Adsorptive Cathodic Stripping Voltammetric Determination of Molybdenum in Synthetic Solutions and Environmental Samples

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Abstract
A sensitive and selective voltammetric methods has been developed for the determination of trace amounts of Mo(VI) ions. This method is based on controlled adsorptive preconcentration of molybdenum species on the hanging mercury drop electrode (HMDE) using mixtures of nitrate and phosphate as supporting electrolytes. The adsorptive stripping response was evaluated with respect to preconcentration time, potential and composition of supporting electrolyte. The method used is cathodic linear sweep stripping voltammetry (CLSSV). The detection limit found was $1 \times 10^{-5}$ M using 120 s. as accumulation time. The precision of the method is satisfactory with relative standard deviation of 1.4% with five replicates at $1 \times 10^{-6}$ M Mo(VI). The effect of various surface active substances (SAS) as well as different metal cations and anions in synthetic aqueous solutions has been investigated. Also this method has been applied for the determination of Mo(VI) in environmental samples; e.g., soil, natural water and indoor airborne particulate.

Keywords: Molybdenum Adsorptive cathodic stripping voltammetry, Surface active substance, Different metal cations and anions

Molybdenum is the only element in the second and the third row of the transition elements that is essential to all organisms [1]. Its biochemical role is extremely important in the nitrogen metabolism of plants. Nevertheless, excess of this element becomes harmful to ruminants since the absorption of copper by the liver is depressed [2]. The low concentrations of molybdenum found in plants, seawater, soil, fresh water and other make it necessary to find very sensitive methods for its determination. Electroanalytical procedures have been reported for the determination of traces of molybdenum at hanging/static mercury drop electrodes, i.e., anodic [3] or cathodic [4] stripping voltammetry and direct polarography [5]. Adsorptive stripping voltammetry has been shown to be useful for this purpose [6, 7]. Therefore, differential pulse adsorptive stripping voltammetric techniques [8–11] have been used for the determination of trace amount of molybdenum based on accumulation of the complex at a hanging mercury drop electrode. Also, the combination of a wall-jet mercury film electrode and square-wave adsorptive stripping voltammetry has been applied for this purpose [12]. Carbon paste electrodes modified in situ with cetyltrimethyl ammonium bromide [13] have been used. Ultratrace determination of Mo(VI) in the presence of 2-(2-thiazolylazo)-p-cresol by catalytic adsorptive stripping voltammetric method has been studied [14]. Recently, the coupling of catalytic and adsorption process, via controlled adsorptive accumulation of the catalyst yields a remarkable sensitivity and detectability down to the picomolar level [15, 16]. The catalytic-adsorptive stripping voltammetric determination of ultratrace levels of molybdenum in the presence of 3-methoxy-4-hydroxymandelic acid has been studied [17]. Calalytic currents of molybdenum have permitted convenient polarographic determination of nanomolar concentrations [18, 19]. A number of ligands have been tested at mercury drop electrodes, such as 8-hydroxyquinoline [20, 21, 22], phosphate [23], toluidine blueoxalic acid [24] and gallic acid [22].

In this work the cathodic adsorptive preconcentration of Mo(VI) at HMDE in presence of a mixture from 0.01 M (NaH2PO4, Na2HPO4) and 0.01 M. NaNO3 was used for the determination of trace amount of Mo(VI). The method has been applied for detecting Mo(VI) in soil, natural water and airborne particulates.

Preliminary investigations show that small and unusable peaks were observed in the presence of $1 \times 10^{-2}$ M universal or bicine buffer or potassium nitrate and $1 \times 10^{-6}$ M Mo(VI). Cyclic voltamograms for $1 \times 10^{-6}$ M Mo(VI) in presence of 5 mM mixture from sodium monohydrogen phosphate (H2A−) di-sodium hydrogen phosphate (HA2−) 10 mM sodium nitrate, pH ca. 2.5 are shown in Figure 1. This was due to the formation of 12-molybdo-phosphate which is more strongly adsorbed at the hanging mercury drop electrode than molybdic acid [23]. The first peak is attributed to the reduction of Mo(VI) to Mo(V), the second one is for Mo(V) to Mo(III) [22] and the third peak may be due to Mo(III) to Mo. The peaks which are observed in the reverse scan, mean that the electrochemical process is reversible.

The effect of potential scan rate $n$ on the peak current and peak potential were studied for the three peaks in the presence of $5 \times 10^{-3}$ M mixed (H2A− − HA2−), $5 \times 10^{-7}$ M Mo(VI) and deposition 60 s. The log $i_P$ (peak current) versus log $n$ (scan rate) are plotted over the range 5–200 mV/s. The slopes are 1.473, 1.23, and 1.061 for the first, second and the third peak, respectively. These slopes are in close proximity to the slope of 1.0 and is expected for the ideal reaction of surface species [25]. A 25 mV negative shift in the peak potential was observed in each case when the scan was increased in the range given. This is more evidence for the adsorption of Mo(VI) onto the electrode surface. The correlation coefficient being 0.969, 0.66, and 0.959 for the first, second and third peak, individually.

