

CHAPTER 4

ANODIC STRIPPING ANALYSIS OF LEAD (II)

Lead (II) in various samples are determined by anodic stripping voltammetry and a list of applications is shown in Table 4. Since lead metal forms amalgam with mercury, a one step process which can be used to improve the sensitivity of lead determination is mercury plating "in situ" (28). Mercuric nitrate is added to the test solution and a simultaneous deposition is made for both mercury and lead in the sample. This results in extremely thin film with a thickness depending on plating time and mercuric nitrate concentration.

The study of the cathodic and anodic stripping voltammetry of lead (II), mercury (II) and mixture of lead (II) - mercury (II) are reported in this chapter. The cathodic peak potential of Pb(II), Hg(II) and Pb(II) - Hg(II) in 0.10 M KNO_3 are listed in Table 5. Since the cathodic peak of lead (II) in 4.00×10^{-3} M $\text{Hg}(\text{NO}_3)_2$ and 0.10 M in KNO_3 showed at -0.52 V, the potential of -0.80 V was chosen for the deposition. After deposition, the anodic voltammetry of Pb, Hg and Pb(Hg) were studied. The conditions and results of this study are shown in Table 6. The anodic voltammogram from this study showed a very well peak separation of lead (-0.47 V) and mercury (+0.28 V) (see Table 6 and Figure 7).

The sensitivity for determination of lead (II) was studied in 0.10 M KNO_3 and in 1.00×10^{-5} M $\text{Hg}(\text{NO}_3)_2$ - 0.10 M KNO_3 . As seen in Table 7,

Table 4 Summary of selected ASV application of lead (II) in samples.

Sample	Working electrode used ^a	Reference
Sea water	HMDE	15
Atmospheric particulate	HMDE	16
Natural water	HMDE	17, 18
Estaurine waters	HMDE	19
Blood	HMDE	20
Atmospheric particulates	HMDE	21
Atmospheric particulates	MTFE	22
Natural water	MTFE	23
Blood	MTFE	24, 25
Natural water	MTFE	26, 27
Natural water and reagents	rotating glassy carbon electrode mercury plated in situ	28
Natural water, blood and urine	MTFGC	29
Natural water, blood and biological tissue	MTFGC	30
Environmental water	MTFGC	31
In an acetate buffer	mercury-coated wax-impregnated graphite electrode	32

Table 4
(continued)

Sample	Working electrode used ^a	Reference
In unstirred KNO_3 solution at pH 3.5	MTFE	33
In 10^{-4} M HNO_3	rotating Hg-amalgamated Cu - disk electrode	34

^a

HMDE = hanging mercury drop electrodes;

MTFE = mercury thin-film electrodes;

MTFGC = mercury thin-film on glassy carbon.

the anodic peak current of Pb(Hg) is higher than the one of Pb(II). These results insist the sensitivity improvement of amalgamated formation.

The concentration ratio of Pb(II) to Hg(II) was also studied. It has been noticed that the anodic peak of Hg is not given in the anodic stripping voltammogram if the concentration ratio of Hg(II) to Pb(II) is less than 1000. Though, this concentration ratio is higher than 1000 and the anodic peak of Hg is shown, its anodic peak current does not interfere the anodic peak current of Pb; since they are about 0.7 volt separated.

