (HMDE) in the presence of rhodanine, followed by reduction of adsorbed gold by voltammetric scan using differential pulse modulation The optimum experimental conditions are: rhodanine concentration of 0.20 $\mu$g mL$^{-1}$, pH 5.0, accumulation potential of -600 mV versus Ag/AgCl, accumulation time of 100 sec, scan rate of 30 mV s$^{-1}$ and pulse height of 100 mV. The calibration matrix for partial least squares (PLS) regression was designed with 9 samples. Orthogonal signal correction (OSC) is a preprocessing technique used for removing the information unrelated to the target variables based on constrained principal component analysis. OSC is a suitable preprocessing method for PLS calibration without loss of prediction capacity using electrochemical method. The RMSEP for gold determination with PLS and OSC-PLS were 8.51 and 1.94, respectively. This procedure allows the determination of gold in synthetic and real samples with good reliability of the determination.

**Keywords:** Gold; Determination; Stripping; Voltammetric; PLS; OSC

## INTRODUCTION

Interest in the development of analytical techniques for determination of the noble metals is growing because of their applications in chemical engineering, micromechanics and medicine. Gold has been used in different areas of science and technology, including agents, brazing alloys, petroleum, electrical industries and catalytic chemical reactions [1, 2]. The metal may enter the environmental and interact with complexing materials, such as humic substances. In recent years, stripping voltammetry techniques, particularly anodic and adsorptive cathodic stripping voltammetry, have shown numerous advantages, including speed of analysis, good selectivity and sensitivity, and low costs of instrumentation compared with other techniques [3-10]. The present investigation was prompted by a desire to develop an alternative method for determination of gold based on adsorptive accumulation stripping voltammetry. The present scheme, based on the accumulation and reduction of gold-rhodanine complex, offers both sensitivity and selectivity, and represents an attractive alternative to conventional stripping measurements of gold.

The basic principle of the multivariate calibration is the simultaneous utilization of many independent variables, $x_1, x_2, \ldots, x_n$, to quantify one or more dependent variables of interest, $y$. The partial least squares (PLS) regression analysis [11] is the most widely used method for this purpose, and it is based on the latent variable decomposition relating two blocks of variables, matrices $X$ and $Y$, which may contain current and concentration data, respectively. These matrices can be simultaneously decomposed into a sum of $f$ latent variables, as follows:

$$Y = TP^T + E = \sum t_f p'_f + E \qquad (1)$$

$$Y = UQ^T + F = \sum u_f q'_f + F \qquad (2)$$

in which $T$ and $U$ are the score matrices for $X$ and $Y$, respectively; $P$ and $Q$ are the loadings matrices for $X$ and $Y$, respectively, $E$ and $F$ are the residual matrices. The two matrices are correlated by the scores $T$ and $U$, for each latent variable, as follows:

$$u_f = b_f t_f \qquad (3)$$

in which $b_f$ is the regression coefficient for the $f$ latent variable. The matrix $Y$ can be calculated from $u_f$, as in Eq. (4), and the concentration of the new samples can be estimated from the new scores $T^*$, which are substituted in Eq. (4), holding to Eq. (5)

$$\mathrm{Y} = \mathrm{TBQ}^{\mathrm{T}} + \mathrm{F} \qquad (4)$$

$$Y_{new} = T^* BQ^T \qquad (5)$$

In this procedure, it is necessary to find the best number of latent variables, which normally is performed by using cross-validation, based on determination of minimum prediction error [12]. Several determinations based on the application of this method to spectrophotometric and electrochemical data have been reported by several studies [13-17].

Orthogonal signal correction (OSC) was introduced by Wold et al. [18] to remove systematic variation from the response matrix $X$ that is unrelated, or orthogonal, to the property matrix $Y$. Therefore, one can be certain that important information regarding the analyte is retained. Since then, several groups [18-23] have published various OSC algorithms in an attempt to reduce model complexity by removing orthogonal components from the signal. Recently, application of OSC in spectrophotometry and electrochemistry data for determination by PLS has been reported [24-26].

