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Cathodic Adsorptive Stripping Voltammetric Determination of Molybdenum Using Mo (VI)-Cr (VI)-Pyrocatechol Violet Ternary Complex

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Abstract

In this study a new selective method for determination of trace amounts of molybdenum by adsorptive stripping voltammetry at pH= 4.5 is proposed. The method is based on adsorptive accumulation of Mo-pyrocatechol violet (PCV) complex onto hanging mercury drop electrode (HMDE) at accumulation potential of +0.10 V (vs Ag/AgCl), followed by reduction of adsorbed species by voltammetric scanning in the potential range of -0.40 and 0.80 V (vs Ag/AgCl) in differential modulation. The reduction peak current at -0.68 V (vs Ag/AgCl) is enhanced by addition of dichromate. The effect of instrumental and chemical variable on the sensitivity of the method were studied and optimized. In the optimum condition the limit of detection was found 0.050 ng mL^{-1}. The relationship between the peak current and molybdenum concentration is linear in the range of 1.0 – 70.0 ng mL^{-1}. The relative standard deviations for ten replicate determinations of 40.0 and 25.0 ng mL^{-1} Mo(VI) are 0.85 and 1.3%, respectively. The effects of interferences ion were studied and it was found that the method is free from interferences of some common cations. The procedure is applied to the determination of molybdenum in real and synthetic samples with satisfactory recoveries (92.5-104%).

Keywords: Molybdenum; Adsorptive stripping voltammetry; pyrocatechol violet; Chromium

1. Introduction

Molybdenum is a trace element found in the soil and is required for growth of most biological organisms including plants and animals. Molybdenum is a transition element, which can exist in several oxidation states ranging from zero to VI, where Mo(VI) is the most common form found in most agricultural soils. Similar to most metals required for plant growth, molybdenum has been utilized by specific plant enzymes to participate in reduction and oxidative reactions [1]. Molybdenum itself is not biologically active but is rather predominantly found to be an integral part of an organic complex called the molybdenum co-factor. Molybdenum co-factor binds to molybdenum-requiring enzymes (molybdoenzymes) found in most biological systems including plants, animals and prokaryotes [2]. It is also widely used in a

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variety of industrial processes, being an important constituent of metal alloys, pigments, lubricants and chemical catalysis, among others. Hence, the development of new methods for the sensitive and selective determination of molybdenum in ultra trace levels is still a challenging problem. A large number of papers have been published on the determination of molybdenum. Some of these methods include neutron activation analysis (NAA) [3], inductively coupled plasma-mass spectrometry (ICP-MS) [4], inductively coupled plasma-atomic emission spectrometry (ICP-AES) [5], atomic absorption spectrometry using flame (nitrous oxide-acetylene) (FAAS) [6] or electrothermal atomization (ETAAS) [7,8], spectrofluorimetry [9] and spectrophotometry [10–19]. Atomic spectrometric methods often lack sensitivity, so they generally need preconcentration. Most of these techniques such as NAA and ICP-MS necessitate the use of rather sophisticated and high cost instruments.

The development of adsorptive cathodic stripping voltammetry (ACSV) has allowed the determination of many trace metals including those that could not be determined by conventional anodic stripping voltammetry (ASV). ACSV has received increasing attention in recent years [20]. Several ACSV procedures have been developed for the determination of molybdenum using different complexing agents such as oxine [21], cupferron [22], 1,10-Phenanthroline [23], and α-benzoin oxime [24]. All of these methods have high limit of detection and/or suffer from metallic interferences. Many catalytic stripping voltammetric procedures have been reported for the highly sensitive determination of traces of molybdenum using complexing agents of oxine [25], methyl thymol blue [26], a-benzoin oxime [27], dihydroxy naphthalene [28], *p*-cresol derivative [29], methyl orange [30], pyrogallol red [31], mandelic acid [32] and morin [33]. Some of these methods suffer from non-linearity of the relationship between peak current and concentration at higher concentration [30-33], a large number of interferences [26-28, 32] and high limits of detection [30]. Thus, some improvements are still desirable, especially, for the analytical case of interference species and non-linearity of the relationship between peak current and concentration.

Pyrocatechol violet (Fig. 1) is a catechol sulphophthalein dye, which forms colored complexes with various metal ions including Al(III), Sn(II), Sn(IV), Cu(II), Cd(II), Pb(II), Fe(II), Fe(III), Mo(VI) and Zn(II), and its selectivity to certain ion(s) may be achieved or improved by appropriate separation or combination with masking agents [34]. The detail of complexation reaction of Mo(VI) with pyrocatechol violet (PCV) in the absence and presence of surfactants has been reported [35].

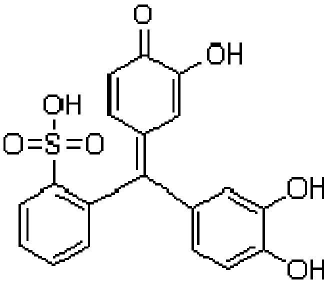

Fig. 1. Chemical structure of pyrocatechol violet (PCV)

In the presented studies, the conditions for ACSV determination of molybdenum (VI) on the HMDE with pyrocatechol violet (PVC) as complexing agent were investigated in details. It was possible to enhance the molybdenum (VI) reduction peak current with the addition of dichromate ions and consequently enhance the sensitivity of the presented method. The proposed method has the novelty over the other voltammetric procedures, because it is the first report on the usage of dichromate ions at low concentration as an adsorption enhancer agent for ACSV determination of trace molybdenum (VI).