The effect of pH on the second peak has been studied for $5 \times 10^{-7}$ M Mo(VI) at the same conditions as before using 60 s.
deposition time. No adsorptive peak was observed at pH > 4, when the pH of the solution was 2.5 the cathodic reduction attained its maximum value.

When cyclic voltammograms of $5 \times 10^{-7}$ M Mo(VI) were recorded in the presence of 5 mM mixed (H$_2$A$^-\text{-HA}^2$) but in the absence of nitrate, illdefined peaks were observed. However, by the addition of different concentrations of nitrate, 1, 5, 10, 20, and 40 mM, the peaks were improved. The three peaks had maximum values at 10 mM NaNO$_3$.

The peak height of $5 \times 10^{-7}$ M Mo(VI), accumulation time 60 s. were studied as to the dependence of $E_{\text{acc}}$. It was noticed that the peak height had a maximum value at $E_{\text{acc}}$ = +0.15 V for the three peaks, then by increasing the potential to the more negative value the height of the peaks decreased. The first and the third peak disappeared while the second peak was still constant and slightly decreased in the current signal by increasing the potential in the negative direction. Therefore, the second peak was used for studying the interferences and other applications.

Hence, the optimal conditions for further measurements in this study are: 5 mM (H$_2$A$^-\text{-HA}^2$) M, 10 mM NO$_3^-$, pH ca. 2.5, $E_{\text{acc}}$ = +0.15 V, S.R $=$ 100 mV/sec.

Figure 2 shows the plots of the peak current vs. preconcentration time for (1.5, 2, 3 and 5) $\times 10^{-7}$ M Mo(VI) for the second peak. The slopes of the linear sections were 0.29, 0.35, 0.78, and 1.67 for (1.5, 2, 3 and 5) $\times 10^{-7}$ M Mo(VI), respectively. It was observed that by increasing the concentration of Mo(VI) shorter times were needed to reach the surface coverage. These times were 300, 240, 180, and 90 s. for (1.5, 2, 3, and 5) $\times 10^{-7}$ M Mo(VI), respectively. The intercept with the current axis was attributed to the fact that the adsorption takes place at equilibrium time [26] and the break in these lines means that the surface coverage was achieved.

The data obtained from the calibration plots over the Mo(VI) concentration range (1 $\times 10^{-7}$-$5 \times 10^{-7}$) M following 60, 120, 240, and 300 s accumulation times are summarized in Table 1. The limit of linearity indicates strong adsorption behavior of the reduction product over all the times applied. As low as $1 \times 10^{-8}$ M (0.95 µg/L) Mo(VI) can be detected using 120 s as preconcentration time. The reproducibility of the adsorption process was examined by repeating 10 experiments on $5 \times 10^{-7}$ M Mo(VI) using 60 s accumulation time. The relative

Fig. 1. Cyclic voltammograms of $1 \times 10^{-6}$ M Mo(VI) in presence of 5 mM mixture from (H$_2$A$^-\text{-HA}^2$) and 10 mM NaNO$_3$ at pH ca. 2.5, scan rate: 100 mV/sec and accumulation time: 40 s.

Fig. 2. Effect of accumulation time on the peak current at 5 mM (H$_2$A$^-\text{-HA}^2$), 10 mM NaNO$_3$, pH ca. 2.5 for the second peak (-0.64 V) a) $1.5 \times 10^{-7}$ M, b) $2 \times 10^{-7}$ M, c) $3 \times 10^{-7}$ and d) $5 \times 10^{-7}$ M Mo(VI).
Table 1. Characteristics of Mo(VI) calibration plots in 10 mM NaNO₃, 5 mM mixed (H₂A⁻·HA²⁻), (pH ca. 2.54) for the second peak (− 0.64 V). Peak height y in nA, concentration x in 10⁻⁷ mol L⁻¹

<table>
<thead>
<tr>
<th>Deposition time [s]</th>
<th>Linearity range [mol L⁻¹]</th>
<th>Equation</th>
<th>Correlation coefficient</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>(1.5–5)×10⁻⁷</td>
<td>y = 44.08×−38</td>
<td>0.9997</td>
</tr>
<tr>
<td>120</td>
<td>(1.5–5)×10⁻⁷</td>
<td>y = 62.61×−22</td>
<td>0.9998</td>
</tr>
<tr>
<td>240</td>
<td>(1.5–5)×10⁻⁷</td>
<td>y = 90.67×−20</td>
<td>0.9997</td>
</tr>
<tr>
<td>300</td>
<td>(1.5–5)×10⁻⁷</td>
<td>y = 100.00×−18</td>
<td>0.9996</td>
</tr>
</tbody>
</table>

