

## Trace Determination of Molybdenum by Adsorptive Cathodic Stripping Voltammetry

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Molybdenum is determined by adsorptive cathodic stripping voltammetry in 0.15 M nitric acid solution containing 15  $\mu\text{M}$  2',3,4',5,7-pentahydroxyflavone (morin) as a ligand. In this medium, molybdenum is preconcentrated on a hanging mercury drop electrode and stripped cathodically in square-wave voltammetry mode, with a peak potential of -350 mV vs. Ag/AgCl (saturated KCl). The effect of various parameters (ligand concentration, supporting electrolyte composition, accumulation potential and collection time) on the sensitivity and linear range of the calibration curve are discussed. With controlled accumulation for 1 min, the detection limit ( $3\sigma$ ) was 0.45  $\text{ng ml}^{-1}$  molybdenum and the calibration curve is linear up to 70  $\text{ng ml}^{-1}$ . The procedure is applied to the determination of molybdenum in real samples with satisfactory results.

**Keywords:** Adsorptive stripping voltammetry, Molybdenum, Morin

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### INTRODUCTION

Molybdenum is a biologically essential trace element. Its biochemical role is extremely important in the nitrogen metabolism of plants. Nevertheless, this element becomes harmful to ruminants at levels high enough to depress the absorption of copper by the liver [1]. Since the concentrations of molybdenum in plants, water and soil are generally at part per billion levels, it is necessary to find very sensitive methods for its determination.

The determination of molybdenum using electroanalytical methods has the advantages of accuracy, sensitivity, selectivity and simplicity. Many electroanalytical procedures including anodic, cathodic [2], adsorptive and catalytic adsorptive stripping voltammetry [3-14] have been reported for the determination of trace amounts of molybdenum.

Although there are many reports on the determination of

molybdenum based on voltammetric techniques with detection limits at the picomolar level, there is still a need for the development of a method that is superior in accuracy, precision and speed at the levels commonly encountered in different natural samples. The above mentioned methods surmounted these problems, however, some of these methods do not have sufficiently low detection limits and others (especially methods based on catalytic adsorptive stripping voltammetry) need a great deal of work to lower the value of their blank sample. Another drawback of some of these methods is that tungsten and iron, commonly found with molybdenum, interfere a great deal with the determination of molybdenum.

In this study, we present a new adsorptive cathodic stripping voltammetric procedure based on the adsorptive accumulation of molybdenum-morin complex into the surface of a hanging mercury drop electrode (HMDE), followed by the reduction of the adsorbed species by voltammetric scan using square wave modulation.

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## EXPERIMENTAL

### Reagents and Solutions

All reagents were of suprapur or proanalytical grade from Merck or Fluka companies. All solutions were prepared with triply distilled deionized water.

Stock solutions of 2',3,4',5,7-pentahydroxyflavone (morin) (Fluka) ( $1.2 \times 10^{-3}$  M) were prepared by dissolving 0.0338 g of morin in 100.0 ml slightly alkaline water. A 100 ppm solution of molybdenum(VI) was prepared by dissolving 0.0252 g of sodium molybdate dihydrate in water and diluting to 100.0 ml; more dilute solutions were prepared by diluting this solution with water. A stock solution of nitric acid (1 M) was prepared by diluting 6.9 ml of 65% nitric acid with water up to 100 ml in a volumetric flask.

### Apparatus

Voltammetric measurements were taken with a Metrohm 746/747 VA processor, with a three electrode system consisting of an HMDE as the working electrode, an Ag/AgCl (saturated KCl) reference electrode and a platinum counter electrode. A Mettler MP 225 pH meter with a combined glass electrode was used for pH measurements.

### Procedure

The general procedure used to obtain cathodic adsorptive stripping voltammograms was as follows. To approximately 8 ml of sample solution in a 10 ml volumetric flask, 1.5 ml nitric acid (1 M) and 150  $\mu$ l of morin solution ( $1 \times 10^{-3}$  M) were added. The volume was adjusted to 10 ml with distilled water. The solution was then transferred to a voltammetric cell. The stirrer was switched on and the solution was purged with nitrogen gas for 5 min. After forming a new HMDE, accumulation was affected for 60 s at -50 mV while stirring the solution. At the end of the accumulation time the stirrer was switched off. After 10 s had elapsed to allow the solution to become quiescent, the potential was scanned in a negative direction.

