

# DETERMINATION OF MOLYBDENUM BY ADSORPTIVE CATALYTIC STRIPPING VOLTAMMETRY IN THE PRESENCE OF ALIZARIN RED S AND PERSULPHATE

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## ABSTRACT

An alternative and sensitive method by adsorptive catalytic stripping voltammetry for the determination of trace molybdenum is proposed. The method is based on the adsorption collection of the Mo(VI)–Alizarin Red S complex on a hanging mercury drop electrode (HMDE) following the catalytic reduction of both Mo(VI) and Alizarin Red S (ARS) in the complex in the presence of persulphate as oxidizing reagent. The experimental parameters such as accumulation time, accumulation potential, scan rate, pH, concentration of ARS and persulphate were optimized. Under the optimized conditions, the relationship between the peak current and molybdenum concentration is linear in the range of 0.15–5.0 µg/L. The detection limit and quantitation limit of the method based on the standard deviation of blank for accumulation time of 30 s were calculated as 0.046 µg/L ( $4.79 \times 10^{-10}$  M) and 0.15 µg/L ( $1.56 \times 10^{-9}$  M), respectively. The method was applied to the determination of molybdenum in drinking water samples. The recoveries for 1 and 3 µg/L molybdenum in the drinking water samples were found as 90% and 93%, respectively. Relative standard deviation for 3 µg/L molybdenum is 2.88%. 100 µg/L As(III), Ni(II) and Zn, 50 µg/L Al(III) did not interfere while serious interference was observed from Sb(III). Voltammetric characteristics and mechanism of the Mo(VI)–ARS–S<sub>2</sub>O<sub>8</sub><sup>2-</sup> system were also investigated.

**KEYWORDS:** Molybdenum, Alizarin Red S, persulphate, catalytic, stripping voltammetry.

## 1. INTRODUCTION

Molybdenum is an essential trace element to all living organisms, especially plants [1], animals and humans. However, excess concentrations of molybdenum can cause adverse effects. It has been reported that molybdenum con-

tent higher than 5 µg/g in plants and equals to 10 µg/g for ruminants can be toxic [2]. The U.S. EPA drinking water health advisories recommended long-term limits of 10 µg/L for children and 50 µg/L for adults and the United Nations Food and Agriculture Organization recommended a maximum level for irrigation water of 10 µg/L. The concentrations of molybdenum in human serum have been reported as lower than 1 µg/L while 42.5 µg/L in urine. Whole blood concentrations for most people have been reported as <5 ng Mo/mL. On the other hand, molybdenum contents of seawater and mineral waters have been reported in the range of 6–20 µg/L and 0.25–1.0 µg/L, respectively [2]. Most natural waters contain low levels of molybdenum in the range of <2–3 µg/L [3]. Therefore, sensitive, selective and precise methods are needed for determination of molybdenum in industrial, environmental and biological samples.

Various techniques such as ultra-violet visible spectrophotometry [4], neutron activation analysis [5], flame atomic absorption spectrometry (FAAS) [6], electrothermal atomic absorption spectrometry (ETAAS)[7,8], inductively coupled plasma–atomic emission spectrometry (ICP-AES) [9,10], and inductively coupled plasma– mass spectrometry (ICP-MS) [11–13]. However, these methods have common disadvantages such as the requirement of preconcentration and separation steps and high instrument cost. On the other hand, adsorptive catalytic stripping voltammetry (AdCtSV) is a low cost and sensitive technique for determination of metal ions in the complex including molybdenum.

Numerous AdCtSV techniques based on the adsorptive accumulation of a molybdenum complex on to electrode surface have been developed for the determination of molybdenum. Various catalytic systems such as dihydroxynaphthalene-bromate [14], mandelic acid-chlorate [15], methyl thymol blue-chlorate [16], pyrogallol red-chlorate [17], tiron-chlorate [18] and pyrocatechol-violet-chlorate [19] have been used. The adsorptive stripping voltammetric methods reported for determination of Mo(VI) have been well listed in the literature[18]. On the other hand, it has been reported that Mo(VI) forms a 1:1 com-

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plex in 0.1 M acid solution and 1:2 complex with Alizarin Red S (ARS) in the pH ranges 2-5 [20]. The complex has been used for determination of molybdenum by spectrofluorimetry [21] and adsorptive stripping voltammetry [22]. The lowest detection limits obtained at mercury electrode and mercury free electrode for an accumulation time of 60 s were reported as 0.006 µg/L ( $6.25 \times 10^{-11}$  M) [18] and 0.086 µg/L ( $9 \times 10^{-10}$  M) [22], respectively.

