CHAPTER 3

ANODIC STRIPPING ANALYSIS OF MOLYBDENUM

Various methods of electrochemical microdetermination of
molybdenum were compared and the lower limit of determination was
found to be about 0.5 ppm by electrodeposition, 10 ppm by polaro-
graphic reduction in 0.1 M citric acid or citrate buffer containing
3 M NaCl, 0.1 ppm by polarographic catalytic current, and about the
same value as polarographic method by indirect coulometry with
electrogenerated Ti (III) (16,17). The polarographic behavior of
molybdenum (VI) in 1-12 M H_3PO_4 (18), H_3PO_4- KCl (19), H_2SO_4(20),
H_2SO_4- Na_2SO_4(21), 0.1 M EDTA -0.1 M NaOAc (22), HCl (23, 24, 25),
citric acid (16,17, 26), malic acid (27), tartaric acid (27),
trihydroxyglutaric acid (27,28), glyceric acid (28), mandelic
acid (28), lactic acid (28, 29·), and thioacetamide solution (30)
were investigated. In addition, polarographic catalytic currents
in solutions of molybdenum (VI)-potassium chlorate-oxalic acid were
reported (31).

Molybdenum was determined potentiometrically with sodium
sulfite solution (32) and amperometrically with thiooxine (33),
mercurous nitrate (34), hydrogen peroxide (35), K_3Fe (CN)$_6$ or $CuSO_4$
(36), and Pb (II) or complexon (III) (37).

The determination of Mo (VI) by ac polarography in 0.5 M
citric acid with no interference from Pb, Cd, Zn, and W (38) and by
oscillography in 0.5 M lactic acid without the interference from Co,
Ni, Cr, W, Re, and V (39) were possible. The oscillographic analysis

of $1 \mu g/cm^3$ of Mo (VI) in saturated tartaric acid solution (pH 1) using scan rate of 0.5 volt/second (40) and 2 volts/ second (41) were reported. Oscillopolarographic determination of Mo in niobium alloys in 0.75 M HNO_3 at scan rate of 0.25 volt/second (42) was also claimed. In addition, the oscillopolarographic behavior of Mo (VI) was studied in glyceric acid and in 0.04 M glyceric acid 0.05 M K_2SO_4 (pH 2.7) (43).

Better voltammetric behavior of molybdenum in H_2SO_4 medium was obtained by the DME/Mo electrode system than the DME/SCE system (44). The formation of absorbed surface films played a predominant role in the polarographic and voltammetric reduction of Mo (VI) in potassium hydrogen phthalate buffer at various pH (45). The lower limit of detection of Mo (VI) in 0.05 M KNO_3 was 3.00×10^{-7}M by inverse polarography (46). The microdetermination of molybdenum by anodic stripping analysis at constant current using the hanging mercury drop electrode yielded 5×10^{-6}M to 1×10^{-4}M with a 1.7% to 1% relative standard deviation(47). Moreover, $10^{-8} - 10^{-5}$M molybdenum was possible to be determined in the medium containing 3 M NaCl, 0.02 M acetic acid and 0.02 M sodium acetate (48).

In this chapter the conditions for anodic stripping analysis of Mo (VI) at a glassy carbon electrode are described. The optimum conditions for stripping analysis and the sensitivity of Mo (VI) in the electrolyte chosen are reported.

3.1 Evaluation of Electrolyte

Since the supporting electrolyte (near pH 5) containing
0.02 M acetic acid, 0.02 M sodium acetate and 3 M in NaCl was used
for the anodic stripping analysis of Mo (VI) at the hanging mercury
drop electrode (48), the anodic stripping analysis of Mo (VI) in
this study (using GCE) was tried in this supporting electrolyte.
A well-defined cathodic peak (-0.68 volt) and anodic peak (-0.25
volt) of 6.00×10^{-6} M molybdenum are shown. To obtain the optimum
conditions for the anodic stripping analysis of Mo (VI) at the GCE,
the effect of NaCl, acetic acid, and sodium acetate concentration
is studied.

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3.1.1 Variation of NaCl concentration in 0.02 M acetic acid
and 0.02 M acetate solution (buffer of pH 4.5)

The cathodic voltammogram of 6.00×10^{-6} M Mo (VI) in
0.02 M acetic acid, 0.02 M sodium acetate and various concentration
of NaCl (0.05, 0.10, 1.00, and 3.00 M), pH 4.5, shows a well-defined
peak at -0.73 V. Using 10 minutes for electrodeposition at -0.80 V,
the stripping voltammogram of 6.00×10^{-6} M molybdenum results a
well-defined anodic peak at ca. -0.25 V with the peak current affected
by NaCl concentration (see Table 3). The maximum anodic peak current
is obtained from the NaCl concentration of 0.10 M. The cathodic
and anodic voltammogram of molybdenum are shown in Figure 1.

