Electrochemical co-detection of Heavy Metals in *Astragalus Membranaceus* by Anodic Stripping Voltammetry

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*Astragalus membranaceus*, as an important medicinal herb, is widely used all over the world. But, the presence of toxic heavy metals in herbal chains due to the rapid industrialization possesses a serious threat on human health. For rapid screening the positive samples in medicinal herbs, an environment-friendly strategy is reported for the determination of heavy metals by using the square wave anodic stripping voltammetry method. The method showed good selectivity, linearity, recovery and precision. It is demonstrated that the intensity of the anodic peak at -0.87 V, -0.61 V and -0.24 V is proportional (R² = 0.9978, 0.9805, 0.9870) to the concentration of Cd²⁺ in the electrolyte over the range of 0.01-0.10 µg·mL⁻¹, and Pb²⁺, Cu²⁺ in the range of 0.10-1.00 µg·mL⁻¹. The proposed method has been successfully applied to the determination of the three heavy metal ions in *Astragalus membranaceus* samples with satisfactory recoveries of 88.00-110.00 %. Meanwhile, the detection limits achieved 0.0010, 0.0007 and 0.0028 µg·mL⁻¹ for Cd²⁺, Pb²⁺ and Cu²⁺, respectively, which are much lower than the guideline values in herbs given by the Chinese pharmacopoeia. Real sample analysis of Cd²⁺, Pb²⁺ and Cu²⁺ in *Astragalus membranaceus* by the electrochemical method of anodic stripping voltammetry has demonstrated that the proposed method can be applied in rapid screening the positive samples of *Astragalus membranaceus*.

**Keywords:** Rapid screening, Heavy metal, *Astragalus membranaceus*, Micromorphologies, Electroanalysis
1. INTRODUCTION

Heavy metal contamination is available in most of agricultural commodities during their growth, harvest, transportation or storage processes [1]. Heavy metals in medicinal herbs, adsorbed from soil, water or improper storage materials have become an interesting topic over the past decades due to their wide range of toxic effects [2-4]. Heavy metal exposure can lead to psychotic disorders and debilitating diseases which is irreversible change in human [5, 6]. Besides, arsenic (As) and lead (Pb) are classified as carcinogenic elements, whereas cadmium (Cd), chromium (Cr), cobalt (Co), copper (Cu), iron (Fe), aluminum (Al) and zinc (Zn) are classified as non-carcinogenic elements by the International Agency for Research on Cancer [7]. However, the five main toxic elements of Cd, Pb, Cu, As and Hg have been strictly limited by several countries and organizations [8, 9] according to their toxic of nephrotoxicity [10, 11], hepatotoxicity [12, 13], the injury of lung [14] and nervous system [15].

*Astragalus membranaceus* is widely distributed in Northeast, North and Northwest China and also other countries [16]. Currently, it is commonly used as one of the main herbal medicines in many prescriptions [17] based on its pharmacological activities for improving immunity, protecting cardiovascular system, anti-aging and treatment of cancer clinical effects [18]. The studies have shown that heavy metal content in *Astragalus membranaceus* and heavy metal pollution degree in soil are strong positive correlation, the heavy metal content in *Astragalus membranaceus* increases with the increase heavy metal concentration in soil [19, 20]. Due to the improper of ecological environment and storage conditions, it is susceptible to the accumulation of heavy metals. Hence, it is of great importance to routinely test the contamination level of Cd, Pb and Cu before being consumed.

Commonly, most of herbal medicine matrices can be contaminated with various kinds of heavy metals, which implies a risk of additional or even synergetic toxic effects [21-23]. Therefore, a direct and sensitive determination of heavy metals in complex herbal matrix is crucial, and huge efforts have been made to achieve efficient methods to realize fast and accurate detection. Although the conventional analytical methods, such as inductively-coupled plasma mass spectrometry (ICP-MS) [24, 25], atomic absorption spectrometry [26-28] and atomic fluorescence spectrometry (AFS) [29, 30] have relatively low detection limits and high precision, the disadvantages of time-consuming, costliest, complicated analytical procedures and being limited to single metal detection seriously restrict their widespread application in real-time and continuous monitoring. Alternatively, the electrochemical analysis method with square wave anodic stripping voltammetry (SWASV) can achieve the above purposes due to its low cost, good selectivity, high sensitivity and portability and has attracted much attention in the detection field, especially for heavy metal ions [31]. Typically, SWASV includes two independent pre-concentration and stripping procedures [32-34]. First, in the pre-concentration process, different kinds of metal ions can be respectively accumulated to heavy metals under specific potential from the herbal digestion solution to the surface of working electrode. Then the measurement (stripping) step is followed, the heavy metals are oxidized to their cation under different oxidation potential, and a potential-current response is perfect proportional to the heavy metals in herbal medicines. For the SWASV methods, the ability to dynamically assess low metal concentrations in complex matrix is critical for the highly efficient detection of trace heavy metals [35, 36].
Consequently, the digestion system of *Astragalus membranaceus* and electrochemical parameters are optimized in order to achieve above purposes.

