Determination and validation method of molybdenum by adsorptive catalytic stripping voltammetry at lead film electrode

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Abstract: A new, selective, sensitive and accurate method for determination of molybdenum by adsorptive catalytic stripping voltammetry was described. The method is based on catalytic reduction of adsorbed Mo(VI)-ARS complex onto the lead film electrode in the presence of chlorate used as oxidizing agent. The instrumental and solution parameters affecting the peak current were optimized. The calibration graph is linear between 2.65-20.00 µg/L Mo(VI) and limit of detection is estimated as 0.79 µg/L. The proposed method was applied to drinking water samples with satisfactorily recovery results and the uncertainty calculation of the method was performed.

1. Introduction

Molybdenum is used the most in metallurgy area such as alloys, superalloys, stainless steel, structural steel, tool and high speed steels [1]. Besides molybdenum is essential element that acts as catalytically active along enzyme catalysis reactions. There are five Mo-dependent enzymes, four of them are for humans, one of them is for plants [2]. Molybdenum deficiency causes to functioning disorder of sulfite oxidase, affecting easily toxic reactions of sulfite in foods and tooth decay [1]. World Health Organization prefers to 2 µg/kg molybdenum intake daily for humans [3]. The molybdenum limits in drinking water released by The U.S. Environmental Protection Agency are 10 µg/L for children and 50 µg/L for adults and for irrigation water released by The United Nations Food and Agriculture Organization is 10 µg/L [4].

Due to simple, rapid, cheap and sensitive features of voltammetric techniques, the researchers have tended to voltammetric methods. The complexing agents are generally used for voltammetric determination of molybdenum to form stable Mo(VI)-organic ligand complexes and all methods are based on adsorption controlled electrode reaction. These ligands are oxine [5-7], methyl thymol blue [8,9], chloranilic acid [10-14], α-benzoin oxime [15-18], cupferron [19,20], dihydroxynaphtalene [21],

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p-cresol derivative [22], 1,10-phenanthroline [23], methyl orange [24], 8-hydroxyquinoline [25], pyrogallol red [26,27], mandelic acid [28], cetyltrimethylammonium bromide (CTAB) [29], tiron [30], morin [31], alizarin violet [32], alizarin red s [4,33,34] and azo compounds [35]. These methods were summarized in Table 1.

Mercury based methods have a great drawback owing to toxicity effect for environment and humans. Therefore there has been a tendency to the using of solid electrodes. The dependence on our best knowledge, there is no comprehensive study for voltammetric determination of molybdenum in terms of validation and using Mo-ARS-chlorate catalytic system. It is aimed to develop new, simple, sensitive and selective voltammetric determination method of molybdenum and also to calculate several validation parameters and uncertainty of the method.

