SIMULTANEOUS TRACE METAL ANALYSIS IN SEAWATER BY LINEAR SWEEP ANODIC STRIPPING VOLTAMMETRY

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Voltammetric methods for trace metal analysis of seawater were developed using the linear sweep anodic stripping voltammetry (LSASV). A rotating gold disc electrode was used for the simultaneous determination of Cu(II) and Hg(II), while a mercury thin-film (*in situ*) on a rotating glassy carbon disc electrode was employed for the determination of Cd(II), Pb(II), and Zn(II) in acetate buffers.

Stripping peak potentials observed at +0.51 V, +0.28 V, -0.47 V, -0.65 V, and -1.04 V (vs SCE) for Hg(II), Cu(II), Pb(II), Cd(II) and Zn(II), respectively, were used for quantitative analysis. The following limits of detection were obtained: 0.04 µg/L for Cd(II), 0.05 µg/L for Pb(II), 0.11 µg/L for Zn(II), 0.15 µg/L for Cu(II), and 0.13 µg/L for Hg(II). Linear responses were observed for the trace metals determined in the mg/L range with correlation factors of 0.997 or better. Analytical precision within the concentration levels of µg/L were less than 10% rsd.

This voltammetric method was applied to some water samples taken from the Manila Bay with the following results for total metal analysis: Cu, 0.61-1.08 µg/L; Hg, 0.42-3.06 µg/L; Cd, 0.53-0.78 µg/L; Pb, 0.85-2.16 µg/L; and Zn, 3.63-4.00 µg/L.

INTRODUCTION

Our natural water systems are very vital not only to aquatic organisms and plants thriving on them but also to human beings utilizing these resources. In recent years, we have become aware of the increasing amount of pollutants in the water systems. Among these hazardous substances, heavy metals pollute all types of natural waters and aquatic ecosystems. Heavy metals in natural waters exist in trace levels (typical range between 0.001 and 1000 µg/L), but their high degree of ecotoxicity makes them an important class in aquatic ecochemistry [1].

It is therefore of utmost importance to be able to determine these heavy metals with great accuracy. Advanced modes of voltammetry have served as the basis for the most powerful and convenient method for the analysis of heavy metals of prime environmental concern in all types of natural waters [2-7]. Anodic stripping voltammetry (ASV) is one of such modes. The ASV technique is specific, outstandingly sensitive, suited for direct determination of heavy metals in natural waters and has an intrinsic capability for speciation work [8,9].

In the Philippines, the most important shipping port is in the Manila Bay which is located in the western fringes of the City of Manila in the main island of Luzon. Manila Bay has a vast fishing potentials and is currently the main source of livelihood of fisherman from Manila and the neighboring provinces. Major rivers empty into this bay, silt-laden and with polluted water. There is thus a need to safeguard the water quality of this valuable bay and to preserve its marine resources.

There has been very limited literature on trace metal analysis of Manila Bay. Coastal waters and bottom sediments from Manila Bay have been previously analyzed for total metal contents utilizing the atomic absorption spectrophotometry (AAS) [10]. AAS was also employed in the analysis of heavy metals in shellfish from Manila Bay [11]. Recently, arsenic species in Manila Bay water were determined using selective hydride generation--atomic absorption spectrophotometry technique [12]. An electrochemical technique potentiometric stripping analysis (PSA) was also used in the analysis of some trace metals in the Manila Bay water [13].

This paper aims to develop a suitable voltammetric method for the simultaneous detection of the trace metals, Cd(II), Cu(II), Hg(II), Pb(II), and Zn(II), in seawater.

EXPERIMENTAL

Reagents. Ultrapure water (deionized water which was first triple-distilled and then passed through Barnstead Nanopure II Water Filter System) was used in preparing all solutions. All chemicals were of analytical reagent grade.

Instrumentation. The Gerhard Bank Electronik potentiostat (Wenking Model LB75L) with a voltage scan generator (Wenking Model VSG 72) and a Rhode and Schwarz X-Y recorder were used for all voltammetric measurements. Potentials were monitored using an Escort EDM 1111A digital multimeter. All potentials were measured against a saturated calomel electrode (SCE).