In the present investigation, to realize a real-time and continuous monitoring method with good sensitivity and selectivity, an electrochemical method of SWASV is used for quick analysis of Cd, Pb and Cu in *Astragalus membranaceus* by optimizing technique parameters and digestion system. It is worth mentioning that the morphologies characteristics of deposited heavy metals are excellently used to prove and screen the deposition potentials, which can further improve the response current signals in SWASV. To the best of our knowledge, this is the first report for simultaneous analysis of three main heavy metals in medicinal herb matrices, which provides significant references and guidance for economical analysis of heavy metals in other complex matrices.

2. EXPERIMENTAL

2.1 Apparatus and conditions

All electrochemical measurements were performed with an Electrochemistry Workstation (CHI660E) at room temperature (25°C). All electrochemical measurements were using a three electrodes system with a platinum plate as the auxiliary electrode and a Hg/Hg₂Cl₂ electrode (SCE) as the reference electrode. A glassy carbon electrode (GCE, d = 3 mm) was employed as the working electrode due to its electrochemical stability and simplicity of surface renew. The GC electrode was cleaned carefully before use, which has been described in previous work[37, 38]. The simultaneously determination of Cd²⁺, Pb²⁺ and Cu²⁺ by SWASV were performed in 0.1 mol·L⁻¹ pH 4.7 acetate buffer solution, respectively depositing at -1.1V, -1.0V and -0.6V under stirring for 120s, stripping conditions: from each deposition potential to 0V at frequency of 25 Hz, step potential of 2 mV and amplitude of 25 mV. The electrode was cleaned in sulfuric acid solution (1 mol·L⁻¹) with constant oxidation potential at 0.5V under stirring for 30s. The digestion was carried out using a Berghof microwave system (Speedwave-3⁺, Berghof, Germany) and the detailed digestion condition are shown in Table 1. The morphologies of the deposited heavy metals were investigated by scanning electron microscope (SEM, Zeiss SUPRA 55 with an accelerating voltage of 20 kV). The confirmation of heavy metals content in *Astragalus membranaceus* samples was proved by inductively coupled plasma mass spectrometry (ICAP-Q, Thermo Fisher Scientific, Germany)

<table>
<thead>
<tr>
<th>Procedure</th>
<th>Temperature (°C)</th>
<th>Time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>150-160</td>
<td>5</td>
</tr>
<tr>
<td>2</td>
<td>160</td>
<td>10</td>
</tr>
<tr>
<td>3</td>
<td>180-200</td>
<td>10</td>
</tr>
<tr>
<td>4</td>
<td>100</td>
<td>10</td>
</tr>
</tbody>
</table>
2.2 Reagents

All chemicals are guaranteed grade produced by Thermo Fisher. The standard stock solutions of Cd$^{2+}$, Pb$^{2+}$ and Cu$^{2+}$ (1000 µg·mL$^{-1}$) are obtained from National institute of metrology (Beijing, China) and diluted as required. All dilutions and sample preparations were made using ultrapure water (the resistance is 18.2 Ω·cm$^{-1}$) produced by a Milli-Q system (Millipore Corporation, Bedford, MA, USA). The standard reference material of *Astragalus membranaceus* (GBW 10028) was obtained from National institute of standards and technology (Beijing, China), and was used to illustrate the matrix effect and the accuracy of the analysis results.

2.3 Sample collection and preparation

A total of ten samples of *Astragalus membranaceus* were collected from Shanxi provinces, Inner Mongolia Autonomous Region and Beijing city, China. The samples were washed with tap water followed by deionized water and ultrapure water. All the samples and also standard reference material were dried in oven at 80 °C until to achieve constant weight, and the dried samples were powdered with a stainless steel blender and stored at 4 °C in the plastic bags for further determination. For electrochemical analysis, 0.5 g of *Astragalus membranaceus* was accurately weighted into a Teflon digestion vessel. Next, 10.0 mL of HNO$_3$ and 2.0 mL H$_2$O$_2$ (5:1, v/v) were added and immersed more than 10 hours. The vessels were closed and placed in the microwave oven, and then set the condition of digestion procedure according to Table 1 and the digestion process was started. After the digestion solution cooling down, the solutions were filtered and diluted to 50.0 g with ultrapure water.

