



## SQUARE WAVE ADSORPTIVE STRIPPING VOLTAMMETRY OF MOLYBDENUM(VI) IN CONTINUOUS FLOW AT A WALL-JET MERCURY FILM ELECTRODE SENSOR

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**Summary**—An adsorptive stripping voltammetry method for the determination of traces of molybdenum(VI) in flowing solution at a wall-jet electrode sensor has been developed. After adsorption of a molybdenum complex on a wall-jet mercury film electrode, the complex is reduced by a square wave scan. More satisfactory results were obtained using 8-hydroxyquinoline as a complexing agent in nitrate medium than using Toluidine Blue in oxalic acid. Enhanced sensitivity was achieved by optimizing adsorption time and square wave parameter values. The detection limit of Mo(VI) was found to be at the nanomolar level. Interference of some other metallic species in the determination of nanomolar Mo(VI) was also investigated: Cu(II), Zn(II), Mn(II) do not interfere at 10  $\mu$ M, whereas 1  $\mu$ M FeEDTA<sup>-</sup> causes an increase in peak current. This iron interference was removed effectively with citric acid.

Molybdenum is a transition metal which is essential to all living organisms. Its biochemical role is extremely important in the nitrogen metabolism of plants. Nevertheless, excess of this element becomes harmful to ruminants since the absorption of copper by the liver is depressed.<sup>1</sup>

Very low concentrations of molybdenum can be found in plants, soils, sea water and other aqueous matrices; therefore, it is important from the analytical point of view to find sensitive methods for its determination. Electroanalytical procedures have been reported for the determination of traces of molybdenum at hanging/static mercury drop electrodes. Adsorptive stripping voltammetry (AdSV) has been shown to be useful for this purpose.<sup>2,3</sup> Molybdenum(VI) is accumulated by adsorption at the mercury electrode as a complex, which is electrochemically reduced by a potential scan; the reduction current is measured. A number of ligands have been tested at mercury drop electrodes, such as 8-hydroxyquinoline,<sup>4</sup> phosphate,<sup>5</sup> Toluidine Blue-oxalic acid,<sup>6</sup> galic acid.<sup>4</sup>

Calibration curves exhibit linearity down to 10<sup>-10</sup>M.<sup>6</sup> Recently, the coupling of catalytic and adsorption processes has led to a significant improvement in the selectivity and sensitivity of the stripping voltammetry of molybdenum at static mercury drop electrodes.<sup>7</sup>

The present paper describes a sensitive, continuous flow method for the determination of traces of molybdenum, using the combination of a wall-jet mercury film electrode (MFE) and square wave adsorptive stripping voltammetry (SWAdSV).

In the wall-jet electrode system a fine jet of fluid strikes the centre of a disc electrode perpendicularly and spreads out radially over the electrode surface.<sup>8</sup> The hydrodynamics is well-defined and leads to high sensitivity. Wall-jet cells exhibit ease of use and ease of maintenance. An important analytical advantage is to enable on-line detection, thus avoiding sampling and handling steps. The application of a square wave potential scan allows fast scan rates and leads to good rejection of background currents.<sup>9</sup>

Two different ligands were tested as chelating agents—Toluidine Blue in oxalic acid and 8-hydroxyquinoline in potassium nitrate solution.

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The dependences of peak current with adsorption time and with the square wave parameters were studied in order to optimize the technique.

## EXPERIMENTAL

### *Reagents and equipment*

Chemicals of Analar grade and triply distilled water were used in the preparation of all solutions. Mo(VI) solutions were obtained by serial dilution from 0.01M ammonium heptamolybdate (Merck) stock solutions. Supporting electrolytes and mercury plating solutions were prepared from stock solutions of 0.2M 8-hydroxyquinoline (Merck) in 0.45M HCl, 0.10M potassium nitrate (BDH), 0.01M mercury(II) nitrate (BDH), 0.40M oxalic acid (Merck) and 1.0 mM Toluidine Blue (Merck).

A glassy carbon disc working electrode, area 0.327 cm<sup>2</sup>, used as substrate for the mercury film, was polished regularly with 0.3 μm alumina in a slurry and then washed thoroughly with doubly distilled water. The wall-jet cell has been previously described;<sup>8</sup> it also includes a platinum tube counter electrode and a silver/silver chloride (saturated KCl) reference.

Solutions were pumped through the electrode assembly by a Pharmacia P-3 peristaltic pump; solution flow rates were calibrated volumetrically. Experiments were conducted at 22 ± 0.5°C.

