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Determination of traces molybdenum by catalytic adsorptive stripping voltammetry

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Abstract

A reliable and very sensitive procedure for the determination of ultra trace of molybdenum is proposed. Molybdenum was determined by cathodic stripping differential pulse voltammetry based on the adsorption collection of the Mo(VI)–Tiron complex on a hanging mercury drop electrode (HMDE). The variation of peak current with pH, concentration of Tiron and chlorate, plus several instrumental parameters such as accumulation time, accumulation potential and scan rate, were optimized. Under optimized condition, the relationship between the peak current and molybdenum concentration is linear in the range of 0.010–21.0 ng $\mathrm{ml^{-1}}$. The limit of detection was found to be 0.006 ng $\mathrm{ml^{-1}}$. The relative standard deviation for 10 replicates determination of 0.6 and 10 ng $\mathrm{ml^{-1}}$ Mo(VI) is equal to 1.3 and 0.9%, respectively. The method was applied to the determination of molybdenum in river water, tap water, well water, plant foodstuff samples such as cucumber, tomato, carrot, and certified steel reference materials.

Keywords: Molybdenum; Stripping voltammetry; Electrocatalysis; Adsorption; Tiron

1. Introduction

Molybdenum has important role in enzymatic redox reaction. In biological systems, molybdenum is an essential constituent of enzymes, which catalyze redox reactions, e.g. oxidation of aldehydes, xanthine, and other purines [1,2], and reduction of nitrates and molecular nitrogen [3–5]. Molybdenum plays an important role in a wide variety of plants and animals particularly ruminants and is an essential trace element in plant nutrition. Some lands are barren for lack of this element in the soil. Typically deficiency symptoms of molybdenum in animals are poor hatchability, weak chicks, and poor feathering [6]. Delay puberty, reduced growth rate and reduced egg production are typical toxicity symptoms of molybdenum in animals [7]. Molybdenum also affects self purification processes of natural water and is valuable as a catalyst in the refining of petroleum [8]. High soil and water molybdenum levels can intensify nitrate toxicity.

Since the concentration of molybdenum in plants, water and soil is generally at parts per billion levels, therefore, sufficient sensitivity method is required for the determination of molybdenum. Many electrochemical procedures have been proposed for the determination of trace amount of molybdenum [9–14]. In the last ten years, several cathodic adsorptive stripping voltammetric (ADSV) procedures have been developed for the determination of molybdenum using different complexing agents such as oxine [9–11], chloranilic acid [12], methyl thymol blue [13,14], cupferron [15,32], α-benzoin oxime [16–18], 1,10-phenanthroline [19], dihydroxynaphthalene [20,29], *p*-cresol derivative [21], resorcinol derivative [22], cetyltrimethylammonium bromide [23], methyl orange [24], 8-hydroxyquinoline [25], α-benzoin oxime [26], pyrogallol red [27], and mandelic acid [31]. A critical assessment is given in Table 1. As shown in this table, a few papers have been reported are electrocatalytic based voltammetric method for molybdenum determination [10,13,18,20,21,24,27,31]. Tiron (1,2-dihydroxy-3,5-benzenedisulfonic acid) is used as a metal indicator for titration of iron ions, and as a colorimetric reagent for Fe, Al,

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Table 1
List of the adsorptive stripping voltammetric methods have been reported for determination of Mo(VI)