Table 1. Summary of the voltammetric methods for determination of molybdenum

Method	Electrode	Ligand	Analytical Range	Limit of Detection	Reference
DPSV	HgFE	Oxine	0-300 µg/L	0.5 µg/L	5
LSSV	SMDE	Oxine	0.01-5 nM	0.0017 nM	6
SWSV	HMDE	Oxine	0-150 µg/L	0.1 µg/L	7
DPSV	HMDE	Methyl thymol blue	0.01-150 µg/L	2 ng/L	8
DPSV	HMDE	Methyl thymol blue	-	-	9
DPSV	HMDE	Chloranilic acid	0-50 µg/L	0.07 µg/L	10
DPSV	HgFE	Chloranilic acid	2-200 nM	83 pM	11,12
SWSV	BiFE	Chloranilic acid	5-50 µg/L	0.2 µg/L	13
DPSV	HMDE	Chloranilic acid	0-200 µg/L	0.4 µg/L	14
DPSV	HMDE	α-benzoin oxime	0-0.2 µg/L	20 ng/L	15
DPSV	HMDE	α-benzoin oxime	-	-	16
LSSV	CMCPE	α-benzoin oxime	0.1-80 µM	20 nM	17
LSSV	HMDE	α-benzoin oxime	2-100 nM	0.35 nM	18
DPSV	HMDE	Cupferron	0.1-20 µg/L	0.06 µg/L	19
DPSV	HMDE	Cupferron	0.2-50 nM	0.1 nM	20
SWSV	HMDE	Dihydroxynaphtalene	0.01-1 nM	6 pM	21
SWSV	SMDE	p-cresol derivative	1-10 µg/L	0.06 µg/L	22
SWSV	SMDE	1,10-phenanthroline	0-0.5 µM	0.6 nM	23
LSSV	DME	Methyl orange	1-80 µg/L	0.3 µg/L	24
SWSV	HgFE	8-hydroxyquinoline	1-100 nM	0.15 nM	25
DPSV	HMDE	Pyrogallol red	0.8-80 µg/L	0.1 µg/L	26
Centri-V	GCE	Pyrogallol red	20-100 nM	14 nM	27
DPSV	SMDE	Mandelic acid	0-20 nM	1.4 pM	28
DPSV	CMCPE	CTAB	0.5-500 µg/L	0.04 µg/L	29
DPSV	HMDE	Tiron	0.01-21 µg/L	0.006 µg/L	30
LSSV	CMCPE	Morin	0.8-60 nM 0.06-6 µM	0.4 nM	31
LSSV	CMCPE	Alizarin violet	0.006-10 µM	2 nM	32
DPSV	HMDE	Alizarin red s	0.15-5 µg/L	0.046 µg/L	4
SWSV	PbFE	Alizarin red s	2-50 nM	0.9 nM	33
DPSV	HMDE	Alizarin red s	1-25 µg/L	0.25 µg/L	34
LSSW	DME	Azo compounds	0.5-2.5 µM	0.15 µM	35
DPSV	PbFE	Alizarin red s	2.65-20 µg/L	0.79 µg/L (with low deposition time)	This study

LSSV: Linear sweep stripping voltammetry   DPSV: Differential pulse stripping voltammetry
SWSV: Square wave stripping voltammetry   Centri-V: Centri-voltammetry
DME: Dropping mercury electrode   SMDE: Static mercury drop electrode
HMDE: Hanging mercury drop electrode   HgFE: Mercury film electrode
BiFE: Bismuth film electrode   PbFE: Lead film electrode
GCE: Glassy carbon electrode   CMCPE: Chemically modified carbon paste electrode

2. Experimental

2.1. Chemicals and Apparatus

Molybdenum ICP standard (Merck, 1000 mg/L Mo(VI) from $(NH_4)_6Mo_7O_{24}$ in H_2O) was used for complexation and determination of molybdenum. The other chemicals were analytical reagent grade. Deionized water (18.2 MΩ) obtained from ELGA PureLab Flex 2 ultra pure water system was used for preparation of all solutions.

Voltammetric measurements were performed using Ivium Compactstat potentiostat/galvanostat connected to a BASi C3 cell stand. A three-electrode system was used, which are lead film electrode (PbFE) supported with glassy carbon electrode (GCE) as working electrode, Ag/AgCl/3 M NaCl as reference electrode and platinum wire electrode as auxiliary electrode.

An Isolab ultrasonic bath was used for the cleaning of GCE.

pH measurements were made using Hanna HI-121 model pH meter with combined pH electrode. pH calibration was performed using standard buffer solutions prior to the measurements.

2.2. Preparation of Lead Film Electrode (PbFE) and Measurement Procedure

Afterwards the cleaning of GCE with alumina slurry on the felt plate, the GCE was ultrasonicated in 1:1 ethanol:ultra pure water and ultra pure water for 3 minutes, respectively. The GCE was activated in 0.1 M pH 5 acetic acid/acetate buffer solution with waiting at +1.2 V for 120 s and cyclic scanning between -1 V and +1 V until obtaining a stable baseline.

Lead film formation was performed in 0.4 mM Pb^{2+} and 0.1 M pH 5 acetic acid/acetate buffer solution with waiting at -1.45 V for 30 s. Mo(VI)-ARS complex adsorption was made with electrodeposition at -0.56 V for 60 s and the adsorbed complex was stripped of from -0.56 V to -1 V.