Table 3 Anodic peak current of molybdenum in 0.02 M

acetic acid, 0.02 M sodium acetate and various

NaCl concentration; using 10 minutes for

electrodeposition of 6.00×10^{-6} M Mo (VI) at

the potential of -0.80 V.

Conc of NaCl (M)	$i_{p, a}^{a}$ (μa)
0.05	2.05 ± 0.21
0.10	2.96 ± 0.13
1.00	2.33 ± 0.16
3.00	0.84 ± 0.05

[a]
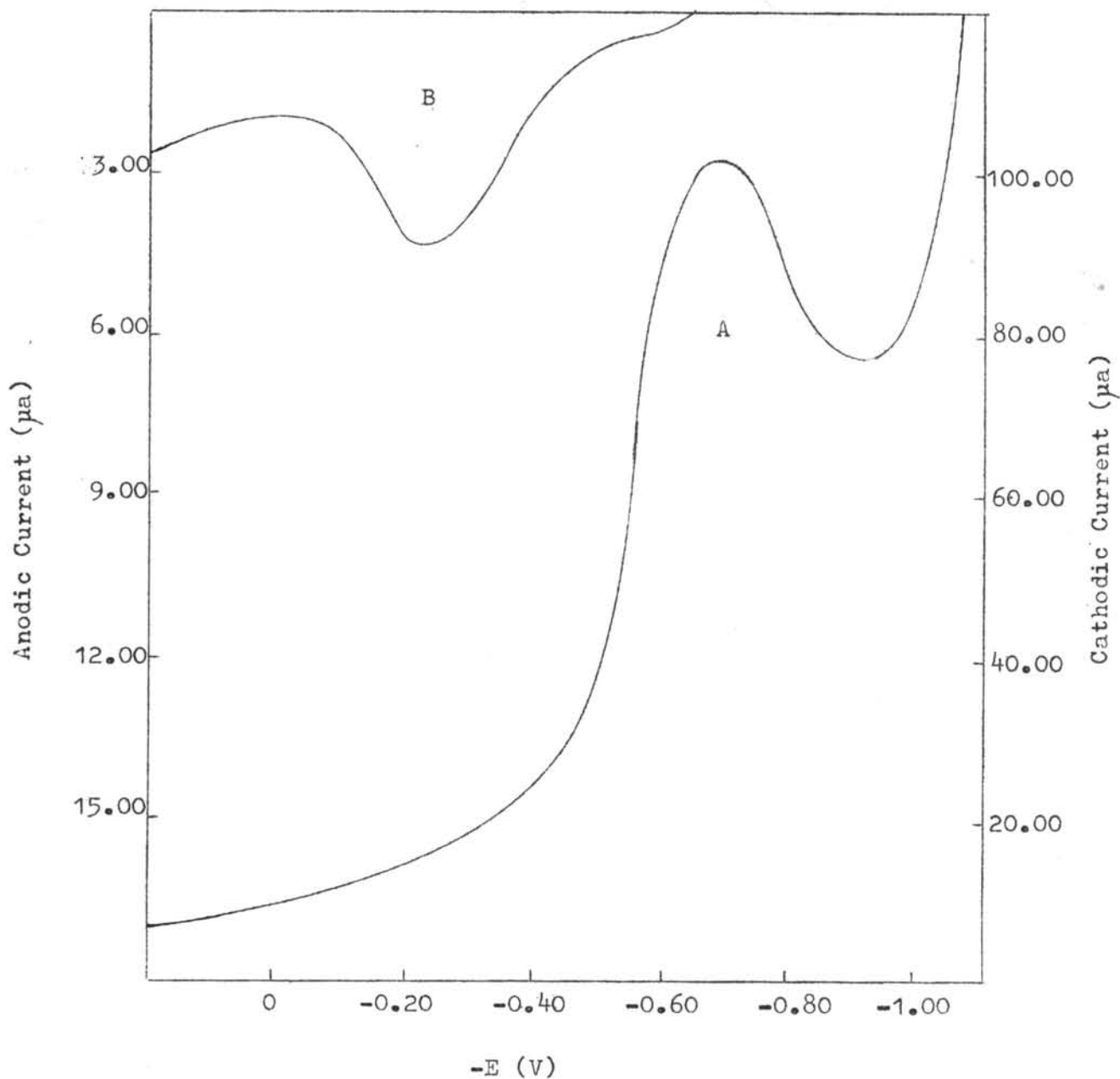average anodic peak current ± average deviation

of more than four trials.