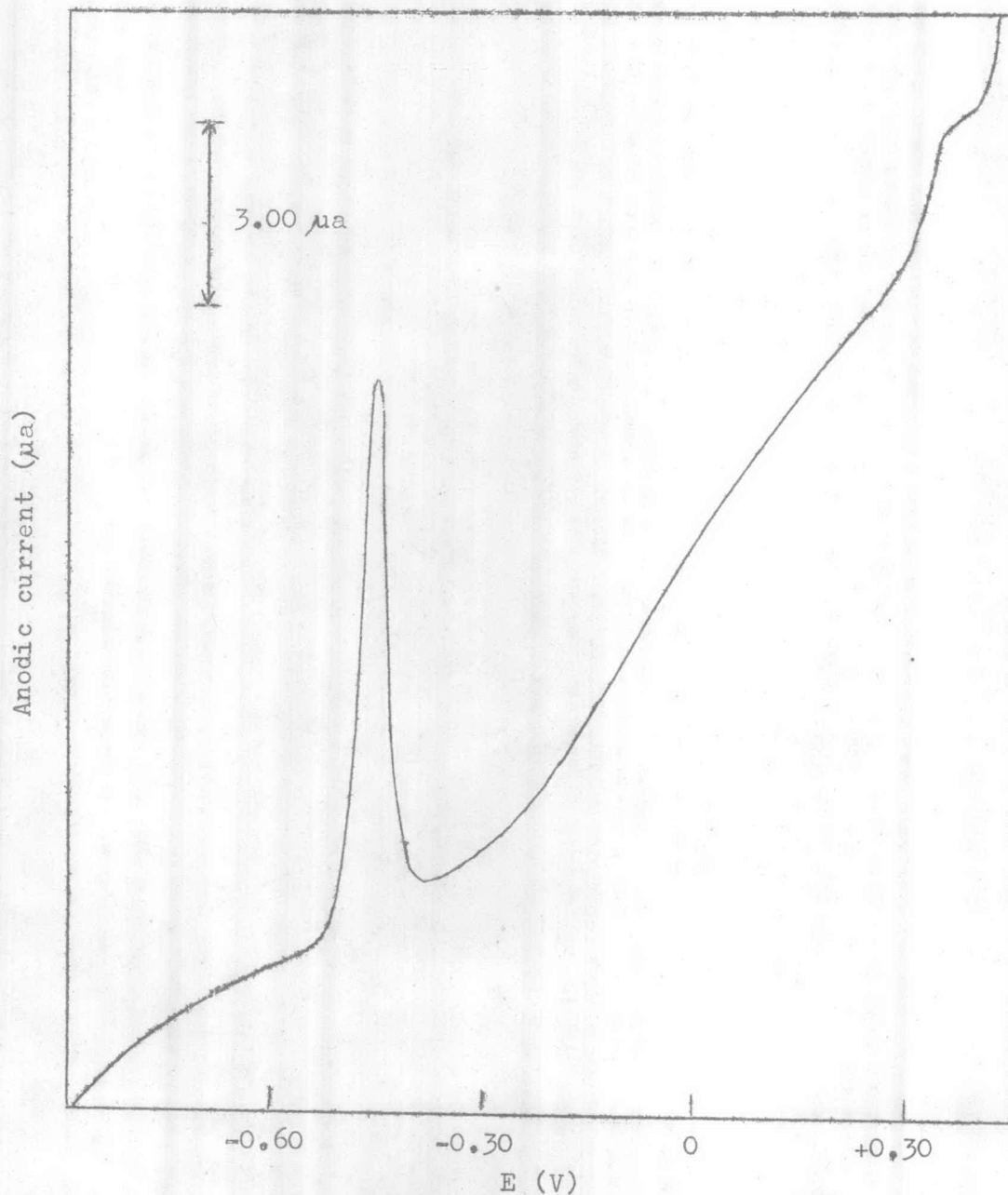


Figure 7 The anodic voltammogram of $1.00 \times 10^{-5} \text{ M Pb(II)}$ and $8.00 \times 10^{-3} \text{ M Hg (II)}$ in 0.10 M KNO_3 .

Table 5 Cathodic voltammetric data of metal ion in 0.10 M KNO_3 , using the scan rate of 0.8 V/minute .

Metal ion	Concentration, M	$E_{P,c}$ (V)
Pb(II)	1.00×10^{-2}	-0.57
Hg(II)	8.00×10^{-3}	+0.20
Pb(II) + Hg(II)	$5.00 \times 10^{-3} + 4.00 \times 10^{-3}$	-0.52, +0.20

Table 6 Anodic stripping voltammetric data of metal ion in 0.10 M KNO_3 , using the scan rate of 0.8 V/minute .

Metal ion	Concentration, M	Deposition		$E_{P,a}$ (V)
		Potential (V)	Time (min)	
Pb(II)	1.00×10^{-5}	-0.80	5	-0.47
Hg(II)	1.00×10^{-3}	-0.80	10	+0.28
Pb(II) + Hg(II)	$2.50 \times 10^{-7} + 4.00 \times 10^{-3}$	-0.80	10	-0.47, +0.28

Table 7 Comparison of anodic stripping voltammetric data of $1.50 \times 10^{-6} \text{ M Pb(II)}$ in 0.10 M KNO_3 and in $1.00 \times 10^{-5} \text{ M Hg(NO}_3)_2 - 0.10 \text{ M KNO}_3$, using the scan rate of 0.8 V/minute .

Deposition		Electrolyte	$i_{P,a}$ (μa) at -0.48 V
Potential (V)	Time (min)		
-0.80	20	0.10 M KNO_3	1.46
		$1.50 \times 10^{-5} \text{ M Hg(NO}_3)_2 - 0.10 \text{ M KNO}_3$	2.60

It is this thesis purpose to determine trace amount of lead (II) as small as possible. Thus, a series of concentration less than 2×10^{-6} M Pb(II) in 1.00×10^{-5} M $\text{Hg}(\text{NO}_3)_2$ and 0.10 M in KNO_3 was investigated by anodic stripping analysis (see Table 8). The suitable time for deposition of this amount of Pb(II) is 20 minutes at -0.80 V. The stripping voltammogram shows a single peak at ca. -0.48 V which is the anodic peak of lead (II). As seen in Figure 8, the anodic peak current is directly proportional to Pb(II) concentration in the range of 1.50×10^{-6} M to 2.00×10^{-7} M Pb(II).