2.2. Sample Preparation Procedure

Drinking water samples collected from Balıkesir and spiked with 1 and 3 µg/L molybdenum. All samples were diluted as 1:1 ratio and standard addition method was used for determination of molybdenum.

3. Results and discussion

3.1. Voltammetric Behaviour of Mo(VI)-ARS Complex

Differential pulse stripping voltammograms were recorded the absence and the presence of potassium chlorate to prove the catalytic effect. It can be seen from Figure 1, the peak current of Mo(VI)-ARS complex is folded 7 times.
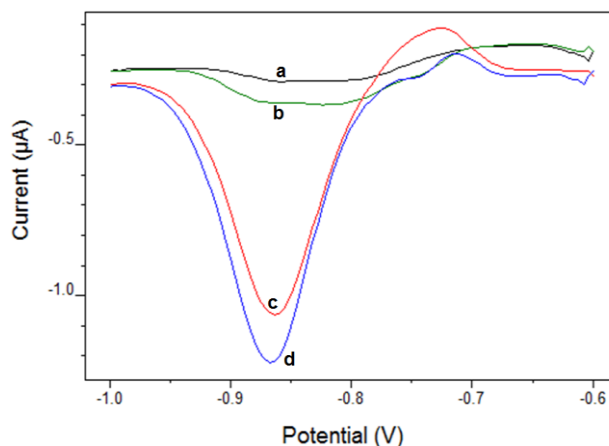

Figure 1. Stripping voltammograms of $7x10^{-7}$ M ARS (a), a + 10 µg/L Mo(VI) (b), b + 0.08 M KClO$_3$ (c) and c + 15 µg/L Mo(VI) (d) in the presence of 0.1 M acetic acid/acetate buffer solution (pH=5) and $4x10^{-4}$ M Pb^{2+}.

Moreover the cyclic voltammograms for various scan rates were recorded of the complex to prove the catalytic effect. The current function was plotted against to scan rates (Figure 2), the exponential decreasing depicts the catalytic system.
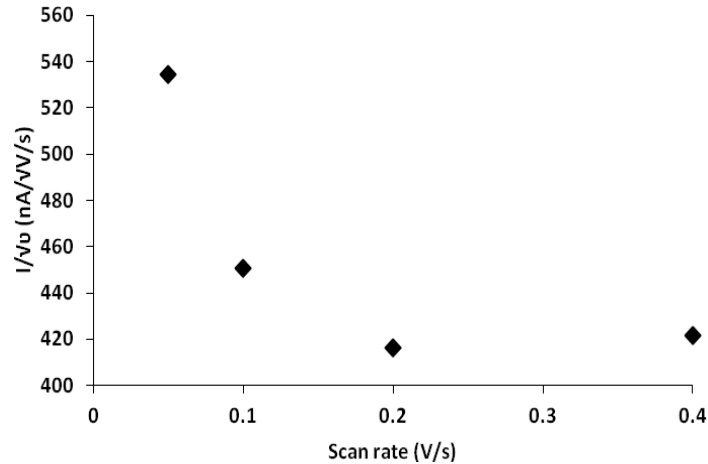

Figure 2. The current function ($I/\sqrt{\upsilon}$)-scan rate (υ) graph (4×10^{-4} M Pb^{2+}, 8×10^{-2} M $KClO_3$, 7×10^{-7} M ARS and 5 µg/L Mo(VI) in 0.1 M pH 5 acetic acid/acetate buffer solution. Scan rates: 50-400 mV/s)