Electrochemical Cell. The electrochemical cell was a three-electrode assembly consisting of the working electrode, the platinum wire auxiliary electrode and the SCE reference electrode. The Metrohm 628 rotating electrode unit was utilized as the working electrode. For Cu and Hg analysis, a gold electrode was used while a glassy carbon electrode (GCE) plated *in situ* with a thin-film of mercury was employed for Cd, Pb and Zn analysis. In all the test samples, the plating Hg(II) solution concentration was 15 mg/L.

The solutions were deaerated with high purity nitrogen and maintained under a nitrogen atmosphere throughout the measurements.

Electrode pre-treatment was conducted before every voltammetric analysis to activate the electrode surface. The GCE was pre-treated by polishing with alumina suspension (0.3 micron) while the gold electrode was electrochemically pre-treated by applying a potential of +1.700 V in the stripping solution.

Seawater Sample Collection. The surface water samples used in this study were taken from the Bacoor, Cavite shoreline of the Manila Bay. Samples were collected from a depth of about 30 cm from the water surface. The collected samples were first filtered using the Millipore vacuum filtration set-up with 0.45 μm cellulose acetate filters (Millipore). Samples were analyzed within 24 hours after sampling.

Total Metal Analysis. A 50-mL aliquot sample was treated with 0.50 mL concentrated HNO_3 and boiled down to half its original volume. After cooling the sample, the pH was adjusted to 4.8 using a saturated solution of NaOAc. The resulting solution was then diluted to 50.00 mL with ultrapure water. Reagent blanks were prepared for all determinations.

Electroanalytical Procedure. The samples were analyzed by the standard addition method due to the complex nature of the sample. The test solution consisted of either ultrapure water or seawater and the supporting electrolyte (NaOAc-HOAc or NaOAc-HNO_3 buffer, pH 4.8) with the appropriate metal standards.

Cu(II) and Hg(II) Analysis. For the simultaneous analysis of Cu(II) and Hg(II) the method of Sipos et. al. [14], was applied. This medium exchange method involves the simultaneous deposition of Cu(II) and Hg(II) on a gold disc electrode followed by stripping in another electrolyte. The medium exchange was done to prevent the destruction of the gold electrode in the sample of high chloride content (seawater). The medium exchange solution was 0.010M $HClO_4$ + 0.0025M HCl.

Cd(II), Pb(II), and Zn(II) Analysis. Simultaneous analysis for Cd(II), Pb(II), and Zn(II) were applied using a mercury thin-film electrode (MFE) plated *in situ* with a rotating glassy-carbon disc electrode (RGCE) as support.

RESULTS AND DISCUSSION

Individual Metal Analysis. Each of the five trace metals were first analyzed separately by ASV using ultrapure water and then a relatively clean and unpolluted seawater as solvent. Two different supporting electrolytes were used in this study. The NaOAc-HOAc buffer can be used for labile ("free") metal analysis while the NaOAc-HNO_3 buffer for total metal analysis. The NaOAc-HNO_3 buffer was needed since the sample had to be oxidized with HNO_3 to convert each metal into the electroactive form. Sharp voltammetric peaks were obtained in both supporting electrolytes in either ultrapure water or seawater. Linear calibration plots were obtained with correlation factors of 0.997 or better and are shown in Figure 1.

Simultaneous Metal Analysis. Two methods of simultaneous analysis were studied using each of the acetate buffers. Method 1 involved the simultaneous analysis of Cd(II), Pb(II), and Zn(II) while method 2 involved the simultaneous analysis of Cd(II), Pb(II) and Cu(II) before Zn(II) analysis.

