

## Anodic stripping voltammetry of mercury, zinc, cadmium, and lead in a ricefarm ecosystem

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Analytical procedures based on differential pulse anodic stripping voltammetry were developed and applied to the analysis of some trace metals in a ricefarm ecosystem. A gold wire served as working electrode for the analysis of mercury in 0.1M HNO<sub>3</sub>; a hanging mercury drop electrode was used for the simultaneous analyses of zinc, cadmium, and lead in 0.1M sodium acetate buffer (pH 4.5). Mercury was pre-concentrated for five minutes at +0.20 V vs SCE. The area of the anodic stripping peaks varied linearly over the concentration range  $3 \times 10^{-10}$  -  $2 \times 10^{-8}$  M Hg(II); the limit of detection was 0.06 ppb or  $3 \times 10^{-10}$  M Hg(II). The simultaneous analytical method involved pre-electrolysis at -1.2 V vs SCE for ten minutes. The heights of the individual anodic stripping peaks varied linearly with concentration in a mixture of the ions over the concentration range 0.020-0.10 ppm for each ion; the limits of detection were 0.004 ppm, 0.01 ppm, and 0.01 ppm for Cd, Pb, and Zn, respectively. The developed procedures were used to determine the baseline levels of these metals in soil, water, and riceplant samples from a one-hectare traditional ricefarm in San Pedro, Laguna.

**Keywords:** anodic stripping voltammetry, gold wire electrode, heavy metals, ricefarm soil.

Heavy metals, such as mercury, cadmium, and lead are known to be highly toxic. These metals are typically present in the environment at submicrogram levels and, hence, require very sensitive methods of analysis. The most popular and accepted standard technique for trace metal analysis is atomic absorption spectrophotometry (AAS). However, anodic stripping voltammetry (ASV) is potentially a more sensitive technique than AAS because the former includes a pre-electrolysis step, which could readily concentrate metals 10-1000 times its original concentration without introducing any contamination (1). It has been successfully employed in the determination of some trace metals in natural waters at concentrations of  $10^{-9}$  M or less (2).

There appears to be very limited efforts in the Philippines to determine the extent of heavy metal pollution in ricefarms of agricultural lands. This paper describes the development of simple, sensitive, and inexpensive ASV methods for the analyses of mercury, cadmium, lead, and zinc in ricefarm samples.

The determination of mercury is based on the anodic stripping of submonolayer amounts of underpotential (UPD) mercury deposit on a gold wire. Several studies have described the underpotential deposition and stripping of mercury at gold electrodes in acidic media (3-7). Generally, multiple anodic stripping peaks have been observed in stripping analysis, indicating more than one surface state for the deposited mercury. However, at very low concentrations (less than  $10^{-8}$  M) of Hg(II), only UPD mercury is deposited and a single anodic stripping peak is obtained, which could be utilized in the quantitative analysis of Hg(II) at the ppb level (7,8).

The hanging mercury drop electrode (HMDE) was employed as the working electrode in the analysis of zinc, cadmium, and lead. The preparation of the electrode is simple and its performance in differential pulse ASV is comparable to the reportedly superior thin mercury-film electrode (9).

### Experimental

**Gold Wire Electrode (GWE).** The working electrode for mercury determination was a gold wire (0.05 mm. diameter) sealed in a 5-mm o.d. soft glass tube, exposing only about one centimeter of the wire. A copper wire, tightly wound around the concealed portion of the gold wire, provided electrical contact to the external circuit.

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The GWE was electrochemically pretreated by repeated potential cyclic scans (usually 5 to 10 scans) in the supporting electrolyte between +0.0V to +1.4V until reproducible current-potential curves (voltammograms) were obtained (usually after 5 to 10 scans). The electrode was then rinsed with deionized water, dried with tissue paper, and transferred into the test solution. The quality of the seal between the gold wire and the soft glass may be recognized from the shape of the residual current-potential curve or voltammogram (Figure 1); a slanting voltammogram indicates a leaking electrode.

