Scientific Paper

Trace Determination of Mo(VI) by Adsorptive Cathodic Stripping Voltammetry

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Abstract

A rapid differential pulse adsorptive cathodic stripping voltammetric method has been developed for trace determination of Mo(VI) using alizarin red S as a complexing agent. The base electrolyte used is 0.01M acetate buffer at pH 4.0 at which a well defined peak is observed with Ep at –0.76 V. The optimum conditions for the analysis of molybdenum include 3.0 μM alizarin red S, accumulation potential of –0.4 V (versus Ag:AgCl), accumulation period of 60 s, rest period of 15 s, scan rate of 20 mV/s and pulse amplitude of 30 mV. The peak current is proportional to the concentration of molybdenum over the concentration range of 1–25 ppb with a detection limit of 0.25 ppb. The method has been applied to the determination of Mo(VI) in water samples.

Key words: Adsorptive, stripping, differential pulse, voltammetry, molybdenum

Introduction

Molybdenum is a metal of great concern especially in marine ecosystem due to its role in enzymatic redox reaction and specific geochemical behavior.[1] Molybdenum and iron are the trace metals required for nitrogen fixation in seawater. Various analytical methods known for determination of molybdenum have been reviewed by Ivanov et al.[2] The most widely used methods include spectrophotometry,[3] spectrofluorimetry,[4] DPP,[5] flame AAS,[6] ETAAS[7] and ICPAES.[8] The spectrophotometric and spectrofluorimetric methods suffer for low sensitivity values while the AAS and ICPAES methods, though sensitive, need rigorous sample pretreatment.

Adsorptive stripping voltammetric methods for estimation of molybdenum using chloranilic acid,[9] oxine,[10] mandelic acid,[11] eriochrome blue black R,[12] tropolone,[13] diethyldithiocarbamate[14] and pyrogallol red[15] have been reported.

This paper suggests a new adsorptive stripping voltammetric method for trace determination of molybdenum using alizarin red S as a ligand.

Experimental

Apparatus: Differential Pulse Adsorptive Cathodic Stripping Voltammetric (DPAdCSV) studies were carried out using Metrohm Polarecord E-506 serie-03 working on 220 volts stabilized AC mains. To it was connected the Metrohm polarography stand E-505. The instrument was kept in an air-conditioned room maintained at 25±1 °C with humidity between 50 to 60%.

The electrode assembly consisted of the hanging mercury drop electrode (Kemula type) as the working electrode, Ag/AgCl (sat. KCl) electrode as reference electrode and a platinum electrode as an auxiliary electrode. Nitrogen gas was used for deaeration and micropipette (25μL) was used for addition of Mo(VI) solution. Mercury was purified by aeration method followed by distillation under reduced pressure in a mercury distillation unit.

Reagents and Solutions: All the chemicals used were of AR grade and the solutions were prepared in double distilled water. A stock solution of 100 ppb Mo(VI) was prepared by dissolving appropriate weight of ammonium molybdate and desired dilutions were made as per the requirements. Stock 0.1M solutions of ARS and sodium acetate were prepared by dissolving appropriate weight of AR grade reagents in double distilled water. pH of the solution was adjusted using dilute acetic acid solution.

General procedure: In each determination, 2.5 mL of 0.1M sodium acetate was taken, pH was adjusted to 4.0 using dilute acetic acid solution and volume made up to 25 mL. To it 25μL of 3.0 mM ARS solution was added that made the concentration of ligand 3.0 μM. 25 μL and 50 μl of 10 ppm solutions of Mo(VI) were added, the solution was deaerated with nitrogen for 10 min and voltmmogram was recorded. In all cases, blank recordings were performed and necessary corrections, if any, were made in the calculations. Typical voltammograms obtained for blank as well as for three different concentration of Mo(VI) are shown in figure 1.