2. Experimental

2.1. Equipment and instrumentation

Voltammetric measurements were carried out using a 746 VA trace analyzer (Metrohm) and a 747 VA electrode stand (Metrohm) with a multimode electrode (MME) operating in the HMDE mode. An Ag/AgCl reference electrode and a platinum auxiliary electrode were used. All potentials are quoted relative to this reference electrode. Solutions were stirred during the purging and accumulation steps bye a rotating PTFE rod. A 744 pH-meter (Metrohm) with a combined glass/calomel electrode was used for pH measurements.

2.2 Reagents and solutions

All reagents were of analytical grade and were used without further purification. All solutions were prepared with doubly distilled water.

The stocks solution of Mo (VI) with concentration of 1.0 g L^{-1} was prepared by dissolving 185.8 mg of ammonium heptamolybdatetetrahydrate (Merck) in a 100 mL volumetric flask. More dilute solutions were prepared by diluting appropriate volumes of this solution.

Pyrocatechol violet (PCV) stocks solution of 1.25×10^{-4} mol L^{-1} was prepared by dissolving 4.8 mg of PCV (Merck) in 100 mL volumetric flask. A dilute solution of 1.25×10^{-5} mol L^{-1} was prepared by dilution.

The stocks solution of chromium 1.0 g L^{-1} was prepared by dissolving appropriate amount of $K_2Cr_2O_7$ (Merck) in 100 mL volumetric flask. Further dilute solutions were appropriately made again with water.

Buffer solution of pH 4.5 was prepared by mixing of 0.10 mol L^{-1} potassium hydrogen phthalate and 0.050 mol L^{-1} sodium hydroxide solutions in appropriate ratio.

Using analytical grade reagents of Merck or Fluka made other solutions that were used in interference study and sample preparation procedure.

2.3. General procedure

All containers and voltammetric cell were carefully cleaned sequentially, first with detergent, then by rinsing with water and by soaking (24 h) with 2 mol L^{-1} nitric acid and finally through rinses with water. The experiments were performed as follows: an appropriate volume of Mo (VI) solution containing 10 to 700 ng Mo (VI), 1.0 mL 1.25×10^{-5} mol L^{-1} PCV and 1.0 mL 1.6 µg mL^{-1} dichromate ions were transferred to the electrochemical cell. The pH of the solution was adjusted to 4.5 by addition of 1.0 mL 0.025 mol L^{-1} phthalate buffer and then the solution was made up to 10.0 mL with water. After replacement of electrochemical cell, the stirrer was switched on and the solution was de aerated with high-purified nitrogen gas for 4.0 min. An accumulation potential of +0.10 V was applied to the fresh mercury drop electrode for 50 sec while solution was stirred at 1000 rpm. After end of accumulation time, stirring was stopped and after equilibration of 10.0 sec, the differential pulse voltammogram was recorded by applying a negative–going potential scanning from -0.40 to -0.80 V (pulse duration, 40 ms; pulse amplitude, 70 mV, interval time, 0.4 sec and potential step 6 mV, resulting in a scan rate of 15 mV s^{-1}). The reduction peak current of Mo (VI)-PCV was measured about -0.68 V. A blank solution without Mo (VI) was used to obtain the blank current. Each scan was repeated three times with a new drop for each analyzed solution and mean of these voltammograms were obtained. Difference between peak current of sample (i_s) and blank (i_b) was extracted and used as analytical signal in the calibration curve construction. All experiments were carried out at room temperature.

2.4. Sample preparation procedures for Lucerne analysis:

5.00 of oven-dried ground plant tissue was transferred to a porcelain crucible and laid in ashes at 550–600 °C for 4 h in a furnace. The resulting ashes was dissolved with 10 mL 4.0 mol L^{-1} HNO_3 and dried at 60 °C in a water bath followed by dissolution using 10 mL 2.0 mol L^{-1} HNO_3. Then, a drop of 0.1% $KMnO_4$ was added in order to oxidize all molybdenum into molybdenum (VI). After that, 1% urea solution was added to remove excess KMnO4 (until the purple color disappeared entirely), and then the solution was boiled to decompose excess urea. After neutralization with drop-wise addition of sodium hydroxide (1.0 mol L^{-1}) the solution was filtrated. The filtrates were quantitatively transferred to 50.0 mL volumetric flasks and diluted to the mark with water. Exactly 1.0 mL of this solution was analyzed using proposed method by standard addition approach.

3. Results and Discussion

3.1. Voltammetric studies

Preliminary experiments were carried out to identify the general features, which characterize the behavior of the Mo (VI)–Cr (VI)–PCV systems on mercury electrode.