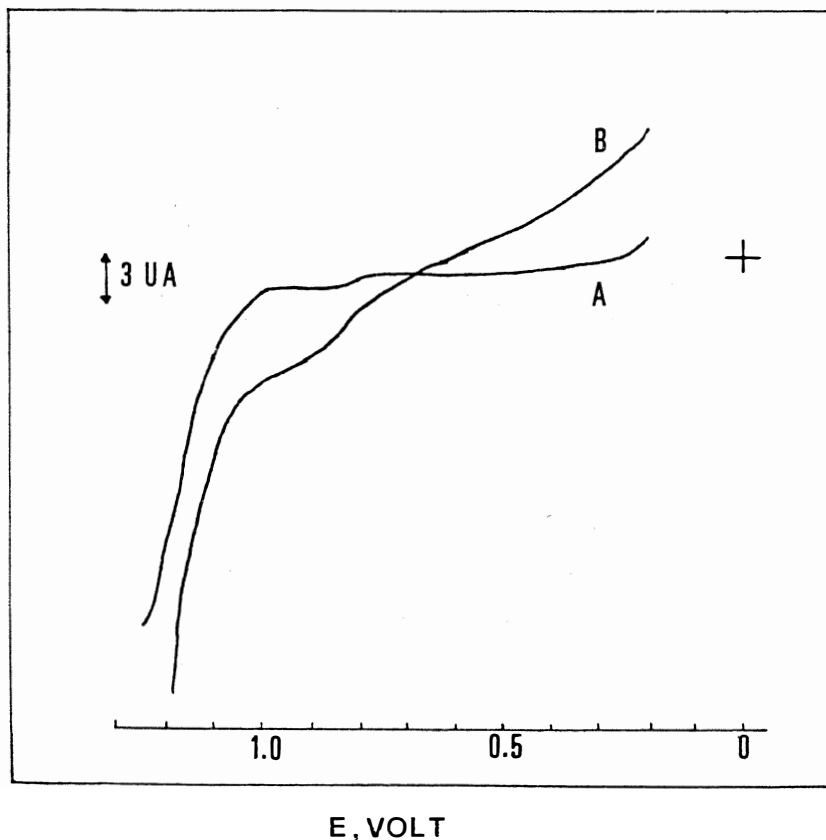


Figure 1. Residual voltammogram at GWE in 0.1 M  $\text{HNO}_3$ : (A) electrode with good seal; (B) electrode with poor seal.

**Hanging Mercury Drop Electrode (HMDE).** A short piece of platinum wire (0.016 in. diameter) was sealed in a 5-mm o.d. soft glass tube and a copper wire was soldered to the portion inside the tube to provide external contact. The exposed tip (one to two mm) of the platinum wire was polished on fine sand paper to a smooth surface flush with the glass. It was then etched slightly with aqua regia and plated with mercury for easier attachment of mercury drops; this procedure was performed routinely to ensure that there was no bare platinum (on which hydrogen evolution could occur, thus limiting the useful cathodic potential region of the electrode) exposed to the solution.

One to four drops of mercury (dispensed from a dropping mercury electrode capillary set-up, with its tip immersed in deionized distilled water) were collected, dried with a lint-free tissue paper, and attached to the platinum wire. A fresh HMDE was generally used for each determination. The average Hg drop weight was  $42.9 \text{ mg} \pm 1.5 \text{ mg}$ , corresponding to an average surface area of  $.102 \text{ cm}^2$ .

**Electrochemical Cell.** The cell consisted of a 150-ml pyrex beaker (pre-cleaned and soaked overnight in 1:1  $\text{HNO}_3$ ), covered with a plexiglass lid with ports for nitrogen gas dispersion tube, the platinum foil (ca.  $1 \text{ cm}^2$ ) auxiliary electrode, the working electrode (HMDE or GWE), and the Luggin capillary salt bridge. A saturated calomel electrode (SCE), served as the reference electrode, and was introduced into the cell via an H-salt bridge with a Luggin capillary tip to minimize chloride contamination (from the SCE) of the test solution. The cell was located in a fixed position over a constant-speed magnetic stirrer.

*Reagents.* All solutions were prepared with doubly-distilled deionized water. All acids were analytical-reagent grade (Merck). Stock solutions of Hg(II) were prepared from reagent-grade mercury (II) monohydrate salt (Merck). Standard solutions of zinc, cadmium, and lead were prepared from 1000 ppm standard solutions of zinc acetate, cadmium sulfate, and lead nitrate (BDH Chemicals Ltd., Poole, England), the final solution being 0.3M in nitric acid. The acetate buffer was prepared from reagent-grade sodium acetate (BDH Laboratory Reagents) and glacial acetic acid (Merck).

*Instrumentation.* The voltammetric equipment was either a Sargent-Welch polarograph (Model 4001) with a differential pulse module, or a modular set-up consisting of a Gerhard Bank Elektronik potentiostat (Wenking Model LB75L), coupled with a voltage scan generator (Wenking Model VSG 72) and a Rhode and Schwarz X-Y recorder. Potential were monitored with a Keithley 160 digital multimeter.

*Test Farm.* Test samples were taken from a one-hectare ricefarm located in Barrio San Vicente, San Pedro (Laguna), which employed traditional ricefarming practices. Samples of the surface (0-10 cm deep) soil, core (one meter deep) soil, paddy water, and rice plants were taken in 1983-1984. More details regarding the farm, the sampling procedure, and preliminary sample treatment are found in an earlier study on this farm, which reported that zinc, cadmium, lead, and mercury were below the detection limit of the AAS technique used (10). Since said study found relatively insignificant differences in the metal levels in samples from three sampling sites, test samples from only one site were generally used in the present study.

*Sample Digestion for Mercury Analysis.* A 100-ml aliquot of the water sample was acidified to pH 2, (with 5.0 ml concentrated  $\text{H}_2\text{SO}_4$  and 2.5 ml of concentrated  $\text{HNO}_3$ ) and left to stand for about two hours to decompose any mercury complexes present. Soil and rice plant samples were subjected to acid permanganate oxidation (11,12).

Reagent blanks were prepared for each type of test sample.