The aim of this paper was to investigate, for the first time, the possibility of using voltammetry and OSC-PLS methods for quantifying gold, in synthetic and real

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samples such as different water samples. The results obtained, with and without OSC algorithm as a preprocessing treatment of original data, were compared.

To our knowledge this is the first voltammetric report on the direct determination of gold, without any primary chemical reaction or separating steps and first application of OSC as preprocessing of voltammetric data.

## EXPERIMENTAL

### *Apparatus and software*

Voltammograms were obtained by using an Autolab instrument (Eco Chemie, The Netherlands), Model PGSTAT12 processor, and a three electrodes system consisting of a HMDE ($r_0$ = 0.20 mm, 0.450 mg) as working electrode, an Ag/AgCl (3.0 mol $L^{-1}$ KCl) reference electrode and a carbon counter auxiliary electrode. Solutions were deoxygenated with high-purity nitrogen for 3 min prior to each experiment. Data acquisitions were accomplished with a personal computer (CPU 3.0 GHz and RAM 2 Gb) using MATLAB software, version 7.0 (The MathWorks). OSC and PLS calculus were carried out in the PLS Toolbox, version 2.0 (Eigenvector Technologies).

### *Reagents*

All chemicals were of analytical grade. Doubly distilled water was used for preparation of the solutions. Standard stock solution (1000 μg $mL^{-1}$) of gold was prepared from commercial salt (bromide) from Fluka. Standard working solutions were made by appropriate dilution daily as required. More dilute solutions were prepared by diluting this solution with water. Britton-Robinson (B-R) buffer [27] was prepared by dissolving appropriate amounts of boric acid, orthophosphoric acid and glacial acetic acid in water and adjusting to the desired pH value with sodium hydroxide and hydrochloric acid solutions.

### *General procedure*

The general procedure used to obtain cathodic adsorptive stripping voltammograms was as follows. All experiments were performed at room temperature. A 5 mL aliquot of buffer (B-R) solution (pH 5.0) and appropriate volumes of the rhodanine and sample solutions were pipetted into a 25 mL volumetric flask, diluted to the mark, and transferred to the electrochemical cell. The solution was purged with nitrogen first for 5 min and then for 50 s before each adsorptive stripping step. Then an accumulation potential of -600 mV versus Ag/AgCl was applied to a fresh HMDE during stirring the solution for a period of 100 s. Following this preconcentration stirrer was stopped and after equilibrium of 10 s, the differential pulse voltammograms was recorded from 425 to 305 mV with a potential scan rate of 30 mV $s^{-1}$ and pulse amplitude of 100 mV. The current was measured and recorded for the sample solution. Peak heights were evaluated as the difference between each voltammograms and the background electrolyte voltammograms.

## RESULTS AND DISCUSSION

### *Preliminary investigation*

Preliminary experiments were carried out to identify the general features, which characterize the behavior of the metal ion-rhodanine systems on hanging mercury drop electrode. Figure 1 displays the stripping voltammograms of 0.06 μg $mL^{-1}$ of gold in presence of rhodanine at pH 5.0 after 100 s accumulation at -600 mV. As can be seen in Figure 1, in the absence of rhodanine the reduction current is rather small. Addition of 0.20 μg $mL^{-1}$ rhodanine causes an increases of the gold reduction current in comparison to the gold current (Figure 1d).