Fig. 2 displays differential pulse voltammograms of solutions at pH 4.5 (phthalate buffer) containing only 50 ng mL^{-1} Mo (VI), 1.25×10^{-6} mol L^{-1} PCV and both 50 ng mL^{-1} of Mo (VI) and 1.25×10^{-6} M PCV after 50 s accumulation at +0.10 V. As can be seen from Fig. 2a and 2b, in a potassium hydrogen phthalate buffer solution of pH 4.5, any considerable peaks are not observed for Mo (VI) and PCV alone. When a trace amount of Mo (VI) is added to the solution containing PCV, a new weak peak is appeared at -0.67 V. (Fig. 2c) It seems reasonable to assume that the new peak results from the Mo (VI) complex with PCV. The current response of this peak is very low for sensitive determination of Mo (VI). Thus some efforts were made for increasing the sensitivity of Mo (VI)-PCV reduction peak current. Some agents with electro-catalytic effects (such as chlorate, bromate and nitrite) were tried and no significant enhancements were observed within the pH range of 1.5 - 7.0.

In the further studies it was found that in the presence of Cr (VI) the peak current increases considerable. Fig. 3 shows differential pulse voltammograms for Cr(VI), Cr(VI)–Mo(VI), Cr(VI)–PCV and Cr(VI)-Mo(VI)-PCV in phthalate buffer solution (pH 4.5). As seen in Fig. 3c, a reduction peak was observed at about –0.80 V, corresponding to the reduction of Cr (III) to Cr (II) [36]. Addition of small amounts of Mo (VI) causes an intensive reduction peak at –0.68 V (Fig. 3d). S. Himeno *et. al* have been reported that the water soluble $[CrMo_6O_{24}H_6]^{3-}$ anion is formed at very low concentrations of Mo(VI) and Cr(III), and the complex formation reaction proceeds rapidly even at ambient temperature and no complex formation of Mo(VI) with Cr(VI) occurs [37]. On the other hand, it has been well established that Cr (VI) is reduced by Hg(0) to Cr(III) in accumulation step [38]. On the other hand, addition of Cr(III) caused the same voltammograms with that Cr(VI) ions. Therefore it seems reasonable to assume that, in the accumulation step Cr(VI) is reduced to Cr(III) and subsequently forms a ternary complex of Cr(III)-Mo(VI)-PCV in the presences of PCV and the reduction peak at potential of –0.68 V can be related to reduction of Cr(III)-Mo(VI)-PCV ternary complex. The Mo(VI)-Cr(III)-PCV complex is more adsorbable than Mo(VI)-PCV complex. Consequently, it has higher reduction current in comparison to the Mo(VI)–PCV. With respect to the facts that, the metal reduction current appeared and increased by the addition of PCV, and the dependence of peak current to the accumulation time (Fig. 4), it can be concluded that the complex was adsorbed on the surface of electrode.

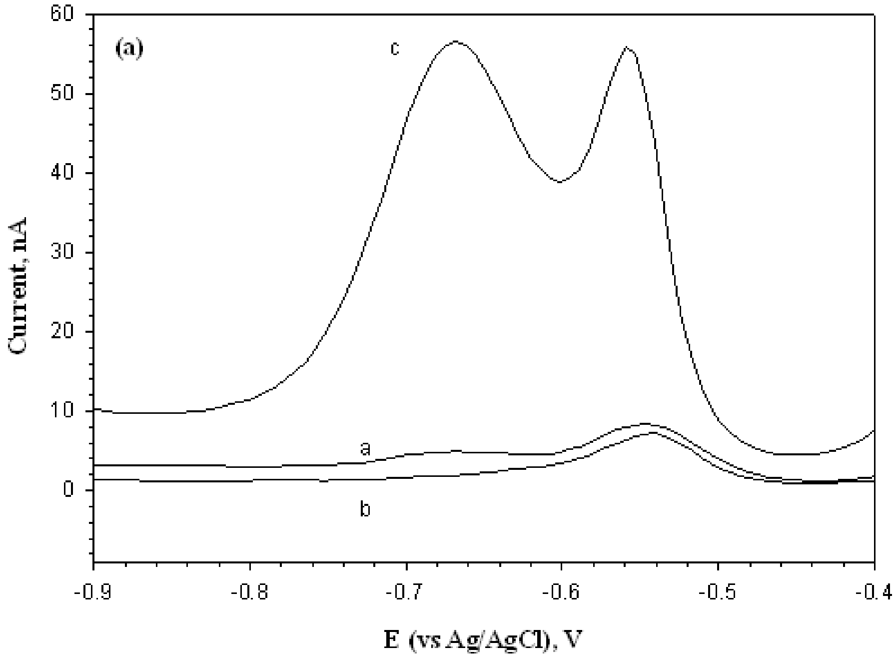

Fig.2. Differential pulse voltammograms for Mo(VI), PCV and Mo(VI)-PCV in phthalate buffer (pH 4.5) and 50 s accumulation at +0.10 V. (a): 50.0 ng mL^{-1} Mo (VI), (b) 1.25 × 10^{-6} mol L^{-1} PCV and (c) a plus b.