For Method 1, about 1 μg/L Pb was added to the solution containing added standards of the other three trace metals to simulate a sample containing Cu(II). The resulting voltammogram showed a very much depressed Zn(II) peak and broad Cu(II) peak with displaced peak potential. This was due to the intermetallic formation of Cu-Zn (15). Cd and Pb exhibited no intermetallic effects. Addition of Ga(III) prevented Cu-Zn intermetallic formation since the Cu-Ga intermetallic compound is more stable than that of Cu-Zn. Simultaneous analysis of Cd(II), Pb(II) and Zn(II) was thus possible with the addition of Ga(III) ions to remove intermetallic interference.
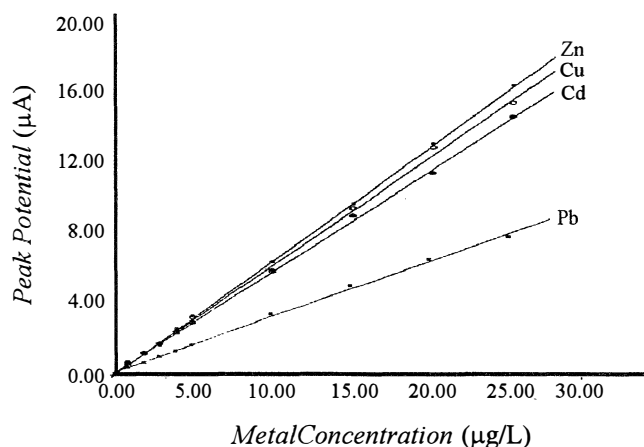
Fig. 1. Calibration plots for Cd(II), Pb(II), Zn(II) and Cu(II) in ultrapure water matrix. NaOAc-HOAc (0.016M) buffer, pH 4.8; using MFE (in situ); t_{dep}=3 minutes; scan rate=200 mV/s; E_{dep}=1.200 V(0.900 V for Cu); and concentration range, 0.00-25.0 μg/L
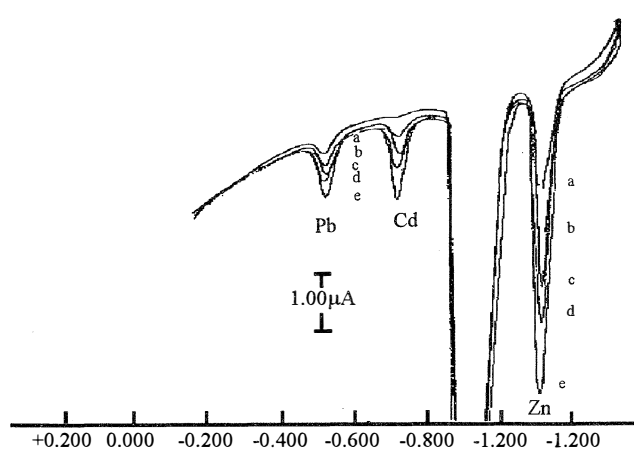

Fig. 2. Typical stripping voltammograms for the simultaneous analysis of Cd(II), Pb(II) and Zn(II) in NaOAc-HOAc (0.016M), pH 4.8; using MFE (in situ); E_{dep} = −1.2000 V; t_{dep} = 3 minutes; and scan rate = 200 mV/s. Metal standards used, (a) 0, (b) 1.00, (c) 2.00, (d) 3.00, (e) 4.00, and (f) 5.00 μg/L.

In Method 2, the deposition potential was set at a value more positive than the peak potential of Zn so no Zn(II) would be reduced and no Cu-Zn intermetallic formation would take place. Zn(II) analysis was carried out after the simultaneous analysis of Cu(II), Pb(II) and after addition of Ga(III). Figure 2 shows the typical voltammograms. The stripping peak potentials were −1.04 V for Zn(II), −0.65 V for Cd(II), and −0.47 V for Pb(II).

Cu(II) and Hg(II) were analyzed simultaneously using a gold disc electrode and the typical voltammograms are shown in Figure 3. The voltammograms showed well-defined stripping peaks for Cu(II) at a potential of +0.28 V and Hg(II) at +0.61 V.

In general, the metal ion behavior was the same whether analyzed individually or simultaneously, in either ultrapure water or seawater. The results also showed that Cu(II) is preferably analyzed using the gold electrode, since larger slopes were obtained compared to that from the mercury thin-film electrode. Thus Cu(II) and Hg(II) were simultaneously determined in the water samples and Method 1 involving simultaneous analysis of Cd(II), Pb(II) and Zn(II) was also adopted.