3. RESULTS AND DISCUSSION

3.1 Electrochemical characterizations of Cd$^{2+}$, Pb$^{2+}$ and Cu$^{2+}$ in *Astragalus membranaceus* matrix
Figure 1. SWASV analysis of toxic heavy metal ions in Astragalus membranaceus matrix in the presence of (a) Cd$^{2+}$, (b) Pb$^{2+}$ and (c) Cu$^{2+}$

The voltammograms for these heavy metals were well separated from one another with the potential differences of ΔE, which were large enough for simultaneous detection of these three heavy metals in one solution. As was shown in Figure 1, there were three remarkable anodic peaks at the potential of -0.87 V (a), -0.61 V (b) and -0.24 V (c) after the heavy metal ions were added in Astragalus membranaceus matrix. These three peaks correspond to the oxidation of Cd$^{2+}$, Pb$^{2+}$ and Cu$^{2+}$ on the surface of GCE. It was worth noting that, after careful digestion, there were no obvious interferences in this complex matrix of Astragalus membranaceus. According to the maximum residue limits (MRL) of heavy metals in medicinal herbs, the flagrant contrast between the MRL and the value in liner range of SWASV have been proved that the sensitivity of the proposed method can be used for rapid screening the large scale of positive samples [39-41] that exceed the MRL in limited time.

3.2 The optimization of deposition potential

In addition to detecting heavy metal ions in Astragalus membranaceus with relatively high repeatability and accuracy, the deposited heavy metals need to achieve maximum stability and parallelism for practical application. Thus, optimizing the deposition parameters to obtain an apparent signal is particularly important. The analytical parameters of the developed method were evaluated,
where the deposition potential was taken into consideration. Except for the deposition time and any other factors [42, 43], deposition potential is a very important factor, which could influence on repeatability and accuracy through the process of heavy metals reduction on the surface of bare GCE and the oxidation of deposited elemental metals [44]. Reported articles have been shown that how to optimize the best deposition condition by the method of electrochemical analysis [45-48], which was easily to calculate the current values but was limited by current interference in such complex herbal matrix. For the first time, SEM was used to optimize the deposition potential due to the morphology characteristic under different conditions, and then the parameters were validated by the electrochemical data as usual [49-51]. Moreover, in most of the published articles, only one deposition potential was choose to reduce all cations and the deposition potential was selected due to the cations which has the lowest reduction potential, such as the potential of -1.1V (reduction potential of Cd$^{2+}$) in this proposed investigation [52-54].

![Figure 2](image1.png)  
**Figure 2.** SEM images of Pb-GCE surface formed under the potential of (a) -1.1 V and (b) -1.0V, 120s. Magnification: 3000

![Figure 3](image2.png)  
**Figure 3.** SEM images of Cu-GCE surface formed under the potential of (a) -1.1 V and (b) -0.6 V, 120s. Magnification: 3000
However, a variety of metal staggered deposition led to incomplete dissolution, thereby affecting the reproducibility and accuracy of the analysis [55]. Here, a much more indicative method was given to optimized deposition potential through the observation of morphology changes under different potential. Based on reduction potential of those three heavy metals, the potential of -1.1V, -1.0V and -0.6V were chosen for the contrast experiments. The SEM images of deposited Pb and Cu on GCE were shown in Figure 2 and Figure 3, dendritic crystal and club-shape crystal were obtained at the potential of -1.1V (Figure 2a and Figure 3a), in which the twigs stretched out of the substrate leading to part of the substrate uncovered. While the reduction potentials of Pb\(^{2+}\) (-1.0V) and Cu\(^{2+}\) (-0.6V) were respectively adopted, the crystal became tinier and the friction of coverage to the substrate was significantly improved, as were shown in Figure 2(b) and Figure 3(b). According to Winand theory, the more compact crystal is, the more stable performance is \([56, 57]\). As was shown in Table 2, the optimized deposition potentials of -1.0V (Pb\(^{2+}\)) and -0.6V (Cu\(^{2+}\)) express better repeatability and accuracy, coincided with the prediction of morphology theory.

