# DETERMINATION OF TRACE AMOUNTS OF MOLYBDENUM BY ADSORPTIVE STRIPPING VOLTAMMETRY USING MORIN AS CHELATING AGENT

**Mihaela Buleandră***, **I.G. Tănase***, **M. Ionică**** and **M.M. Buleandră***

**abstract:** A highly selective and sensitive procedure for the determination of ultra-trace concentrations of molybdenum by adsorptive stripping voltammetry is presented. The method is based on adsorptive accumulation of the molybdenum - morin complex onto a hanging mercury drop electrode, followed by reduction of the adsorbed species by voltammetric scan using square wave modulation. Optimal analytical conditions were found to be a morin concentration of 5 μM, $pH = 2.3$ (Britton-Robinson buffer), and an adsorption potential at –0.25 V versus SCE. The peak current is proportional to the concentration of molybdenum over the range of $10^{-9} – 10^{-6}$ M with a detection limit of 0.1 nM for an accumulation time of 60 s. The method has been applied to the determination of molybdenum in seawater samples and results were in good agreement with atomic absorption spectrometry determinations.

## Introduction

Molybdenum is an essential trace element for all living organisms [1]. Since the concentrations of molybdenum in plants, water and soil are generally at parts per billion levels, selective and sensitive methods for the determination of molybdenum are required. According to literature data methods for determination of molybdenum are mainly spectrophotometric techniques [2,3], spectrofluorimetry [4], atomic absorption spectrometry [5,6], neutron activation analysis [7], plasma emission spectrometry [8], ion chromatography [9] and electroanalytical techniques [10-31].

Many electroanalytical procedures based on the catalytic reduction of some oxianions like nitrate [10,11], bromate [12] and chlorate [13], the adsorptive accumulation of molybdenum complexes onto a HMDE [14-20] or the combination of the adsorptive accumulation with a catalytic current system [21-31]] have been used in the determination of molybdenum in environmental and biological samples. The adsorptive accumulation of molybdenum complexes onto a HMDE has been used by means of chemical interactions of the substrate with specific ligands such as 8-hydroxyquinoline (detection limit of 4 nM for 120 s) [14], phosphate (4 nM for 120 s) [15], tropolone (0.3 nmol $L^{-1}$ for 60s) [16],

---

\*    University of Bucharest, Faculty of Chemistry, Department of Analytical Chemistry, Panduri 90-92, Bucharest-5, 76231, Romania
\*\*   Army Center for Medical Research, Toxicology Laboratory, Calea Floreasca 8, Bucharest-2, Romania

chloranilic acid (0.3 nmol $L^{-1}$) [17], Eriochrome Blue Black R (5.2 nmol $L^{-1}$ for 30s) [18], phenanthroline (0.6 nM for 20 min) [19], toluidine blue (0.1 nM for 240 s) [20].

In order to develop a new sensitive method for determination of molybdenum, the present work deals with a study of electrochemical behavior of the trace amounts of molybdenum in presence of 3,5,7,2',4'-pentahydroxy-flavone (morin) and determination of this element from seawater samples.

## Experimental

All reagents were of analytical grade and were used without further purification (Sigma). Solutions were prepared by dissolving the salt or concentrated solution in three-distilled water. The Mo(VI) solution was prepared by dissolving $(NH_4)_6Mo_7O_{24} \cdot 4H_2O$ in three-distilled water to give a $10^{-2}$ M stock solutions. Solutions of lower concentration were prepared daily by appropriate dilution of the stock solution. The 3,5,7,2',4'-pentahydroxy-flavone (morin) stock solution, $10^{-3}$ M, was prepared by dissolving the necessary amount of dye in three-distilled water. A 0.04 M stock Britton-Robinson buffer solution with respect to o-boric, o-phosphoric acid and acetic acid was prepared. From this solution of different pH values were prepared by additions of 0.2 M sodium hydroxide.