As can be seen in Figure 3, Mo(VI) in the adsorbed Mo(VI)-ARS complex onto the electrode surface is reduced to Mo(V) by the driving force of potential. Afterwards Mo(V) oxidizes to Mo(VI) by chlorate then, Mo(VI)-ARS complex occurs again on the electrode surface. Therefore, the reduction process of Mo (VI) to Mo (V) called adsorptive catalytic procedure recreates.
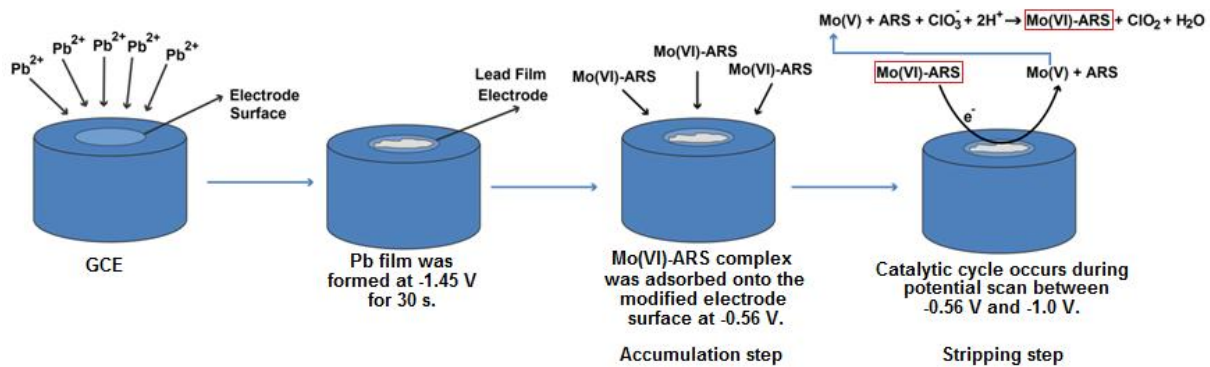

Figure 3. Schematic representation of the procedure and the electrode reactions

3.2. Optimization studies for molybdenum determination

Solution parameters which are pH, concentration of ARS, potassium chlorate and lead and instrumental parameters which are deposition potential and time were optimized.

pH effect on peak current was investigated in the range of 3.50 - 5.75 in acidic acid/acetate solutions. pH-peak current curve can be seen in Figure 4. The peak current has a maximum level at pH 5, then decreased. Therefore pH 5 was selected as optimum pH. Also the peak potential (mV)-pH graph (not shown) was plotted and the slope of the graph is 57.6 mV that is close to 59 mV. This situation shows the Mo(VI)-ARS electrode reaction realizes with equal proton and electron.
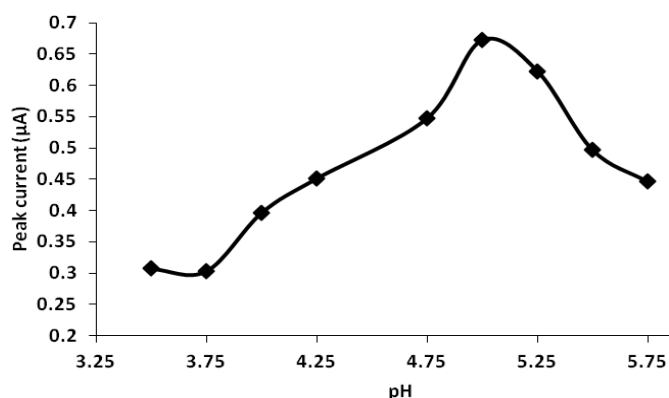
Figure 4. Peak current (μA)-pH curve (4×10^{-4} M Pb^{2+}, 8×10^{-2} M $KClO_3$, 7×10^{-7} M ARS and 2×10^{-8} M Mo(VI) in 0.1 M pH 3.50-5.75 acetic acid/acetate solutions)