### Determination of Molybdenum in Foodstuff

A 3.0 g sample of dry foodstuff material was ashed for 7 hours at 500 °C in a crucible. After cooling, the ash was moistened with 2 ml 1:1 nitric acid and heated until dry. Nitric

acid (1 mM) was added to give a total volume of 8 ml and the mixture was boiled for 10 min. After cooling, the solution was filtered and diluted with distilled water to 10.0 ml in a volumetric flask. The resulting solution was analyzed using the general procedure.

In spiking the samples, known amounts of molybdenum(VI) were added to the solutions of foodstuff samples and the resulting solutions were analyzed using the proposed procedure.

## RESULTS AND DISCUSSIONS

### Preliminary Investigations

Morin (structure shown in Fig. 1) has been used as a chelating agent in the cathodic adsorptive stripping voltammetry of indium [15], antimony [16], copper [17], bismuth [17], and the simultaneous determination of copper, zinc and lead [18].

Figure 2 displays square wave voltammograms of the molybdenum-morin system between -100 to -700 mV (*vs.* Ag/AgCl), in the absence of molybdenum (curve a) and morin (curve b) after a 60 s accumulation at -300 mV. The voltammograms of the molybdenum-morin mixture after 0 s (curve c) and 60 s (curve d) accumulation at -300 mV are also shown. Comparison of the voltammograms shows that the height of the molybdenum reduction peak depends on the duration of the concentration stage and also on the presence or absence of morin, which reveals the adsorption nature of the currents.

### Effect of Operational Parameters

In order to find the optimum conditions with the highest sensitivity and larger linear dynamic range for the determination of Mo(VI), the influence of various parameters,

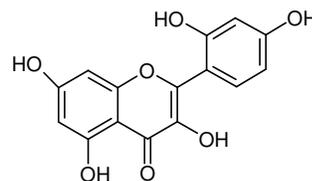
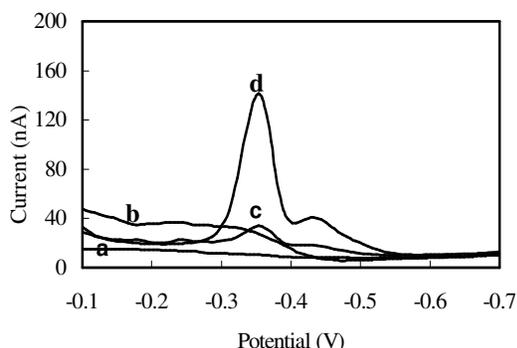


Fig. 1. Structural formula of morin.

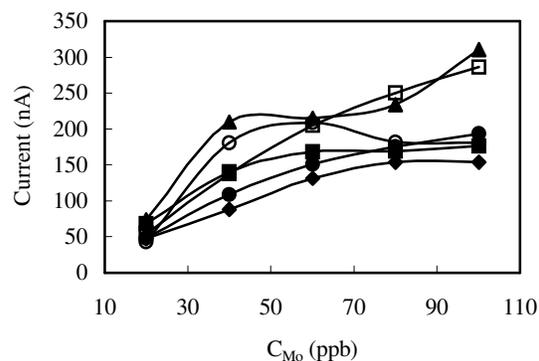


**Fig. 2.** Square wave voltammograms of 10  $\mu\text{M}$  morin (curve a), 40  $\text{ng ml}^{-1}$  Mo (curve b), Mo(VI)-morin (curve d) after 60 s accumulation at -300 mV, and Mo(VI)-morin (curve c) without accumulation in 0.1 M nitric acid.

including acid concentration, accumulation potential, morin concentration and accumulation time, were studied. To be able to compare both sensitivity and linear dynamic range of the method under different experimental conditions, the adsorptive stripping peak currents of different concentrations of molybdenum were measured and a calibration graph was constructed for each of the experimental conditions.

