

# Fundamental Studies on the Determination of Trace Heavy Metals by Anodic Stripping Voltammetry (ASV) using Glassy Carbon Electrode

—Effect of Supporting Electrolyte—

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## Introduction

The usual method of trace heavy metals are generally known to atomic absorbance, colorimetry, and polarography. These methods must be carried out pretreatment by solvent-extraction, concentration of sample, etc. Recently, anodic stripping voltammetry (ASV) of analytical method take the place of above method get into the spotlight. The method was a simple and conveniently apparatus system that the trace heavy metal ions were first concentrated on an electrode by pre-electrolysis and oxidized after words by anodic potential scanning. The most currently electrode of ASV are metallic mercury such as hanging mercury drop electrode (HMDE)<sup>1),2)</sup>, thin film mercury electrode (TFME)<sup>3),4)</sup>, tubular mercury-graphite electrode<sup>5)</sup>, rotating mercury coated glassy carbon electrode<sup>6)</sup>. Using the metallic mercury electrode, Franke et al<sup>7)</sup> reported to the analysis of toxic metals in urine by ASV, and Duinker et al<sup>8)</sup> also on the speciation of dissolved zinc, cadmium, lead, and copper in river by DPASV (differential pulsed anodic stripping voltammetry). However, the effect of supporting electrolyte on the determination of trace heavy metals did not reported.

Therefore, the present report was concerned with the effect of supporting electrolyte as fundamental studies on the determination of trace heavy metals by ASV using glassy carbon electrode.

## Experimental

### Apparatus

The apparatus was used voltammetric analyzer (Model P-1000) of Yanagimoto

Co. This apparatus is possible to the various analytical method, especially pulse and differential pulse methods are used to ultramicroanalysis of  $10^{-7}$ - $10^{-8}$  M using HMDE. The working and reference electrodes used to glassy carbon and saturated calomel electrode (SCE) respectively.

#### Reagents

The reagents used to the all analytical grade. The standard solutions of copper, lead, cadmium, and zinc used by dilute with distilled water to the required consistency. Twice-distilled water used through the experiment.

#### Procedure

About 20.0 ml of sample solution was poured into the electrolytic cell and flushed with a purified nitrogen gas for 10 min to remove dissolved oxygen. The heavy metals in sample solution were then concentrated on the working electrode at a defined time. During the pre-electrolysis, the solution was stirred by magnetic stirrer using teflon-coated spin bar. After the pre-electrolysis, stop the stirrer, and the solution was left quiescent for 15 sec under the applied potential. Then, the potential was swept anodically and recorded the stripping voltammogram for heavy metals in sample solution.

## Results and Discussion

#### Specificity of apparatus

We were investigated for the specificity of apparatus, i. e. the effect of lowpass filter (sec), current range ( $\mu\text{A}/\text{V}$ ), modulation amplitude (V), scan rate (mV/sec), and pulse interval (sec). Sample solution used lead standard solution (1 ppm) in 0.1 M phthalate (pH=5.0) as supporting electrolyte. Sample solution flushed with purified nitrogen for 10 min to remove the dissolved oxygen and electrolysis time was 3 min.

On the lowpass filter, the peak current of 3 sec showed a tendency of decrease than off, 0.3, and 1 sec. The lowpass filter is necessary to establishing the optimum value to be fit for the purpose of analysis. Modulation amplitude was modulated the trace pulse potential overlapping to direct voltage in differential pulse polarography. Peak potential showed a tendency to leaning toward minus side as changing 5 to 100V on the modulation amplitude. In the case of scan rate and pulse interval, peak potential showed a tendency to leaning toward plus side as opposed to modulation amplitude. These specificity of apparatus was considered to be playing important role on the analysis of unknown sample.

Comparison with single and simultaneous determination of copper, lead, cadmium, and zinc in the various supporting electrolyte

Generally, the simultaneous determination of various trace heavy metals must be set up the region of suitable pH. Therefore, the single and simultaneous determination of copper, lead, cadmium, and zinc in the various supporting electrolyte were investigated. The relationship between the various supporting electrolyte (pH=1.0–11.0) and the peak current of heavy metals is shown in Table 1. The