Square wave adsorptive stripping voltammetry was carried out using a ICCMU interface rack (Imperial College Chemistry Microprocessor Unit) which includes: CPU-2 rack computer (Z 80), ADC-4 4 channel 12 bit ADC converter, DAC-2 2 channel 12 bit DAC outputs, ELEC-2 electrode controllers which can function as a potentiostat/voltage follower or galvanostat, PIO 32 channel digital input and output, TIMER 32 bit timer and MEM-1 board for holding EPROM version of programs. Suitable software was employed. The host computer was a IBM compatible machine Amstrad PC 1640.

### *Procedure*

Solutions were continuously purged with oxygen-free nitrogen prior to analysis and pumped to the cell by the peristaltic pump with a flow rate of 90 mm<sup>3</sup>/sec. A thin mercury film was plated *in situ* onto the wall-jet glassy carbon electrode from a solution of 5 × 10<sup>-5</sup>M Hg(NO<sub>3</sub>)<sub>2</sub> in the corresponding background electrolyte, at 0.0 V for 60 sec. Preliminary

voltammograms of 10<sup>-4</sup>M Mo(VI) solutions were recorded in order to select the deposition potential in both background electrolytes— -0.1 V in 0.048M oxalic acid/6 × 10<sup>-5</sup>M Toluidine Blue (pH 1.8) and -0.2 V in 0.1M KNO<sub>3</sub>/10<sup>-3</sup>M 8-hydroxyquinoline (pH 3.02). In the adsorptive stripping voltammetry method presented here, preconcentration of Mo(VI) was performed by adsorption of its complexes on the mercury film electrode at the potential values mentioned above; following this, a square wave scan was done in the negative direction to reduce the adsorbed electroactive molybdenum complexes. Reduction peak currents, *I<sub>p</sub>*, were recorded. For the nitrate/8-hydroxyquinoline system calibration curves were obtained by the standard addition method.

## RESULTS AND DISCUSSION

Experiments were conducted using Toluidine Blue complexing agent in oxalic acid electrolyte, and 8-hydroxyquinoline complexing agent in potassium nitrate electrolyte. Although the AdSV experiments could be conducted in the presence of oxygen, since the square wave reduction in the determination step suppressed its effects, it was found beneficial to deaerate solutions with oxygen-free nitrogen in order to reduce the background current and permit an increase of the sensitivity of the current scale. This oxygen removal was, nevertheless, not total, since inevitably, some air got into the flow system through the walls of plastic tubing; thus all results presented in the figures were obtained in the presence of a small amount of oxygen remaining in solutions.

First results were obtained using oxalic acid electrolyte and Toluidine Blue complexing agent as described by Zhao *et al.* at the mercury drop electrode (an example is given in Fig. 1a). Whereas at the mercury drop electrode two peaks corresponding to the reduction of Mo(VI) appear,<sup>6</sup> here there is only one at ~ -0.28 V *vs.* Ag/AgCl. Reduction peaks are ill-defined and peak currents were not reproducible. This is probably due to the magnitude of the required adsorption time, 540 sec, in order to achieve reasonable sensitivity.

The method was applied successfully in nitrate electrolyte with 8-hydroxyquinoline complexing agent. Adsorption accumulation was done at -0.2 V, followed by square wave reduction and led to a fairly broad but well-defined peak at ~ -0.55 V (Fig. 1b).