Figure 3 shows the variation of adsorptive stripping peak currents with molybdenum concentration in the presence of different acid concentrations. It was found that by changing the acid concentration from 0.001 M to 0.05 M, the sensitivity of the method increased but the linear dynamic range decreased. By increasing the acid concentration up to 0.2 M, the sensitivity decreased and the linear dynamic range increased. The best results were obtained at an acid concentration of 0.15 M, which was selected for further studies.

Figure 4 shows the effect of accumulation potential on the sensitivity and linear dynamic range of the proposed method over the potential range of 0.20 to -0.50 V. As shown in Fig. 4, both the sensitivity and linear dynamic range increased with the decrease in potential, from 0.20 to -0.050 V. However, sensitivity and linear dynamic range decreased upon an increase potential from -0.05 to -0.5 V, probably due to complex reduction during the adsorption step. An accumulation potential of -0.05 V was used for the optimized



**Fig. 3.** Variation of adsorptive stripping peak current with change in molybdenum concentration after 60 s accumulation at -300 mV, in the presence of 10  $\mu\text{M}$  morin and different acid concentrations (M): (◆) 0.001, (■) 0.01, (▲) 0.05, (○) 0.1, (◻) 0.15, (●) 0.2.

analytical procedure.

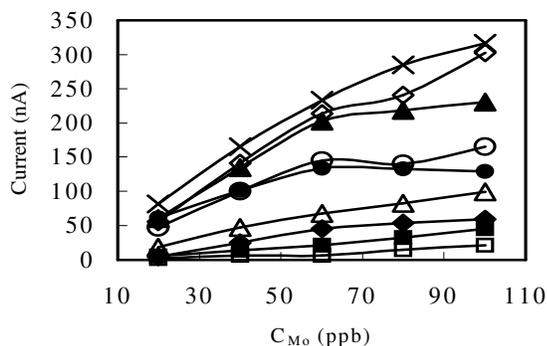
Figure 5 shows the effect of the variation of the morin concentration on the sensitivity and linear dynamic range of the method. Both the sensitivity and linear dynamic range increased with an increase in morin concentration (up to 15  $\mu\text{M}$  morin); at higher concentrations both the sensitivity and linear dynamic range decreased with an increase in morin concentration. A concentration of 15  $\mu\text{M}$  was selected as the optimum morin concentration.

In order to obtain the coordination number of the complex adsorbed on the surface of the electrode ( $m$ ), the following equation can be used [19]:

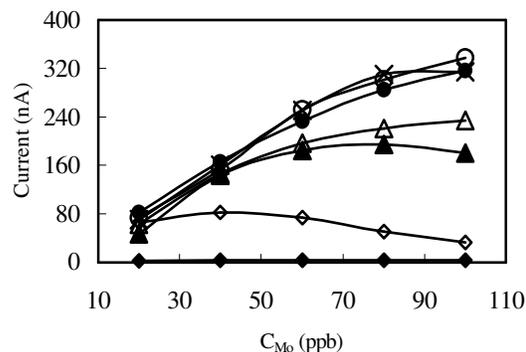
$$1/i_p = 1/i_{p \max} + 1/(i_{p \max} \beta c^m) \quad (1)$$

where  $i_p$  is the measured peak current,  $i_{p \max}$  is the peak current when all the metal ions form the complex and  $c$  is the concentration of the ligand. When  $m = 1$ , a straight line with  $r = 0.9998$  is obtained. This indicates that the composition of the electroactive complex on the surface of the mercury electrode is 1:1, and the complex of molybdenum with morin can be written as Mo(VI)-morin. According to these results the electrode processes can be summarized as follows:





**Fig. 4.** Effect of accumulation potential on the sensitivity and linear dynamic range in 0.15 M nitric acid solution. Conditions as in Fig. 3: (◆) 200, (○) 100, (▲) 0, (×) -50, (◇) -100, (●) -200, (△) -300, (■) -400, (□) -500 mV.



**Fig. 5.** Variation of adsorptive stripping peak current with change in molybdenum concentration after 60 s accumulation at -50 mV in 0.15 M nitric acid and different morin concentrations ( $\mu\text{M}$ ): (◆) 0, (◇) 3, (▲) 5, (△) 7, (●) 10, (○) 15, (×) 20.