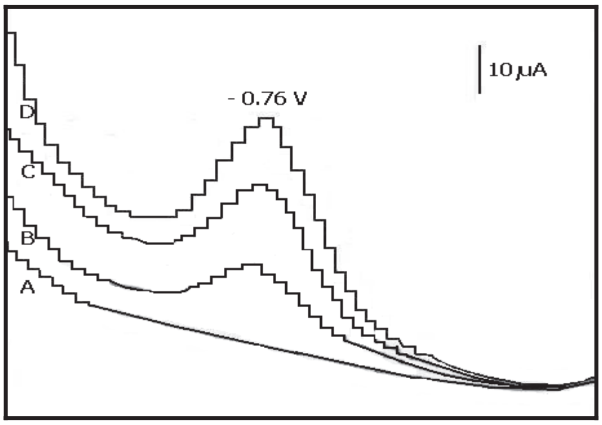

Figure1. Typical voltammograms of (A) 0.01M acetate buffer containing 3 µM ARS with (B) 10 ppb (C) 20 ppb and (D) 30 ppb Mo(VI).

Results and discussion

Concentration of sodium acetate was varied from 0.002 to 0.06 M in a total volume of 25 mL maintaining pH 4.0 and other conditions as above. Voltammograms were recorded for 10 ppb and 20 ppb of Mo(VI). Peak current and peak potential were found to be unaffected with change in concentration of sodium acetate but the peak symmetry was affected. Peak was found to be unsymmetrical below 0.01M sodium acetate. A symmetrical and reproducible peak was obtained for Mo(VI) in 0.01M sodium acetate, which was used for further studies. At concentrations of sodium acetate more than 0.01M, reproducibility of peak signal was not satisfactory.

The pH of 0.01 M sodium acetate solution was varied from 2.5 to 5.0 using acetic acid solution and voltammograms were recorded for 10 ppb and 20 ppb Mo(VI). The peak height was found to increase substantially upto pH 4.0 and then decreased. This is probably due to higher stability of the complex at pH 4.0. No peak was observed above pH 5.0. There was cathodic shift in peak potential with increase in pH (Figure 2). A sharp and symmetrical peak was observed at pH 4.0 with Ep at –0.76 V, which was selected for further studies.

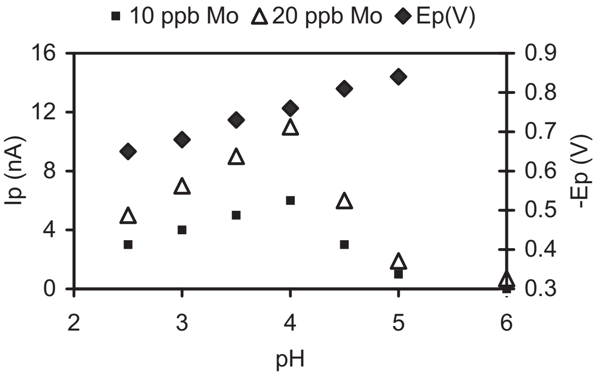

Figure 2. Effect of pH on peak current and peak potential.

To 25 mL 0.01 M sodium acetate solution containing 10 ppb Mo(VI) at pH 4.0, varying concentrations of alizarin red S were added in the range 0–5 µM. No peak was obtained in the absence of alizarin red S, but a distinct peak was observed after its addition. The peak current increased upto ligand concentration of 2 µM and then remained almost constant (Figure 3). Slight decrease in peak current at ligand concentration above 4.0 µM has been attributed to competitive adsorption of alizarin red S on HMDE. Same trend was observed for 20 ppb Mo(VI). Similar trend and reasoning have been reported for zirconium studies by J. N. Li et al[16] with alizarin red S ligand and by Safavi et al[17] for cobalt studies with methyl thymol blue ligand. In all further studies, 3.0 µM of alizarin red S was selected as optimum ligand concentration.

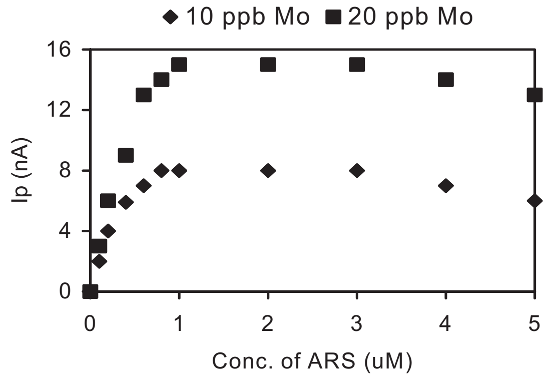

Figure 3. Effect of concentration of alizarin red S on peak current.

