ELECTROCHEMICAL EXTRACTION OF COPPER, SILVER, AND GOLD FROM ENVIRONMENTAL WATER AND SOIL SAMPLES

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ABSTRACT

This present work presents an extraction technique for copper, silver and gold, from water and soil environmental samples based on electrodeposition. The methodology involves potentiostatic electrodeposition of the metals from a large-volume sample at a large platinum gauze electrode. The deposited metal at the electrode was then stripped off in a small-volume by application of a high positive potential to the electrode. The optimal conditions were potentiostatic electrodeposition at extreme negative potential, and the stripping at an extreme potential in the allowed potential window of platinum in 0.5 M H₂SO₄ solution, -0.26 V and 1.2 V, respectively. The kinetics of deposition was found to follow a pseudo-first order, and the time of electrodeposition was found to be not greater than 120 min for 5.00 ppm concentrations. The method was evaluated and found to exhibit high precision (relative standard deviation <5% for most of the analyzed samples), high accuracy (recoveries between 95 and 103%, for most of the samples).

KEYWORDS: electrochemical extraction, electrodeposition of metals, preconcentration of metals, copper, silver, and gold electrodeposition

1 INTRODUCTION

The quest for simple, reliable and 'green" extraction is attracting considerable attention in chemical analysis [1]. Generally, extraction techniques involve reagents that might not be classified as environment-friendly ones [2-4], simply because all chemicals are inherently characterized by a degree of toxicity [5].

Electrochemical deposition of metals, on the other hand, only involves the use of electrons as reducing agents [6]. Deposition can be carried out at ambient conditions, at a wide range of pH values, and on a wide range of metallic, semiconductor or carbon electrode types to be selected [7].

On the premise that electrochemical extraction provides an environment-friendly approach for extraction and utilization of electrodeposition as a preconcentration setup in the subsequent analysis, the present work was undertaken and aims at electrochemical extraction of copper, silver and gold from water and soil environmental samples, followed by analysis of the three metals by AAS analysis.

2 MATERIALS AND METHODS

2.1 Materials, Instruments, cell and electrodes

A potentiostat (273 A, Princeton Applied Research) interfaced to a computer through GPIB interface along with Echem® software was used for potentiostatic control during the deposition step. A conventional H-shape electrochemical cell, composed of two demountable compartments, equipped with a multiple inlet system for admission of supporting electrolyte, purging and blanketing the solution with oxygen-free nitrogen, was used. The two compartments were interconnected by ground glass joints and a fine sintered glass frit. The capacity of the working electrode compartment was about 1 L. The reference electrode was a Ag/AgCl/[Cl⁻] =1.0 M, and all the potentials reported in this paper are referenced to this electrode. The working electrode was a 3x4 cm gauze platinum electrode (99.99% pure, Goodfellow). The auxiliary electrode was a 10x3 cm cylindrically rounded nickel sheet (99.9% minimum purity, Goodfellow). The working electrode was housed in one compartment while the auxiliary and the reference electrodes were housed in the other compartment. Analyst Varian Spectra AA-250 pulse atomic spectrometer was used for the quantitative determination of the three metals under optimal conditions given in Table 1.

All chemicals used were highly pure certified analytical reagent (A.R.) chemicals, and used as received from the suppliers without further purification. The purging nitrogen was G5 grade (99.999% minimum purity) supplied by the National Gas Company, and coupled with anOxisorb® cartridge (Supelco) to remove any traces of oxygen. All solutions were made from the above-mentioned reagents dissolved in Millipore-Q or triple distilled water where the

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second distillation was carried out from basic potassium permanganate solution to get rid of any traces of organic impurities.

2.3 Procedures

2.3.1 Preparation of the working electrode

At the beginning of each experiment, the platinum working electrode was cleaned by dipping it in freshly prepared chromic acid for 5 min, followed by extensive rinsing with Millipore-Q water or with triple distilled water. Then, the electrode was transferred to a beaker containing concentrated nitric acid for 15 min. The clean electrode was placed in the working electrode compartment of the electrochemical cell which contained 100 ml of 0.15 M HNO₃. The electrode potential was held at 1.5 V for 30 min for stripping any deposits at the electrode surface. This procedure was carried out before each experiment to ensure cleanliness of the electrode.