The effect of accumulation time on the sensitivity and linear dynamic range of the proposed method was also studied. As shown in Fig. 6, with short accumulation times, the calibration curves were linear over the whole molybdenum concentration range studied, but the sensitivity of the method was low. Increasing the accumulation time leads to an increase in sensitivity and a decrease in the linear dynamic range. An accumulation time of 60 s was selected for further studies.

### Figures of Merit

A calibration graph for the determination of molybdenum was prepared according to the general procedure under the optimum conditions developed above from its square wave voltammograms with different molybdenum concentrations. A detection limit ( $3\sigma$ ) of  $0.45 \text{ ng ml}^{-1}$  of molybdenum was obtained [20]. The calibration plot was linear up to  $70 \text{ ng ml}^{-1}$  using the regression equation:  $i_p = 3.56c + 1.83$ , where  $i_p$  is the adsorptive stripping peak current in nA and  $c$  is the concentration in  $\text{ng ml}^{-1}$ .

Possible interference by other metals with the adsorptive stripping voltammetry of molybdenum was investigated by the addition of the interfering ion to a solution containing 20 ng

$\text{ml}^{-1}$  of molybdenum using the optimized conditions. The tolerance limit was defined as the concentration of interfering ion that gave an error of 5.0% or less in the determination of  $20.0 \text{ ng ml}^{-1}$  of molybdenum. The results are presented in Table 1.

### Determination of Molybdenum in Foodstuffs

The utility of the developed method was tested by determining molybdenum in some foodstuff samples. In order to test the accuracy of the proposed method, samples were spiked with a standard solution of molybdenum. The data obtained for samples spiked with molybdenum showed good recoveries (Table 2).

### CONCLUSION

The present study demonstrates that the adsorptive stripping analysis of molybdenum in the presence of morin is a good method for the determination of trace amounts of molybdenum. By studying the effect of the experimental variables on the adsorptive stripping peak current in the presence of different amounts of molybdenum, it was possible to select the best conditions for the determination of molybdenum with respect to both sensitivity and linear dynamic range.

In conclusion, the above system offers a practical potential

## Trace Determination of Molybdenum

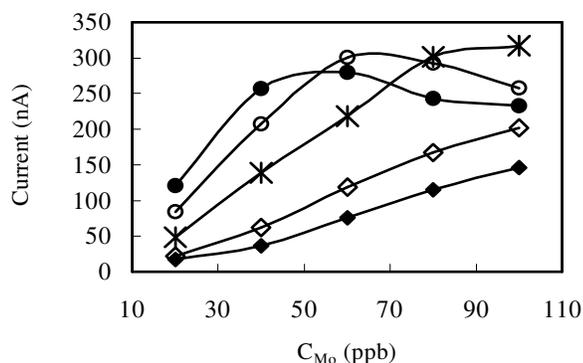
**Table 1.** Maximum Tolerable Concentration of Interfering Species<sup>a</sup>

Species	Tolerance limit (w/w)
Alkali and Alkaline earth metals, Cd <sup>2+</sup> , Tl <sup>+</sup> , Zn <sup>2+</sup> , Fe <sup>3+</sup> , Cr <sup>3+</sup> , Mn <sup>2+</sup> , Al <sup>3+</sup> , Ni <sup>2+</sup> , Co <sup>2+</sup> , Fe <sup>2+</sup> , CN <sup>-</sup> , ClO <sub>4</sub> <sup>-</sup> , Cl <sup>-</sup>	500 <sup>b</sup>
V <sup>4+</sup> , Hg <sup>2+</sup>	250
C <sub>2</sub> O <sub>4</sub> <sup>2-</sup>	25
WO <sub>4</sub> <sup>2-</sup> , CrO <sub>4</sub> <sup>2-</sup> , I <sup>-</sup> , Bi <sup>3+</sup> , Cu <sup>2+</sup> , In <sup>3+</sup>	10

<sup>a</sup>Conditions: optimum reagent concentration, 60 s accumulation time, -50 mV accumulation potential, 20.0 ng ml<sup>-1</sup> Mo(VI). <sup>b</sup>Maximum concentration of foreign species tested.

