

담수 및 퇴적물에 함유된 아연, 카드뮴, 납 및 구리의 산화전극 빗김 전압전류법 정량

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Anodic Stripping Voltammetric Determinations of Zinc, Cadmium, Lead and Copper in Freshwater and Sediment

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요 약. 매달린 수은 방울 전극(HMDE) 또는 얇은 수은막 전극(TMFE)을 사용하여 금속이온들을 은/염화 은(포화 KCl) 기준전극에 대하여 -1.200 V에서 150초 동안 전해시켜서 수은전극에 농축시키고 펄스 차이 전압전류법(DPASV)과 네모파 전압전류법(SWASV)으로 산화전극 빗김 분석을 하여 동시에 아연, 카드뮴, 납 및 구리를 정량분석하였다. HMDE를 사용하여 DPASV로 네 가지 금속이온을 동시 정량분석시 각각의 금속이온의 붕우리 전류는 20~100 ppb 농도범위에서 직선성을 보여주었으나 TMFE를 사용하여 DPASV 또는 SWASV로 네 가지 금속이온을 동시 정량분석시에는 Cd^{2+} 와 Pb^{2+} 의 붕우리 전류만 DPASV의 경우 100 ppb까지 SWASV의 경우 10 ppb까지 직선성을 나타내었다. Cd^{2+} 와 Pb^{2+} 의 동시 정량분석의 경우 TMFE를 사용한 DPASV분석은 HMDE를 사용한 DPASV보다 약 15배 더 민감하였으며 TMFE에서 SWASV는 DPASV보다 약 5배 더 민감하였다. 퇴적물에 함유된 아연의 농도를 HMDE를 사용한 DPASV분석법과 유도 결합 플라즈마-질량분석법으로 일곱개의 시료에 대하여 정량분석하여 비교하였더니 상관계수가 0.9993으로 높았고 t-test 결과 두 방법 사이에는 유의성 있는 차이가 없었다.

ABSTRACT. Zinc, cadmium, lead and copper were simultaneously determined by depositing metals at -1.200 V vs. a Ag/AgCl(sat. KCl) reference electrode for 150 seconds on a hanging mercury drop electrode(HMDE) or a thin mercury film electrode(TMFE), followed by scanning towards anodic direction using differential pulse voltammetric(DPASV) and square wave voltammetric(SWASV) techniques. The linear calibration curves were obtained for four metal ions simultaneously determined by DPASV with a HMDE in the concentration range between 20 and 100 ppb. However, the linear calibration plots were obtained only for Cd^{2+} and Pb^{2+} in the simultaneous determinations with a TMFE in the concentration range up to 100 ppb using DPASV and up to 10 ppb using SWASV. DPASV with a TMFE was about 15 times more sensitive than DPASV with a HMDE for simultaneous determinations of Cd^{2+} and Pb^{2+} . SWASV was about 5 times more sensitive than DPASV at a TMFE. Concentrations of zinc in seven different sediment samples determined by DPASV with a HMDE and inductively coupled plasma-mass spectrometry were compared, resulting with an excellent correlation coefficient of 0.9993 and with no significant difference between two methods after t-test.

INTRODUCTION

Anodic stripping voltammetric(ASV) techniques with different stripping steps have been applied for the determinations of copper, lead and cadmium in

sea water.¹⁻⁴ Longer deposition time of 60 min was required when using a linear sweep ASV at a hanging mercury drop electrode(HMDE),¹ comparing with 5 min deposition using differential

pulse anodic stripping voltammetry(DPASV) at a thin mercury film electrode(TMFE)⁴ for the analyses of ppb level concentrations of these metals in sea water. Other applications of ASV were reported to determine metals in the environmental samples.⁵⁻⁷ Analysis time for Zn, Cd, Pb and Cu by square wave anodic stripping voltammetry (SWASV)⁷ was found to be only one half the time needed by DPASV and similar to the time needed for the determinations of one element by ET AAS.⁷ ASV was proposed for the determinations of lead and cadmium in the recent 18th edition of standard methods for the examination of water and wastewater, which states ASV is as much as 10 to 100 times more sensitive than electrothermal atomic absorption for some metals.⁸

In this study the proposed ASV in the 18th edition of standard methods⁸ are evaluated with some modification including deposition and final potentials for simultaneous determinations of zinc, cadmium, lead and copper in freshwater and sediment sampled from Han river downstream.