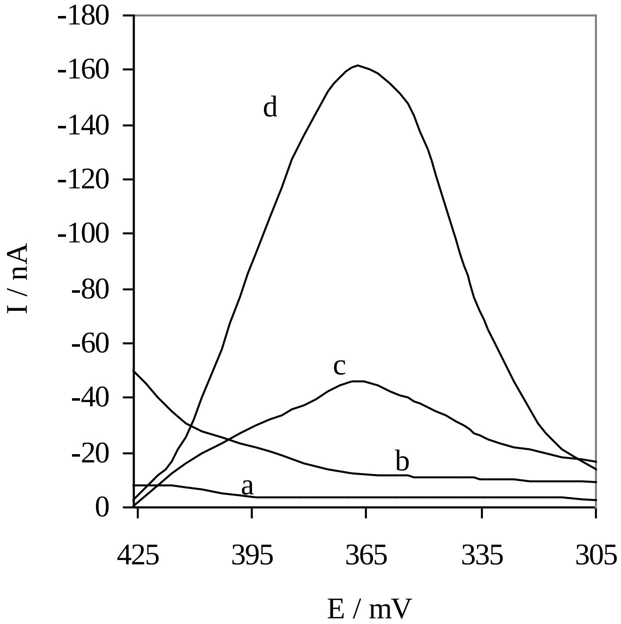

Fig 1. Differential pulse voltammograms for (a) background, (b) 0.2 μg $mL^{-1}$ of rhodanine, (c) 0.06 μg $mL^{-1}$ of gold and (d) 0.06 μg $mL^{-1}$ of gold and 0.2 μg $mL^{-1}$ rhodanine in B-R buffer (pH 5.0). Other conditions were accumulation time 100 s, accumulation potential -600 mV, pulse amplitude of 100 mV and scan rate of 30 mV $s^{-1}$.

*Effect of operational parameters*

Taking into account that the differential pulse voltammetry technique was used to develop the method for quantitative determination of gold, and in order to choose the optimum conditions, some analytical and instrumental parameters were studied.

*Effect of chemical variables*

The influence of the pH on the stripping peak current of gold was studied in the pH range 1.0 to 12.0 (Figure 2). The results showed that by increasing pH values from 1.0 to 5.0 the peak current of gold increased. Therefore, pH = 5.0 was selected as the optimum pH. At this pH, the sensitivity was highest, the peak was well defined. Thus, a pH of 5.0 was adopted for further studies.

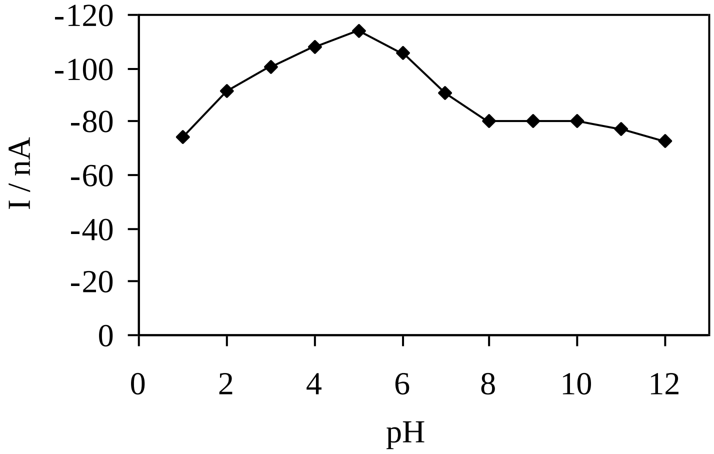

Fig 2. Effect of the pH on the peak current of 0.06 μg $mL^{-1}$ of gold in presence of 0.2 μg $mL^{-1}$ of rhodanine

The concentration of rhodanine has a significant effect on peak current. It can be seen from Figure 3 that the peak current increases with an increase in the rhodanine concentration up to 0.20 μg $mL^{-1}$, above which it starts to decline. Therefore, 0.20 μg $mL^{-1}$ rhodanine was selected.