*Sample Digestion for Simultaneous Determination of Zinc, Cadmium and Lead.* The soil digestion procedure was taken from Pinta (13). Two-gram surface soil sample were taken for analysis, while only one-gram core soil samples per 100 ml of the test solution was used since the core soil consisted of coarser particles (14), and required more acid for digestion than the surface samples.

The procedure prescribed by the U.S. Environmental Protection Agency (12) was used in water analysis. Water samples were preconcentrated from 500 ml to 100 ml.

Rice plant sample were digested according to the method of the Association of Official Analytical Chemists (15).

Reagent blanks were prepared for each test sample.

Digested samples which could not be analyzed immediately were kept in the freezer and later thawed gently prior to analysis.

*Analysis of Mercury.* The voltammetric method of Sipos et al. (16) was modified for application to mercury analysis of ricefarm samples. The pH of a 25-ml aliquot of the digested sample was adjusted to 4.5 with 4 M sodium acetate buffer; final volumes were 100 ml for soil and 50 ml for water and rice plant samples.

The sample was deaerated for 10 minutes with nitrogen, which was kept flowing above the solution during measurements. Pre-electrolysis was done either at 0.20 V for ten minutes under stirred conditions using conventional or linear scan ASV, or for five minutes at 0.30 V using the differential pulse mode (DPASV). The applied potential was then switched off and the cell rapidly replaced by another containing 100 ml of freshly prepared 0.1 M  $\text{HNO}_3$ . This medium exchange was a precautionary measure, in case the environmental samples contained chloride, which may damage the gold electrode during the stripping stage by forming gold chloro-complexes (17). The potential,  $E_{\text{dep}}$ , was immediately re-applied and anodic stripping carried out in a quiescent condition.

The mercury concentration was evaluated by two standard additions (using Eppendorf micropipets). The anodic stripping peak area (in microcoulombs,  $\mu\text{C}$ ) was measured with a polar planimeter and served as the analytical signal. Each analysis consisted of five to ten replicate runs on the same solution. Duplicate trials were made.

*Analysis of Zinc, Cadmium, and Lead.* The pH of a 25-ml aliquot of the digested sample was adjusted to 4.5, and the solution deaerated as described in the mercury analysis. Pre-electrolysis was at -1.20 V for 10 minutes under stirred conditions. Stirring was then stopped, the background current allowed to decay for 30 seconds, and anodic stripping carried out in the quiescent solution.

Each analysis consisted of five to ten replicate runs on the same solution; duplicate trials were performed. At least two standard additions (using Eppendorf micropipets) were done for quantitative analysis. The maximum current of the anodic stripping peak, or peak height (the perpendicular distance from the peak to the baseline drawn through the minima on either side of the peak), served as the analytical signal.

## Results and Discussion

### Anodic Stripping Voltammetry of Mercury on Gold

*$E_{\text{dep}}$  and the Mercury Stripping Peak.* The relationship of the deposition potential ( $E_{\text{dep}}$ ) and the anodic stripping signal after a three-minute pre-electrolysis was studied in  $1 \times 10^{-9}$  M Hg(II) solution in 0.1 M  $\text{HNO}_3$  (see Figure 2). As  $E_{\text{dep}}$  became more negative, the area of the mercury anodic stripping peak at +0.87 V increased; however, at more negative values ( $E_{\text{dep}} < -0.3$  V), this peak became less symmetrical and broader, and at  $E_{\text{dep}} \leq -0.5$  mercury deposition was difficult, probably due to simultaneous hydrogen evolution at the electrode surface.