2.3.2 Deposition experiments

Extraction followed by determination of the concentration was applied to spiked water samples and spiked montmorillonite samples for method validation and optimization of experimental parameters. Real water and soil samples from the Jordanian environment were also collected from Zarqa river basin (northeast of Amman), Wadi Ben Hammad (Karak, about 140 km from Amman) and Majhoul Falls, from Tafelah area, about 250 km to the south of Amman). Soil samples were collected from Zarqa, Dana Natural Reservation (Tafelah), Karak (south of Jordan), and Irbid (north of Jordan).

Two concentrations of the ions were adopted for elucidation of the optimal experimental conditions for electrochemical extractions, 1.0 ppm and 5.00 ppm. Deposition of the two metals was carried out at two potentials, -0.16 V and -0.26 V, for exploring the influence of the deposition potential. Calibration curves comprising the concentration of the analytes were prepared starting from an initially prepared 100-ppm stock solution by successive dilution. A 0.10 M HNO₃ solution was used as a blank in AAS analysis.

Deposition experiment was carried out by placing a measured volume of the solution to be analyzed (250 ml, unless something else is stated) which contained, in addition to the analyte, 0.50 M H₂SO₄ as a supporting electrolyte. Deposition was carried out potentiostatically at the above-mentioned potentials. For recording the concentration profiles, a sample was taken from the solution, and the concentration of the ion was determined by FAAS.

### TABLE 1 - The operational conditions for atomic absorption spectrometry (AAS) analysis.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Wavelength (nm)</th>
<th>Lamp Current (mA)</th>
<th>Slit width (mm)</th>
<th>Burner Height (mm)</th>
<th>Acetylene Flow-Rate (L/min)</th>
<th>Air Flow (L/min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>324.8</td>
<td>4</td>
<td>0.5</td>
<td>10</td>
<td>2</td>
<td>13.5</td>
</tr>
<tr>
<td>Ag</td>
<td>328.1</td>
<td>4</td>
<td>0.5</td>
<td>10</td>
<td>2</td>
<td>13.5</td>
</tr>
<tr>
<td>Au</td>
<td>267.6</td>
<td>4</td>
<td>1.00</td>
<td>10</td>
<td>2</td>
<td>13.5</td>
</tr>
</tbody>
</table>

### 3 RESULTS AND DISCUSSION

3.1 Concentration profiles and electrodeposition kinetics

Figure 1 shows the concentration profiles as a function of time for copper, at a deposition potential of -0.16 V and -0.26 V, at two initial concentrations of 5.00 and 1.00 ppm. Concentration profiles for silver and gold are displayed in Figs. 2 and 3.

Investigation of the concentration profiles indicates that for both tested concentrations, 5 and 1 ppm, at the two tested deposition potentials, there was a direct relationship between the time needed for quantitative removal of the ion from the solution and the initial concentration of the ion. This finding is not unexpected because larger initial concentration demands longer time for quantitative deposition. This finding holds true for all three metals.

Applying the equations of the integrated rate laws to the concentration profiles indicated that the kinetics of deposition generally follow a pseudo-first order kinetics, with respect to the metal ion concentration. The kinetic parameters for deposition of the three metals are displayed in Table 2. Table 2 shows that the first-order model is applicable for the kinetic data of the deposition of the three metals (correlation coefficient, R > 0.98 for all cases). The values of the specific rate constants are slightly higher at -0.26 V than those obtained at -0.16 V. This indicates that the rate of electrodeposition is largely influenced by mass transfer to the electrode but slightly influenced by potential activation (a quasi-reversible system) [6]. The concentration profiles along with the kinetics of the electrodeposition reveal that the electrodeposition under our experimental conditions is completed within 120 min for deposition of copper at 5 ppm concentration, and much shorter for lower concentrations, and also for silver and gold.