EXPERIMENTAL

Instrumentation. DPASV measurements using a HMDE were carried out with a 174A polarographic analyzer, a 303 static mercury drop electrode and a RE0074 X-Y recorder(EG & G, Princeton Applied Research). DPASV and SWASV measurements using a TMFE were carried out with a 263 potentiostat/galvanostat and a 616 rotating disk electrode system(EG & G, PAR). A home made glassy carbon disk electrode(area; 0.196 cm²) compartment was inserted into a Kel-F body of a RDE 001 disk electrode assembly. The software program was model 270 research electrochemistry v. 4.11(EG & G, PAR).

Reagents and solutions. Nitric acid(Songyawon Pharm. Co.), sulfuric acid(Wako Pure Chem. Co.) and ammonia water(Junsei Chem. Co.) were harmful metal analysis grades. Atomic absorption standard solutions of Zn, Cd, Pb and Cu were purchased from Aldrich Chemical Company. Three kinds of supporting electrolytes at the ionic strength of 0.10 M, which were a pH 3.0 ammonium citrate

buffer, a pH 4.5 acetate buffer and a pH 6.4 phosphate buffer, were prepared with ACS grade or GR grade chemicals dissolved in pure HPLC grade water(J. T. Baker). Triply distilled mercury (Merck) was used for a HMDE. The oxidizing mixture for digestion was prepared by adding 1.5 g of K₂S₂O₈(GR grade; Hayashi Pure Chem.) in 10 mL of conc. H₂SO₄ and diluting up to 100 mL with ultra pure water passed through a Milli-QII deionizer (Millipore).

Pretreatment of freshwater and sediment samples. Freshwater and sediment were sampled randomly between Mapo bridge and Nanjido in Han river downstream in July, 1995. Sediment samples for comparison studies were collected in the same area in January, 1996. Freshwater at 50 cm below the surface of river was transferred with a van Dorn water sampler into a pre-cleaned polyethylene bottle which was stored in an ice-box and was carried to the lab on the same day. All glass and plastic labware used in the experiment were soaked in a 6 N nitric acid solution overnight and rinsed with ultra pure water thoroughly. Measurements were carried out on the sampling day, otherwise one mL of conc. nitric acid was added to each liter of freshwater sample which was kept in a refrigerator until analysis. Freshwater sample was filtered using a 0.45 μm Millex-HV filter unit (Millipore). Five mL of filtrate was accurately pipetted into a Teflon-lined digestion beaker in which 0.1 mL of the oxidizing mixture was added for digestion to destroy organic materials in the sample matrix. The solution was slowly heated for about 25 min to dryness without boiling. After cooling it to room temperature, ten mL of a supporting electrolyte solution was added to the residue to redissolve it, which was used as the analytical solution in the ASV measurement. Sediment at the bottom of the river was collected using a Ponar grab and was frozen until analysis. After thawing it at room temperature about 50 g of sediment was dried in the oven at 105 ± 2 °C and grinded in a mortar, which was then sieved with a 100-mesh screen. About 0.5 g of the sediment powder was accurately weighed, transferred into a Teflon-lined

digestion beaker and saturated with one mL of the oxidizing mixture, which was heated for about 15 min to dryness. A supporting electrolyte solution was added into the digested sediment up to total weight of 50 g. The mixed sediment solution was filtered using a 0.45 μm Millex-HV filter unit. The diluted filtrate by 25–50 times with a supporting electrolyte solution was used as the analytical solution in the ASV measurement.

DPASV with a HMDE. Accurately 10 mL of analytical solution was transferred into a cell bottom which was deaerated using purified nitrogen gas for 4 min while stirring a solution with a Teflon-coated magnetic stirring bar. Deposition step was carried out using a new medium size HMDE by applying a potential of -1.200 V vs. a Ag/AgCl(sat. KCl) reference electrode for 120 sec with stirring and for 30 sec without stirring while keeping nitrogen atmosphere above the solution. Stripping step was carried out by scanning anodically up to 0.100 V with a differential pulse mode, a scan rate of 5 mV/s , a modulation amplitude of 25 mV and a pulse period of 0.5 sec .