This work presents an AdCtSV method for the determination of molybdenum, using Alizarin Red S (monosodium salt of 1,2-dihydroxyanthraquinone-3-sulphonic acid) as ligand and persulphate (firstly used for the determination of molybdenum) as oxidizing reagent. The proposed method is based on the catalytic reduction of Mo(VI)-ARS complex accumulated at the HMDE in the presence of persulphate. As the potential is scanned in the negative direction, Mo(VI) in the complex adsorbed on the electrode surface is reduced to Mo(V). Then, Mo(V) is immediately oxidized back to Mo(VI) by the persulphate and the catalytic cycle resulting in high sensitivity is completed. The proposed method has been applied to determination of molybdenum in different water samples.

## 2. MATERIAL AND METHODS

### 2.1. Apparatus and Reagents

The voltammetric measurements were carried out using a Radiometer Pol 150 Polarographic Analyzer in combination with a MDE 150 polarographic stand. The analyzer was controlled with Trace Master 5 Software. Three-electrode system consisting of a hanging mercury drop electrode (HMDE) as the working electrode, an Ag/AgCl with saturated KCl as the reference electrode and a platinum wire as the auxiliary electrode were used. Hexadistilled mercury (Radiometer-Copenhagen) was used throughout the study for HMDE. WTW pH-meter with combined pH electrode was used for pH measurement.  $1 \times 10^{-2}$  M stock solution of ARS was prepared from Fluka. The working solutions were prepared daily. The other chemicals used throughout the study were of analytical grade. All the solutions were prepared with deionized water having the resistivity of 18.2 MΩ.

### 2.2. Procedure

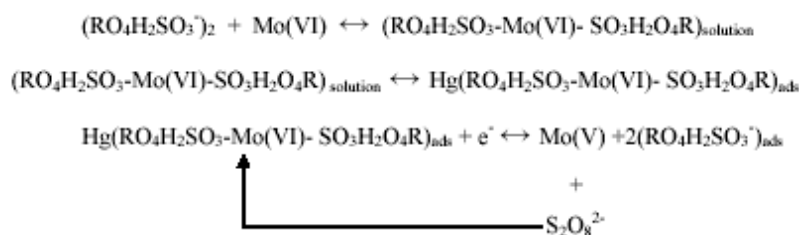
Twenty five microliters of  $5 \times 10^{-5}$  M of ARS and the required amount of Mo(VI) (or water sample) was pipet-

ted into a 10 mL of volumetric flask and completed to the mark with 0.04 mol/L acetate-phosphate buffer at pH 4.25. The solution was transferred to the quartz voltammetric cell and nitrogen was purged for 5 min after addition of 100 µL of 0.1 M  $K_2S_2O_8$ . A new mercury drop was extruded and then, accumulation on HMDE was performed at 0.00 mV by stirring the solution at 400 rpm for 30 s. The stripping was initiated toward cathodic direction and differential puls voltammogram with a potential scan rate of 25 mV/s was recorded. All of the measurements were performed at room temperature.

## 3. RESULTS AND DISCUSSION

### 3.1. Voltammetric peak characteristics of the Mo(VI)-ARS-persulphate system

Voltammetric behaviours of Mo(VI)-ARS-persulphate system were summarized in Figure 1. No significant peak was observed when scanning the electrode potential to the negative direction for the solution containing 3 µg/L of Mo(VI) (Fig.1b) in 0.04 mol/L acetate-phosphate buffer at pH 4.25. On the other hand, a cathodic peak at -276 mV vs Ag/AgCl reference electrode was observed for  $1.25 \times 10^{-7}$  mol/L of ARS in the absence of Mo(VI) and persulphate in the same conditions (Fig.1c). However, a peak at -214 mV in addition to the peak at -276 mV appears when 3 µg/L of Mo(VI) was added to the solution containing  $1.25 \times 10^{-7}$  mol/L of ARS (Fig.1d). Addition of  $1 \times 10^{-3}$  mol/L of persulphate causes an increase of the peak current at -214 mV (Fig.1e). This suggests that the reduction of Mo(VI) in the complex is catalyzed by persulphate. Additionally, it is noted that current of the peak at -276 mV increased and the peak at -214 mV also appeared when the persulphate was added to the solution containing ARS alone in 0.04 mol/L acetate-phosphate buffer at pH 4.25 (not shown in here). This implies that the reduction of ARS is also catalysed by persulphate. On the other hand, it was noted above that Mo(VI) forms 1:2 complex with ARS in the pH ranges 2-5. From all of the information mentioned above, the possible reaction mechanism is that the Mo(VI)-(ARS)<sub>2</sub> complex formed in the bulk solution was accumulated onto the mercury electrode at 0.0 V. Both Mo(VI) and ARS in the complex are then reduced during the potential scan. At the same time, the reduction products are oxidized back to Mo(VI) and ARS, which formed a catalytic cycle to increase the reduction current. The following catalytic mechanism can be suggested;