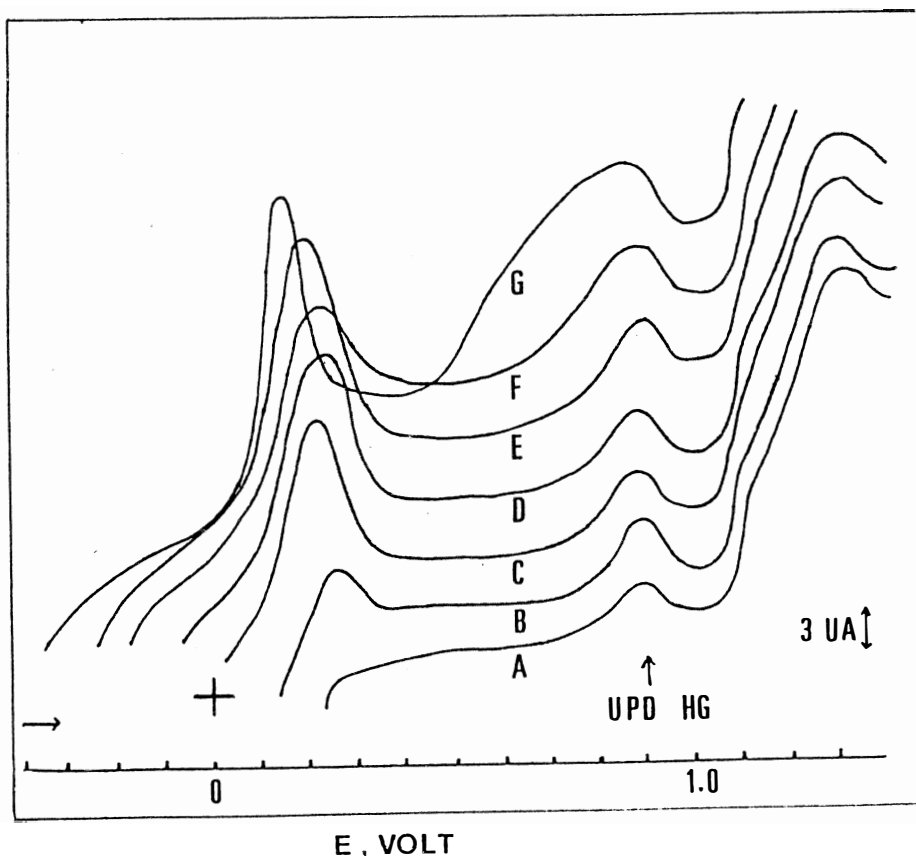


Figure 2. The dependence of conventional or linear scan ASV stripping curves on  $E_{\text{dep}}$ .  $1 \times 10^{-9}$  M Hg(II) in 0.1 M  $\text{HNO}_3$ ,  $t_{\text{dep}} = 10$  min., anodic scan rate = 100 mV/sec.  $E_{\text{dep}}$  (V), peak area ( $\mu\text{C}/\text{cm}^2$ ): (A) 0.20, 31; (B) 0.10, 50; (C) 0.00, 37; (D) -0.10, 54; (E) -0.20, 54; (F) -0.30, 92; (G) -0.40, 3750.

Co-deposition of copper was indicated by a second larger anodic peak at +0.20 V (cf. Figure 2); this peak increased in area and its peak potential shifted more negatively with increasingly negative  $E_{\text{dep}}$ . It was verified to be due to copper impurity present in the supporting electrolyte by spiking the solution with copper(II) ions (18). Other workers have also observed this simultaneous deposition of mercury and copper (7, 8, 17, 18).

*Time-Dependence of the Mercury Stripping Peak.* Anodic stripping curves as a function of deposition time ( $t_{\text{dep}}$ ) at  $E_{\text{dep}} = 0.00$  V in  $1 \times 10^{-9}$  M Hg(II) are shown in Figure 3. For  $t_{\text{dep}} \leq 11$  minutes, a single stripping peak at +0.88 V was observed, with peak area varying from 18 to 105  $\mu\text{C}/\text{cm}^2$ . This peak corresponds to the stripping of less than one monolayer of UPD mercury (7). After prolonged deposition ( $t_{\text{dep}} \geq 14$  minutes), three anodic stripping peaks were obtained: the peak at +0.86 V is associated with UPD Hg, the peak at +0.48 V with bulk mercury (i.e., Hg bonded to Hg), while the peak at +0.59 V with mercury-gold intermetallic compounds. The peak at +0.28 V corresponds to the stripping of co-deposited copper (as noted above), while the huge peak at +1.2 V is largely due to gold oxide formation (3,7).

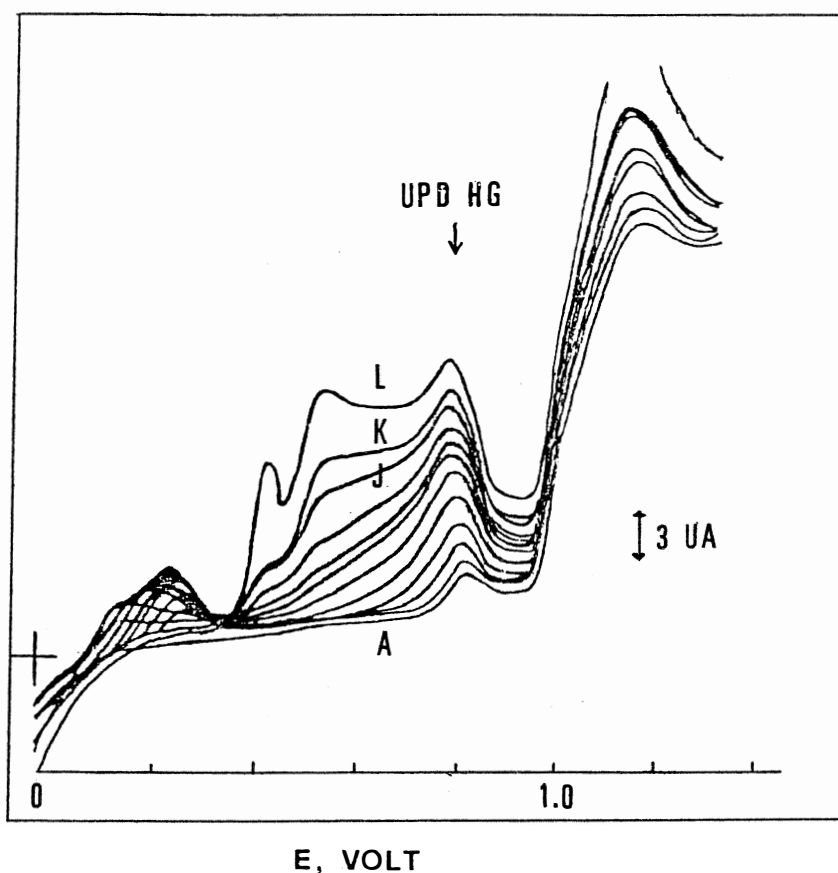


Figure 3. ASV stripping curves at a GWE for a  $1 \times 10^{-9}$  M Hg (II) in 0.1 M  $\text{HNO}_3$ ,  $E_{\text{dep}} = 0.00$  V, scan rate = 100 mV/sec.  $t_{\text{dep}}$  (min.): (A) 0; (B) 2; (C) 4; (D) 6; (E) 8; (F) 11; (G) 14; (H) 15; (I) 20; (J) 25; (K) 30; (L) 60.