DPASV and SWASV with a TMFE. Accurately 50 mL of analytical solution was transferred into a cell bottom in which $100\ \mu\text{L}$ of 0.02 M mercuric nitrate solution was added. The solution was deaerated with purified nitrogen gas while stirring it with a rotating glassy carbon electrode(GCE) at 2700 rpm . To form a TMFE in situ, the GCE was stabilized by scanning the potential five times between -1.200 V and 0.100 V at a scan rate of 100 mV/s . For every ASV measurement the GCE was conditioned at 0.100 V for 60 sec . Deposition step was carried out at -1.200 V for 120 sec with rotating the electrode and for 30 sec without rotation. Stripping step was carried out by DPASV or SWASV. For DPASV a TMFE was scanned from -1.200 V to 0.100 V at a scan rate of 5 mV/s , a step time of 0.4 sec , a step increment of 2 mV and a pulse height of 25 mV . For SWASV a TMFE was scanned from -1.200 V to 0.100 V at a scan rate of 30 mV/s , a scan increment of 2 mV , a frequency of 15 Hz and a pulse height of 25 mV .

RESULTS AND DISCUSSION

Supporting electrolytes. Since metal impurities in the supporting electrolyte solution could limit the detection of ASV, three kinds of supporting electrolytes which were a 0.10 M pH 3.0 ammonium citrate buffer, a 0.10 M pH 4.5 acetate buffer and a 0.10 M pH 6.4 phosphate buffer were investigated by DPASV at a HMDE. Concentrations of impure metals in each buffer were determined by the standard addition method. The peak potentials of Zn^{2+} , Cd^{2+} , Pb^{2+} and Cu^{2+} were appeared at -1.07 V , -0.65 V , -0.47 V and -0.08 V vs. a Ag/AgCl(sat. KCl) reference electrode, respectively and were not varied depending on the pH of the buffer. However, the Pb^{2+} peak, even in the standard added solution did not appear in the phosphate buffer. Since $\text{pK}_{\text{sp}}^{\circ}$ of $\text{Pb}(\text{HPO}_4)$ is 9.859 , solubility of $\text{Pb}(\text{HPO}_4)$ in a pH 6.4, 0.10 M phosphate buffer was calculated to be $1.03 \times 10^{-8}\text{ M}$, that was equivalent to 2.13 ppb of Pb^{2+} which could not be detected with electrolysis time of 150 sec . Therefore, the phosphate buffer was not suitable for the determination of lead. The concentrations of Zn^{2+} , Cd^{2+} , Pb^{2+} and Cu^{2+} in pH 3.0 ammonium citrate buffer were 5.2 , not detectable (nd), 1.9 and 0.9 ppb , respectively, while those ions in pH 4.5 acetate buffer were 33.2 , 1.1 and 0.4 ppb , respectively. Ammonium citrate buffer with a much lower concentration of zinc was selected in the following studies.

ASV of metal standard solutions. DPASV was carried out at a HMDE for simultaneous analyses of Zn^{2+} , Cd^{2+} , Pb^{2+} and Cu^{2+} in each standard solution in the concentration range between 20 and 100 ppb . A plot of peak currents vs. ppb concentrations of each metal ion yields a straight line passing almost zero point as shown in Fig. 1. DPASV and SWASV of a standard solution containing 8.13 ppb of Zn^{2+} , 7.97 ppb of Cd^{2+} , 8.05 ppb of Pb^{2+} and 8.13 ppb of Cu^{2+} were carried out at a TMFE and voltammograms are shown in Fig. 2. DPASV with a TMFE yielded peak potentials of Zn^{2+} at -0.98 V , Cd^{2+} at -0.56 V , Pb^{2+} at -0.38 V and Cu^{2+} at -0.09 V vs. a Ag/AgCl(sat. KCl)

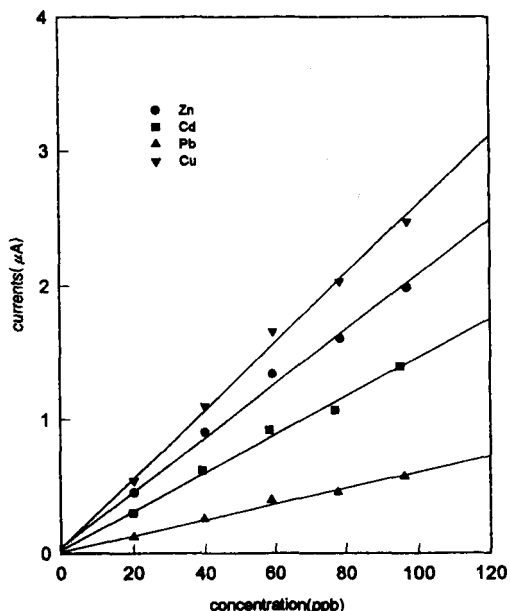


Fig. 1. A plot of peak currents(μA) vs. concentration (ppb).