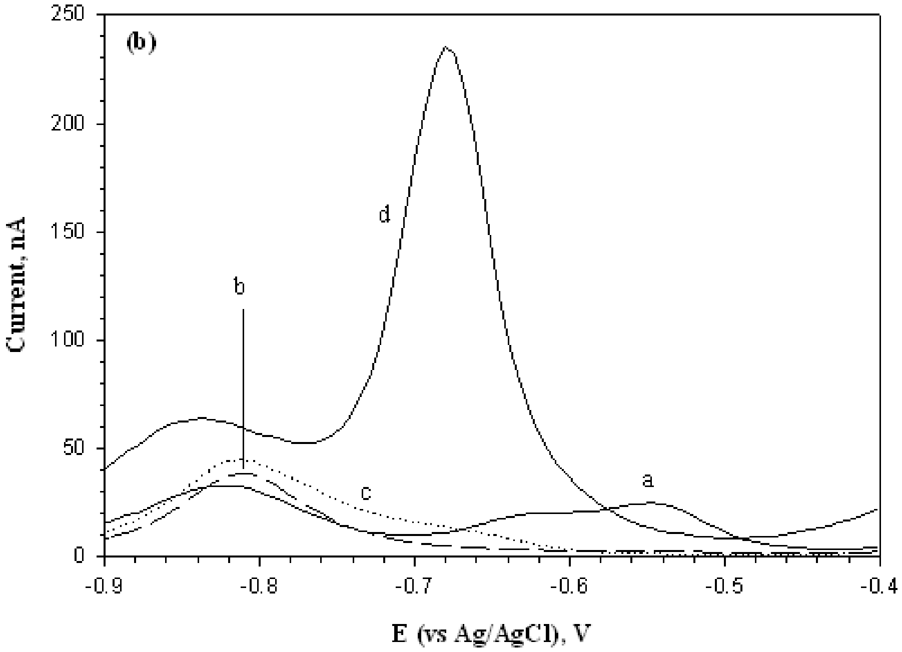

Fig. 3. Differential pulse voltammograms for Cr(VI), Mo(VI)-Cr(VI), Cr(VI)-PCV and Mo(VI)-Cr(VI)-PCV in phthalate buffer (pH 4.5) and 50 s accumulation at +0.10 V. (a) 50.0 ng mL^{-1} Mo(VI) and 0.16 µg mL^{-1} Cr (VI), (b) 0.16 µg mL^{-1} Cr(VI), (c) 0.16 µg mL^{-1} Cr(VI) and 1.25 × 10^{-6} mol L^{-1} PCV and (d) C plus 50.0 ng mL^{-1} Mo(VI).

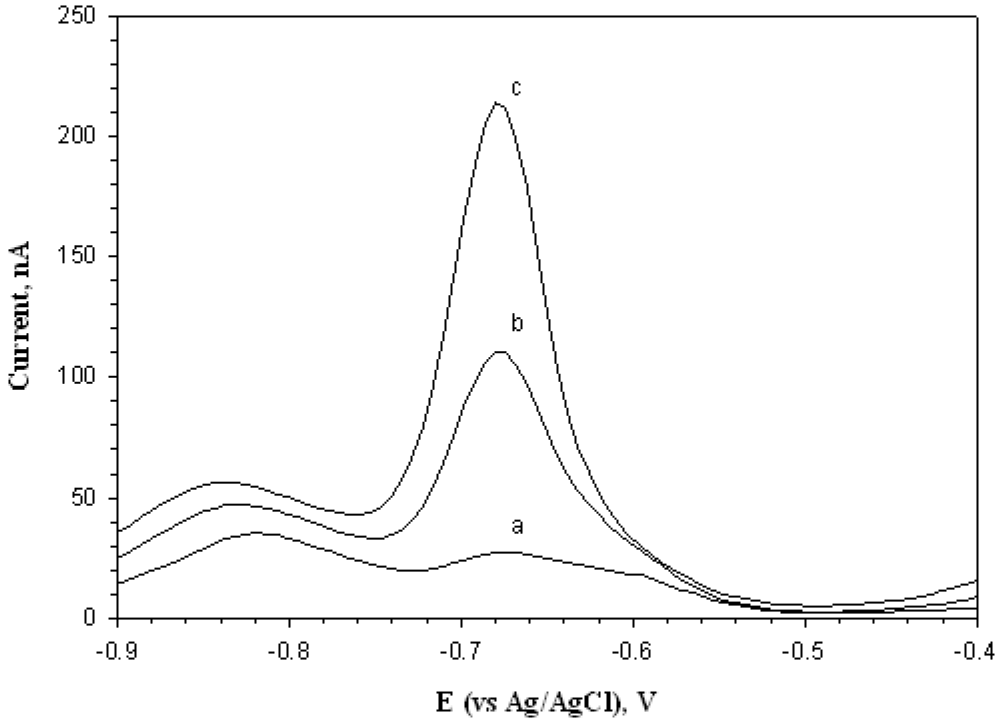

Fig. 4. Differential pulse voltammograms of Mo(VI)-PCV-Cr(VI) in phthalate buffer after a) 0, b) 20 and c) 40 s accumulation at +0.10 V. Conditions: 0.16 µg mL^{-1} Cr(VI), 1.25 × 10^{-6} mol L^{-1} PCV and 50.0 ng mL^{-1} Mo(VI).