The catalytic process could be further confirmed by plotting the current function,  $I_p v^{1/2}$ , versus potential scan rate,  $v$ . The current function of the catalytic peak decreased dramatically with the increasing potential scan rate in the range of 100–200  $\text{mVs}^{-1}$  then leveled off (Fig.2). This result also confirmed the catalytic process.

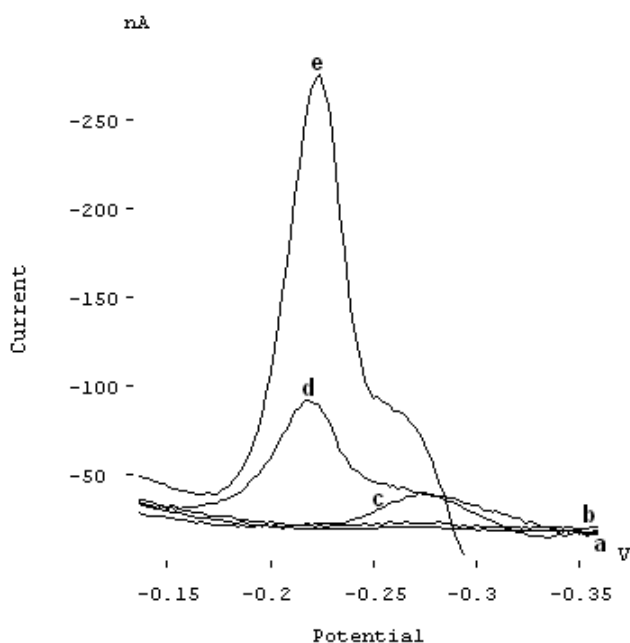


FIGURE 1 - Voltammograms representing the behaviour of Mo-ARS-persulphate system. (a) 0.04 mol/L acetate-fosfat buffer at pH 4.25, (b) a+3  $\mu\text{g/L}$  Mo(VI), (c) a+ $1.25 \times 10^{-7}$  mol/L ARS, (d) c + 3  $\mu\text{g/L}$  Mo(VI) and (e) d +  $1 \times 10^{-3}$  mol/L  $\text{S}_2\text{O}_8^{2-}$ ,  $E_{\text{acc}}=0$  mV,  $t_{\text{acc}}=30$  s.

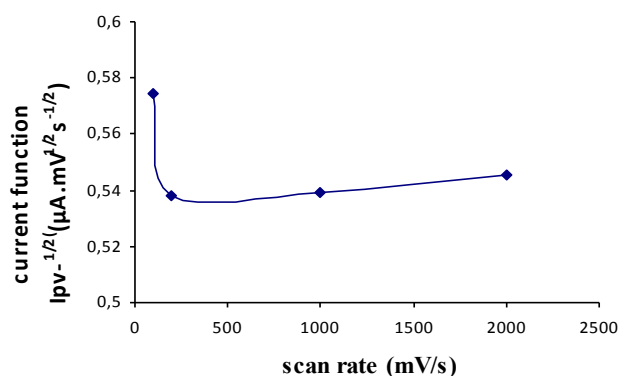


FIGURE 2 - Dependence of current function on the potential scan rate.

### 3.2. Effect of pH

The effect of pH on the peak current of Mo(VI)-ARS-persulphate system was studied in the range of 3.0 and 5.0, because no significant signal related to the complex was obtained below pH 3.0. As can be seen in Fig.3, the peak current slightly increases from pH 3.0 and gives a maximum at pH 4.25 and then, decreases by increasing of

pH. A negative shift in the peak potential was observed as the pH increases. Therefore, the optimum pH was selected as 4.25 to carry out subsequent experiments. Additionally, various buffer system at pH 4.25 were tested such as citrate, tartarate, acetate, phosphate, hydrogen phthalate and acetate-phosphate mixture. Among these, acetate-phosphate mixture (0.04 mol/L of each) was found to be suitable.