### Table 2. Accuracy and repeatability of Pb\(^{2+}\) and Cu\(^{2+}\) by SWASV under different deposition potentials.

<table>
<thead>
<tr>
<th>Ions</th>
<th>Deposition voltage (V)</th>
<th>Sensitivity ((\mu A \cdot \mu g \cdot mL^{-1}))</th>
<th>Er (%)</th>
<th>RSD (%), n=20</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pb(^{2+})</td>
<td>-1.1</td>
<td>8.35</td>
<td>11.90</td>
<td>6.45</td>
</tr>
<tr>
<td>Pb(^{2+})</td>
<td>-1.0</td>
<td>4.32</td>
<td>2.60</td>
<td>2.40</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>-1.1</td>
<td>9.18</td>
<td>18.37</td>
<td>8.44</td>
</tr>
<tr>
<td>Cu(^{2+})</td>
<td>-0.6</td>
<td>6.28</td>
<td>3.50</td>
<td>2.79</td>
</tr>
</tbody>
</table>

Er: Relative error between electroanalysis and label values

### Table 3. Comparison of analytical performance of electrochemical method for the determination of heavy metals.

<table>
<thead>
<tr>
<th>Electrodes</th>
<th>Techniques</th>
<th>Heavy metals</th>
<th>Repeatability (RSD %)</th>
<th>Test times</th>
<th>Refs.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bismuth-coated porous screen-printed carbon electrode</td>
<td>SV</td>
<td>Pb;Cd</td>
<td>4.75</td>
<td>7</td>
<td>[58]</td>
</tr>
<tr>
<td>Gold microelectrode</td>
<td>ASV</td>
<td>Cu</td>
<td>3.2</td>
<td>3</td>
<td>[59]</td>
</tr>
<tr>
<td>Chitosan modified screen-printed carbon electrode</td>
<td>DPASV</td>
<td>Pb</td>
<td>4.1</td>
<td>5</td>
<td>[60]</td>
</tr>
</tbody>
</table>
A comparison of analytical characteristics between the previous reports and our work for the simultaneous determination of Pb$^{2+}$, Cd$^{2+}$, and Cu$^{2+}$ was summarized in Table 3. The RSD for repeatability of the currently developed method is much lower than that of the reported methods using any other modified electrodes [58-62]. In addition, the repeatability of the electrode in this study is still satisfactory even it is used for 20 times. So, the proposed method has accomplished to improve the repeatability of all three heavy metals.

### 3.3 SWASV of the heavy metals ions and calibration plots

To examine whether the data provided by SWASV was precise, accurate, the recoveries were determined using three standard solution spiked by 0.08 µg·mL$^{-1}$, 0.1 µg·mL$^{-1}$ and 0.12 µg·mL$^{-1}$ in a sample solution including 0.1 µg·mL$^{-1}$ Cd$^{2+}$, Pb$^{2+}$ and Cu$^{2+}$. The results obtained from three repeated measurements were shown in Table 4, and it can be observed that the obtained values were very close to the label values. Moreover, the values of recoveries, RSD and Er indicating that this proposed method were both reliable and sensitive.

#### Table 4. Analysis of the recovery for Cd$^{2+}$, Pb$^{2+}$ and Cu$^{2+}$ in commercially available Astragalus membranaceus matrix

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Original content (µg·mL$^{-1}$)</th>
<th>Added content (µg·mL$^{-1}$)</th>
<th>Peak current (µA)</th>
<th>Found value (µg·mL$^{-1}$)</th>
<th>Er (%)</th>
<th>Recovery (%)</th>
<th>RSD (%)</th>
<th>n=3</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd$^{2+}$</td>
<td>0.01</td>
<td>0.008</td>
<td>0.947</td>
<td>0.0168</td>
<td>6.67</td>
<td>88.00</td>
<td>5.01</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>0.01</td>
<td>1.135</td>
<td>0.0190</td>
<td>5.00</td>
<td>89.84</td>
<td>4.68</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.01</td>
<td>0.012</td>
<td>1.35</td>
<td>0.0215</td>
<td>2.27</td>
<td>94.81</td>
<td>0.68</td>
<td></td>
</tr>
<tr>
<td>Pb$^{2+}$</td>
<td>0.1</td>
<td>0.08</td>
<td>2.982</td>
<td>0.1847</td>
<td>2.61</td>
<td>104.67</td>
<td>0.96</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.1</td>
<td>5.06</td>
<td>0.2021</td>
<td>1.05</td>
<td>102.11</td>
<td>3.36</td>
<td></td>
</tr>
<tr>
<td>Cu$^{2+}$</td>
<td>0.1</td>
<td>0.08</td>
<td>1.136</td>
<td>0.1737</td>
<td>3.50</td>
<td>93.74</td>
<td>1.65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.1</td>
<td>1.386</td>
<td>0.1964</td>
<td>1.80</td>
<td>96.38</td>
<td>2.45</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.1</td>
<td>0.12</td>
<td>1.756</td>
<td>0.2299</td>
<td>4.50</td>
<td>109.88</td>
<td>4.90</td>
<td></td>
</tr>
</tbody>
</table>
A series of stripping voltammograms were respectively shown in Figure 4 with 0.01-0.1 μg·mL⁻¹ of Cd²⁺, and 0.1-1.0 μg·mL⁻¹ of Pb²⁺ and Cu²⁺, the insets which were studied in triplicate shown the respective calibration curves of Cd²⁺, Pb²⁺ and Cu²⁺. The regression data were calculated for Cd²⁺, Pb²⁺ and Cu²⁺ as the following equations and shown in Figure 4:

Ip (µA) = 86.0935C - 0.4994
Ip (µA) = 78.9854 C - 11.8711
Ip (µA) = 11.0445 C - 0.78292

**Table 5.** The quantitative analysis of Cd²⁺, Pb²⁺ and Cu²⁺ based on the anodic peak of -0.87V, -0.61V and -0.24V in Astragalus membranaceus.

<table>
<thead>
<tr>
<th>Ions</th>
<th>LOD (µg·mL⁻¹)</th>
<th>LOQ (µg·mL⁻¹)</th>
<th>Linear range (µg·mL⁻¹)</th>
<th>R²</th>
<th>RSD (%) (n=20)</th>
<th>Standard error of slope (×10⁻⁶)</th>
<th>Standard error of intercept (×10⁻⁶)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cd²⁺</td>
<td>0.0010</td>
<td>0.0034</td>
<td>0.01 - 0.10</td>
<td>0.9978</td>
<td>2.68</td>
<td>1.8173</td>
<td>0.1103</td>
</tr>
<tr>
<td>Pb²⁺</td>
<td>0.0007</td>
<td>0.0022</td>
<td>0.10 - 1.00</td>
<td>0.9805</td>
<td>2.40</td>
<td>4.9777</td>
<td>3.0210</td>
</tr>
<tr>
<td>Cu²⁺</td>
<td>0.0028</td>
<td>0.0093</td>
<td>0.10 - 1.00</td>
<td>0.9870</td>
<td>2.79</td>
<td>0.5650</td>
<td>0.3429</td>
</tr>
</tbody>
</table>

The LODs were 0.0010 µg·mL⁻¹ for Cd²⁺, 0.0007 µg·mL⁻¹ for Pb²⁺ and 0.0028 µg·mL⁻¹ for Cu²⁺, and the LOQs were 0.0034 µg·mL⁻¹ for Cd²⁺, 0.0022 µg·mL⁻¹ for Pb²⁺ and 0.0093 µg·mL⁻¹ for Cu²⁺, respectively (Table 5), which were much lower than the limits of 0.30 µg·mL⁻¹ (Cd²⁺), 5.00 µg·mL⁻¹ (Pb²⁺) and 20.00 µg·mL⁻¹ (Cu²⁺) in Chinese Pharmacopeia. Therefore, the analytical performance indicated that the proposed method can be applied in rapid screening positive herbal samples.
Figure 4. SWASV curves measured in 0.1 mol·L⁻¹ acetic acid (pH 4.7) with the concentration varying from 0.01 µg·mL⁻¹ to 0.1 µg·mL⁻¹ of (a) Cd²⁺, and 0.1 µg·mL⁻¹ to 1.0 µg·mL⁻¹ of (b) Pb²⁺ and (c) Cu²⁺. Inset shows the calibration curve for the SWASV peaks current against the concentration of Cd²⁺, Pb²⁺ and Cu²⁺.