Cyclic voltammetry was used for the study of the Mo–PCV and Cr-Mo-PCV systems. Fig.5 shows the cyclic voltammograms obtained for PCV, Mo(VI), Mo-PCV and Cr-Mo-PCV systems in phthalate buffer of pH 4.5 after adsorption for 50 s at a potential of +0.100 V followed by a cyclic scan between -0.100 V and -1.10 V at scan rate of 200 mV s^{-1}. In the cyclic voltammograms of 1.25 ×10^{-6} M PCV (Fig. 5a), and 20 ng mL^{-1} Mo(VI) (Fig. 5b) in a phthalate buffer solution no peaks were observed. Cyclic voltamogram of a solution contain both PCV and Mo(VI) at the same condition (Fig. 5c) shows a well-developed reduction peak around -0.67 V due to reduction of Mo(VI)-PCV complex. Fig. 5d shows the voltammogram after addition of 0.16 µg mL^{-1} of Cr(VI) ions. The new peak at -0.68 V was concluded due to the reduction of Cr(III)-Mo(VI)-PCV complex. Because of formation Cr(III)-Mo(VI)-PCV ternary complex a slight negative potential shift was observed. From the results in Fig. 6, the dependence of logarithm of cathodic peak currents (log i_p) versus logarithm of scan rate (log υ) is linear (r=0.9990) with a slope near to unite. Additionally, the ratio, $I_{P,a}/I_{P,c}$, is a function of scan rate, and is smaller than the value of unity, which is expected for an ideal diffusion controlling**.** These results improve the weakly adsorption of corresponding complex [39].

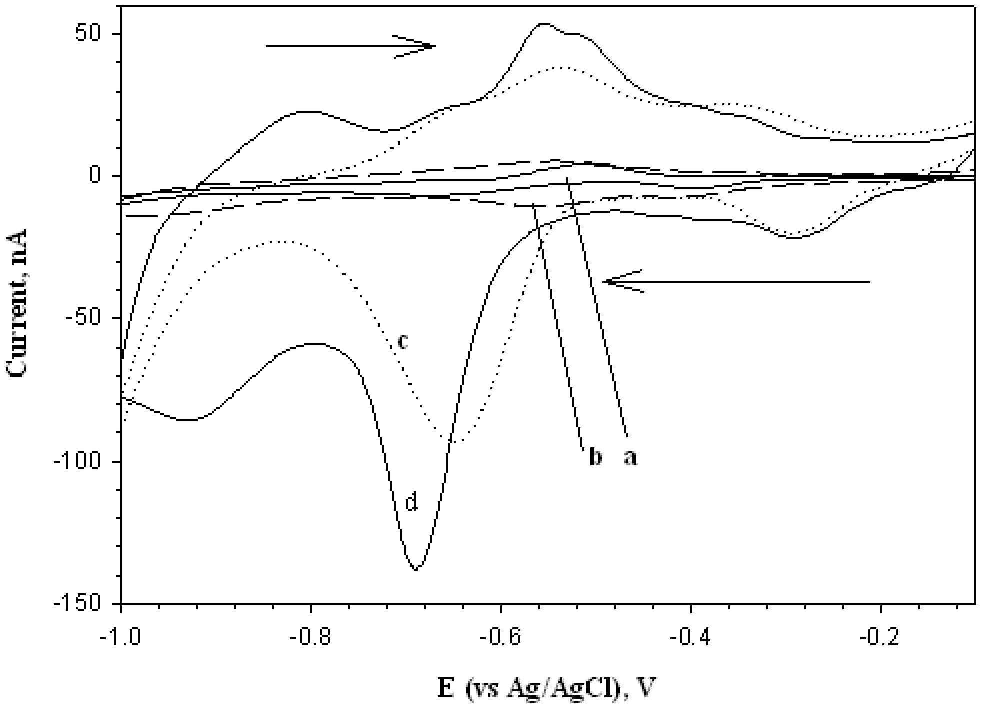

Fig. 5. Cyclic voltammograms of (a) 1.25 × 10^{-6} M PCV, (b) 20.0 ng mL^{-1}Mo(VI), (c) b plus 1.25 × 10^{-6} M PCV and (d) b plus 0.16 µg mL^{-1} Cr(VI). Conditions: phthalate buffer (pH 4.5), 50 s accumulation at +0.10 V and scan rate of 200 mVs^{-1}.