Table 1. Comparison with single (A) and simultaneous (B) determination of  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cd}^{2+}$  and  $\text{Zn}^{2+}$  (each final concentration is 1-ppm) on the change of pH

pH	$\text{Cu}^{2+}$		$\text{Pb}^{2+}$		$\text{Cd}^{2+}$		$\text{Zn}^{2+}$	
	( $\mu\text{A}$ )	(V)						
1.0 (A)	0.46	-0.16	6.10	-0.51	0.53	-0.78	0.73	-1.05
" (B)	2.66	-0.16	1.96	-0.51	0.20	-0.78	0.04	-1.05
3.0 (A)	4.43	-0.06	1.59	-0.50	3.25	-0.74	1.61	-1.02
" (B)	3.32	-0.06	1.34	-0.50	0.38	-0.74	0.04	-1.02
5.0 (A)	2.47	-0.03	3.18	-0.53	2.43	-0.76	1.67	-1.08
" (B)	5.39	-0.03	5.47	-0.52	3.87	-0.76	1.18	-1.08
7.0 (A)	1.66	-0.10	0.07	-0.59	2.71	-0.74	2.02	-1.09
" (B)	3.38	-0.10	0.03*	-0.59	3.00	-0.74	2.18	-1.09
9.0 (A)	0.38	-0.18	0.19	-0.58	9.03	-0.72	1.64	-1.16
" (B)	0.36	-0.18	0.25	-0.58	7.73	-0.72	3.27	-1.16
11.0 (A)	0.33	-0.33	0.05	-0.66	0.08	-0.83	0.89	-1.30
" (B)	0.09*	-0.33	0.02*	-0.66	0.04*	-0.83	0.32*	-1.30

\* This value is 0.5  $\mu\text{A}/\text{V}$ , and other value is 5  $\mu\text{A}/\text{V}$  in sensitivity.

working electrode used to the glassy carbon, and the each heavy metal ions (each final concentration is 1 ppm) used to dilute of standard solution (1000 ppm). In the case of a single metal determination, the peak current of each heavy metals indicated a high value at an acidity side (copper and lead) and an alkali side (cadmium and zinc), respectively. On the other hand, the peak current of each heavy metals on the simultaneous determination showed approximately similar results to those of single determination. Moreover, the overall peak current of the simultaneous determination showed higher value than the single on the any pH region.

However, the overall sensitivity on the simultaneous determination of copper, lead, cadmium, and zinc was excellent at pH=5.0 and also the peak current is high. Copper, lead, cadmium, and zinc in this pH were readily determined, but the peak current of zinc was lower than that of copper, lead, cadmium.

Comparison with the limit of detection of trace heavy metals in phthalate supporting electrolyte and of adding mercuric nitrate on the heavy metals determination

The study of the polished glassy carbon electrode with in situ mercury film

deposition has recently become an interesting subject of discussion among investigators and is applicable to a wide range of supporting electrolytes. Thus, the limit of detection of copper, lead, cadmium, and zinc in phthalate supporting electrolyte and of adding mercuric nitrate were investigated. The results shown in Table 2. The limit of detection of copper, lead, cadmium, and zinc in phthalate supporting

Table 2. Comparison with the limit of detection of trace heavy metals in phthalate supporting electrolyte and of adding mercuric nitrate

	Conc. of Metals (ppm)	Cu ( $\mu\text{A}$ )*	Pb ( $\mu\text{A}$ )*	Cd ( $\mu\text{A}$ )*	Zn ( $\mu\text{A}$ )*
(A)	1	5.39	5.47	3.87	1.18
	0.1	0.48	0.34	0.51	0.27
	0.01	0.07	0.03	0.01	0.02
	0.001	ND**	ND**	ND**	ND**
(B)	1	8.75	7.32	6.65	3.95
	0.1	1.54	1.37	1.05	1.55
	0.01	0.27	0.13	0.10	0.12
	0.001	0.03	0.05	0.02	0.05

(A): Phthalate supporting electrolyte

(B): Phthalate supporting electrolyte + mercuric nitrate

\*: Peak current, \*\*: Non-detect

electrolyte is estimated as about 0.01 ppm, and 0.001 ppm by adding mercuric nitrate. The limit of detection by adding mercuric nitrate, therefore, showed 10 times higher value compared with only phthalate supporting electrolyte. It seems that a very thin mercury film is formed on a polished glassy carbon electrode by adding mercuric nitrate to the sample solution. After the analysis the mercury film can be completely removed from the electrode by a simply wiping tissue. Moreover, the value of determination of copper, lead, cadmium, and zinc gradually increases with increasing mercuric ion.

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