reference electrode, while SWASV with a TMFE yielded peak potentials of Zn^{2+} at -0.95 V , Cd^{2+} at -0.54 V and Pb^{2+} at -0.36 V . However, a Cu^{2+} peak on SWASV voltammogram was not well defined to assign a peak potential in contrast to that obtained by DPASV. Since SWASV peak potentials of Cd^{2+} , Pb^{2+} and Zn^{2+} were shifted by 20~30 mV towards positive potentials with respect to those of DPASV, the peak potential of Cu^{2+} might be shifted to the more anodic potential than -0.09 V , at which oxidation of mercury commenced. The peak currents of SWASV were about five times larger than the corresponding peak currents of DPASV. Each standard solution containing all Zn^{2+} , Cd^{2+} , Pb^{2+} and Cu^{2+} in the concentration range between 1 and 100 ppb was analyzed by DPASV and SWASV at a TMFE. The linear calibration plots were obtained for Cd^{2+} as well as Pb^{2+} up to 100 ppb by DPASV and up to 10 ppb by SWASV. However, the linear plots were not obtained for Zn^{2+} and Cu^{2+} , because they formed an intermetallic compound in a TMFE.¹⁰ Without adding Cu^{2+} in the standard solutions, a linear plot was obtained for Zn^{2+} in the concentration range between

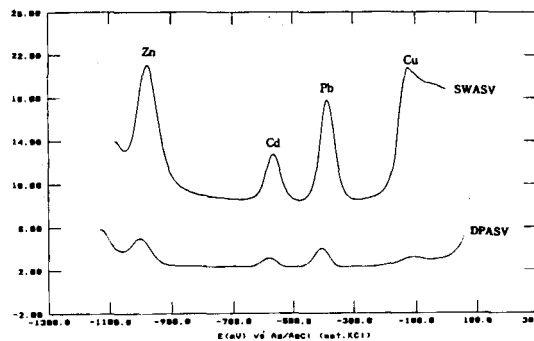


Fig. 2. DPASV and SWASV voltammograms of 8.13 ppb of Zn^{2+} , 7.97 ppb of Cd^{2+} , 8.05 ppb of Pb^{2+} and 8.13 ppb of Cu^{2+} in pH 3.0 ammonium citrate buffer at a TMFE.

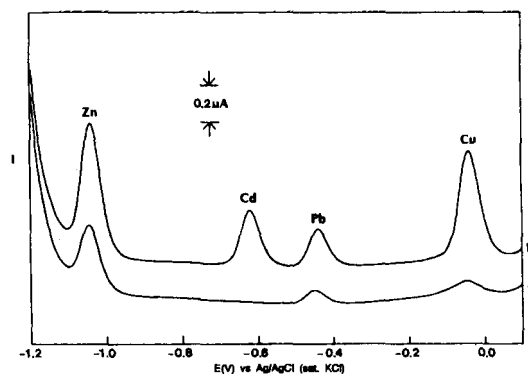


Fig. 3. DPASV voltammograms of freshwater(A) and standard added freshwater(B) at a HMDE. Final concentrations of 20.3 ppb Zn^{2+} , 19.9 ppb Cd^{2+} , 20.1 ppb Pb^{2+} and 20.3 ppb Cu^{2+} were added to freshwater.

1 and 10 ppb by DPASV. Above 50 ppb concentrations, the Zn^{2+} peak was splitted and was not increased as the concentration was increased. DPASV with a TMFE was about 15 times more sensitive than DPASV with a HMDE for simultaneous determinations of Cd^{2+} and Pb^{2+} . DPASV with a HMDE was preferred in the analyses of zinc, cadmium, lead and copper contained in freshwater and sediment, since this technique was sensitive enough to detect ppb level of Zn^{2+} , Cd^{2+} , Pb^{2+} and Cu^{2+} simultaneously and the practical limit of detection was set by the magnitude of contaminated heavy metals in the supporting electrolyte solution.

ASV of metals in freshwater and sediment.