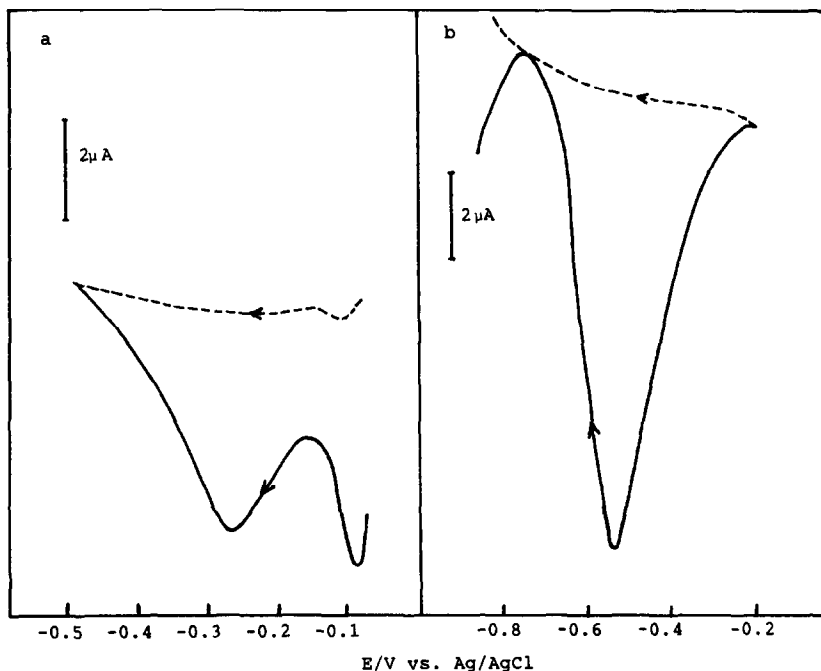


Fig. 1. Square wave voltammograms at the wall-jet MFE for SWAdSV of solutions containing Mo(VI). (a) 0.048M oxalic acid/ $6.0 \times 10^{-5}M$  Toluidine Blue complexant/ $5.0 \times 10^{-5}M$   $Hg(NO_3)_2$ ; [Mo(VI)] =  $1.0 \times 10^{-9}M$ ; pH 1.80. Adsorption time: 540 sec; square wave amplitude: 100 mV; staircase increment: 5 mV; frequency: 100 Hz. (b) 0.10M  $KNO_3$ / $1.0 \times 10^{-3}M$  8-hydroxyquinoline/ $5.0 \times 10^{-5}M$   $Hg(NO_3)_2$ ; pH 3.02; [Mo(VI)] =  $1.3 \times 10^{-9}M$ ; pH 3.02. Adsorption time: 360 sec; square wave amplitude: 25 mV; staircase increment: 5 mV; frequency: 100 Hz. Dotted lines show blank response in the same solutions, but in the absence of Mo(VI).

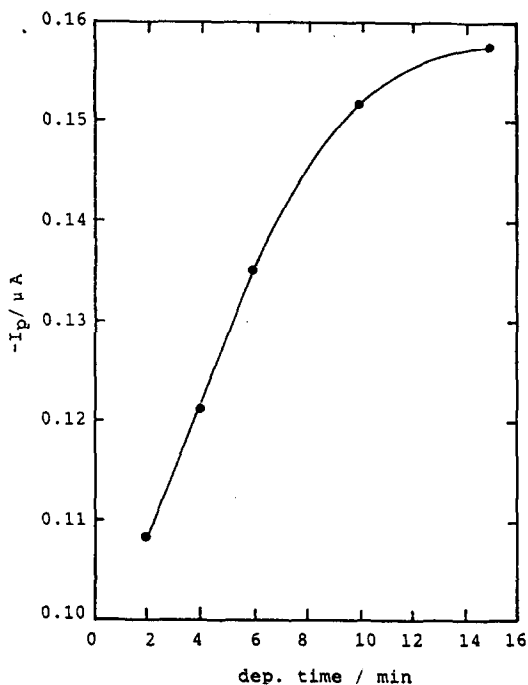


Fig. 2. The relationship between adsorption time and peak current for  $10^{-9}M$  Mo(VI). Conditions as in Fig. 1b.

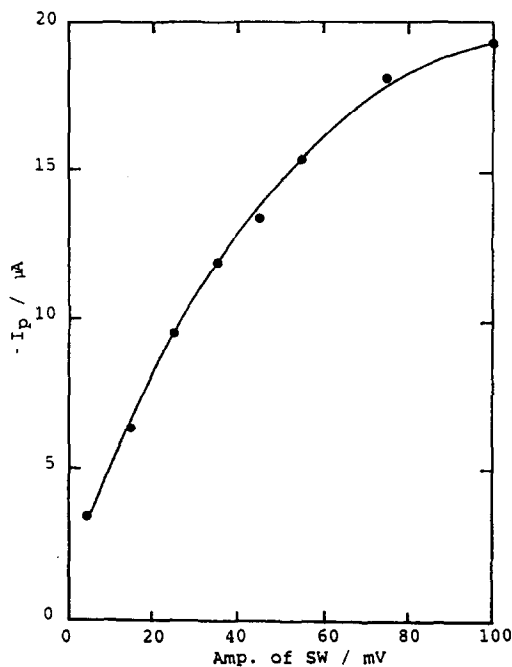


Fig. 3. The dependence of peak current on square wave amplitude. Adsorption time: 360 sec; staircase increment: 5 mV; period of square wave: 10 msec. Solution:  $10^{-7}M$  Mo(VI) in  $10^{-1}M$   $KNO_3$ / $10^{-3}M$  8-hydroxyquinoline and  $5 \times 10^{-5}M$   $Hg(NO_3)_2$ .

Comparison with the oxalic acid/Toluidine Blue system (such as by comparing Fig. 1a and b and taking the different concentrations and adsorption times into account) shows an increase in peak current by a factor of about five. Sensitivity could be further increased by extending the adsorption time but higher values are inconvenient, since the saturation region is reached (Fig. 2), 360 sec was the maximum possible adsorption time in order to remain in the linear part of the curve.

With a view to optimizing the experimental conditions, square wave parameters were adjusted. Although peak currents were greater for higher square wave amplitude values (Fig. 3), a sharper peak was found at  $-0.53$  V using a square wave amplitude of 25 mV. A staircase increment of 5 mV and a square wave period of 10 msec were selected.