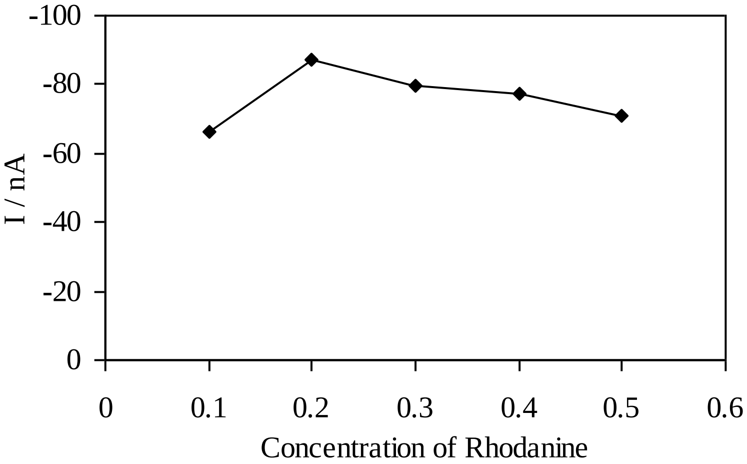

Fig 3. Effect of rhodanine concentration on the peak current at pH 5.0

*Effect of variation of accumulation potential and accumulation time*

The accumulation potential was varied between 0.0 and -1.1 V during a constant accumulation time of 100 s. The cathodic voltammetric scan was started after an equilibrium time of 10 s without stirring to allow the electrode to equilibrate before performing the measurement process. Maximum peak currents were observed at accumulation potentials of -0.6 to -1.1 V for gold (Figure 4). Generally, an accumulation potential of -600 mV vs. Ag/AgCl was used for further investigation. Variation of the accumulation time between 0 and 200 s at an accumulation potential of -600 mV was investigated. The influence of accumulation time on the stripping peaks of gold was investigated.

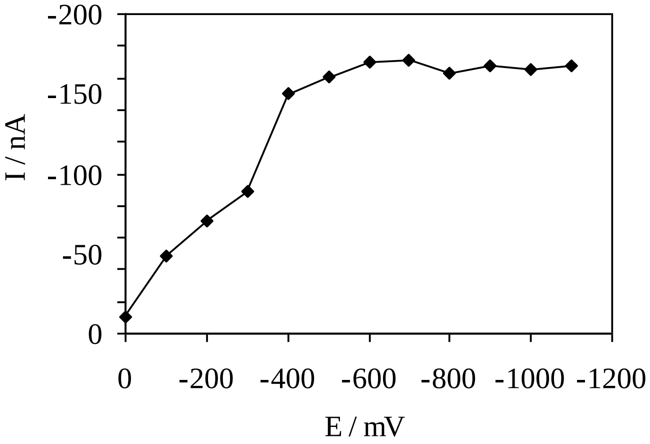

Fig 4. Effect of the accumulation potential on the peak current

The time required for accumulation of the gold complex onto the electrode depends on the concentration of the complex, less time required for higher concentrations. As mentioned before ligand concentrations that are higher than required may cause inhibition of the chelates adsorption by competitive coverage by the free ligand. An increase in the stripping peaks current with accumulation time was observed for Au(III)-rhodanine complex. As is expected for adsorption processes, the dependence of the peak current on the accumulation time is limited by the saturation of the electrode, resulting in the current reaching a plateau at high accumulation time, as shown in Figure 5. Thus, deposition time of 100 s was used throughout, as it combines good sensitivity and relatively short analysis time.

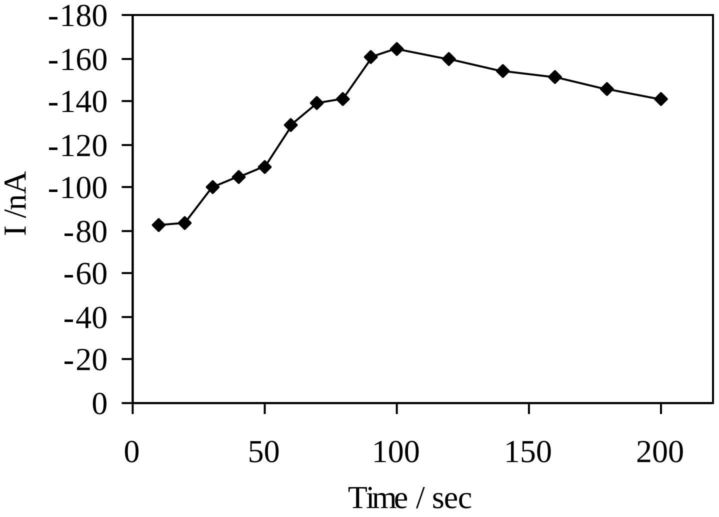

Fig 5. Variation of the peak current with the accumulation time at the optimum conditions.