The adsorptive voltammetric measurements were performed using a Radiometer POL 150 polarographic analyzer coupled to a Radiometer MDE stand with a hanging mercury drop electrode (HMDE), a saturated calomel electrode (SCE) reference electrode and a platinum wire counter-electrode. The potential was scanned from +0 to -1.2 V for the screening experiments and from –0.25 to –1.00 V for the Mo(VI) calibration and sample determination, at a scan rate of 50 mV $s^{-1}$. The solutions were de-aerated with highly purified argon at the beginning of each experiment and a flow of argon was maintained over the solution during the experiment to prevent oxygen interference. All experiments were performed at room temperature. The data acquisition and the scan recordings were done by means of Trace Master 5.0 software.

A sea water sample was filtered to remove suspended particles. The sample solution (10 mL), containing 5 μM morin and Britton-Robinson buffer ($p$H = 2.3) was pipetted into the voltammetric cell. The stirrer was switched on and the solution was purged with argon gas for 5 min. The accumulation potential (–0.25 V) was applied to a fresh HMDE for 60 s. Following the accumulation period, the stirrer was stopped, and, after 10 s, the voltammogram was recorded by applying a negative-going square wave scan from –0.25 to –1.00 V. Each standard addition was 0.1 mL of Mo(VI) solution with a concentration of 10 mg $L^{-1}$.

An atomic absorption spectrometer SpectrAA 880 - Varian with a GTA 100 - Varian graphite furnace was used for the determination of molybdenum. The spectrometer was operated using a hollow cathode lamp for molybdenum ($\lambda$ = 313.3 nm, 0.5R nm spectral slit width). A volume of 20 μL of both reference and sample solutions were transferred into graphite tube through the autosampler. Argon 99.999% was used as protective and purge gas.

High purity standard reference solutions of Mo(VI) (from $(NH_4)_6Mo_7O_{24}$ $4H_2O$ in 0.5 M $NH_4OH$ AAS standard solutions) in 0.1% $HNO_3$ (v/v) were used to prepare the analytical solutions (0 – 200 μg/L) for calibration of the graphite furnace atomic absorption spectrometer. All measurements were made with three replicates and based on integrated absorbance.

## Results of discussions

### SWAdSV response of Mo(VI)-morin complex

Molybdenum (VI) forms a soluble complex with morin in aqueous acidic medium [32]. In aqueous acidic medium Mo(VI) additions to a solution containing morin give rise to the formation of a Mo(VI)-morin complex, which is susceptible to be adsorbed onto mercury drop electrode and is, therefore, able to be analytically determined using Square Wave Adsorptive Stripping Voltammetry (SWAdSV). The voltammogram Mo(VI) in presence of morin at $pH = 2.3$ has showed one cathodic peak at about -0.55 V. This peak is proportional with molybdenum concentration.

In order to obtain the coordination number (m) of the adsorbed complex on the electrode surface, the following equation can be used [33]:

$$\frac{1}{i_p} = \frac{1}{i_{p,max}} + \frac{1}{i_{p,max}\beta[L]^m} \, ,$$

where $i_p$ and $i_{p,max}$ are the current and the maximum current of the reduction peak of the complex $MoL_m$, [L] the concentration of the ligand and $\beta$ the stability constant of the complex. For a given concentration of molybdenum, additions of morin in the range of 0.1 - 8 μM give rise to a saturation curve, typical of adsorption phenomena. Fig. 1 shows that, for a Mo(VI) concentration of 1 nM, the peak current increases with the morin concentration up to 5 μM, and then becomes constant. Analyzing this curve by plotting $1/i$ as function of $1/[L]^m$ for $m = 1, 2, 3, \ldots$, it results a straight line for $m = 2$ which corresponding to the number of ligand molecules bound to the metal. This shows that the composition of the electroactive complex of Mo(VI) is 1:2, thus it can be written as $Mo(L)_2$.