Calibration plots of peak current *vs.* molybdenum(VI) concentration were obtained by the standard addition method (see Fig. 4). There is good linearity from  $10^{-9}$  to  $10^{-7}M$ ; above  $10^{-7}M$  deviation from linearity occurred owing to saturation of the mercury film electrode.

The detection limit was estimated with five blank solutions using 360 sec adsorption time. The blank was equivalent to  $4.5 \times 10^{-10}M$  Mo(VI) with a relative standard deviation of

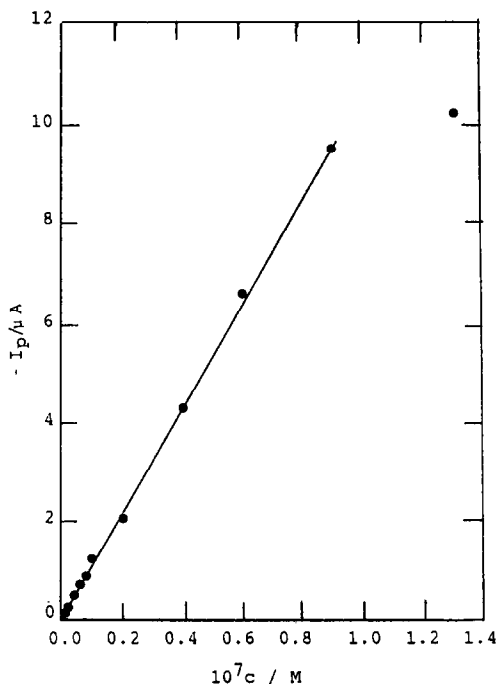


Fig. 4. Effect of Mo(VI) concentration on the peak height (at  $-545$  mV) after 360 sec accumulation. Other conditions as in Fig. 1b.

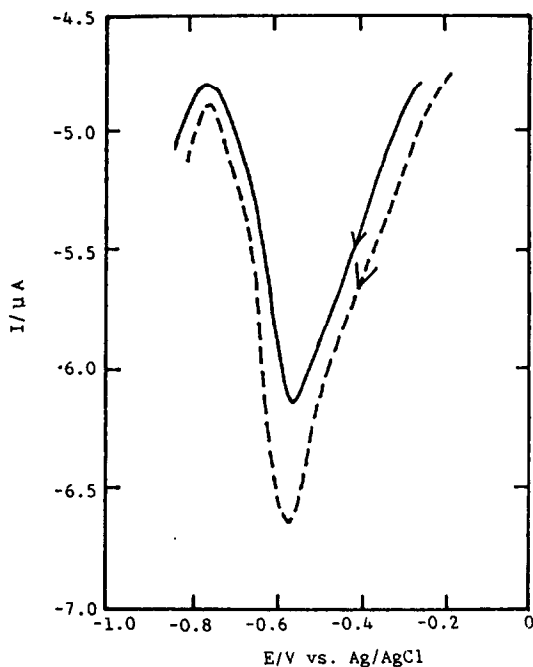


Fig. 5. SWAdSV of: (—)  $10^{-6}M$  Mo(VI); (—)  $10^{-6}M$  Mo(VI) and  $10^{-5}M$  {Cu(II)+Zn(II)+Mn(II)}; (---)  $10^{-6}M$  Mo(VI) and  $10^{-6}M$  FeEDTA<sup>-</sup> in nitrate/8-hydroxyquinoline (pH 3.02). Conditions as in Fig. 1b.

$\pm 11.8\%$ . The detection limit,  $3\sigma$ , where  $\sigma$  is the standard deviation of the blank, is therefore estimated as  $1.5 \times 10^{-10}M$ .

The method was developed for future application in plant nutrition studies. Some other species which could cause interference should be present in plant material. It was found that at pH 3.02 the presence of  $10^{-5}M$  Cu(II), Zn(II) and Mn(II) was tolerated, but  $10^{-6}M$  FeEDTA<sup>-</sup> interferes and leads to an increase in peak current, as illustrated in Fig. 5. This is caused by the reduction of the iron complex at similar potential values.<sup>10</sup> Experiments carried out after addition of 0.1M citric acid led to suppression of the FeEDTA<sup>-</sup> interference. The effect of citric acid in remaining interferences involving EDTA complexes has already been reported elsewhere.<sup>11</sup>

The proposed procedure for the determination of molybdenum using square wave adsorptive stripping voltammetry at an *in situ* mercury-plated wall-jet electrode provides a quick and easy method for the determination of traces of molybdenum in flowing aqueous solutions. It is highly sensitive and shows good reproducibility. The automation of the method for on-line detection is presently being undertaken with microprocessor-based equipment.

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