Method	Ligand	Catalyzed with	Linear dynamic range	Detection limit (less than 10-fold)	Interference elements	Reference
DPSV[a]	Oxine	–	0–300 μg l^{-1}	0.5 μg l^{-1}	Pb, Cd, Ti, W	[9]
LSV[b]	Oxine	Chlorate	10–5000 pM	1.7 pM	Sb, W, I^{-}	[10]
SWV[c]	Oxine	–	0–150 μg l^{-1}	0.1 μg l^{-1}	Fe, Pb, Cd, Cu	[11]
DPSV	Chloranilic acid	–	0–50 μg l^{-1}	0.07 μg l^{-1}	Not reported	[12]
DPSV	Methyl thymol blue	Chlorate	0.01–150 ng ml^{-1}	2 pg ml^{-1}	Zn, Pb, Cd, Cu	[13,14]
DPSV	Cupferron	–	0.1–20 ng ml^{-1}	0.06 ng ml^{-1}	Fe, Br^{-}	[15]
DPSV	α-Benzoin oxime[e]	–	0–0.2 μg l^{-1}	20 ng l^{-1}	–	[16,17]
LSV	α-Benzoin oxime	Chlorate	0.1–80 μM	20 nM	Fe, Pb, Cd, Cu, Zn	[18]
SWV	1,10-Phenanthroline	–	0–0.5 μM	0.6 nM	Fe, Cu, Zn, Pb, Cd	[19]
SWV	Dihydroxy naphthalene	Bromate	0.01–1.0 nM	6 pM	Fe, Cd, Cu, Zn	[20]
SWV	*p*-Cresol derivative	Chlorate	1–10 μg l^{-1}	62 nM	Not reported	[21]
LSW	Azo compounds	–	0.5–2.5 μM	0.15 μM	Fe, Pb, Cd, Cu, Zn	[22]
DPASV[d]	Cetyltrimethylammonium bromide	–	0.5–500 μg l^{-1}	0.04 μg l^{-1}	Cd, Cu, Fe, Pb	[23]
Polarography	Methyl orange	Hydrazine	1–80 ng ml^{-1}	0.3 ngml^{-1}	Not reported	[24]
SWV	8-Hydroxy quinoline	–	1–100 nM	0.15 nM	Fe	[25]
LSV	α-Benzoin oxime	–	2–100 nM	0.35 nM	Fe, Pb, Cd, Cu	[26]
DPSV	Pyrogallol red	Chlorate	0.8–80 ng ml^{-1}	0.1 ng ml^{-1}	Pb	[27]
SWV	Dihydroxy naphthalene	Bromate	0.01–1 nM	6 pM	Fe, Pb, Cd, Cu	[29]
DPSV	Mandelic acid	Chlorate	0–20 nM	1.4 pM	W, Cu, Sn, Cd, Sb, Fe	[31]
DPSV	Cupferron	–	0.2–50 nM	0.1 nM	Fe, Pb, Cd, Cu	[32]
DPSV	Tiron	Chlorate	0.01–21 ng ml^{-1}	0.006 ng ml^{-1}	$S_2O_3^{2-}$	The proposed method

[a] Differential pulse stripping voltammetry.
[b] Linear sweep voltammetry.
[c] Square wave voltammetry.
[d] Differential pulse anodic voltammetry.
[e] Organic solvents was used.

and Ti ions determination [28]. Despite the availability of a number of methods for the determination of trace of molybdenum, there is still a need for the development of a method that is superior in accuracy, sensitivity and speed at the levels that commonly encountered in different real samples.

The proposed method described in this paper is based on the adsorptive accumulation of the molybdenum–Tiron complex on a hanging mercury drop electrode (HMDE) and its catalytic effect on the electrochemical reduction of chlorate in an acidic medium is used for determination of low levels of molybdenum(VI) ions. The method is extremely sensitive, precise, and simple for determination of ultra trace level of molybdenum in real samples.

2. Experimental

2.1. Reagents

All chemicals were reagent grade chemicals and doubly distilled water was used in preparation of all solutions.

Stock solution (1000 μg ml^{-1}) of Mo(VI) was prepared by dissolving 0.2573 g of $Na_2MoO_4{\cdot}2H_2O$ in water in a 100-ml volumetric flasks.

Tiron solution, 0.0010 M, was prepared by dissolving 0.3322 g of the reagent in water in a 100-ml volumetric flask. Working solutions were prepared daily by dilution.

Chlorate stock solution, 1.0 M, was prepared each week by dissolving 10.8612 g of $NaClO_3$ in water in a 100-ml volumetric flask.

2.2. Apparatus

Experiments were conducted by using a PAR Model 384B polarographic analyzer equipped with a Model 303A electrode system (EG&G). A conventional three electrodes system, comprising a medium-sized hanging mercury drop electrode with a surface area of 1.8 mm^2, a platinum wire counter electrode and an Ag/AgCl (saturated KCl) reference electrode was used in all experiments. Solutions were deoxygenated with high-purity nitrogen for 4 min prior to each experiment.

2.3. Procedure

Ten millilitres of supporting electrolyte solution (0.02 M KNO_3 solution with the pH adjusted 2 with nitric acid), 0.10 M sodium chlorate and 3.0×10^{-6} M Tiron were added the electrochemical cell and the solution was purged with a nitrogen gas for at least 4 min. The adsorption preconcentration was carried out from the stirred solution for a period of 60 s at +0.15 V versus Ag/AgCl, at a fresh mercury drop. Afterward, a differential pulse voltammogram was recorded from +0.16 to −0.20 V, with a potential scan rate of 20 mV s^{-1}. The current for the blank solution (I_b) was measured. Then, the molybdenum standard solution (max., 210 ng Mo(VI)) was added to the cell while maintaining a nitrogen atmosphere over the solution, and a differential pulse voltammogram was recorded as before and the current I_s was measured. The calibration graph was constructed by plotting ΔI_p (i.e. $I_s - I_b$) versus Mo(VI) concentration. All data were obtained at room temperature (25 °C).