*Concentration Dependence of Mercury Stripping Peaks.* Multiple stripping peaks are not desirable in quantitative stripping voltammetry, since they decrease the precision of measurements. Therefore,  $E_{\text{dep}}$  and  $t_{\text{dep}}$  must be precisely controlled to ensure that only the UPD mercury peak is obtained; these conditions are summarized in Table 1.

Figure 4A depicts the linear relationship between  $t_{\text{dep}}$  ( $E_{\text{dep}} = 0.00$  V) and stripping charge (peak area) at +0.88 V for  $1 \times 10^{-10}$  M  $\leq C_{\text{Hg(II)}} \leq 8 \times 10^{-9}$  M; correlation coefficients ( $r$ ) are indicated in the figure caption. Zero deposition time meant that the electrode potential was scanned anodically immediately upon applying  $E_{\text{dep}}$ . Figure 4B shows the relationship between stripping charge and Hg(II) concentration under the specified conditions. All data were corrected for the blank. The average relative standard deviation (RSD) of

$C_{\text{Hg(II)}}$  exceeded  $2 \times 10^{-8}$  M (cf. Figure 4B-3) wherein multiple stripping peaks occurred even with very short  $t_{\text{dep}}$ . However, it was found that the differential pulse mode of ASV (DPASV) could be employed at the higher mercury(II) concentrations.

Table 1. Experimental conditions for deposition of UPD Hg		
$E_{\text{dep}}$ (V)	$t_{\text{dep}}$ (min)	Hg (II) concentration range (M)
0.00	10	$1 \times 10^{-10} - 8 \times 10^{-9}$
0.00 to 0.20	10	$8 \times 10^{-9} - 2 \times 10^{-8}$
0.20 to 0.30	5	$> 2 \times 10^{-8}$