3.2 Precision and accuracy of the electrochemical extraction technique

To prove the accuracy of the electrochemical extraction, water samples and samples of montmorillonite, as a model for natural clay mineral, were spiked with a controlled amount of copper. The samples were extracted according to the proposed procedure. The absorbance values of the solutions measured and the solutions were calculated in the final stripping solution. The results are given in Tables 3 and 4.

Close inspection of Tables 3 and 4 demonstrates the precision of the method where the standard deviation (based on three runs) does not exceed ±0.3 ppm. Similarly, the high percent recoveries for water samples range from...
FIGURE 1 - Copper concentration profiles for (A) 5.0 initial concentration and (B) 1.0 ppm initial concentration at a deposition potential of (■) -0.16 V and (•) -0.26 V. The supporting electrolyte was 0.5 M H$_2$SO$_4$.

FIGURE 2 - Silver concentration profiles for (A) 5.0 initial Ag$^+$ concentration and (B) 1.0 ppm Ag$^+$ initial concentration at a deposition potential of (■) -0.16 V and (•) -0.26 V. The supporting electrolyte was 0.5 M H$_2$SO$_4$. 
FIGURE 3 - Gold concentration profiles for (A) 5.0 initial gold concentration and (B) 1.0 ppm initial gold concentration at a deposition potential of (■) -0.16 V and (●) -0.26 V. The supporting electrolyte was 0.5 M H₂SO₄.

TABLE 2 - Kinetic parameters for electrodeposition of copper, silver and gold at a polycrystalline platinum electrode.

<table>
<thead>
<tr>
<th>Metal</th>
<th>Deposition</th>
<th>First-order specific rate constant, k, min⁻¹</th>
<th>R²</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cu</td>
<td>-0.16</td>
<td>2.2x10⁻²</td>
<td>0.9729</td>
</tr>
<tr>
<td></td>
<td>-0.26</td>
<td>6.193x10⁻²</td>
<td>0.9956</td>
</tr>
<tr>
<td>Ag</td>
<td>-0.16</td>
<td>3.393x10⁻²</td>
<td>0.9893</td>
</tr>
<tr>
<td></td>
<td>-0.26</td>
<td>5.315x10⁻²</td>
<td>0.9944</td>
</tr>
<tr>
<td>Au</td>
<td>-0.16</td>
<td>2.699x10⁻²</td>
<td>0.9804</td>
</tr>
<tr>
<td></td>
<td>-0.26</td>
<td>8.72x10⁻²</td>
<td>0.9901</td>
</tr>
</tbody>
</table>

TABLE 3 - Percent recoveries upon performing extraction and analysis of triple-distilled water spiked samples with controlled amounts of copper to make solutions of known concentrations.

<table>
<thead>
<tr>
<th>Concentration of spiked solution (250 ml)</th>
<th>Found concentration (ppm) in 50 ml</th>
<th>Expected concentration (ppm) in 50 ml stripping solution</th>
<th>Enrichment factor</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.05 ppm</td>
<td>0.241</td>
<td>0.236 ± 0.02</td>
<td>4.713</td>
<td>94.267</td>
</tr>
<tr>
<td>0.10 ppm</td>
<td>0.517</td>
<td>0.492 ± 0.06</td>
<td>4.917</td>
<td>98.333</td>
</tr>
<tr>
<td>0.25 ppm</td>
<td>1.226</td>
<td>1.289 ± 0.15</td>
<td>5.155</td>
<td>103.093</td>
</tr>
<tr>
<td>0.50 ppm</td>
<td>2.577</td>
<td>2.453 ± 0.27</td>
<td>4.905</td>
<td>98.107</td>
</tr>
<tr>
<td>0.75 ppm</td>
<td>3.649</td>
<td>3.622 ± 0.29</td>
<td>4.829</td>
<td>96.578</td>
</tr>
</tbody>
</table>
### TABLE 4 - Percent recoveries upon performing extraction and analysis of Montmorillonite spiked samples with controlled amounts of copper.