2.4. Analysis of real samples

Analyses of alloy samples were conducted by weighing about 0.4 g of steel BS XCCS, BS 2932, IRON 464, and IRON 467 (certified reference material, USA). The samples were transferred to four separate 100-ml Erlenmeyer flasks, then 25 ml of HNO_3 (2.0 M) were added and the mixtures were heated to ca. 50 °C for 3 h to dissolve the samples. Then the solutions were transferred into 50-ml volumetric flasks and diluted to the mark with double distilled water. Then, the alloy sample solutions were diluted 100 times with water and 1.0 ml of the each result solution was analyzed for molybdenum contents by the proposed method using standard addition method and by using of 3 μM Tiron.

For water analysis, three water samples given from Zayandeh Roud river (Isfahan city), well water and tap water (Isfahan city) were selected for analysis. Each sample was filtered using filter paper (Whatman No. 1). Then, 1.0 ml of nitric acid was added into 100 ml of the sample and heated up to dryness to destroy any surfactant. The residue was dissolved in 50 ml of water in a volumetric flask, and 0.5 ml of each sample was used for determination of molybdenum contents by standard addition method.

For the determination of molybdenum in plant and foodstuffs, about 1.0 g of the dried sample (cucumber, carrot, and tomato) was first ashed for 5–6 h at 500 °C in a crucible. After cooling, the ash was carefully moistened with 2 ml of 1:1 nitric acid and the mixture was heated on a hotplate to near dryness. The residue was dissolved in 1.0 mM nitric acid. The solution was filtered using filter paper (Whatman No. 1) and collected in a 25.0 ml volumetric flask. The result solution (1.0 ml) was transferred into the voltammetric cell and the concentrations of molybdenum were determined using standard addition method.

3. Results and discussion

Tiron is readily soluble in water and gives a colorless solution. Preliminary experiments for elucidation of the electrochemical activity of the Tiron–Mo(VI)–Chlorate system showed that the ligand can acts as a good complexing agent for accumulation of Mo(VI) ions at a HMDE. Different supporting electrolytes containing Briton–Robinson buffer, phosphate buffer, glycine buffer, and sodium nitrate solution were tested to ensure a sufficient sensitivity and a good peak shape. The results showed that the peak current of 3.0 ng ml^{-1} Mo(VI) is higher for 0.02 M $NaNO_3$ adjusted to pH 2 with nitric acid. This may be due to the fact that the phosphate presents in the Briton–Robinson and phosphate buffer interact with molybdenum to produce molybdophosphate [30], therefore, decreases the peak current of the molybdenum. In addition, in glycine buffer, glycine or chloride ions interact with Mo(VI) and cause decreasing the peak current. Fig. 1 shows the adsorptive stripping differential pulse polarograms for different combination of Mo(VI), Tiron and ClO_3^- in 0.02 M $NaNO_3$ solution at pH 2, that were recorded in the potential range of +0.16 to −0.20 V versus Ag/AgCl reference electrode. For a solution containing a mixture of Mo(VI) and Tiron in the supporting electrolyte, no current peak was observed. However, in the presence of chlorate, the system gave a catalytic current peak at approximately 0.0 V. This current increased linearly with increasing molybdenum(VI) concentration. Fig. 2 shows the voltammograms of Mo(VI)–Tiron–ClO_3^- system recorded without accumulation time (curve A) and with accumulation time of 5 s (curve B), 15 s (curve C) and 30 s (curve D). The results show that the peaks current increase with increasing accumulation time prior to the potential scan, indicating that the Mo(VI)–Tiron complex is readily adsorbed onto the HMDE. In addition, depression of the peak current upon addition of 10 μg ml^{-1} Triton X-100 into the solution, shows the adsorptive characteristic of the complex onto the HMDE. The overall results suggest a catalytic adsorptive mechanism, as described by Gao and Siow [10]. The adsorbed Mo(VI)–Tiron is