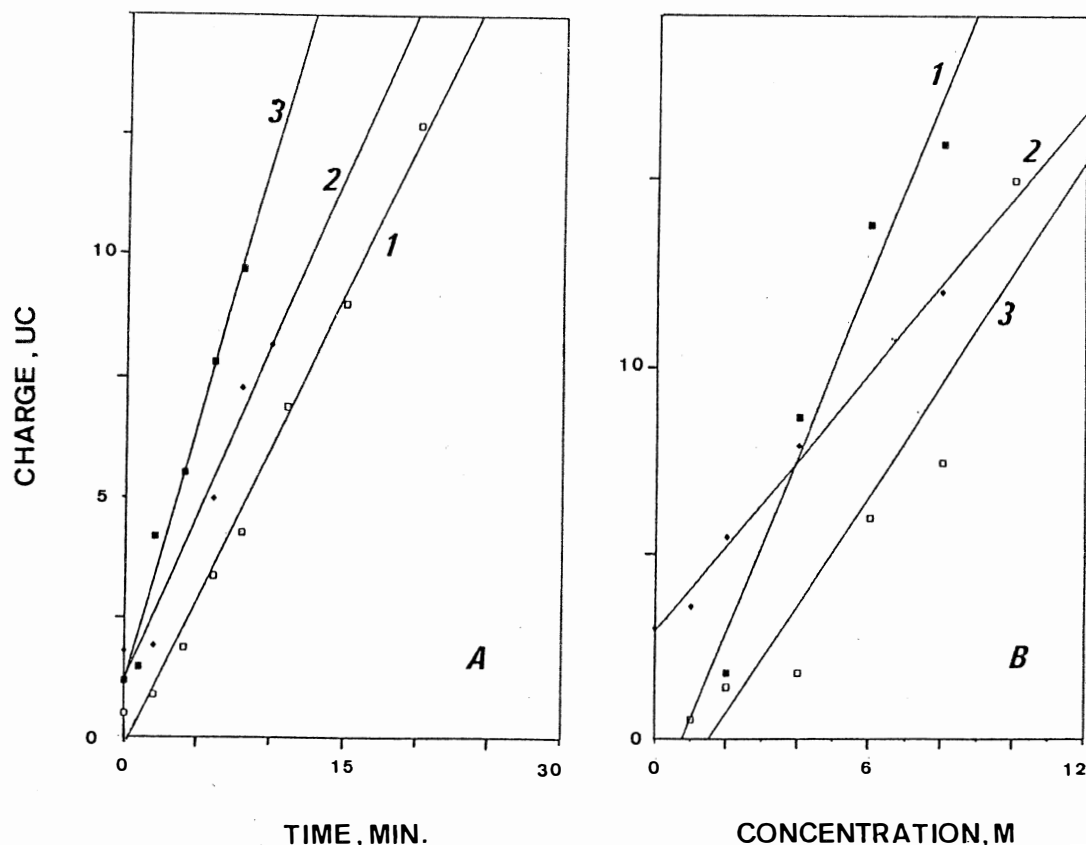


Figure 4. A. Charge (peak area) vs. deposition time in 0.1 M  $\text{HNO}_3$   $E_{\text{dep}} = 0.00$  V, anodic scan rate = 100mV/sec. molar concentration of Hg(II), correlation coefficient (r): (1)  $2 \times 10^{-10}$ , .9955; (2)  $1 \times 10^{-9}$ , .9819; (3)  $1 \times 10^{-8}$ , .9917.

B. Charge vs. Hg(II) concentration.  $E_{\text{dep}} = 0.00$  V, anodic scan rate = 100mV/sec.  $t_{\text{dep}}$ , Hg(II) concentration scale, correlation coefficient (r): (1) 10 min,  $1 \times 10^{-10}$  M, .9760; (2) 10 min,  $1 \times 10^{-9}$  M, .9904; (3) 5 min,  $1 \times 10^{-8}$  M, .9417.

**DPASV.** Figure 5, curves A-D show that when  $0 < C_{\text{Hg(II)}} \leq 5 \times 10^{-6}$  M, a single, fairly symmetrical anodic peak, corresponding to the stripping of UPD Hg, is obtained at +0.80 V after  $t_{\text{dep}} \leq 10$  minutes. At  $C_{\text{Hg(II)}} 5 \times 10^{-6}$  M (Figure 5, curves E-G), bulk mercury (which stripped at +0.50 V) and some intermetallic Au-Hg compounds formed (stripping peaks at +0.68 V and at +0.84 V) after a two-minute deposition.

The charge equivalent to the stripping peak at 0.8 V for UPD Hg obtained at  $E_{\text{dep}} = +0.20$  V and  $t_{\text{dep}} \leq 5$  minutes varied linearly with mercury concentration in the range of 0.06-0.40 ppb or  $3 \times 10^{-10}$  -  $2 \times 10^{-9}$  M. The average RSD of peak areas at each concentration level was 8%. The limit of detection as determined on the blank was 0.06 ppb or  $3 \times 10^{-10}$  M Hg(II).

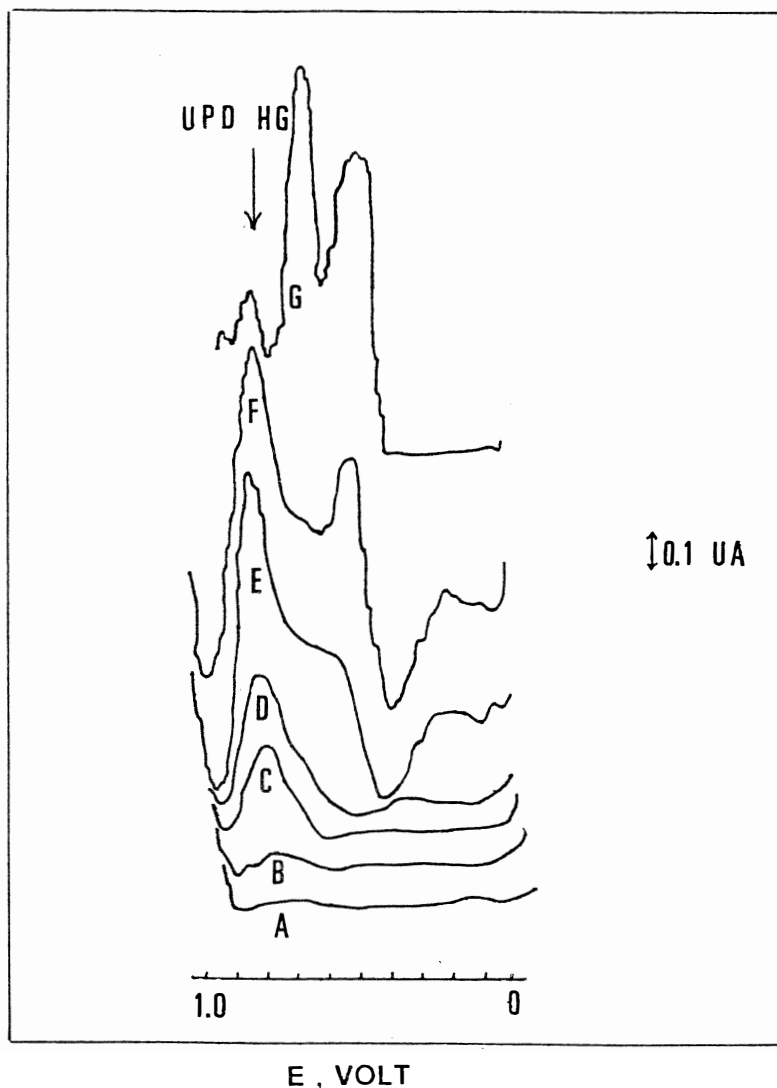


Figure 5. DPASV stripping curves (displaced origin) in 0.1M  $\text{HNO}_3$ ,  $E_{\text{dep}} = 0.00$  V,  $t_{\text{dep}} = 2$  min., anodic scan rate = 100 mV/sec, pulse height = 50 mV. Hg (II) concentration, M: (A) 0; (B)  $2 \times 10^{-7}$ ; (C)  $1 \times 10^{-6}$ ; (D)  $5 \times 10^{-6}$ ; (E)  $1 \times 10^{-5}$ ; (F)  $2 \times 10^{-5}$ ; (G)  $5 \times 10^{-5}$