3.4 Rapid screen of commercially available samples

To demonstrate the applicability of the developed rapidly electrochemical method, 10 batches of commercial Astragalus membranaceus samples including ten main genuine producing areas in China were analyzed for three main heavy metals. The specific heavy metal ions in positive samples were identified based on the appropriate potential and further confirmed by ICP-MS. The test results obtained by SWASV from three repeated measurements were given in Table 6. The results showed that residual levels of heavy metals in most of the Astragalus membranaceus samples were below LODs, while there are 2 positive samples (No. 4 and No. 9) contaminated by Cu²⁺ at concentrations of 0.1533 and 0.1107 mg·kg⁻¹. The confirmed result of Cu²⁺ by ICP-MS was shown in Table 7, which was similar to the result of SWASV and much lower than the regulatory MRLs suggested by EU (European Commission, 2007) and China (Chinese Pharmacopoeia Committee, 2015). As was shown in Figure 5, the comparison of negative and positive samples were clearly separated and accurately analyzed by using the proposed SWASV method, although it was difficult to recognize on superficial
characteristics (Figure 6). So, the above results have proved that the proposed SWASV method can be applied in rapid screening of heavy metals in *Astragalus membranaceus*. Because of the occurrence frequency and serious toxicity of these heavy metals, *Astragalus membranaceus* samples should be under careful control to assure its quality and the safety to consumers.

![Figure 5. SWASV analysis of Cu$^{2+}$ in negative and positive samples](image)

**Figure 5.** SWASV analysis of Cu$^{2+}$ in negative and positive samples

![Figure 6. *Astragalus membranaceus* images of (a) positive and (b) negative samples.](image)

**Figure 6.** *Astragalus membranaceus* images of (a) positive and (b) negative samples.

**Table 6.** Electrochemical co-detection of real *Astragalus membranaceus* samples from different sources in China (n=3).

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Cd$^{2+}$ (mg·kg$^{-1}$)</th>
<th>Pb$^{2+}$ (mg·kg$^{-1}$)</th>
<th>Cu$^{2+}$ (mg·kg$^{-1}$)</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>2</td>
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<td>N</td>
<td>N</td>
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<tr>
<td>3</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
<tr>
<td>4</td>
<td>N</td>
<td>N</td>
<td>0.1533</td>
<td>1.29</td>
</tr>
<tr>
<td>5</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
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<td>N</td>
<td>N</td>
</tr>
<tr>
<td>9</td>
<td>N</td>
<td>N</td>
<td>0.1107</td>
<td>1.08</td>
</tr>
<tr>
<td>10</td>
<td>N</td>
<td>N</td>
<td>N</td>
<td>N</td>
</tr>
</tbody>
</table>
Table 7. Confirmation results of positive samples by ICP-MS (n=3).

<table>
<thead>
<tr>
<th>Sample No.</th>
<th>Cd$^{2+}$ (mg·kg$^{-1}$)</th>
<th>Pb$^{2+}$ (mg·kg$^{-1}$)</th>
<th>Cu$^{2+}$ (mg·kg$^{-1}$)</th>
<th>RSD (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4</td>
<td>0.0002</td>
<td>0.0129</td>
<td>0.1535</td>
<td>1.47</td>
</tr>
<tr>
<td>9</td>
<td>0.0002</td>
<td>0.0147</td>
<td>0.1152</td>
<td>1.88</td>
</tr>
</tbody>
</table>

4. CONCLUSION

An environmental-friendly, fast, green, sensitive and simultaneous method was developed and validated for the co-detection of three heavy metals in *Astragalus membranaceus* by using the electroanalysis method of SWASV. The heavy metals of interest were isolated from complex *Astragalus membranaceus* matrix using an optimized digestion system and low-cost sample preparation procedure. For assuring the high repeatability and accuracy, the deposition condition was carefully optimized based on the properties of morphologies and peak current, it can be concluded that the optimized deposition potential is suitable for the electrochemical co-detection of Cd$^{2+}$, Pb$^{2+}$, Cu$^{2+}$. In addition, it is demonstrated that the intensity of the anodic peaks at -0.87V, -0.61V and -0.24V were proportional ($R^2 = 0.9978, 0.9805, 0.9870$) to the concentrations of Pb$^{2+}$ and Cu$^{2+}$ in the electrolyte over the range of 0.10-1.00 µg·mL$^{-1}$, and the concentration of Cd$^{2+}$ in the range of 0.01-0.10 µg·mL$^{-1}$. The proposed method has been successfully applied to the co-detection of those three heavy metal ions in *Astragalus membranaceus* standard reference material with satisfactory recoveries of 88.00-110.00%. Then, the optimized method was applied for fast screening of 3 heavy metals in 10 commercially available AM samples and the results showed that two samples were positive for Cu$^{2+}$ with levels much lower than the set MRLs. The study of electrochemical analysis of heavy metals will make big progress toward the rapid screening of more contaminants in other medicinal herbs or related products with complex matrix.

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