<table>
<thead>
<tr>
<th>Concentration of spiked solution (250 ml)</th>
<th>Found concentration (ppm) in 50 ml</th>
<th>Expected concentration (ppm) in 50 ml stripping solution</th>
<th>Enrichment factor</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Trail1</td>
<td>Trail2</td>
<td>Trail3</td>
<td>Average</td>
</tr>
<tr>
<td>0.05 ppm</td>
<td>0.187</td>
<td>0.201</td>
<td>0.208</td>
<td>0.20 ± 0.03</td>
</tr>
<tr>
<td>0.10 ppm</td>
<td>0.489</td>
<td>0.493</td>
<td>0.482</td>
<td>0.49 ± 0.01</td>
</tr>
<tr>
<td>0.25 ppm</td>
<td>1.198</td>
<td>1.207</td>
<td>1.224</td>
<td>1.21 ± 0.03</td>
</tr>
<tr>
<td>0.50 ppm</td>
<td>2.137</td>
<td>2.247</td>
<td>2.182</td>
<td>2.19 ± 0.12</td>
</tr>
<tr>
<td>0.75 ppm</td>
<td>3.709</td>
<td>3.652</td>
<td>3.714</td>
<td>3.69 ± 0.09</td>
</tr>
<tr>
<td>1.00 ppm</td>
<td>4.890</td>
<td>4.908</td>
<td>4.872</td>
<td>4.89 ± 0.04</td>
</tr>
</tbody>
</table>

### TABLE 5 - Percent recoveries upon performing extraction and analysis of Montmorillonite spiked samples with controlled amounts of silver.

<table>
<thead>
<tr>
<th>Concentration of spiked solution (250 ml)</th>
<th>Found concentration (50 ml)</th>
<th>Expected concentration (ppm) in 50 ml stripping solution</th>
<th>Enrichment factor</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Trail1</td>
<td>Trail2</td>
<td>Trail3</td>
<td>Average</td>
</tr>
<tr>
<td>0.005 ppm</td>
<td>0.021</td>
<td>0.024</td>
<td>0.02</td>
<td>0.022 ± 0.005</td>
</tr>
<tr>
<td>0.05 ppm</td>
<td>0.218</td>
<td>0.225</td>
<td>0.222</td>
<td>0.222 ± 0.01</td>
</tr>
<tr>
<td>0.10 ppm</td>
<td>0.445</td>
<td>0.462</td>
<td>0.45</td>
<td>0.452 ± 0.02</td>
</tr>
<tr>
<td>0.25 ppm</td>
<td>1.137</td>
<td>1.167</td>
<td>1.153</td>
<td>1.152 ± 0.04</td>
</tr>
<tr>
<td>0.50 ppm</td>
<td>2.314</td>
<td>2.334</td>
<td>2.329</td>
<td>2.326 ± 0.03</td>
</tr>
<tr>
<td>0.75 ppm</td>
<td>3.576</td>
<td>3.659</td>
<td>3.641</td>
<td>3.625 ± 0.11</td>
</tr>
<tr>
<td>1.00 ppm</td>
<td>4.806</td>
<td>4.836</td>
<td>4.753</td>
<td>4.798 ± 0.1</td>
</tr>
</tbody>
</table>

### TABLE 6 - Percent recoveries upon performing extraction and analysis of Montmorillonite spiked samples with controlled amounts of gold.

<table>
<thead>
<tr>
<th>Concentration of spiked solution (250 ml)</th>
<th>Found concentration (50 ml)</th>
<th>Expected concentration (ppm) in 50 ml stripping solution</th>
<th>Enrichment factor</th>
<th>% Recovery</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Trail1</td>
<td>Trail2</td>
<td>Trail3</td>
<td>Average</td>
</tr>
<tr>
<td>0.005 ppm *</td>
<td>0.042</td>
<td>0.038</td>
<td>0.048</td>
<td>0.043 ± 0.01</td>
</tr>
<tr>
<td>0.05 ppm</td>
<td>0.217</td>
<td>0.214</td>
<td>0.211</td>
<td>0.214 ± 0.01</td>
</tr>
<tr>
<td>0.10 ppm</td>
<td>0.412</td>
<td>0.394</td>
<td>0.407</td>
<td>0.404 ± 0.02</td>
</tr>
<tr>
<td>0.25 ppm</td>
<td>0.985</td>
<td>1.001</td>
<td>0.982</td>
<td>0.989 ± 0.03</td>
</tr>
<tr>
<td>0.50 ppm</td>
<td>1.743</td>
<td>1.845</td>
<td>1.812</td>
<td>1.800 ± 0.13</td>
</tr>
<tr>
<td>0.75 ppm</td>
<td>3.141</td>
<td>3.071</td>
<td>3.11</td>
<td>3.107 ± 0.09</td>
</tr>
<tr>
<td>1.00 ppm</td>
<td>4.687</td>
<td>4.465</td>
<td>4.51</td>
<td>4.554 ± 0.29</td>
</tr>
</tbody>
</table>