Accumulation of the complex on HMDE was carried out at different potentials from 0.0 to –0.6 V followed by cathodic stripping upto –0.9 V. The peak current was found to be maximum for accumulation potential of –0.4 V (Figure 4). This was selected for further studies.

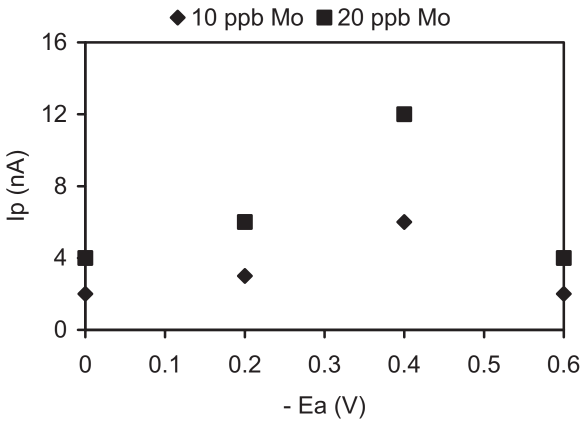

Figure 4. Effect of accumulation potential on peak current.

Effect of time on adsorptive accumulation of the complex was studied by varying time from 10 s to 180 s. The peak current was found to increase with accumulation time upto 60 s. An equilibrium is reached in about 60 s where Ip is maximum. For accumulation period above 75 s, the peak current decreased rapidly, probably due to disorption of the complex. Accumulation period of 60 sec was selected for further studies (Figure 5).

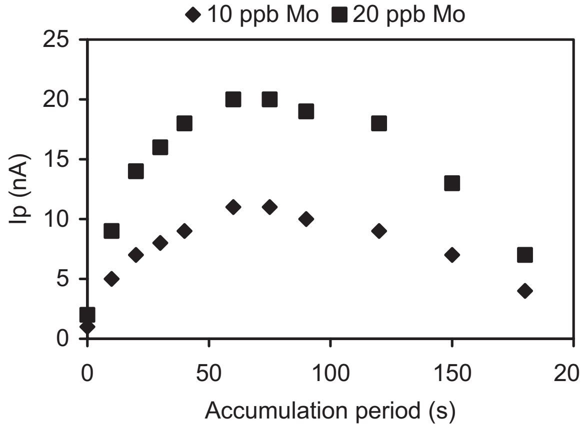

Figure 5. Effect of accumulation period on peak current.

With increase in surface area of the mercury drop from 0.89 mm^2 to 2.20 mm^2, a linear increase in peak current was observed. A drop of 1.4 mm^2 was maintained in all the studies. Increase in the scan rate from 10 mV/s to 50 mV/s and pulse amplitude from 10 mV to 100 mV showed a regular increase in the peak current. Scan rate of 20 mV/s and pulse amplitude of 30 mV were selected as the reproducibility was highly satisfactory at these values.

Effect of presence of various ions on the peak current was studied for 5 ppb Mo(VI). It was observed that Co(II), Mn(II), Cr(III), Fe(II), Fe(III), Pb(II), Cd(II) and Ni(II) did not interfere even when present 100 times in excess. Slight interference was observed from Cr(VI) and V(V). With increase in concentration of these ions, the peak current goes on decreasing. The peak current was found to reduce by about 20% when any of these ions were present 10 times in excess while about 60% reduction in peak current was observed when these ions were present 20 times in excess. This shows a fair degree of selectivity of the method.

Concentration of Mo(VI) was varied in the range 1–50 ppb and corresponding peak current was recorded. It was found that peak current increased linearly with concentration upto 25 ppb and then remained constant. Coefficient of correlation for 1–25 ppb range was found to be 0.9995. Equation of regression line was $y = 1.087x + 0.006$. Detection limit calculated as 3 times standard deviation of 1 ppb Mo(VI) was found to be 0.25 ppb for a series of 10 determinations.