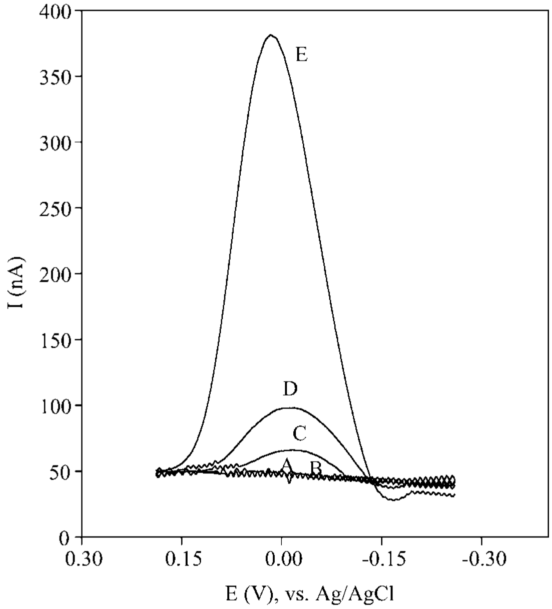

Fig. 1. Differential pulse voltammograms for a solution containing: (A) 3.0 × 10^{-6} M Tiron, 0.02 M $NaNO_3$ at pH 2 and 0.016 ng ml^{-1} Mo(VI); (B) 3.0 × 10^{-6} M Tiron, 0.02 M $NaNO_3$ at pH 2 and 0.10 M ClO_3^-; (C) A plus 0.10 M ClO_3^-; (D) C plus 0.032 ng ml^{-1} Mo(VI); and (E) C plus 0.83 ng ml^{-1} Mo(VI). Conditions: E_{ac} = 0.15 V; t_{ac} = 60 s; E_{pulse} = 0.100 V; and scan rate of 20 mV s^{-1}.

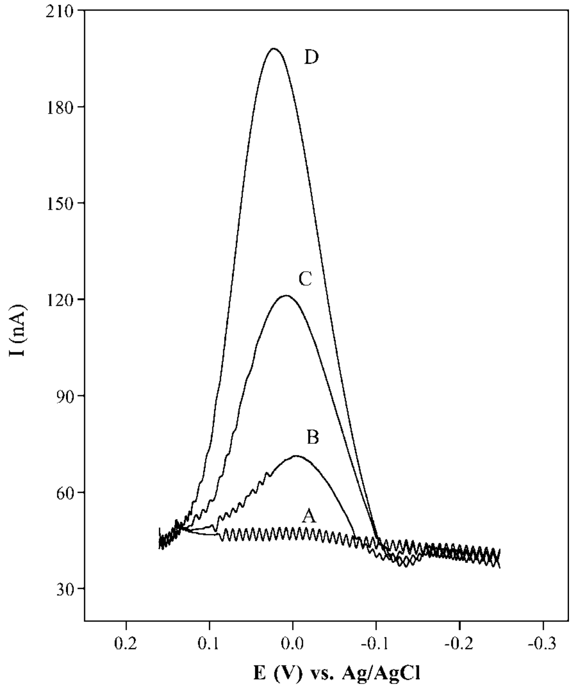

Fig. 2. Differential pulse voltammograms for a solution containing 0.60 ng ml^{-1} Mo(VI) plus 3.0 × 10^{-6} M Tiron and 0.10 M ClO_3^- in 0.02 M $NaNO_3$ at pH 2 with E_{ac} = +0.15 V, E_{pulse} = 0.10 V; and (A) t_{ac} = 0.00 s; (B) t_{ac} = 5.0 s; (C) t_{ac} = 15 s; and (D) t_{ac} = 30 s.

converted to Mo(V), and the oxidizing agent (chlorate) converts Mo(IV) to Mo(V). So that catalytic cycle is between Mo(IV) and Mo(V). Another possible mechanisms [11,31] that observed for systems with the peak potential are negative than −0.5 V versus Ag/AgCl reference electrode are that the catalytic cycle is between Mo(VI) and Mo(V) [31] and/or cycle between Mo(V) and Mo(III) [11].

The formation of the complex, their stability, and the catalytic effect of chlorate are strongly dependent upon the pH of the solution. As seen in Fig. 3, the ΔI_p values were affected by pH in the range of 1–4, and strongly decreased by increasing pH from 2 to 4. The cathodic wave almost disappeared at pH > 3.0. Such a behavior can be related to decreasing oxidation ability of chlorate in higher pH values as we observed in our previous work [27]. Decreasing the ΔI_p in acidic medium (pH < 2) were attributed to the decreasing ability of Tiron in complex formation with Mo(VI), due to protonation of the sulfonic group of the ligand. Therefore, a pH of 2 was selected for the study. In addition, various type of electrolyte such as KCl, KNO_3, and H_3PO_4 on the peak current and shape were studied. The results showed that KNO_3 is the best due to the fact that KCl shifts the oxidation potential of Hg (working electrode) near to zero, and minor overlap with the molybdenum peak. On the other hand, H_3PO_4 decreased the peak current and broad the peak due to phosphate interact with molybdenum to produce molybdophosphate [30]. Therefore, KNO_3 was select as a suitable electrolyte for this study.

Since Tiron is an essential component for the formation of the adsorptive complex, the Tiron concentration would be expected to strongly affect on the peak current. Therefore, the influence of Tiron concentration on the peak current was studied for the concentration range of 0–9.0 μM (Fig. 4). The results show that the peak current increases by increasing Tiron concentration up to 3.0 μM. At higher concentration of Tiron, the peak current tended to level off. Therefore, an optimum Tiron concentration of 3.0 μM was selected for further study.