Figure 1   Voltammograms of molybdenum in 0.02 M acetic acid-
0.02 M sodium acetate -0.1 M NaCl; A) is the cathodic
voltammogram of 1.00 X 10^{-3}M Mo (VI) and B) is the
anodic voltammogram of molybdenum after deposition
of 6.00 X 10^{-6}M Mo (VI) for 10 minutes.

3.1.2 Variation of NaCl concentration in 0.24 M acetic acid
and 0.56 M acetate solution (buffer of pH 5)

The results of anodic stripping voltammograms of
1.00×10^{-5}M Mo (VI) in 0.24 M acetic acid, 0.56 M acetate and
various NaCl concentrations are tabulated in Table 4. The anodic
stripping peak obtained is too small to measure the peak current
correctly. In addition, anodic peak potential is more negative as
the concentration of NaCl increases.

3.1.3 Using 3 M NaCl in 0.06 M acetic acid and 0.14 M acetate
solution (buffer of pH 5)

A cathodic peak of Mo (VI) in 3 M NaCl, 0.06 M acetic
acid and 0.14 M acetate is observed at the potential of -0.73 V.
The anodic stripping peak obtained from 10-minute electrodeposition
of Mo (VI) (2.00×10^{-3}M to 2.00×10^{-6}M) at -0.80 V occurs at the
potential of ca. -0.56 V. The anodic peak is very broad and the
charging current is quite high. Thus, a base line for this anodic
peak cannot be drawn and no datum can be obtained.

Therefore, the supporting electrolyte containing 0.10 M
NaCl in 0.02 M acetic acid and 0.02 M acetate gives the best anodic
voltammetric behavior of molybdenum and it is selected for the anodic
stripping analysis of Mo (VI) in this study.

3.2 Stripping analysis

Since the cathodic peak potential of Mo (VI) in 0.02 M acetic
acid, 0.02 M sodium acetate and 0.10 M NaCl is ca. -0.68 V the

Table 4 Anodic voltammetric behavior of molybdenum

in 0.24 M acetic acid, 0.56 M sodium acetate,

pH 5, and various NaCl concentration; using

10 minutes for electrodeposition of 1.00 X 10^{-5}M

Mo (VI) at potential -0.80 V.

Conc of NaCl (M)	$E_{p,a}$ (V)	$i_{p,a}$ (μa)
3.00	ca. -0.40	very low, cannot be measured
1.00	ca. -0.35	very low, cannot be measured
0.10	ca. -0.22	very low, cannot be measured
0.00	ca. -0.25	very low, cannot be measured

deposition potential of -0.80 V is chosen. The time for electrodeposition of Mo (VI) is varied corresponding to the concentration of Mo (VI) in the test solution. Molybdenum is a multivalent ion, however, a single anodic peak is obtained at -0.24 V in the concentration range of 2.00×10^{-6} M to 1.00×10^{-5} M Mo (VI), using 10 minutes for electrodeposition. In the higher concentration of Mo (VI) ($> 2.00 \times 10^{-5}$ M) and using 10 minutes for electrodeposition, two anodic peaks at the potential of ca. -0.25 V and -0.56 V are observed (see Figure 2). The peak at ca. -0.25 V is the predominant peak. These two peaks are slightly overlapped at the higher concentration of molybdenum. In order to obtain the higher precision and accuracy, the elimination of anodic peak at -0.50 V was tried by decreasing the deposition time. It is found that 5-minute-deposition of Mo (VI) in the concentration greater than 2.00×10^{-5} M gives only one anodic peak at ca. -0.25 V.

The conditions for deposition of Mo (VI) in 0.02 M acetic acid, 0.02 M sodium acetate, and 0.10 M NaCl, data of stripping analysis and the detection limit are given in Table 5. The anodic peak current in each condition is directly proportional to the concentration of Mo (VI) as shown in Figure 3A and 3B. These lines are calculated least squares lines.