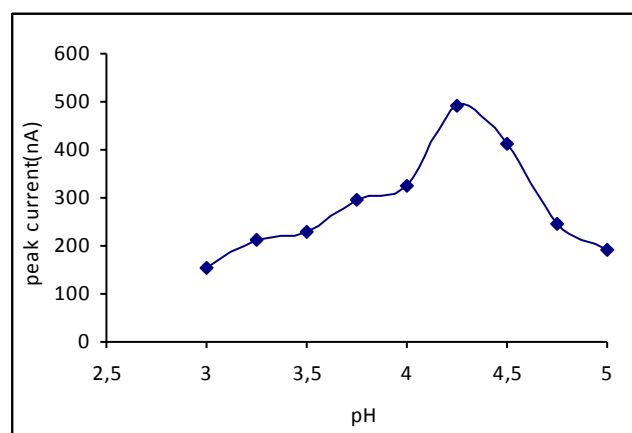


FIGURE 3- The effect of pH on the peak current. ( $10^{-3}$  mol/L  $\text{S}_2\text{O}_8^{2-}$ , 3  $\mu\text{g/L}$  Mo(VI),  $1.5 \times 10^{-7}$  mol/L ARS,  $E_{\text{acc}}=0$  mV,  $t_{\text{acc}}=30$  s).

### 3.3. Effect of ARS Concentration

The effect of the ARS concentration on the peak current of Mo(VI)-ARS-persulphate system was investigated in the range of  $5 \times 10^{-8}$ – $1 \times 10^{-6}$  mol/L of ARS. No significant peak was obtained for concentration of ARS below  $5 \times 10^{-8}$  mol/L. The peak current at -214 mV increases between  $5 \times 10^{-8}$ – $1.5 \times 10^{-7}$  mol/L of ARS concentrations and then decreases at higher concentrations. However, the peak at -214 mV overlaps with the peak at -264 mV for high concentrations of ARS at a concentration of more than  $1.5 \times 10^{-7}$  mol/L and the current of the resulting peak increases independently from concentration of Mo(VI). This is attributed to the change of the stoichiometry of the Mo(VI)-ARS complex. The result suggests that the concentration of the ARS is a critical parameter for selectivity and accuracy of the method. Therefore, the concentration of ARS was selected as  $1.25 \times 10^{-7}$  mol/L.

### 3.4. Effect of persulphate concentration

The effect of persulphate concentration on the peak current of Mo(VI)-ARS-persulphate system was investigated for the solutions containing 3  $\mu\text{g/L}$  of Mo(VI),  $1.25 \times 10^{-7}$  mol/L of ARS in acetate-phosphate buffer. The peak current increased with the increasing persulphate concentrations from  $1.0 \times 10^{-4}$  mol/L up to  $1.0 \times 10^{-3}$  mol/L. The values higher than  $1.0 \times 10^{-3}$  mol/L of persulphate concentrations, no peak was observed belonging to the catalytic system because of whole oxidation of mercury on the electrode by persulphate. For this reason, the persulphate concentration was selected as  $1.0 \times 10^{-3}$  mol/L.

### 3.5. Effect of accumulation potential

Fig. 3 shows the effect of changes of the accumulation potential on the peak current of Mo(VI)-ARS-per sulphate system. The higher peak current was obtained at the potential of zero charge, suggesting the Mo(VI)-ARS complex is a neutral molecule. The study for positive potentials was not performed because of the limitation of the mercury electrode. The accumulation potential, therefore, was preferred as 0 mV.

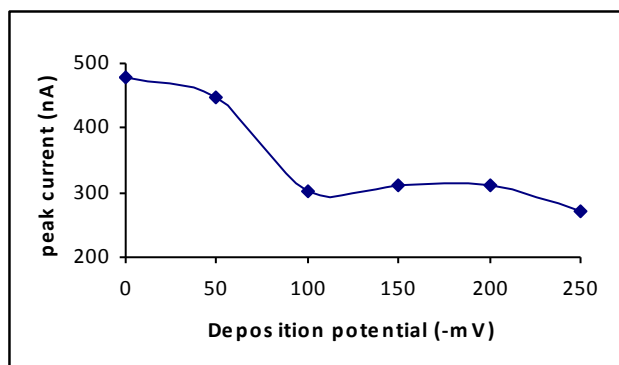


FIGURE 4 - The effect of accumulation potential on the peak current. ( $10^{-3}$  mol/L  $S_2O_8^{2-}$ , 3  $\mu\text{g/L}$  Mo(VI),  $1.25 \times 10^{-7}$  mol/L ARS, 0.04 mol/L acetate-fosfat buffer (pH 4.25),  $t_{acc}=30$  s)

### 3.6. Effect of accumulation time

The effect of accumulation time on the peak current is shown in Fig.4. The peak current increases linearly with accumulation time up to 60 s for 3  $\mu\text{g/L}$  of Mo(VI) and then it tends to level off for the longer accumulation time.