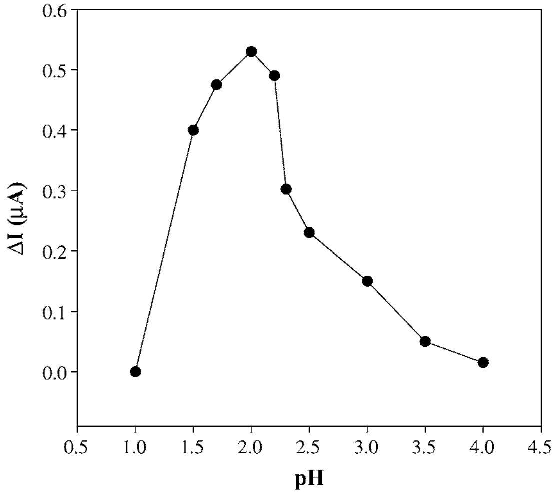

Fig. 3. Influence of pH on the peak current. Conditions: Mo(VI), 10.0 ng ml^{-1}; Tiron, 5.0 × 10^{-6} M; accumulation time, 60 s; accumulation potential, 0.05 V; scan rate, 10 mV s^{-1}; and pulse amplitude, 0.05 V.

Chlorate concentration also has profound effect on the peak current. Fig. 5 shows the influence of chlorate concentration on the peak current for 10.0 ng ml^{-1} molybdenum(VI). As the results shown, the peak current increases linearly with increasing chlorate concentration up to 0.10 M, and then tended to level off. Therefore, an optimum chlorate concentration of 0.10 M was selected for further study.

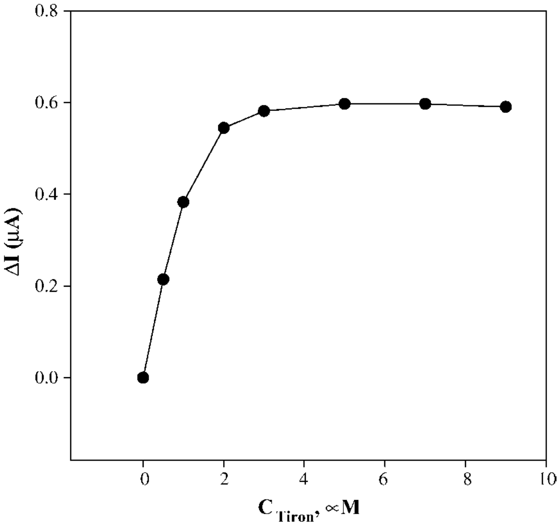

Fig. 4. Influence of Tiron concentration on the peak current of 10.0 ng ml^{-1} Mo(VI). Conditions: such as Fig. 3 with a pH 2.

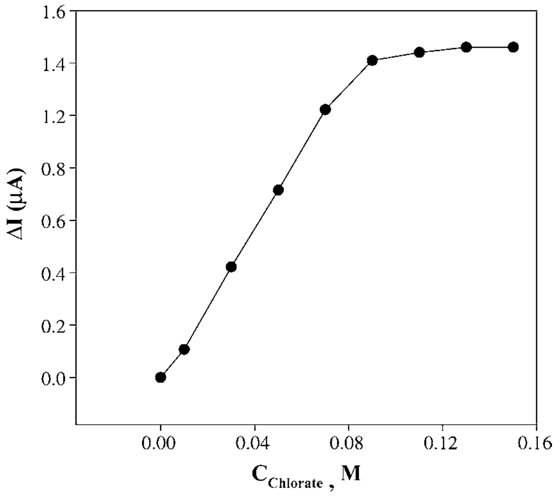

Fig. 5. Influence of chlorate concentration on the peak current of 10.0 ng ml^{-1} Mo(VI). Conditions: such as Fig. 4 with 3.0 × 10^{-6} M Tiron.

For the best sensitivity in determination of molybdenum the influence of instrumental parameters such as accumulation potential, accumulation time, pulse amplitude, and scan rate on the peak current were studied over the range of 0.18 to −0.50 V, 0–140 s, 0.02–0.12 V, and 5–40 mV s^{-1}, respectively. The experiments showed that increasing the accumulation potential from +0.15 to 0.00 V causes strongly decreasing the peak current and then the peak current tended to level off. This may be due to the fact that Mo(VI)–Tiron has negative charge therefore, by changing the potential of the electrode to negative values, the electrostatic interaction between charges of the electrode surface with Mo(VI)–Tiron in the solution was decreases. However, an accumulation potential of +0.15 V gives the best sensitivity and was selected for the study. In addition, the influence of accumulation time on the peak current was also studied. The results showed that at the first, the peak current increased linearly with accumulation time indicating that before adsorptive equilibrium is reached, whereas for the longer accumulation time the peak current tended to level off illustrating that adsorptive equilibrium was achieved. Therefore, a 60 s as an accumulation time was selected for further study.