The sensitivity of this technique seemed to be improved if a rotating glassy carbon electrode mercury plated in situ and higher scan rate were used (28).

Table 8 Condition for deposition of Pb(II) and data of stripping analysis of lead in 1.00×10^{-5} M $\text{Hg}(\text{NO}_3)_2$ and 0.10 M in KNO_3 at pH 1.5, using the scan rate 0.8 V/minute.

Deposition		Concentration of Pb(II) (M)	^a i_p , a (μa)
Potential (V)	Time (min)		
-0.80	20	1.50×10^{-6}	2.60 ± 0.13
		1.00×10^{-6}	1.65 ± 0.13
		8.00×10^{-7}	1.27 ± 0.02
		6.00×10^{-7}	0.89 ± 0.05
		4.00×10^{-7}	0.51 ± 0.05
		2.00×10^{-7}	0.13 ± 0.03

^a average anodic peak current \pm mean deviation of more than 4 trials.

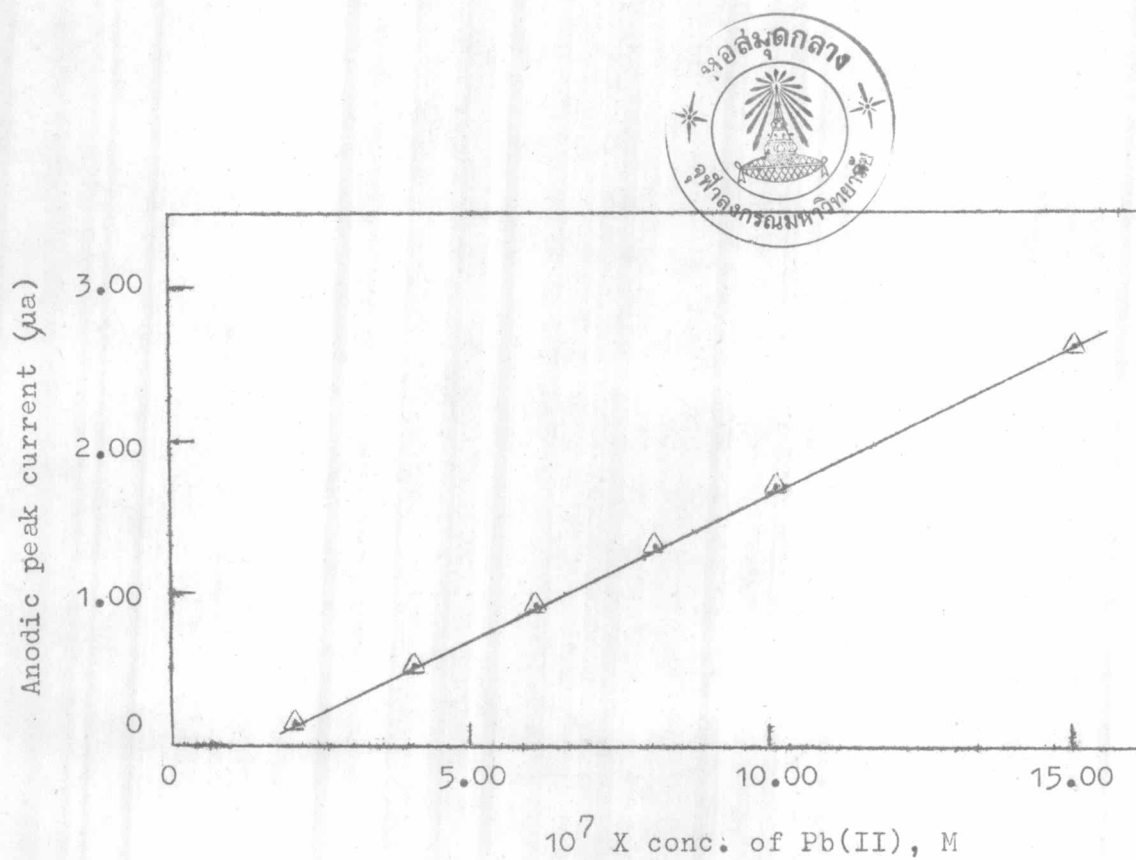


Figure 8 Linear dependence of anodic peak current on concentration for anodic stripping analysis of Pb(II) using electrodeposition time of 20 minutes and scan rate 0.8 V/minute. The line drawn is the calculated least squares line.