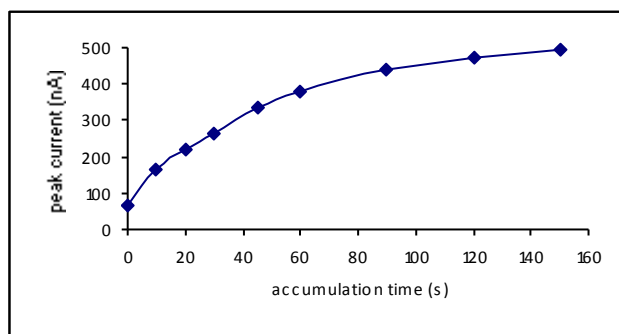


FIGURE 5 - The effect of accumulation time on the peak current ( $10^{-3}$  mol/L  $S_2O_8^{2-}$ , 3  $\mu\text{g/L}$  Mo(VI),  $1.25 \times 10^{-7}$  mol/L ARS, 0.04 mol/L acetate-fosfat buffer (pH 4.25),  $E_{acc}=0$  mV).

### 3.7. Calibration plot, detection limit and repeatability

As a result of the studies above, a calibration curve was constructed for determination of Mo(VI). Some voltammograms are shown in Fig.6. The curve was linear in the concentration range of 0.15–5.0  $\mu\text{g/L}$ . The equation of regression line was calculated as  $I_p = 62.9C_{Mo} + 17.4$  where  $I_p$  is the peak current (in nA) and  $C_{Mo}$  is the concentration of molybdenum. The coefficient of determination,  $r^2$ , was 0.9986 (for  $N=6$ ). The detection limit and quantitation limit of the method based on the standard deviation of blank

( $N=9$ ) for accumulation time of 30 s were calculated as 0.046  $\mu\text{g/L}$  ( $4.79 \times 10^{-10}$  M) and 0.15  $\mu\text{g/L}$  ( $1.56 \times 10^{-9}$  M), respectively. The relative standard deviation of blank solutions was calculated as 6.24%.

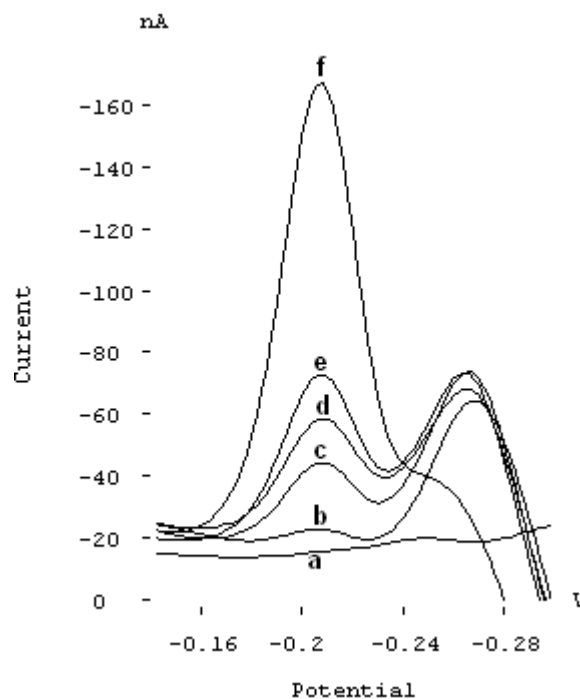


FIGURE 6 - Some voltammograms used for construction of calibration curve (a) blank solution ( $1.25 \times 10^{-7}$  mol/L ARS, 0.04 mol/L acetate-phosphate buffer at pH 4.25), (b) 0.25  $\mu\text{g/L}$  Mo(VI), (c) 0.50  $\mu\text{g/L}$  Mo(VI), (d):0.75  $\mu\text{g/L}$  Mo(VI), (e) 1.0  $\mu\text{g/L}$  Mo(VI) and (f) 2.5  $\mu\text{g/L}$  Mo(VI).