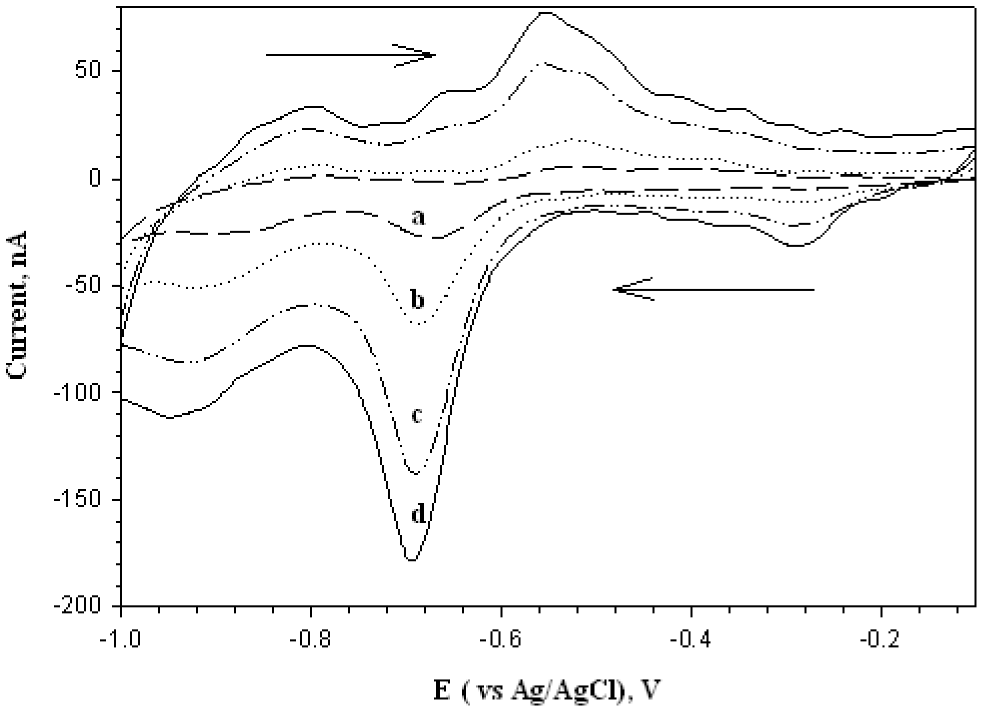

Fig. 6. Cyclic voltammograms of 1.25 × 10^{-6} mol L^{-1} PCV, 20.0 ng mL^{-1} Mo(VI) and 0.16 µg mL^{-1} Cr(VI) in different scan rates of a) 50, b) 100, c) 200 and d) 250 mVs^{-1}. Conditions: phthalate buffer (pH 4.5) and 50 s accumulation at +0.10 V

3.2. Optimization of variables

The influence of pH on the cathodic stripping peak currents of Mo was studied in the pH range of 3.0–5.5 (Fig. 7). It was found that at pH 4.5, the peak current of Mo was at its maximum value. Thus, pH 4.5 was adopted for further studies. Among various electrolytes (such as phthalate, acetate and citrate buffer solution) examined for adsorptive stripping study, the best results were obtained in phthalate buffer media.

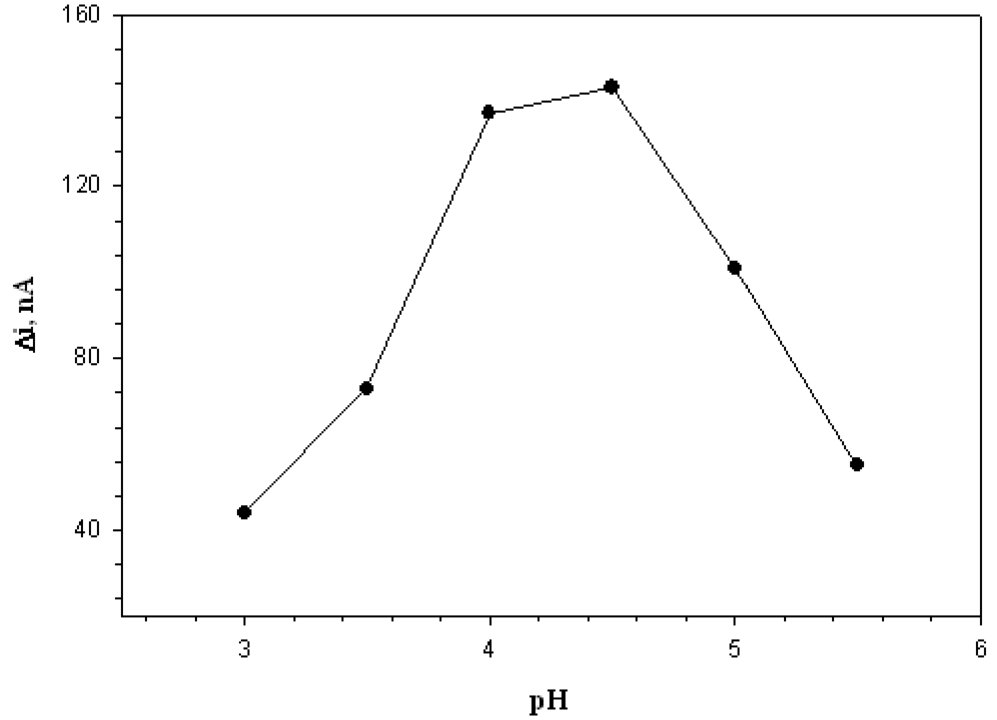

Fig. 7. Influence of pH on the peak current of 50.0 ng mL^{-1} Mo (VI), 1.03 × 10^{-6} mol L^{-1} PCV and 0.20 µg mL^{-1} Cr (VI) with 50 s accumulation at -0.10 V.