* Volume of deposition solution = 500 ml.

### TABLE 7 - Copper, silver and gold concentrations (ppm) in water and soil samples collected from Jordanian environment.

<table>
<thead>
<tr>
<th>Samples</th>
<th>Copper concentration*, ppm</th>
<th>Silver concentration*, ppm</th>
<th>Gold concentration*, ppm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1 a</td>
<td>3.197±0.11</td>
<td>0.626±0.20</td>
<td>0.879±0.11</td>
</tr>
<tr>
<td>Sample 2 b</td>
<td>1.906±0.25</td>
<td>1.431±0.14</td>
<td>1.145±0.17</td>
</tr>
<tr>
<td>Sample 3 c</td>
<td>1.312±0.22</td>
<td>0.056±0.00</td>
<td>ND</td>
</tr>
<tr>
<td>Sample 4 d</td>
<td>4.982±0.25</td>
<td>0.142±0.01</td>
<td>ND</td>
</tr>
<tr>
<td>Sample 5 e</td>
<td>3.730±0.16</td>
<td>0.044±0.003</td>
<td>ND</td>
</tr>
<tr>
<td>Sample 6 f</td>
<td>0.307±0.02</td>
<td>0.028±0.00</td>
<td>ND</td>
</tr>
<tr>
<td>Sample 7 g</td>
<td>3.341±0.32</td>
<td>0.078±0.00</td>
<td>ND</td>
</tr>
</tbody>
</table>

* Average and standard deviation is based on n = 3 for all samples. (a) a soil sample collected from north of Jordan, (b) soil sample collected from north of Jordan, (c) from Zarqa river basin, (d) from Dana reservation (Tafelah), (e) from Zarqa river, (f) water sample Wadi Ben Hammid (Karak), and (g) water sample Majhoul Falls (Tafela).

94.267 to 103.093% attesting to the accuracy of the extraction method, and rules out the existence of determination error. For extraction from montmorillonite samples, the maximum value of standard deviation is about ±0.12 with recoveries ranging from about 80 to 98% attesting to the accuracy of the method.

The same statistical and recovery analysis was applied to silver and gold spiked samples. The results are given in Tables 5 and 6. Investigation of the data in Tables 5 and 6 show that the electrochemical extraction of silver and gold is highly precise and accurate as revealed by the standard deviation and recovery values.
3.3 Analysis of real samples collected from the Jordanian environment

To prove applicability of the electrochemical extraction to real-life samples, samples from the Jordanian Environment were collected, extracted and analyzed by the proposed extraction method. The results are displayed in Table 7. The precision as reflected in the values of standard deviation is attested to the developed extraction procedure and analysis approach.

4 CONCLUSIONS

In the present work, electrochemical extraction of copper, silver and gold from water and soil environmental samples was investigated. The results showed that extraction of metals by electrochemical routes may prove itself as a competitive technique for environmental sample analysis. Platinum is used in the present work but many metals of lower cost than platinum can be used. The state-of-the-art potentiostat which is used in the present work can be replaced with a simple and inexpensive control function circuitry. The simplicity, the lack of the need for extraction reagents, and the pre-concentration of the analyte from the original sample are all major points of strength of the suggested extraction technique.

Extension of the technique to include metals of prime environmental importance like lead or cadmium does not need more than choosing the electrode whose potential window embraces deposition of these metals, which will be tackled in the near future.

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