### 3.8. Interference study

The interference from  $Al^{3+}$ ,  $As^{3+}$ ,  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Ni^{2+}$ ,  $Sb^{3+}$ ,  $Zn^{2+}$ , humic acid and Triton-X-100 was studied in the solution containing 1  $\mu\text{g/L}$  of Mo(VI). The tolerance limits were taken as those concentrations causing changes no greater than  $\pm 5\%$  in the peak current. It was found that 2 mg/L of  $Ca^{2+}$  and  $Mg^{2+}$ , 100  $\mu\text{g/L}$  of  $Al^{3+}$ ,  $Zn^{2+}$ ,  $As^{3+}$ ,  $Ni^{2+}$ , 0.1 mg/L Triton X-100 and 0.5 mg/L humic acid not interfere while 1  $\mu\text{g/L}$  of  $Sb^{3+}$  causes serious interference.

### 3.9. Application of the method

The method proposed applied to three different drinking water samples and molybdenum was not detected in all of samples. The samples were fortified with molybdenum and the recoveries obtained were found acceptable. Voltammograms recorded for determination of molybdenum by standard addition method in fortified water sample were given in Fig.7. Additionally, accuracy of the proposed method was checked by inductively coupled plasma atomic emission spectrometric (ICP-AES) measurement. All of the results obtained are shown in Table 1. Statistical evaluation of the results shows good agreement between the mean concentrations obtained by the two methods in a 95% confidence level.

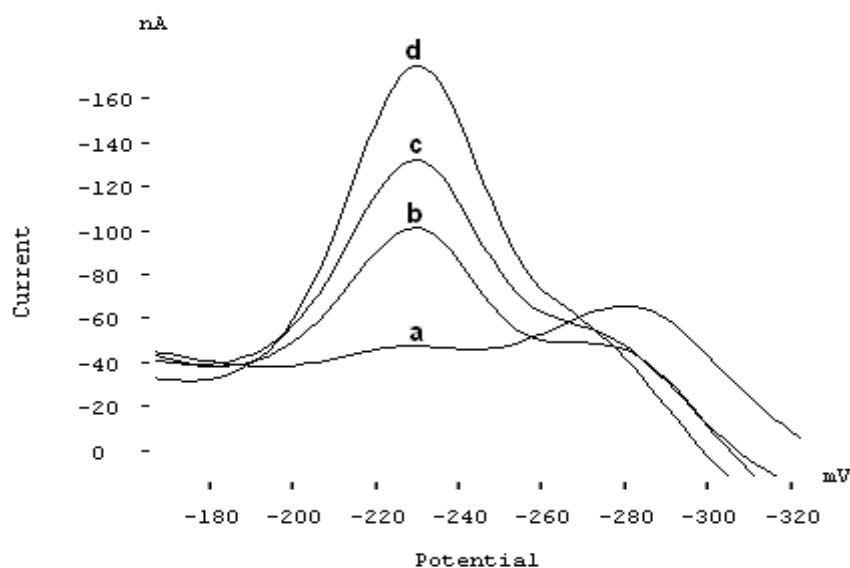


FIGURE 7 - Standard addition voltammograms obtained for the determination of molybdenum in fortified water samples. (a) blank solution ( $1.25 \times 10^{-7}$  mol/L ARS, 0.04 mol/L acetate-phosphate buffer at pH 4.25), (b) sample (c) and (d) upon additions of 0.50 µg/L Mo(VI).

TABLE 1 - Determination of molybdenum in water samples.

Samples	Mo(VI) Added (µg/L)	Mo(VI) Found by proposed method (µg/L±s)	Mo(VI) Found by ICP-OES (µg/L±s)	% R±s
DW1	-	<0.046	-	-
DW1	1	0.90±0.12	-	90±1.2
DW1	3	2.78±0.08	-	93±3.0
DW2	-	<0.046	-	-
DW2*	25	25.4±0.6	25.9±0.3	101.6±2.4
DW3	-	<0.046	-	-

s: standard deviation for three replicate measurements.

\*Sample diluted (1:10) for application of the proposed method.

#### 4. CONCLUSIONS

Sensitive and an alternative adsorptive catalytic stripping voltammetric method for the determination of molybdenum in the presence of ARS and persulphate was described. The method proposed differs from the other voltammetric method given in the literature in terms of persulphate firstly used as oxidizing agent for the determination of molybdenum. The limit of detection of the method can be improved further by extending the deposition time. Voltammetric characteristics and mechanism of the Mo(VI)-ARS- $S_2O_8^{2-}$  system were also investigated. The method can be applied successfully to the water samples with satisfactory results.

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