The effect of phthalate buffer concentration on the sensitivity of the method was also investigated. It was found that increasing phthalate buffer concentration from 0.0013 to 0.005 mol L^{-1} in a solution of 50.0 ng mL^{-1} Mo(VI), 0.20 µg mL^{-1} Cr(VI) and 1.0 ×10^{-6} mol L^{-1} PCV resulted in a substantial decrease in reduction peak height from about 180 to 125 nA. The decrement of peak height with increasing buffer concentration was attributed to the phthalate anion adsorbed onto mercury electrode surface [40]. Consequently, less electrode surface is available for the adsorption of the metal complex in case of increasing phthalate concentration. As a result, a buffer concentration of 0.0013 mol L^{-1} was adequate to give good buffer capacity and maintain pH without reducing sensitivity substantially.

The effect of the accumulation potential on the cathodic stripping peak current was examined over the range –0.50 – +0.20 V after an accumulation time of 50 s. The results indicate that the current is high and almost constant at the range of 0.00 – 0.15 V and exhibits a decrease on going towards more electronegative potential. Thus, an accumulation potential of +0.100 V was selected for the further studies.

Various concentrations of Cr(VI) ranged from 0.040 to 0.28 µg mL^{-1} in the presence of 50.0 ng mL^{-1} Mo(VI) and 0.0013 M phthalate buffer (pH 4.5) were studied. The peak current increased sharply upon increasing of Cr (VI) from 0.040 to 0.16 µg mL^{-1}. For higher dichromate ion, a slight decrease in the peak current was observed. Therefore, 0.16 µg mL^{-1} of Cr(VI) was selected as an optimum concentration.

The peak current of Mo(VI) increased with increasing PCV concentration up to 1.0×10^{-6} mol L^{-1} PCV. An optimum PCV concentration of 1.25×10^{-6} mol L^{-1} was selected for further experiments.

The effect of scan rate was studied from 1.0 to 30 mVs^{-1}. The peak current increased with increasing scan rate up to 15 mV s^{-1} and remained constant at high values. Thus with respect to sensitivity and voltammogram sharpness, scan rate of 15 mV s^{-1} was selected for subsequent studes.

The influence of accumulation time on the peak current was studied (pH 4.5; accumulation potential of +0.10V; scan rate of 15mV s^{-1}) in the mixture of 50.0 ng mL^{-1} Mo(VI), 1.25×10^{-6} mol L^{-1} PCV, 0.16 µg mL^{-1} dichromate. The results showed that the peak current increased linearity with accumulation time from zero to 50 s. The slightly decrements for further deposition was probably due to competition adsorption of other species. Therefore, an accumulation time of 50 s was used for further study.

3.3. Selectivity

The influence of co-exiting ions on the determinations of molybdenum was investigated under the optimum conditions. The voltammograms of the solutions containing 50.0 ng mL^{-1} Mo(VI) and various amounts of foreign ions were recorded. The tolerance limit was defined as the concentration, which gave a change of 3S (S is the standard deviation of five replicate signal measurements for 50.0 ng mL^{-1} of Mo(VI)) in the analytical signal. The experimental results are shown in Table 1. From the results, it is concluded that the method is free from many interferences of foreign ions.

3.4. Analytical parameters

Under the optimum conditions, a linear relationship was observed between the peak current and Mo(VI) concentration in the range of 1.0-70.0 ng mL^{-1} (Fig. 8). The calibration graph regression equation is $\Delta i=4.04C_{Mo}+0.29$ with a correlation coefficient of 0.9980 (n=14) where Δi is the difference between sample and blank peak currents and C_{Mo} is the Mo(VI) concentration in ng mL^{-1}. The detection limit (*S*/*N*=3) was 0.050 ng mL^{-1}. The precision of the method was checked at optimal conditions for 40.0 and 25.0 ng mL^{-1} Mo(VI). For ten replicate determinations, the relative standard deviations were 0.85 and 1.3%, respectively.