*Effect of pulse height and scan rate*

The effect of pulse height on the sensitivity of the reduction current peak was also checked using different pulse heights in the range of 10 and 100 mV with the optimum conditions. The results showed that the peaks current were increased by increasing pulse height to 100 mV, and then leveled off. This is due to the fact, after 100 mV, the peak current broadened. Thus, 100 mV pulse height was selected. The influence of potential scan rate on the peak current of gold was studied in the range of 10-120 mV $s^{-1}$ with the optimum conditions. The results showed that by increasing scan rate from 10 to 30 mV $s^{-1}$, the peak currents increased linearly, whereas for higher scan rate the rate of increasing in peaks current decreased. This is due to the fact that at lower scan rate (30 mV $s^{-1}$) the adsorption processes is the main of phenomena at the electrode surface, whereas at higher scan rate diffusion of the gold from solution to the electrode surface added to the adsorption phenomena. Therefore, a scan rate of 30 mV $s^{-1}$ was selected for study.

*Effect of stirring speed, drop size and equilibrium time*

Figure 6 shows the influence of stirring rate on the voltammetric response and also on R.S.D. [4]. It was found that peak current increased with stirring rate in the range of 500 to 2000 rpm, and levels off at higher stirring rates. The R.S.D. value decreases rapidly from 500 to 2000 rpm and then rises after 2000 rpm. This is because at lower stirring rates the solution was stirred heterogeneously and at higher speed, the solution was stirred turbulently. A stirring rate of 2000 rpm, which gave the best reproducibility, was selected. The effects of drop size and equilibrium time on the voltammetric response were examined in developing a suitable analytical procedure for the determination of gold. The chosen working conditions were: drop size of 3 and equilibrium time of 10 s.

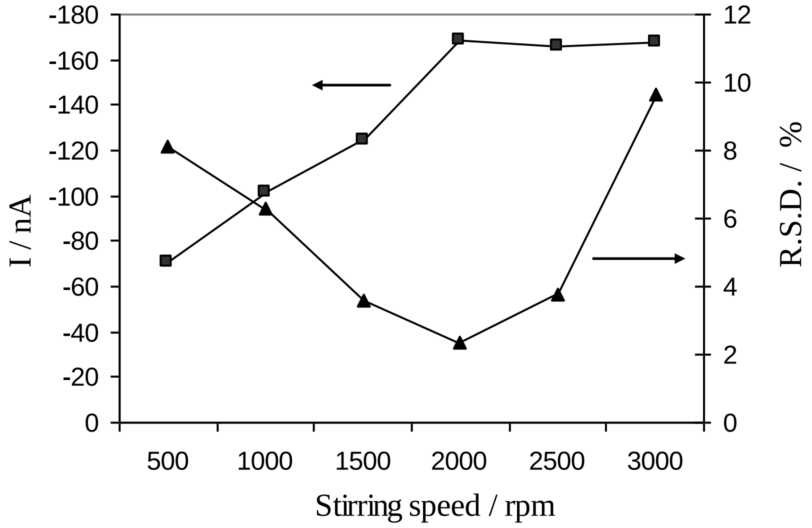

Fig 6. The effect of stirring speed on the peak current and its R.S.D. (%) for 0.06 µg mL$^{-1}$ of gold

*Reproducibility, linear range and detection of the method*
The reproducibility of repeating the determination of low concentration of gold was found under the optimum conditions. The R.S.D. for three determinations was calculated as 0.86% for gold concentrations of 0.06 µg mL$^{-1}$, respectively. Typical adsorptive cathodic differential pulse voltammetry and calibration graph are shown in Figure 7. Under the optimized conditions the peak current of gold was found to be proportional to its concentration over the range 0.02–0.40 µg mL$^{-1}$ and its equation was [current]$_{nA}$ = - 0.3207 × [gold] - 40.5570. The correlation coefficient (R$^2$) was 0.9688. The detection limit $(Y_{LOD} = \hat{X}_B + 3S_B)$, (where $Y_{LOD}$ is the signal for detection limit, $\hat{X}_B$ is the mean of blank signal, and $S_B$ is the standard deviation of blank signal) was obtained as 9.0 ng mL$^{-1}$ [12].