### Optimization of experimental conditions

The formation of the complex, the stability and the potential of reduction are strongly dependent on the $pH$ value of the solution. The influence of pH on stripping current of molybdenum has been studied in the $pH$ range of 1.8 to 5.0 (Fig. 2). In order to keep constant the composition of the buffer, when studying the effect of pH, Britton-Robinson buffers were used. It is clear that higher current can be obtained when pH is in the range of 1.8 – 2.8. Therefore, $pH$ 2.3 identified as the optimum pH value, under these conditions the peak potential being -0.55 V. As illustrated in Fig. 2, the peak potential varied with $pH$ and was shifted in the negative direction by 57 mV/$pH$ unit.

The dependence of the reduction peak current of Mo(VI) complex on the accumulation potential in the range from 0 to –0.40 V was studied using an accumulation period of 60 s.

The optimum accumulation potential was –0.25 V. From the variation of the current peak has been observed that the peak height of the molybdenum-morin complex rapidly increases with the accumulation time during the first 100 s and then slows down. This is confirming that an adsorption process is involved.
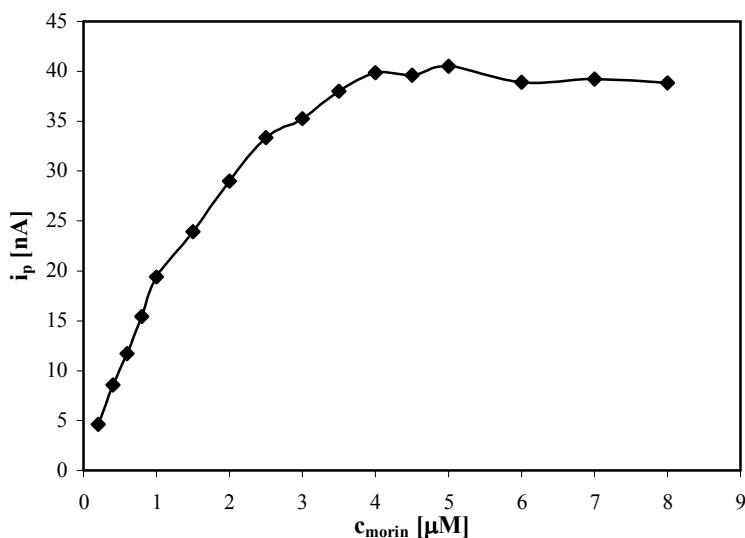


**Fig. 1:** *Effect of the morin concentration on the height of the reduction peak of complex in Britton-Robinson buffer (pH 2.3) for 1 nM Mo(VI), with an accumulation time of 60 s at -0.25 V;* scan rate = 50 mV s$^{-1}$.
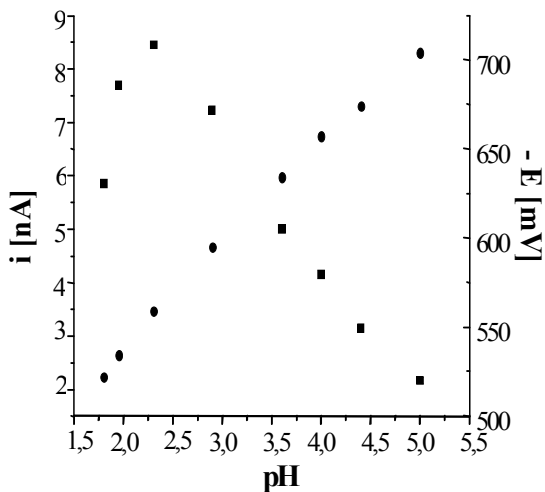


**Fig. 2:** *Variation of the SWV peak height (■) and SWV peak potential (●) as function of the pH in Britton-Robinson buffer using 1 nM Mo(VI) and 5 μM morin, with an accumulation time of 60 s at -0.25 V; scan rate = 50 mV s$^{-1}$.*

In order to examine the effect of different scanning wave-forms on the sensitivity and linear dynamic range for determining molybdenum, the optimum conditions for square-wave adsorptive stripping voltammetry (SWAdSV) were compared to differential pulse adsorptive voltammetry (DPAdSV). The peak heights were greater, and a better resolution of the peak was obtained using SWAdSV.