**Table 2.** Determination of Molybdenum in Foodstuff Samples

Sample	Mo found (ng ml <sup>-1</sup> )	Mo added (ng ml <sup>-1</sup> )	Total Mo found (ng ml <sup>-1</sup> )	Recovery of spiked Mo (%)
Tomato	7.7 ± 0.9	0.0	7.7 ± 0.9	–
Tomato	7.7 ± 0.9	10.0	18.3 ± 1.7	106.0
Cucumber	39.6 ± 3.3	0.0	39.6 ± 3.3	–
Cucumber	39.6 ± 3.3	20.0	58.9 ± 4.5	96.5
Tea	1.2 ± 0.4	0.0	1.2 ± 0.4	–
Tea	1.2 ± 0.4	20.0	20.6 ± 1.3	97.0



**Fig. 6.** Variation of adsorptive stripping peak current with molybdenum concentration in the presence of 15 μM morin in 0.015 M nitric acid solution after different accumulation times at -50 mV: (◆) 20, (◇) 30, (\*) 60, (○) 90, (●) 120 sec.

for the trace determination of molybdenum, especially with its advantages of acceptable sensitivity and linear dynamic range,

high selectivity, simplicity, and speed that were not present together in the previously reported system.

## ACKNOWLEDGMENT

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## REFERENCES

- [1] W.R. Chappel, K.K. Petersen (Eds.), Molybdenum in the Environment, Marcel Dekker, New York, 1976.
- [2] P. Lanza, D. Ferri, P.L. Buldini, *Analyst* 105 (1980) 379.
- [3] G.D. Christian, J.L. Vandenbalck, G.J. Patriarche, *Anal. Chim. Acta* 108 (1979) 149.
- [4] C.M.G. van den Berg, *Anal. Chem.* 57 (1985) 1532.
- [5] S.N. Willie, S.S. Berman, J.A. Page, G.W. van Loon, *Can. J. Chem.* 65 (1987) 957.

- [6] E. Barrado, R. Pardo, P.S. Batanero, *Anal. Lett.* 21 (1988) 1221.
- [7] L. Wang, X. Zhang, G. Cheng, *Anal. Lett.* 23 (1990) 2233.
- [8] K. Yokoi, C.M.G. van den Berg, *Anal. Chim. Acta* 257 (1992) 293.
- [9] K. Jiao, W. Jin, H. Metzner, *Anal. Chim. Acta* 260 (1992) 35.
- [10] J. Wang, J. Lu, Z. Taha, *Analyst* 117 (1992) 35.
- [11] P.A.M. Farias, A.K. Ohara, A.W. Nobrega, J.S. Gold, *Electroanalysis* 9 (1994) 333.
- [12] Z. Gao, K.S. Siow, *Talanta* 43 (1996) 719.
- [13] A. Safavi, E. Shams, *Anal. Chim. Acta* 396 (1999) 215.
- [14] A.M.M. Ali, M.A. Ghandour, S.A. El-Shatoury, S.M. Ahmed, *Electroanalysis* 12 (2000) 155.
- [15] P.A.M. Farias, C.M.L. Martins, A.K. Ohara, J.S. Gold, *Anal. Chim. Acta* 293 (1994) 29.
- [16] Ch. Zhou, Y. Lu, X. Li, Ch. Luo, Zh. Zhang, J. You, *Talanta* 46 (1998) 1531.
- [17] R. Hajian, E. Shams, *Anal. Chim. Acta* 491 (2003) 63.
- [18] E. Shams, A. Babaei, M. Soltaninezhad, *Anal. Chim. Acta* 501 (2004) 119.
- [19] X. Gao, *Handbook on the Physics on the Chemistry of Rare Earths*, Elsevier, Amsterdam, 1986, p. 163.
- [20] J.C. Miller, J.N. Miller, *Statistics for Analytical Chemistry*, 3<sup>rd</sup> ed., Ellis Horwood, New York, 1993.