*Effect of Copper on the Mercury Peak.* AAS yielded average copper levels of 0.02 ppm for water and 88 ppm Cu for soil samples (7). The possibility of Cu-Au intermetallic compound formation during the analysis and its effect on the mercury stripping signal was investigated. A monolayer of underpotential copper (equivalent to  $413 \text{ uC/cm}^2$ ) stripped at +0.14 V, bulk copper at +0.20 V, and some Cu-Au intermetallic compound(s) at +0.59 V. However, it was evident from the stripping curve of a mixture of 159 ppm or  $2.5 \times 10^{-3}$  M Cu(II) and  $2 \times 10^{-10}$  M Hg(II) in 0.1 M  $\text{HNO}_3$  that the copper peak did not interfere with the UPD mercury peak: increasing the Hg(II) concentration in the mixture resulted in a proportionate increase of the Hg stripping peak area at +0.8 V, while the Cu stripping peak area remained essentially constant (18).

*Analyses of the Ricefarm Samples.* Possible interferences by dissolved organic matter (e.g. by adsorption on the electrode during the deposition stage, reduction at a potential in the vicinity of the mercury stripping

solution after addition of a strong oxidant to free the mercury for voltammetry (17). The non-irradiated digested ricefarm water sample revealed a broad anodic Hg peak at about +0.64 V; after uv-irradiation for 17 hours with a 15-watt uv lamp, a sharper peak was observed with peak potential at +0.70 V, suggesting the destruction of some organo-mercury complex. The Hg stripping peak potential is slightly more negative than that obtained in synthetic Hg solutions because of the different sample matrix. For these environmental samples,  $E_{\text{dep}}$  of +0.2 V or 0.3 V was used in the analyses (cf. Table 1) to avoid any intermetallic compound formation.

The DPASV data, are compared with the AAS results (10) in Table 2. In general, soil analyses by the two methods were consistent. However, DPASV yielded lower values than AAS for water and rice plant samples. It will be noted that the DPASV method omits the additional step in the AAS procedure, which involved the chemical reduction of Hg(II) to the elemental form prior to analysis.

Table 2. Mercury content of different components of the ricefarm ecosystem				
			Mercury content, ppm <sup>*</sup>	
Sample	Farm Site	Sampling Date	DPASV	AAS
Paddy Water	5	January, 1984	< 0.00006	< 0.0004
	5	June, 1984	< 0.00006	0.0008
	5	August, 1984	< 0.00006	0.0005
	5	September, 1984	< 0.00006	< 0.0004
Surface soil (0-10 cm)	2	May, 1983	0.010 $\pm$ .002	< .04
	3	May, 1983	0.010 $\pm$ .003	< .04
	5	May, 1983	0.006	< .04
Core soil (1 meter)		June, 1983	0.020 $\pm$ .003	0.14
Bare grain	2,3,5	November, 1983	< .006	.012 - .019
Plant + hull (without grain)	2,3,5	November, 1983	< .006	.032 - .045
<sup>*</sup> Limits of detection (ppm):				
Water			0.00006	0.0004
Soil			0.00006	0.04
Bare rice grain			0.006	0.0001
Plant + hull (without grain)			0.006	0.0001

#### *Simultaneous DPASV of Zn(II), Cd(II) and Pb(II)*

*Useful Potential Range in Different Supporting Electrolytes.* The useful potential window of the HMDE was determined in several supporting electrolytes (18). Ammonia buffer, KCl, and NaOH gave wide cathodic but limited anodic potential windows. Strong acids such as H<sub>2</sub>SO<sub>4</sub>, HNO<sub>3</sub>, and HCl gave narrow cathodic potential ranges due to hydrogen reduction. Acetate buffer gave the widest useful potential range (-1.46 V to +0.19 V vs. SCE) and was used as the supporting electrolyte in the analysis.