The concentration of ARS is important for both formation of stable complex and the situation of competitive adsorption between free ARS and the ARS side of Mo(VI)-ARS complex. As can be seen the peak current (μA)-concentration of ARS (μM) curve (Figure 5), the peak current was increased up to 0.7 μM, then decreased dramatically. It is supposed that the decreasing of peak current resulted from competitive adsorption between free ARS and the ARS side of Mo(VI)-ARS complex. Consequently, 0.7 μM ARS was chosen as an optimal concentration.
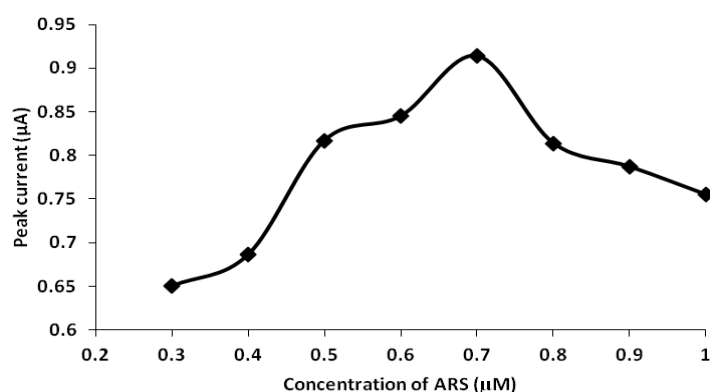

Figure 5. Peak current (μA)-ARS concentration (μM) curve (4×10^{-4} M Pb^{2+}, 8×10^{-2} M $KClO_3$ and 2×10^{-8} M Mo(VI) in 0.1 M pH 5 acetic acid/acetate buffer solution. ARS concentrations: 10^{-9}-10^{-6} M)

Additionally, potassium chlorate concentration for catalytic effect and lead concentration for electrode modification were optimized. The effect of potassium chlorate concentration was investigated between 0.008-0.300 M, the peak current was increased up to 0.250 M (not shown). However, the reason of sufficiency for determination of molybdenum in drinking water samples, 0.08 M potassium chlorate was randomly chosen as an optimal value. The lead concentration was evaluated between 1×10^{-6}-8×10^{-4} M, the peak current reached the maximum value with 4×10^{-4} M, then decreased (not shown). Optimum lead concentration was selected as 4×10^{-4} M.

The effect of deposition potential was examined between -525 mV and -750 mV. The peak current was almost same to -575 mV, then diminished (not shown). The optimum deposition potential was chosen as -560 mV. The effect of deposition time was examined between 0-400 s. It was monitored that the peak current increased up to 400 s (not shown). Similarly to potassium chlorate optimization study because of the sufficiency of the method to applicable to drinking water samples, 60 s was chosen as optimum deposition time.

3.3. Validation and application of the method

　　　Differential stripping voltammograms were taken under optimum conditions (Figure 6) and calibration graph was plotted. The analytical range is between 2.65 and 20.00 µg/L with a regression equation of $I_{pa}(\mu A) = 0.0358C_{Mo}$ (µg/L) + 0.6911 (*n*= 7, *r*= 0.999). The limit of detection ($3s_{y/x}$) and limit of quantification ($10s_{y/x}$) were 0.79 µg/L and 2.65 µg/L, respectively. The regression data analysis was given in Table 2.
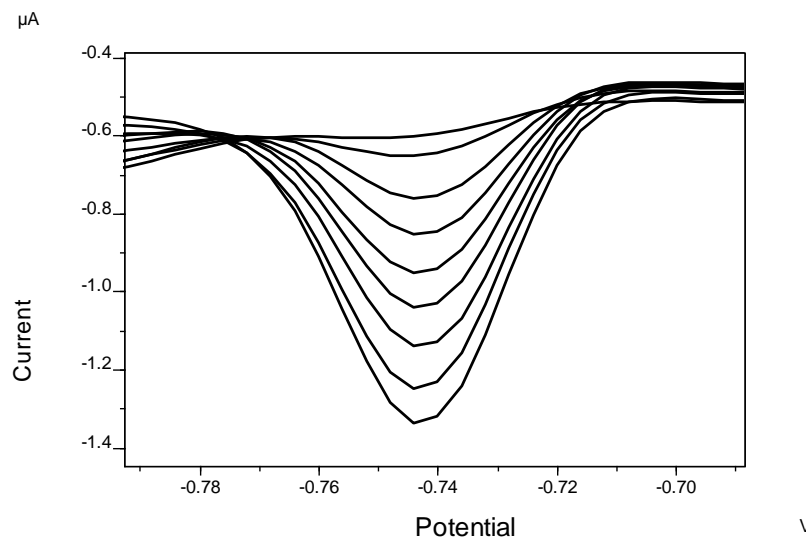