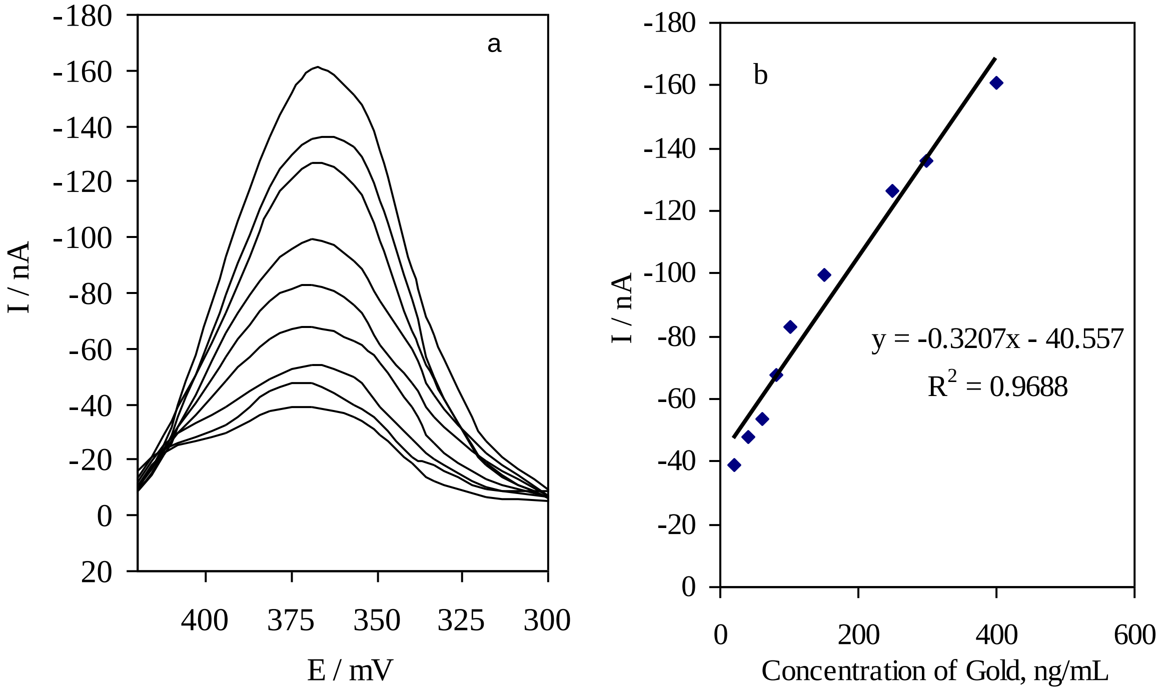

Fig 7. (a): Typical voltammograms and (b): Calibration graph for determination of gold at pH 5.0

*Interferences studies*
To check the selectivity of the proposed stripping voltammetric method for determination of gold, various cationic and ionic ions, as potential interferents, were tested. Interference was taken as the level causing an error in excess of 3%. The results show that less than 500-fold excess of alkaline and alkaline earth metal, $Cr^{6+}$, $Mo^{6+}$, $Th^{4+}$, $Sn^{4+}$, $Al^{3+}$, $Ga^{3+}$, $Bi^{3+}$, $Mn^{2+}$, $Co^{2+}$, $Cu^{2+}$, $Ni^{2+}$, $Zn^{2+}$, $SO_4^{2-}$, $SO_3^{2-}$, $NO_2^-$, $Br^-$, $Cl^-$, $CO_3^{2-}$, $CN^-$; 200-fold excess of $As^{3+}$, $Cr^{3+}$, $Fe^{3+}$, $Fe^{2+}$, $Cd^{2+}$, $Hg^{2+}$, $ClO_3^-$, $ClO_4^-$, $C_2O_4^{2-}$; 50-

fold excess of $Cd^{2+}$ and 10-fold excess of $Tl^{+}$ did not interfere the determination of 0.06 μg $mL^{-1}$ of gold. Thus, the method is highly selective and therefore, has been successfully applied to trace determinations of gold in various synthetic and real samples without any prior separation.