The influences of scan rate and pulse amplitude on the peak current were studied with the other selected optimum conditions. Scan rate and pulse amplitude were varied from 5 to 40 mV s^{-1} and 20–120 mV, respectively. The results showed that by increasing scan rate up to 20 mV s^{-1} and pulse amplitude up to 100 mV the peak current increased, whereas higher scan rate and/or pulse amplitude cause decreasing the sensitivity. This is due to increasing the blank signal at higher rate relation to the sample signal. Very good sensitivity and precision was achieved with 0.15 V as an accumulation potential, 60 s as an accumulation time, 0.10 V as pulse amplitude and a 20 mV s^{-1} as scan rate.

4. Calibration graph and reproducibility

The calibration plot of ΔI_p versus molybdenum(VI) concentration at pH 2 and under the optimum conditions described above is a straight line in the range of 0.010–21.0 ng ml^{-1} Mo(VI) with $\Delta I_p = 0.060 + 0.485C$ ($r^2 = 0.9993$, n = 9) where ΔI_p is the net peak current in μA and C is the Mo(VI) concentration in ng ml^{-1}. A detection limit ($C_{LOD} = 3s_b/m$, where s_b is the standard deviation for 10 replicates determination of the blank signal and m is the slop of the calibration curve) of 0.006 ng ml^{-1} for Mo(VI) was obtained.

The repeatability of the response of the system to molybdenum was studied. The relative standard deviation for 10 replicate measurements for 0.6 and 10.0 ng ml^{-1} molybdenum(VI) was 1.3 and 0.9%, respectively.

5. Interference study

In the voltammetric determination of molybdenum(VI) with the catalytic-adsorptive systems, interference may be caused by the competitive adsorption of ions or their

Table 2
Interference study for determination of 10.0 ng ml^{-1} Mo(VI) under optimum conditions

Species	Tolerance limit ($\mathrm{mol_{ion}\,mol_{Mo(VI)}}^{-1}$) with Triton	
	3.0 μM	30.0 μM
Cd(II), Ca(II), Ba(II), Mg(II), Cr(III), Ga(II), Sr(II), Co(II), Ni(II), Al(III), F$^-$, SO_4^{2-}, Ag(I)	1000[a]	10000
Mn(II), Zn(II), CO_3^{2-}	900	5000[b]
Hg(II), In(III), La(III), Fe(II), V(III), Fe(III), CN$^-$, UO_2^{2+}	500	2000[c]
SCN$^-$, Cr(III), Ti(III)	80	100[d]
Br$^-$	50	100
I$^-$	30	60
$S_2O_3^{2-}$	2	8
SCN$^-$, Br$^-$, I$^-$, $S_2O_3^{2-}$	200[e]	

[a] Maximum concentration was tested.
[b] Not for carbonate.
[c] Not for cyanide.
[d] Not for thiocyanate.
[e] After treatment with 1.0 ml of 0.0012 MAg$^+$.

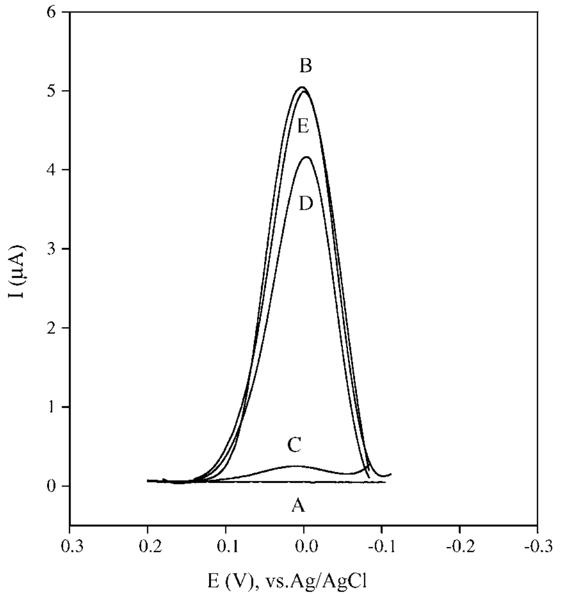

Fig. 6. Typical voltammograms showing the influence of $S_2O_3^{2-}$ as an interfering ion and elimination of the interference for determination of molybdenum in water sample: (A) 3.0 × 10^{-6} M Tiron, 0.10 M ClO_3^-, 0.02 M $NaNO_3$ at pH 2; (B) A plus 10.0 ng ml^{-1} Mo(VI); (C) B plus 2.330 μg ml^{-1} $S_2O_3^{2-}$; (D) C plus 0.5 ml of 0.0006 M $AgNO_3$ solution; (E) C plus 1.0 ml of 0.0006 M $AgNO_3$ solution.