Concentration Dependence. A linear calibration plot similar to Figure 1 was obtained for each metal ion in simultaneous analysis by either of the two methods studied. Typical calibration plots obtained in seawater matrix are shown in Figure 4. Linear responses were obtained in the range of 0-5.00 μg/L. The precision as relative standard deviation (rsd) were within the acceptable levels for the different concentrations in μg/L. The % rsd for Cd(II), ranges from 0.5 to 2.0; for Pb, from 2.0 to 5.0; for Zn, from 1.0 to 7.0; for Cu, from 1.0 to 3.0; and for Hg, from 2.0 to 9.0.
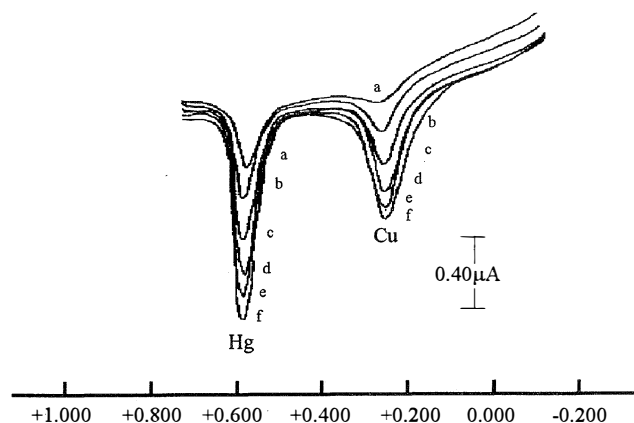

Fig. 3. Typical voltammograms for the simultaneous analysis of Cu(II) and Hg(II) in NaOAc-HOAc (0.016M), pH 4.8; using RGDE; E_{dep}=−0.200 V; t_{dep}=3 minutes; scan rate=200 mV/s; and medium exchange solution, 0.10M $HClO_4$+0.0025 M HCl. Metal standards used, (a) 0, (b) 1.00, (c) 2.00, (d) 3.00, (e) 4.00, and (f) 5.00 μg/L.

Detection Limit. The detection limit was determined for each metal using the simultaneous analysis of Cd(II), Pb(II) and Zn(II) on MFE and simultaneous analysis of Cu(II) and Hg(II) on RGDE. The detection limit is defined as the concentration which produces an analytical signal equal to twice the standard deviation of the background signal. The background signal was taken at the most sensitive setting of the instrument for the analytical method. The corresponding concentration was obtained from the slope of the calibration plot. The detection limit values were: 0.04 μg/L for Cd, 0.05
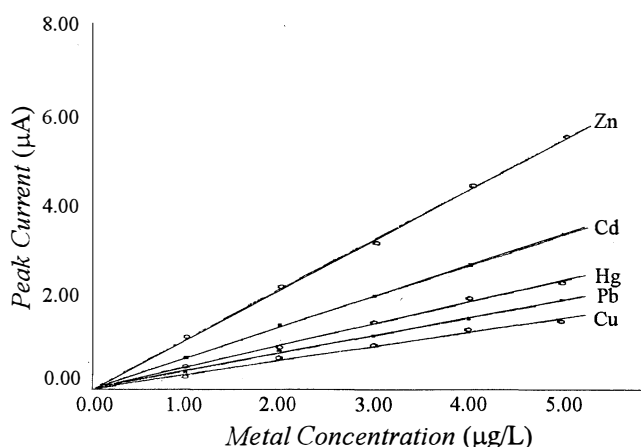
Fig. 4. Calibration plots for the simultaneous analysis of the five metals in seawater matrix. Supporting electrolyte, NaOAc-HOAc (0.016M), pH 4.8; t_{dep}=3 minutes; and scan range, 200 mV/s. Cd(II), Pb(II) and Zn(II) using MFE (in situ) and E_{dep}=−0.2000 V. Cu(II) and Hg(II) using RGDE; E_{dep}=−0.200 V and medium exchange solution, 0.10M $HClO_4$+0.0025 M HCl. Metal concentration range, 0-5.00 µg/L.

µg/L for Pb, 0.11 µg/L for Zn, 0.15 µg/L for Cu, and 0.13 µg/L for Hg.