### *Determination of gold using OSC-PLS*

The multivariate calibration is a powerful tool for determinations, because it extracts more information from the data and allows building more robust models. Therefore, it was decided to perform a multivariate calibration using PLS model built using voltammogram curve and compare it with OSC-PLS method. According to an experimental design (Table 1), 9 solutions were used to construct the models (calibration set) and another 3 solutions to validate them (validation set). The models were validated using cross-validation.

Table 1. Concentration data of the calibration and prediction set of gold for multivariate models (ng $mL^{-1}$)

| Calibration | Concentration | Calibration | Concentration | Prediction | Concentration |
|---|---|---|---|---|---|
| C1 | 20.0 | C6 | 150.0 | P1 | 30.0 |
| C2 | 40.0 | C7 | 200.0 | P2 | 170.0 |
| C3 | 60.0 | C8 | 300.0 | P3 | 350.0 |
| C4 | 80.0 | C9 | 400.0 | | |
| C5 | 100.0 | | | | |

Orthogonal signal correction (OSC) is a preprocessing technique used for removes the information unrelated to the target variables based on constrained principal component analysis. OSC is a suitable preprocessing method for partial least squares calibration of mixtures without loss of prediction capacity using electrochemical method. For calibration set one OSC components were used for filtering. Evaluation of the prediction errors for the validation set reveals that the OSC treated data give substantially lower root mean squares error of prediction values than original data. Also, the OSC-filtered data give much simpler calibration models with fewer components than the ones based on original data. The results imply that the OSC method indeed removes information from voltammetry data that is not necessary for fitting of the Y-variables (Table 2). In some cases the OSC method also removes non-linear relationships between X and Y.

Determining how many factors to be used in the calibration is a key step in factor based methods. Only those factors that contain analytical information must be kept. The discarded factors should contain only noise. The cross-validation procedure leaving out one sample at a time is used for this purpose and the predicted residual error sum-of-squares, PRESS is calculated.

$$PRESS = \sum_{i=1}^{n} (y_i - \hat{y}_i)^2 \qquad (6)$$

where $y_i$ is the reference concentration for the ith sample and $\hat{y}_i$ represents the estimated concentration and n is the total number of samples. The optimum number of factors was determined rather than the selection of the model, which yields a minimum in prediction error variance or PRESS, the model selected is the one with the fewest number of factors such that PRESS for that model is not significantly greater than the minimum PRESS. One reasonable choice for the optimum number of factors would be that number which yielded the minimum PRESS. Since there are a finite number of samples in the training set, in many cases the minimum PRESS value causes overfitting for unknown samples that were not included in the model. A solution to this problem has been suggested by Haaland et al. [26] in which the PRESS values for all previous factors are compared to the PRESS values at the minimum. The F-statistical test can be used to determine the significance of PRESS values greater than the minimum. Table 3 shows the optimum number of factor and PRESS values for calibration set. In Figure 8, the PRESS obtained by optimizing the calibration matrix of the electrochemical data with PLS (N.F.=8, PRESS=0.11) and OSC-PLS (N.F.=6 and PRESS=0.89) models is shown.

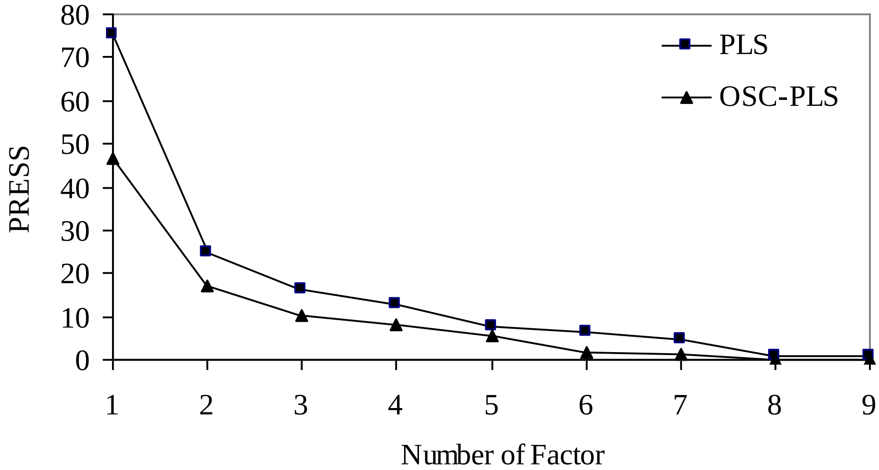

Fig 8. Plots of PRESS versus number of factors by PLS and OSC-PLS.