## Calibration graph, precision, detection limit and interferences

Under optimized conditions, a linear relationship between the reduction peak current of molybdenum complex and the concentration of Mo(VI) can be obtained in the range of $10^{-9}$ - $10^{-6}$ M. The detection limit for Mo(VI) was calculated as $kS_B/b$, where $S_B$ is the standard deviation of blank signal with current values measured at the same potential as for molybdenum-morin signal, and $b$ is the slope of the calibration plot, and $k$ is a constant equal to 3 as recommended by IUPAC [34]. The standard deviation of ten blank curves was 0.54 nA for an accumulation time of 60 s leading to detection limit of 0.1 nM.

Some trace elements can interfere with the determination of molybdenum adsorbing competitively onto HMDE or producing signals close to that of molybdenum. However, no interferences of common interfering ions such as iron and aluminum were caused by the 100-fold excess of these elements for molybdenum determination with tested reagent.

## Application to real samples

The proposed method was successfully applied to the determination of molybdenum in three seawater samples (Black Sea) without interference removal (Fig. 3). In order to eliminate matrix effects, the standard addition method was used. Molybdenum concentrations in the $\mu g\ L^{-1}$ range in seawater samples were found to be in good agreement with values determined by GF-AAS (Table 1).
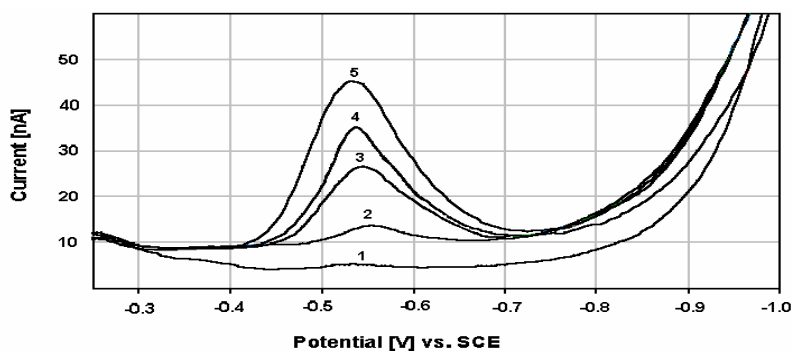


**Fig. 3:** *SWAdSV voltammogram for Mo(VI) determination in water sample no 2 by addition standard method;* 1: water sample; 2: + 5 $10^{-6}$ M morin; 3: first addition; 4: second addition; 5: third addition of Mo(VI)

**Table 1:** Results of molybdenum determination in sea water by AdSV method with morin and GF-AAS

| Sample | AdSV (µg/L) | GF AAS (µg/L) |
| --- | --- | --- |
| No. 1 | 129.33 ± 1.01 | 129.54 ± 0.4 |
| No. 2 | 125.95 ± 1.54 | 127.70 ± 1.6 |
| No. 3 | 125.20 ± 1.23 | 125.89 ± 0.8 |

## Conclusions

A method for determination of Mo(VI) with morin as an electroactive ligand by SWAdSV is developed and successfully applied in seawater samples. The proposed method can be a potential candidate for the practical use of molybdenum determination with high sensitivity, simplicity and speed.