Sample Analysis. Samples taken from Manila Bay were analyzed for the five trace metals using the developed ASV methods. The resulting voltammograms showed very large peaks for Zn(II) and relatively small signals for Cd(II) and Pb(II). A modification of Method 1 had to be carried out to be applicable to the water sample. A shorter deposition time was needed for Zn(II) and a longer one for both Cu(II) and Pb(II). Thus sample analysis involved the simultaneous analysis of Cd(II) and Pb(II) after Zn(II) determination. There was no problem encountered with the simultaneous analysis of Cu(II) and Hg(II). Table 1 gives a summary of the LSASV parameters used in the simultaneous analysis of these metals.

Table 2 shows the results obtained from the seawater samples analyzed. Sample C was also analyzed by the AAS method. Comparable values of Zn were obtained using both

Table 2. Total Metal Analysis Result for Trace Metals in the Manila Bay Seawater Samples (in µg/L)

Metal	Sample A (Near shore sample)	Sample B (Half a kilometer away)	Sample C (One kilometer away)	AAS Analysis (Sample C)*
Cu	1.08	0.61	.06	<3
Hg	3.06	1.20	0.42	<0.2
Cd	0.53	0.64	0.78	<3
Pb	2.16	0.90	0.85	<20
Zn	3.63	4.00	3.70	6

*AAS-MIBK extraction (for Cu, Cd, Pb, and Zn) and cold vapor flameless AAS (for Hg)

techniques. However, the AAS results were mostly below the detection limit of the technique. The ASV technique which is more sensitive than the AAS gave more reliable results.

As shown in Table 2, both Hg and Pb concentrations showed decreasing trend with distance away from the shore while the Cd concentration showed an increasing trend. However, there were very limited sampling stations used in this study and no periodic samplings were carried out due to time constraint. More sampling should have been conducted to be able to explain the trends in the obtained results.

Table 3 shows the reported values of trace metals in other seawater systems. The concentrations of the trace metals in Manila Bay were of comparable range as those reported. These values were still below the maximum allowed limits.

CONCLUSION

This study has shown that the sensitive LSASV technique is applicable to the simultaneous analysis of trace metals in seawater. Cd(II), Pb(II) and Zn(II) can be analyzed simultaneously under proper parameters and conditions to minimize interferences using the mercury film electrode. The most suitable simultaneous analysis of Cu(II) and Hg(II) is using the rotating gold disc electrode with the medium exchange technique.

Table 1. Summary of the LSASV Parameters Used in the Simultaneous Analysis of the Different Trace Metals

Trace Metals Analysis	Electrode	Deposition Potential (V)	Deposition Time (min)	Scan Range (V)	Stripping Potential (V)
Zn	MFE	−1.200	3.0	−1.200-0.000	−1.04
Simultaneous Cd and Pb	MFE	−1.000	5.0	−1.000-0.000	−0.47 [Pb(II)] −0.65 [Cd(II)]
Simultaneous Cu and Hg	RGDC	−0.200	5.0	−0.200-+0.750	+0.28 [Cu(II)] +0.61 [Hg(II)]

Supporting electrolytes: NaOAc-HOAc and NaOAC-HNO₃ buffers (pH 4.8)

**Tabel 3. Recent Typical Dissolved Trace Metals in Seawater (in µg/L)-
Total Metals Analysis.[a]**

Metal	Sample 1	Sample 2	Sample 3	Sample 4	Sample 5	Sample 6	Maximum Allowed Levels[b]
Cu	0.2-0.7	<0.3-2.6	0.127	1.22	0.099	0.060	1000
Hg	-	-	0.009	-	-	-	2
Cd	0.1-0.22	<0.1-0.4	0.014	0.051	0.004	0.002	100
Pb	-	0.2-3.5	0.042	0.827	0.045	0.005	50
Zn	1.9-7.0	0.5-4.0	0.770	-	-	-	5000

[a]Sample 1, N.W. Mediterranean (16); Sample 2, Darwin Harbour, Australia (17); Sample 3, Seawater, Italy (18); Sample 4, Belgian and Dutch Coasts (4); Sample 5, Arctic Ocean (4); and Sample 6, Pacific Ocean (Cook Islands) (4)
[b]DENR-EMB/BFAD standard limits

This voltammetric technique can be utilized for trace metal speciation study. Speciation is needed to assess the true extent of heavy metal pollution in Manila Bay.

ACKNOWLEDGMENT

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