Since the 20-minute-deposition of 1.00×10^{-6} M Mo (VI) gives a very low peak current (see Table 5), the concentration less than 1.00×10^{-6} M Mo (VI) is not worth to try.
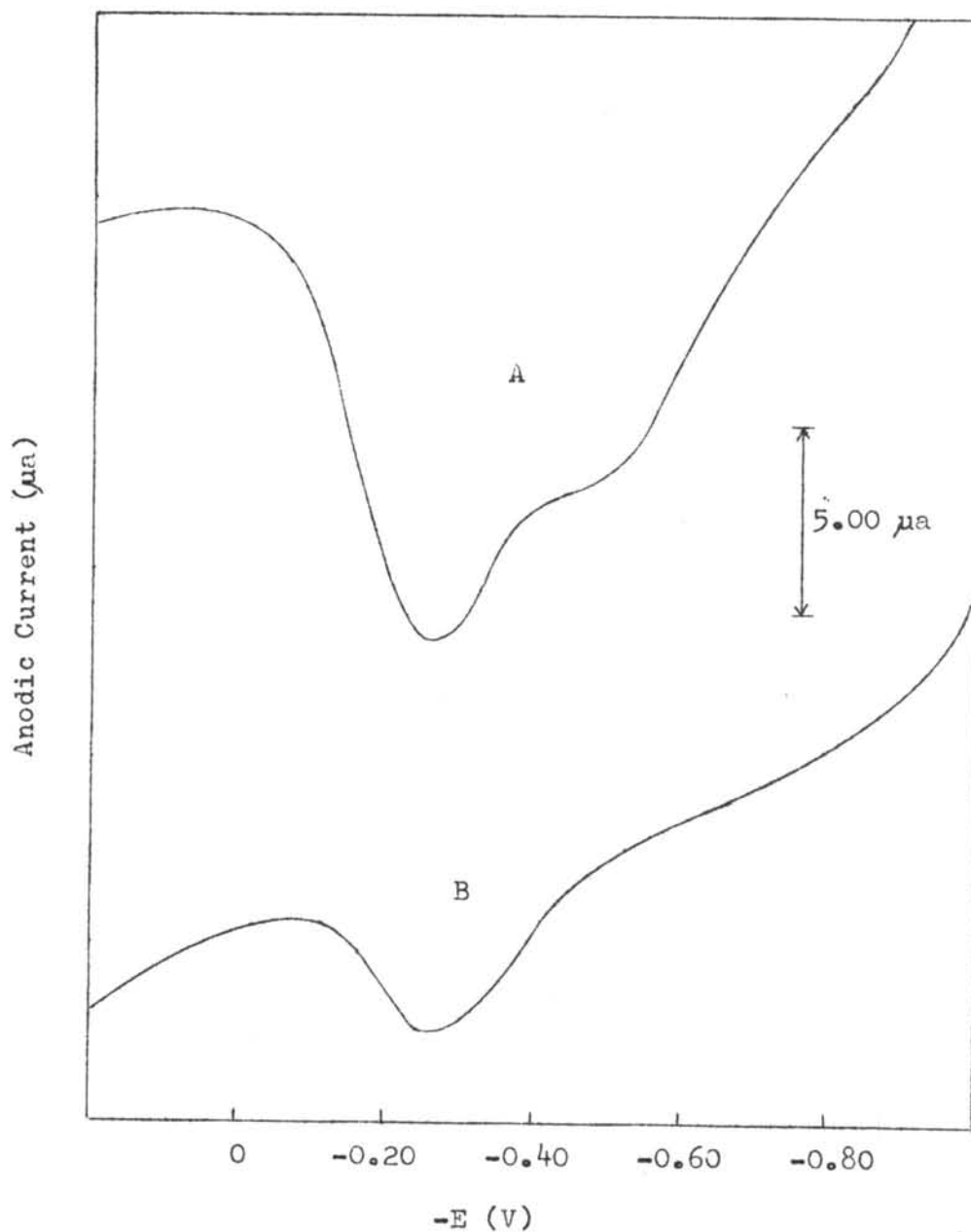
Figure 2 Anodic voltammogram of 2.00 X 10^{-5}M in 0.02 M

acetic acid -0.02 M acetate -0.1 M NaCl, after

A) 10-minute and B) 5-minute electrodeposition

at -0.80 V.

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Table 5 Conditions for deposition of Mo (VI) and data of
stripping analysis of molybdenum in 0.02 M acetic
acid - 0.02 M sodium acetate - 0.10 M NaCl.