Table 3
Determination of molybdenum in water samples

Sample	Mo(VI) added (ng ml^{-1})	Mo(VI) found (ng ml^{-1})[a]	Recovery (%)
River water	–	1.0±(0.1)	–
	1.0	2.1±(0.1)	101
	3.0	4.1±(0.1)	102
Tap water	–	1.06±(0.09)	–
	1.0	2.02±(0.08)	98
	3.0	4.03±(0.08)	99
Well water	–	6.5±(0.1)	–
	2.0	8.3±(0.1)	98
	4.0	10.40±(0.07)	99

[a] Number in the parenthesis show the S.D. for four replicates measurement.

complexes and competitive complexation or participation in the catalytic reaction. They may also be the result of the appearance of reduction peak next to the Mo(VI)–Tiron complex current peak. Owing to the extremely high sensitivity of the method, it is expected that the influence of another species on the determination of molybdenum will be minor. The effect of co-exiting ions was investigated under the optimum conditions and with 10.0 ng ml^{-1} Mo(VI). The tolerance limit was defined as the concentration which gave an error of <3.0% in the determination of 10.0 ng ml^{-1} of molybdenum(VI). The results showed that many potential interfering ions did not affect the peak current. The results are summarized in Table 2. All the other interfering ions decreased the peak current. We found that when higher concentration of Tiron is used (about 30 μM), the tolerance limit of many ions are increased as shown in Table 2. Therefore, for reducing the interferences from foreign ions in real sample analysis, it is recommended that using 30 μM Triton instead of 3.0 μM, to increase the tolerance limit. From the results, it is concluded that the method is free from many interferences of foreign ions, but some anions such as I^-, Br^-, and $S_2O_3^{2-}$ can interfere and decreased the peak current. It may be due to the fact that Mo(VI) forms complex with these anions. But the complexes are sufficiently labile to permit to eliminate their interference completely with addition of silver ions solution to the sample solution, as shown in Fig. 6. Ti(III) interfered at concentration greater than 80-fold (with the optimum conditions) and cause decreasing the peak current. This interference is due to the reduction of Mo(VI) by Ti(III) in acidic media [33] and complexation with Tiron. The influence of surfactants as an interfering species on the determination of molybdenum was also studied using 10 μg ml^{-1} of Triton X-100, and sodium dodecyle sulfate in the presence of 10.0 ng ml^{-1} Mo(VI). The results showed that the peak currents were depression to 45% of the first value upon addition of the surfactants.

Table 4
Determination of molybdenum in certified reference material samples

Alloy sample	Mo(VI) added (ng ml^{-1})	Mo(VI) found (ng ml^{-1})[a]	Recovery (%)	Molybdenum found (%)
BS XCCS	–	0.40 ± (0.01)	–	0.00501
	3	3.4 ± (0.1)	101	
	7	7.6 ± (0.1)	103	
BS 2932	–	2.25 ± (0.09)	–	0.0270
	3	5.5 ± (0.2)	104	
	7	9.8 ± (0.2)	106	
IRON 464	–	1.50 ± (0.07)	–	0.0282
	3	4.2 ± (0.2)	96	
	7	8.2 ± (0.2)	97	
IRON 467	–	1.18 ± (0.05)	–	0.0205
	3	4.1 ± (0.1)	97	
	7	8.0 ± (0.1)	98	

BS XCCS: C, 0.042%; Mg, 0.32%; P, 0.003%; S, 0.014%; Si, 0.010%; Cu, 0.018%; Ni, 0.017%; Cr, 0.014%; Mo, 0.0050%; V,<0.002%; Al, 0.069%; Sb, .0006%; As, 0.002%; Co, 0.003%; Pb, <0.001%; Nb, <0.002%; N, 0.0047%; 0.0047%; Sn, 0.006%; Ti, <0.001%; Zr, <0.002%. BS 2932: C, 0.208%; Mn, 1.2%; P, 0.008%; S, 0.020%; Si, 0.186%, Cu, 0.060%, Ni, 0.034%; Cr, 0.077%; Mo, 0.0260%; Al, 0.022%; Co, 0.004%, N0.0080%; O, 0.0013%; Sn, 0.005%; V, 0.001%. IRON 464: C, 0.54%; Mn, 1.32%; P, 0.017%; S, 0.021%; Si, 0.48%; Cu, 0.094%; Ni, 0.135%; Cr, 0.078%; Mo, 0.0290%; V, <0.29%; Al, 0.005%; Sb, .0006%; As, 0.018%; Co, 0.028%; Pb, <0.020%; Nb, <0.037%; N, 0.005%; O, 0.003%; Sn, 0.043%; Ti, <0.004%; W, 0.022%; Zr, <0.010%, B, 0.005%; Ta, 0.069%. IRON 467: C, 0.11%; Mn, 0.27%; P, 0.033%; S, 0.009%; Si, 0.26%; Cu, 0.067%; Ni, 0.088%; Cr, 0.036%; Mo, 0.0210%; V, <0.041%; Al, 0.005%; Sb, .0006%; W, 0.20%; As, 0.16%; Co, 0.074%; Pb, <0.0006%; Nb, <0.29%; N, 0.004%; O, 0.004%; Sn, 0.10%; Ti, <0.26%; Zr, <0.094%, B, 0.0002%; Ta, 0.23%.