*Determination of gold in synthetic solutions*

The predictive ability of multivariate calibration methods was determined using tree synthetic solutions (their compositions are given in Table 2). The results obtained by applying PLS and OSC-PLS methods to tree synthetic samples are listed in Table 2. Table 2 also shows the percentage recovery for prediction series of gold. As can be seen, OSC-PLS method is the best method in determination of gold.

Table 2. Added and found results of prediction set of gold using PLS and OSC-PLS methods (ng mL$^{-1}$)

| | PLS | | OSC-PLS | |
|---|---|---|---|---|
| Added | Determined | Recovery (%) | Determined | Recovery (%) |
| 30.0 | 26.90 | 89.7 | 29.80 | 99.3 |
| 170.0 | 162.80 | 95.8 | 167.10 | 98.3 |
| 350.0 | 338.00 | 96.6 | 348.30 | 99.5 |
| RMSEP | 8.51 | | 1.94 | |
| RSEP (%) | 3.77 | | 0.86 | |

For the evaluation of the predictive ability of a multivariate calibration model, the root mean square error of prediction (RMSEP) and relative standard error of prediction (RSEP) can be used:

$$RMSEP = \sqrt{\frac{\sum_{i=1}^{n}(y_{pred} - y_{obs})^2}{n}} \qquad (7)$$

$$RSEP(\%) = 100 \times \sqrt{\frac{\sum_{i=1}^{n}(y_{pred} - y_{obs})^2}{\sum (y_{obs})^2}} \qquad (8)$$

where $y_{pred}$ is the predicted concentration in the sample, $y_{obs}$ is the observed value of the concentration in the sample and $n$ is the number of samples in the validation set. The value of RMSEP and RSEP (%) for gold summarized in Table 2.

### 3.4. Analytical application

In order to assess the applicability of the proposed method to real samples with different matrices containing varying amounts of a variety of diverse ions, these methods were applied to the determination of gold in wastewater sample. The results of three replicate analyses of each sample are presented in Table 4.

Table 3. Determination of gold in the real samples by PLS and OSC-PLS (ng mL$^{-1}$).

| Water sample | | PLS | | | OSC-PLS | | |
|---|---|---|---|---|---|---|---|
| | Added | Found | S.D. [b] | Recovery (%) | Found | S.D. [b] | Recovery (%) |
| Tap | 0.0 | N.D [c] | - | - | N.D [c] | - | - |
| | 20.0 | 23.11 | 0.17 | 115.6 | 24.35 | 0.12 | 121.8 |
| Waste [a] | 0.0 | N.D [c] | - | - | N.D [c] | - | - |
| | 40.0 | 36.17 | 0.16 | 90.4 | 37.26 | 0.09 | 93.2 |

[a] Waste water samples were collected in waste water from Arak factories

[b] Standard deviation for n = 3

[c] No detect.

As can be seen in all cases, the gold recovery is approximately quantitative, especially when used the OSC-PLS method. Thus, the proposed method can be applied to environmental and/or other samples having gold levels higher than and the detection limit of the method.

## CONCLUSION

A simple, sensitive, rapid, lower cost and fairly selective procedure is reported for determination of gold by voltammetric techniques and chemometrics methods. The proposed method can be used for the determination of gold at trace levels without use of any preconcentration steps. This is a novel method and it suitable for simple and accurate determination of this element in a variety of real samples with satisfactory results.

## ACKNOWLEDGMENT

The authors gratefully acknowledge the support to this work from Young Researcher Club, Islamic Azad University, Arak Branch, research council.

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