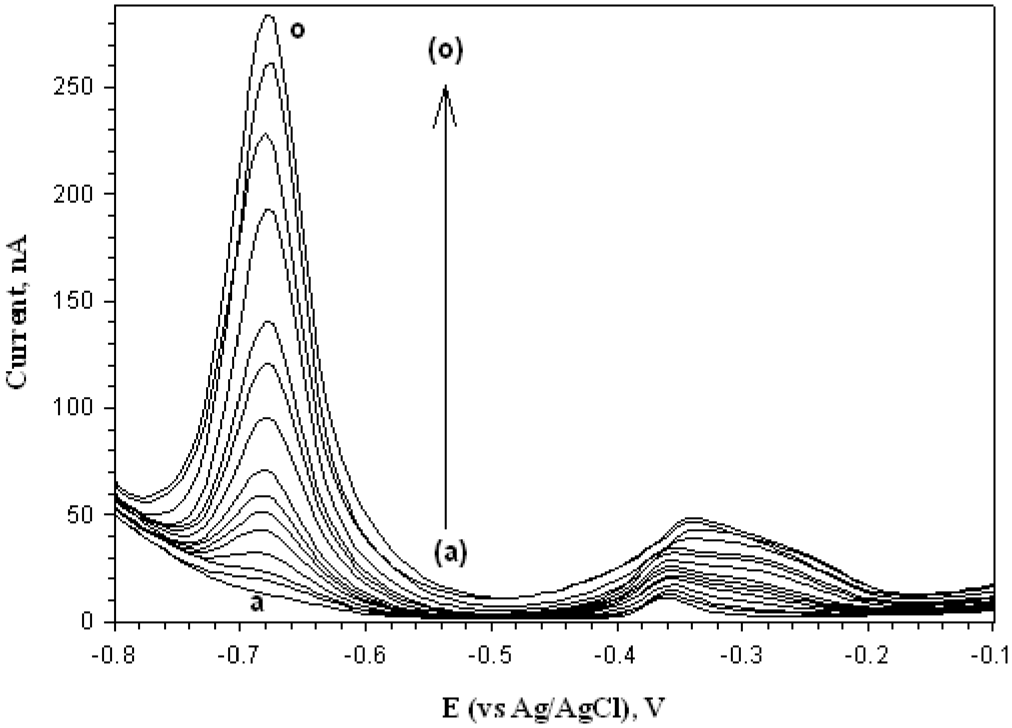

Fig. 8. Typical voltammograms at different concentration of Mo(VI). Conditions: pH 4.5; accumulation potential of +0.10V; accumulation time of 50s; scan rate of 15mV s^{-1}; 1.25 ×10^{-6} mol L^{-1} PCV and 0.16 μg mL^{-1} dichromate in the presence of a) 0.00, b).1.0, c)2.0, d)5.0, e)8, f)10, g)12, h)15.0, i)20.0, j)25.0, k)30.0, l)40.0, m)50, n)60 and o)70 ng mL^{-1} Mo(VI).

Table 1. Interferences for the determination of 50.0 ng mL^{-1} Mo(VI)

Species	Tolerance limit ($W_{ion}/W_{Mo(VI)}$)
Cd^{2+}, Pb^{2+}, K^{+}, Cr^{3+}, Pt^{4+}, NO_3^{-}, Ca^{2+}, Mg^{2+}	1000
Zn^{2+}, Sr^{2+}, F^{-}, Ag^{+}, Ba^{2+}, Tartaric acid	500
Cl^{-}	400
Ni^{2+}, Mn^{2+}, Br^{-}, Cu^{2+}, Co^{2+}, Al^{3+}	250
CN^{-}, Na^{+}, PO_4^{3-}	150
SCN^{-}, $C_2O_4^{2-}$, Fe^{3}+, Fe^{2+}, CO_3^{2}	100
I^{-},WO_4^{2-}, Bi^{3+}, Au^{3+}	25
Sn^{2+}	10

3.5. Analysis of real samples

In order to examine the performance of the proposed method, it was applied for the determination of Mo(VI) in spiked-untreated river water, tap water, synthetic alloy and planet samples (Lucerne), by using standard addition method. Well-defined peaks, similar to those found in the supporting electrolyte solution, were obtained. The results are summarized in Tables 2 and 3. The data obtained by this method reveal the capability of the method for the determination of molybdenum in real samples without considerable error.

Table 2. Determination of Mo(VI) in water sample

Sample	Mo(VI) added (ng mL^{-1})	Mo(VI) found (ng mL^{-1}) [a]	Recovery (%)
Tap Water	-----	N.D	-----
	5.0	4.9 (±0.1)	98.0
	10.0	9.9 (±0.7)	99.0

a) Numbers in the parenthesis show the S.D. for five replicates measurements.

Table 3. Determination of Mo(VI) in Lucerne and synthetic alloy samples

Sample [a]	Mo(VI) added (ng mL^{-1})	Mo(VI) found (ng mL^{-1}) [b]	Mo Content (µg g^{-1})	Recovery (%)
Lucerne	-----	43.0 (±1.4)	4.30	-----
	5.0	48.1 (±1.4)	-----	102
	10.0	53.4 (±1.4)	-----	104
	15.0	58.3 (± 1.5)	-----	102
Alloy-1	20.0	18.5 (±0.2)	-----	92.5
Alloy-2	30.0	29.8 (±0.2)	-----	99.3

a) Composition of synthetic alloys in µg mL^{-1}:

[1]Cd^{2+} (0.40), Pb^{2+} (0.40), Cu^{2+} (0.10), Ni^{2+}(0.10), Co^{2+} (0.10), Al^{3+} (0.10), Zn^{2+} (0.20)

[2]Cd^{2+} (1.8), Pb^{2+} (1.8), Mg^{2+} (1.35), Zn^{2+} (1.0), Al^{3+} (1.0), Sr^{2+} (1.0), Ba^{2+} (1.0), Cl^{-} (0.80), Cu^{2+} (0.45), Ni^{2+} (0.45), Co^{2+} (0.45), CN^{-} (0.30), W(VI) (0.04)

b) Numbers in the parenthesis show the S.D. for five replicates measurements.

4. Conclusion

In this study, the voltammetric behavior of molybdenum (IV) complex with PCV in the presence of Cr(VI) was described. Procedure based on the usage of these reagents is relatively lack interference compared with many previously reported electroanalytical methods [28-30, 33]. Additionally, the procedure shows the adsorption enhancement of the reduction current in the presence of Cr(VI). Coupling the sensitivity with high selectivity and accuracy is a distinguishing factor of the proposed methods. The low detection limit and the excellent selectivity show that this method is the most appropriate for molybdenum analysis in real samples.

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