[a] Molybdenum contents in the final sample solution. Numbers in the parenthesis show the S.D. for three replicates measurement.

Table 5
Determination of Mo(VI) in plant foodstuffs

Sample	Mo(VI) added ng ml^{-1}	Mo(VI) found[a] ng ml^{-1}	Recovery (%)	Mo(VI) found (%) (in dry sample)
Cucumber	–	1.46 ± (0.04)	–	0.0034
	2.0	3.45 ± (0.07)	99.7	–
	4.0	5.6 ± (0.2)	102.0	–
Tomato	–	2.21 ± (0.08)	–	0.0052
	2.0	4.25 ± (0.08)	103.8	–
	4.0	6.3 ± (0.1)	101.0	–
Carrot	–	1.48 ± (0.03)	–	0.0023
	1.0	2.45 ± (0.09)	98.8	–
	3.0	4.4 ± (0.1)	98.0	–

[a] Molybdenum contents in the final sample solution. Numbers in the parenthesis show the S.D. for three replicates measurement.

6. Analysis of real samples

To investigate the applicability of the proposed method for the voltammetric determination of molybdenum, the method was used in the determination of molybdenum in water samples (river water, tap water, and well water), certified steel references materials (BS XCCS, BS 2932, IRON 464, and IRON 467), and foodstuffs including cucumber, tomato, and carrot by standard addition method. The standard was added to the sample solution after preparation of sample and before analysis. The results are given in Tables 3–5. The method is capable to analyzed molybdenum contents in water and food samples. On the other hand, for steel samples, due to competitive reaction between molybdenum and iron ions to form complex with Tiron, we used excess amount of Tiron (10-fold of the optimum value) as described in experimental section. The results obtained by the proposed method reveal the capability of the method for determination of molybdenum in real samples without considerable error. Fig. 7 shows typical voltammograms for determination of molybdenum in steel sample.

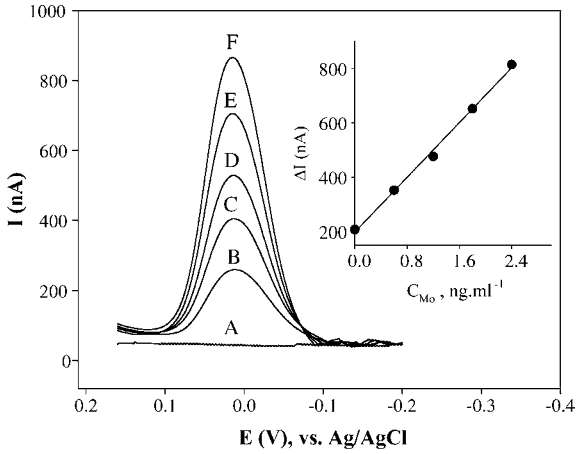

Fig. 7. Typical voltammograms for determination of molybdenum contents in a steel sample (IRON 467) by standard addition method; (A) 3.0×10^{-5} M Tiron, 0.10 M ClO_3^-, 0.02 M $NaNO_3$ at pH 2; (B) A plus 10.0 µl sample solution (containing 0.5778 g/100 ml) of the steel sample; (C) B plus 0.6 ng ml^{-1} Mo(VI); (D) B plus 1.2 ng ml^{-1} Mo(VI); (E) B plus 1.8 ng ml^{-1} Mo(VI); (F) B plus 2.4 ng ml^{-1} Mo(VI) with the optimum instrumental conditions.

7. Conclusion

A new method is developed using Tiron for determination of trace amount of molybdenum by means of adsorption cathodic stripping voltammetry. The proposed method is more sensitive, precise and selective than atomic absorption spectrometry and ICP-AES for molybdenum determination, because aluminum, iron, calcium, magnesium, and vanadium are the important elemental interferences in determination of molybdenum by atomic absorption spectrometry [34]. In addition, calcium, magnesium, and aluminum are the most serious interferences in determination of molybdenum by ICP-AES [34]. The sensitivity and selectivity of the proposed method is better than the other existing electrochemical methods [9–24]. The proposed method is suitable for determining low levels of molybdenum concentration in real samples such as water, food, and steel alloy samples. The disadvantage of the method is that if there is any bromide or iodide greater than 50-fold to Mo(VI) contents, it is needed to suppress the interference by adding silver nitrate solution.

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