Table 1. The precisions of Zn^{2+} , Cd^{2+} , Pb^{2+} and Cu^{2+} analyses with a HMDE by DPASV(All samples were analyzed three times and averaged)

Sample	Zn		Cd		Pb		Cu	
	Conc.	Rsd(%)	Conc.	Rsd(%)	Conc.	Rsd(%)	Conc.	Rsd(%)
Freshwater #1	88.33 ppb	2.3	3.95 ppb	8.0	56.17 ppb	4.8	3.73 ppb	6.6
Freshwater #2	181.6 ppb	3.3	1.15 ppb	20.0	20.38 ppb	8.0	2.48 ppb	4.1
Freshwater #3	66.72 ppb	1.1	N.D.	-	18.68 ppb	9.6	1.62 ppb	15.0
Sediment #1	310.3 ppm	2.2	0.497 ppm	10.6	82.71 ppm	5.6	155.5 ppm	12.0
Sediment #2	410.3 ppm	1.5	1.54 ppm	9.9	99.09 ppm	4.2	278.4 ppm	8.7
Sediment #3	95.87 ppm	4.4	N.D.	-	52.11 ppm	7.2	61.70 ppm	11.1

Fig. 3 shows DPASV voltammograms of the analytical solution prepared with freshwater sampled from Han river downstream and the standards added analytical solution of freshwater using a HMDE. The peak potentials of Zn^{2+} , Cd^{2+} , Pb^{2+} and Cu^{2+} appeared at -1.04 V, -0.62 V, -0.44 V and -0.04 V, respectively vs. a Ag/AgCl(sat. KCl) reference electrode. The peak potentials of metal ions contained in freshwater were shifted by 30–40 mV towards positive potentials with respect to those in supporting electrolyte solution due to the difference in matrix. Comparing Fig. 3 with Fig. 2, the DPASV peak potentials with a HMDE for Zn^{2+} , Cd^{2+} , Pb^{2+} were shifted by 60 mV towards negative potentials, while Cu^{2+} peak was shifted by 50 mV towards positive potentials due to the difference in the type of mercury electrode as well as the difference in matrix. When DPASV was carried out using freshwater sample just diluted twice with ammonium citrate buffer without digestion, the peaks of Cd^{2+} , Pb^{2+} and Cu^{2+} were well defined to measure but a huge background current from the freshwater matrix appeared up to -1.15 V. Therefore it was difficult to measure the peak current of Zn^{2+} accurately. Simultaneous determinations of Cd^{2+} , Pb^{2+} and Cu^{2+} could be performed without digestion. DPASV voltammograms of the analytical solution prepared with sediment sampled from the bottom of Han river downstream and the standards added analytical solution of sediment also yielded well defined peaks as those in Fig. 3. Three freshwater and three sediment samples collected in July, 1995 were analyzed for their metal contents by DPASV with a HMDE. Each

Table 2. Concentrations of zinc in sediment samples by different analytical methods(ppm)

Sample	ICP-MS	DPASV(at HMDE)
1	72.55	75.33
2	55.29	55.41
3	96.32	101.24
4	80.64	73.21
5	111.17	100.95
6	150.71	145.05
7	495.02	504.07

sample was analyzed three times. Average and relative standard deviation of triplicate runs are listed in Table 1. According to the regulation of drinking water(Ordinance No. 11 of the Environmental Ministry) concentrations of zinc, cadmium, lead and copper should be less than 1 mg/L, 0.01 mg/L, 0.05 mg/L and 1 mg/L, respectively. Among the three freshwater samples concentrations of all metal ions except lead in #1 sample were adequate for this regulation. Concentrations of metals in sediments were expressed as μg of metal per g of dried sediment sample. Contents of metal in sediment was increased in the order of $Cd < Pb < Cu < Zn$. As listed in Table 2, concentrations of Zn^{2+} in seven different sediment samples collected in January, 1996 were determined by the present DPASV with a HMDE and the inductively coupled plasma-mass spectrometry(ICP-MS) method analyzed by Korea Basic Science Institute Seoul Branch. Correlation between two methods was excellent($\gamma = 0.9993$). According to a t-test there was no significant difference at the 95% confidence level between the results obtained by DPASV with a

HMDE and ICP-MS.

DPASV using a HMDE with a deposition time of 150 seconds was well suited for the simultaneous determinations of zinc, cadmium, lead and copper in environmental samples at ppb~ppm level concentrations.

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