Applications of the method

Spiked water samples: 100 mL of tap water was taken in each of the 3 beakers and was spiked with 25 μL of 5 ppm Mo(VI) solution which contained 0.125 μg of molybdenum. To it, 1 mL of conc. HNO_3 and 2 drops of $HClO_4$ were added and boiled to destroy organic matter and to oxidize molybdenum to hexavalent state. The solution was evaporated to about 10 ml. To it, 2.5 mL of 0.1 M sodium acetate solution was added and pH was adjusted to 4.0 using dil. NaOH solution. Volume was made up to 25 ml and voltammograms were recorded following above developed procedure. Similar studies were carried out by spiking 0.250 μg of molybdenum. Recovery results obtained by standard addition method were in good agreement with actual values (Table 1).

Table 1. Analysis of spiked water.

S.No.	Actual concentration (μg)	Observed concentration* (μg)
1	0.125	0.125 ± 0.002
2	0.250	0.249 ± 0.009

* (Avg±SD) of 3 observations.

Seawater sample: A synthetic seawater sample was prepared by adding salts in exactly same proportions as in natural seawater. 100 ml of the sample was treated with 0.5 mL $HClO_4$ to oxidize molybdenum to hexavalent state. Suitable aliquots were taken, pH was adjusted to 4.0, and voltammograms were recorded under optimum conditions. Concentration of molybdenum was determined using standard addition method and was found to be (481±10) μg/L (n=3) as against actual concentration of 500 μg/L. This result clearly indicates the applicability of the method in the analysis of molybdenum even in complex matrices.

Effluent samples: The method has been extended to determination of molybdenum in four effluent samples collected from MIDC industrial area of Hingna near Nagpur. 100 mL of each sample was filtered; organic matter was destroyed by treatment with 2 ml conc HNO_3 and 0.5 mL conc. $HClO_4$. It was further concentrated to about 10 mL, neutralized with NaOH solution and volume was made up to 50 mL. Suitable aliquots were taken and analyzed using standard addition method. The results obtained were compared with AAS method and were in good agreement with each other (Table 2).

Table 2. Analysis of effluent samples.

Sample	Concentration of molybdenum (ppm)	
	Present method*	AAS method
1	0.077 ± 0.008	0.08
2	0.085 ± 0.012	0.09
3	0.062 ± 0.004	0.06
4	0.067 ± 0.004	0.07

* (Avg±SD) of 4 observations.

Conclusions

A simple rapid method has been developed for the determination of Mo(VI) at trace level. The method has been found to be reproducible, reliable and accurate. The method is very convenient as 60 s of accumulation period is sufficient to achieve the detection limit of as low as 0.25 ppb. Standard deviation, relative mean deviation and coefficient of variation calculated at 5 ppb Mo(VI) were found to be 0.64, 5.77% and 6.60% respectively. These values clearly show high precision of the method. The method suffers from limitations like smaller linear concentration range (1–25 ppb) as compared to those of Sander[9] and Sun[10] in which ranges are 0.07–20 ppb and 0.1–150 ppb respectively. Application of the method gave reproducible and reliable results for various water samples analyzed for Mo(VI).

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Povzetek

Razvili smo hitro diferencialno pulzno adsorpcijsko inverzno voltametrično metodo za določanje sledov Mo(VI) z uporabo Alizarin rdeče S kot liganda. Kot elektrolit smo uporabili 0,01 M acetatni pufer (pH 4), v katerem je opazen dobro razvit vrh pri E_p -0,76 V. Optimalni pogoji za analizo molibdena so 3.0 μM alizarina, potencial med predkoncentracijo -0,4 V (napram Ag/AgCl), čas predkoncentracije 60 s, čakalni čas 15 s, hitrost spreminjanja napetosti 20 mV/s in amplituda pulza 30 mV. Tok pri vrhu je sorazmeren koncentraciji molibdena v območju 1-25 ppb z mejo detekcije 0,25 ppb. Razvito metodo smo uporabili za določevanje Mo(VI) v vzorcih vode.