## REFERENCES

1.  Chappel, W.R., Petersen, K.K. (1976), **Molybdenum in the Environment**, Marcel Dekker, New York.

2.  Li, Z., Pan, J., Jan, T. (2001) *Analyst* **126**, 1154.

3.  Prasada Rao, T., Reddy, M.L.P., Ramalingom Pillai, A. (1998) *Talanta* **46**, 769.

4.  Blanco, C.C., Campana A.G., Barrero, F.A., Ceba, M.R. (1993) *Anal. Chim. Acta* **283**, 213.

5.  Barrera, P.B., Calvo, C.P., de Juan, J.A.C. (1990) *Anal. Chim. Acta* **231**, 321,

6.  Okutani, T., Noshiro, K., Sakuragawa, A. (1998) *Anal. Sci*. **14**, 621.

7.  Hirai, S. (1999) *Curr. Adv. Mater. Proc*. **12**, 614.

8.  Marczenko, M. (1991) *Pure Appl. Chem*. **63**, 1629.

9.  Zolotov, Yu. A., Shpigun, O.A., Bubchikova, L.A. (1983) *Fresenius J. Anal. Chem.* **316**, 8.

10. Kolthoff, I.M., Hodara, I. (1963) *J. Electroanal. Chem*. **5**, 2.

11. Edmonds, T.E. (1980) *Anal. Chim. Acta* **116**, 323.

12. Barrado, E., Pardo, R., Batanero, P.S. (1998) *Anal. Lett*. **21**, 1221.

13. He, H.B., Siow, K.S, Chi, H., Gao, Z.Q., Hsieh, A.K. (1995) *Anal. Chim. Acta* **309**, 73.

14. van den Berg, C.M.G. (1985) *Anal. Chem*. **57**, 1532.

15. Wang, L., Zhang, X., Cheng, G. (1990) *Anal. Lett*. **23**, 2233.

16. Khan, S.H., van den Berg, C.M.G. (1989) *Mar. Chem*. **27**, 31.

17. Karakaplan, M., Gucer, S., Henze, G. (1992) *Fresenius J. Anal. Chem*. **342**, 186.

18. Willie, S.N., Berman, S.S., Page, J.A., van Loon, G.W. (1987) *Can. J. Chem*. **65**, 957.

19. Quentel, F. (1999) *Electroanalysis* **11**, 1355.

20. Zhao, Z., Pei, J., Zhang, X., Zhou X. (1990) *Talanta* **37**, 1007.

21. Yokoi, K., van den Berg, C.M.G. (1992) *Anal. Chim. Acta* **257**, 293.

22. Gao, Z., Siow, K.S. (1996) *Talanta* **43**, 719.

23. Farias, P.A.M., Ohara, A.K., Nobrega, A.W., Gold, J.S. (1994) *Electroanalysis* **9**, 333.

24. Wang, J., Serra, B., Ly, S.Y., Lu, J., Pingarron, J.M. (2000) *Talanta* **54**, 147.

25. Jiao, K., Jin, W., Metzer, H. (1992) *Anal. Chim. Acta* **260**, 35.

26. Fraga, I.C.S., Farias, P.A.M., Ohara, A.K. (2000) *Fresenius J. Anal. Chem*. **366**, 307.

27. Safavi, E., Shams, E. (1999) *Anal. Chim. Acta* **396**, 215.

28. Li, H., Smart, R.B. (1997) *J. Electroanal. Chem*. **429**, 169.

29. Tănase, I., Buleandră, M., Iorgulescu, E.E., Radu, G.L. (2001) *U.P.B. Sci. Bull., Series B* **63**(3), 375.

30. Tănase, I., Radu, G. L., Buleandra, M., Litescu, S. (1998) **Aplicatii ale tehnicilor electroanalitice in bioanaliza**, Protransilvania Publishing House, Bucuresti.

31. Tănase, I. (2000) **Tehnici şi metode electrometrice de analiză**, Ars Docendi, Bucureşti.

32. Tarek, M., Yaki, M., Abdel-Kader, A.K., Abdalla, M.M. (1991) *Fresenius J. Anal. Chem*. **339**, 197.

33. Wang, L., Ma, C., Zhang, X., Wang J. (1994) *Anal. Lett*. **27**, 1165.

34. IUPAC, (1978) *Spectrochim. Acta B* **33**, 242.