Table 2. Determination of Mo(VI) (µg/L, ppb) in water sample, and (µg/Kg, ppb) in soil sample and airborne particulates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>pH</th>
<th>Mo(VI)</th>
<th>Correlation coefficient</th>
<th>Tₚ [s]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Potable water from different sources</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(EGYPT) S₁</td>
<td>7.86</td>
<td>1.72±0.01</td>
<td>0.987</td>
<td>120</td>
</tr>
<tr>
<td>S₂</td>
<td>8.30</td>
<td>4.80±0.02</td>
<td>0.972</td>
<td></td>
</tr>
<tr>
<td>S₃</td>
<td>8.29</td>
<td>9.58±0.01</td>
<td>0.955</td>
<td></td>
</tr>
<tr>
<td>S₄</td>
<td>8.30</td>
<td>0.48±0.01</td>
<td>0.978</td>
<td></td>
</tr>
<tr>
<td>Tap water (Nile) S₅</td>
<td>7.50</td>
<td>3.93±0.01</td>
<td>0.969</td>
<td>60</td>
</tr>
<tr>
<td>Tap water (well) S₆</td>
<td>7.71</td>
<td>5.76±0.01</td>
<td>0.954</td>
<td>90</td>
</tr>
<tr>
<td>Natural (Nile) water (Assiut city) after filtration S₇</td>
<td>7.80</td>
<td>8.15±0.02</td>
<td>0.979</td>
<td>180</td>
</tr>
<tr>
<td>Natural (Nile) water filtered then digested with nitric acid S₈</td>
<td>6.80</td>
<td>40.5±0.0</td>
<td>0.964</td>
<td>180</td>
</tr>
<tr>
<td>Soil sample, filtrate of the water soluble portion and digested with nitric acid S₉</td>
<td>2.5</td>
<td>407.75±0.02</td>
<td>0.979</td>
<td>15</td>
</tr>
<tr>
<td>Soil sample before digested the sample S₁₀</td>
<td>–</td>
<td>not detected</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Airborne particulates S₁₁</td>
<td>–</td>
<td>not detected</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

standard deviation RSD and coefficient of variation (r) were 3.25 and 0.997, respectively.

The effect of surface active substances (SAS): for a cell containing 5×10⁻⁸ M Mo(VI), 5 mM (H₂A⁻·HA²⁻), 10 mM NaNO₃, deposition time 90 s the adsorption voltammetric peak height of Mo(VI) was decreased to one seventh of its original value by the addition of 5×10⁻³ M neutral (SAS) (Triton X-100) or 4×10⁻³ M anionic SAS (sodium dodecylsulfate). However, the addition of 1.5×10⁻⁴ M cationic SAS (cetyltrimethyl ammonium bromide, CTAB) the adsorption peak completely disappeared. Therefore, the peak signal of 0.5×10⁻⁷ M Mo(VI) depends on the type of surface active substance (SAS) and its concentration.

Also, the interferences with cations or anions were studied in the cell containing 5×10⁻⁸ M Mo(VI) using 90 s deposition time. No change on the peak height of Mo(VI) was observed by the addition of 5×10⁻⁷ M Co(II), Ni(II), Cr(III), Cd(II), Pb(II), Br⁻ and Cl⁻ ions individually or in admixture.

The standard addition method was applied to the determination of Mo(VI) in different samples viz., potable water from different sources in Egypt, S₁-S₄, tap water either Nile, S₅ or well, S₆. These samples were used without any treatment. However, natural Nile water (Assiut city) were used after filtration, S₇, or after filtration and digestion with nitric acid, S₈. Furthermore, the method was also used for the determination of Mo(VI) in soil and airborne particulate samples which were dissolved in water and filtered S₁₀ and S₁₁, while soil sample, S₁₀ was treated with nitric acid after filtration. Table 2 summarizes the Mo(VI) contents in each of the samples.

Experimental

The instrument used was an EG&G Princeton Applied Research (PAR, Princeton, NJ, USA) Model 264A stripping analyzer, coupled with a PAR 303A static mercury drop electrode (SMDE) (drop size; medium, area of the drop: 0.014 cm²). The polarographic cell was equipped with a platinum wire used as an auxiliary electrode and a Ag/AgCl saturated KCl as a reference electrode. A PAR 305 stirrer was connected to the 303A SMDE. The (CLSSV) signals were displayed on 0151 X − Y recorder.

Molybdenum(VI) was prepared by dissolving the appropriate mass of molybdenum salt (Merck) in doubly distilled water. All standard methods [27] Phosphate buffer and other supporting electrolytes were prepared from analytical grade. Solutions of 10⁻³ M from (SAS) and metal ions were prepared and used as interferences.

References