Figure 6. DPSV voltammograms with increasing Mo(VI) concentrations ($4x10^{-4}$ M Pb^{2+}, $8x10^{-2}$ M $KClO_3$ and $7x10^{-7}$ M ARS in 0.1 M acetic acid/acetate buffer solution at pH 5. Mo(VI) concentrations: 0, 0.5, 2, 5, 8, 11, 14, 17, 20 µg/L)

Table 2. The regression data and validation analysis of voltammetric determination of molybdenum

Parameter	Value
Slope (µA.L/µg)	0.0358
Intercept (µA)	0.6911
Standard deviation of slope (µA.L/µg)	0.0015
Standard deviation of intercept (µA)	0.0192
Standard error of estimate (µA)	0.0095
Coefficient of variation (R^2)	0.9986

　　　The interference effects of Co^{2+}, Cu^{2+}, Mg^{2+}, Cr^{3+}, Fe^{3+}, Sb^{3+}, Cd^{2+} and Triton X-100 were investigated with 2 µg/L molybdenum. 200 fold Co^{2+} and Triton X-100, 150 fold Cr^{3+}, 100 fold Cu^{2+} and Fe^{3+} have no effect on the peak current according to ±%5 change. On the other hand, Mg^{2+}, Sb^{3+} and Cd^{2+} are seriously interfere, but the interference effect of Mg^{2+} and Cu^{2+} were eliminated with addition of the EDTA into the solution.

　　　The real sample applications were given in Table 3. The recovery values of drinking water samples change between 98.3% and 110.7% and RSD values of these samples are between 3.86 and 14.86. Since the content of molybdenum in drinking water is very close to LOD, obtaining the high RSD value around the LOD is ordinary.

Table 3. Real sample applications in drinking water

Spiked Mo(VI) (µg/L)	Found Mo(VI) (µg/L)	Recovery (%)	RSD (%)
-	0.74 ± 0.11^a	-	14.86
1	1.71 ± 0.14^a	98.3	8.19
3	4.14 ± 0.16^b	110.7	3.86

[a]: the mean of six measurements, [b]: the mean of three measurements

Since variations of influence quantities may affect a measurement result in both random and systematic ways, the qualitative performance characteristics of the measurements includes both trueness and precision,

Measurement uncertainty of a result is formed from a combination of systematic error and random error [36]. From this point of view the following equation for calculation of expanded uncertainty can be written;

$$U\% = \sqrt{\left(\left|100-T\%\right| + 2xRSD\%\right)} \tag{1}$$

where, U is expanded uncertainty of the result obtained in the method, T is the trueness and RSD is the relative standard deviation. In this equation, the term $\left|100-T\%\right|$ represents the total systematic error of the method while the term 2xRSD% represents the total random error. Six independent drinking water samples spiked with 12 µg/L Mo(VI) were analysed by the proposed method. The mean of six measurements, T% and RSD were calculated as 11.915 µg/L, 99.289% and 2.172%, respectively. From the equation (1), U% was calculated as 2.248 and it was transformed to U which was 0.268. The result can be expressed as (11.915 ± 0.268) µg/L ($\rho = 0.025$).

4. Conclusions

A new, selective, sensitive and accurate method for voltammetric determination of molybdenum was described. As far as we know there is no study that consisting of comprehensive validation and uncertainty examinations. Accuracy of the method has been successfully proved in drinking water samples for 95% confidence level.

The sensitivity of the method can be terrifically improved with increasing of potassium chlorate concentration or deposition time. As the limit values of molybdenum in drinking waters (the least: 10 µg/L) are examined, the proposed method has good LOD value (0.79 µg/L). Because of this reason the higher concentrations of potassium chlorate or the higher deposition time were not used.

The proposed method is comparable to all voltammetric molybdenum determination methods used solid electrodes.

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