Deposition		Conc. of Mo (VI) (M)	$i_{p,a}^{a}$ (μa)	Detection limit (M)
Potential (V)	Time (min.)			
-0.80	5	1.00×10^{-4}	11.32 ± 0.22	
		8.00×10^{-5}	9.77 ± 0.58	
		6.00×10^{-5}	8.18 ± 0.20	
		4.00×10^{-5}	6.27 ± 0.49	
		2.00×10^{-5}	4.09 ± 0.32	
		1.00×10^{-5}	2.44 ± 0.23	1.00×10^{-5}
-0.80	10	1.00×10^{-5}	4.67 ± 0.21	
		8.00×10^{-6}	3.84 ± 0.32	
		6.00×10^{-6}	2.97 ± 0.13	
		4.00×10^{-6}	1.64 ± 0.16	
		2.00×10^{-6}	0.57 ± 0.01	2.00×10^{-6}
-0.80	20	1.00×10^{-6}	0.60 ± 0.01	

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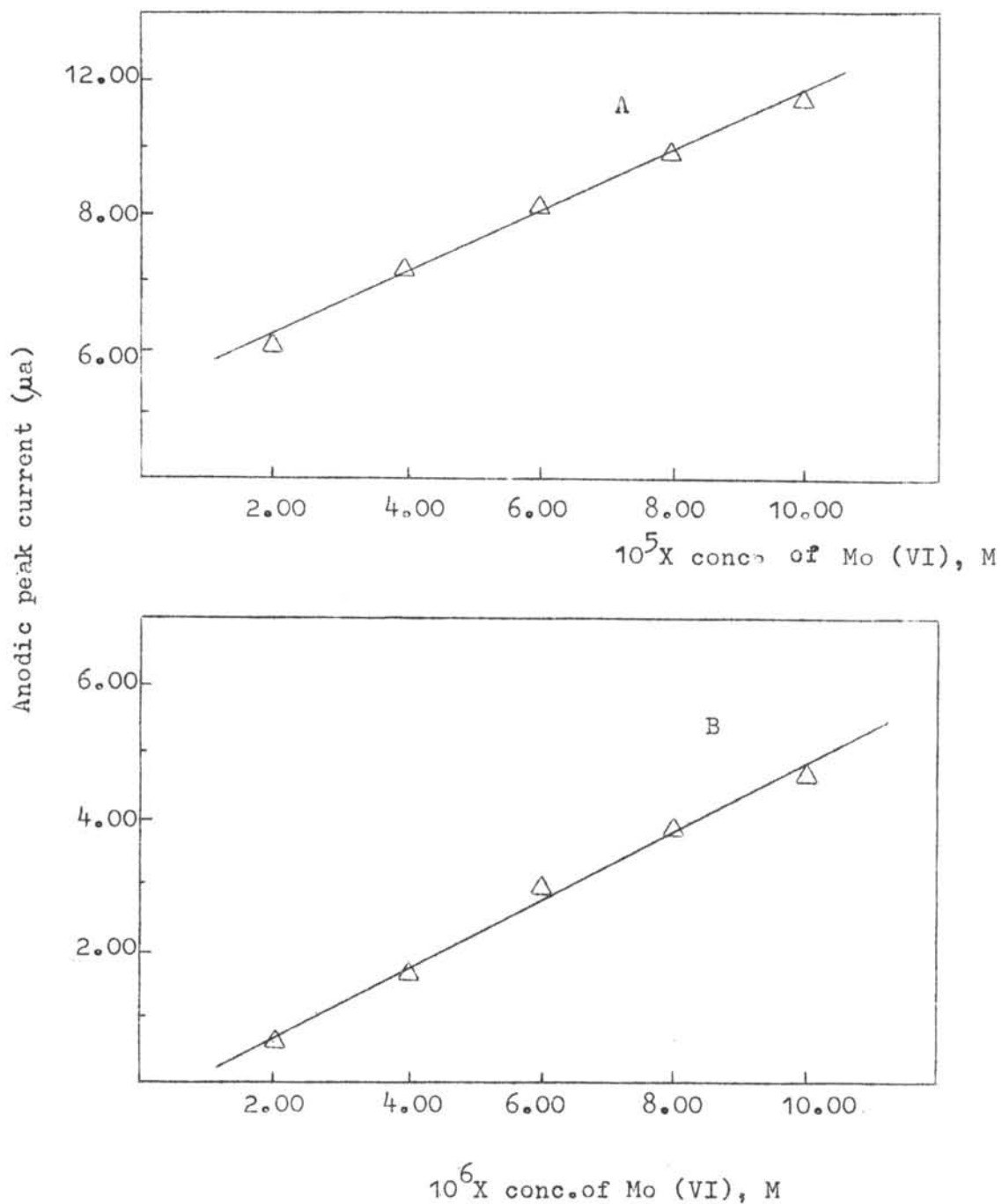average anodic peak current $\pm$ average deviation of more than 5 trials.

Figure 3   The linear dependence of anodic peak current on
concentration for anodic stripping analysis of
Mo (VI) using electrodeposition time of A) 5
minutes and B) 10 minutes.