*Effect of Potential Scan Rate.* Current or peak heights were dependent on potential scan rate (Figure 6). A scan rate of 0.50 V/min gave the optimum peak resolution and speed of analysis. The faster scan rate (1.0 V/min) showed decreased sensitivity, while the slower rate (0.20 V/min) gave excellent resolution but required a longer run time. The figure also shows that the sensitivity of the Zn signal at the medium scan rate is more comparable to those of Pb and Cd. The relative precision (RSD) of the peak heights for three consecutive runs were: Zn =  $\pm 2.7\%$ ; Cd =  $\pm 1.9\%$ ; Pb =  $\pm 4.4\%$ ; the average day-to-day reproducibility (obtained on three



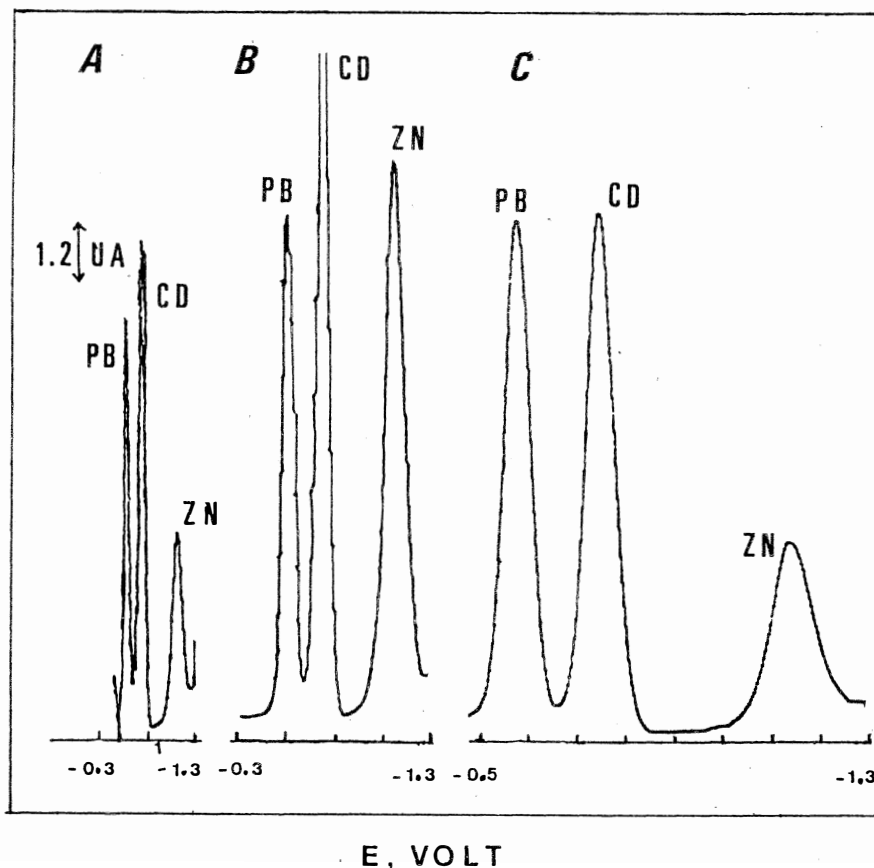


Figure 6. DPASV stripping voltammogram as a function of potential scan rate. 2 ppm each in Pb, Cd, and Zn, in 0.1 M NaAc buffer (pH = 4.5),  $E_{\text{dep}} = -1.3\text{V}$ ,  $t_{\text{dep}} = 1\text{ min}$ . Scan rate (V/min): (A) 1.00; (B) 0.50; (C) 0.20.

**Effect of pH.** The electroanalytical behavior of a mixture containing 2.0 ppm each in Zn(II), Cd(II) and Pb(II) in different supporting electrolytes of varying pH (1-13) was also studied (18). Well-defined anodic stripping peaks of zinc, cadmium, and lead were observed at pH 4.4 - 5.9. At very low pH (pH 1-2) cadmium and lead also gave well-defined anodic peaks; however the zinc peak was hardly discernible, quite unsymmetrical, and occurred very close to the rising portion of the background current near the cathodic limit. At pH 9, the lead stripping peak appeared small and broad; while at pH 13 a small, unsymmetrical broad zinc peak, and poorly resolved cadmium and lead peaks were obtained. It was concluded that pH 4.4 (acetate buffer) was the optimum value for the simultaneous determination of zinc, cadmium, and lead.

**Deposition Potential ( $E_{\text{dep}}$ ).** The optimum value of  $E_{\text{dep}}$  was determined in a mixture of 2.0 ppm each in zinc, cadmium, and lead standards in 0.1 M NaAc buffer using one-minute electrodeposition.  $E_{\text{dep}}$  was varied from -1.50 V to -1.10 V in increments of 100 mV: the anodic potential limit was -0.1 V. The sharpest anodic stripping peaks were obtained using  $E_{\text{dep}} = -1.30$  or 1.20 V.

**Effect of Pulse Height or Modulation Amplitude.** Peak current increased with pulse height as expected in differential pulse voltammetry (21). In addition, the peak width at half-peak current increased with pulse height, resulting in decreased resolution. A pulse height of 30 mV was chosen as the compromise value (18).

**Calibration Curves.** Figure 7 shows that the measured peak heights for each metal were linear (correlation coefficients,  $r$ , are indicated in the figure caption) with concentration for mixed standards in the concentration range 0.020-0.10 ppm each in Zn, Cd, and Pb. Peak heights for Pb were corrected for the blank, which contained approximately 0.01 ppm Pb. The limits of detection, taken as twice the standard deviation of the pertinent peak height, were: Cd = 0.004 ppm, Pb = 0.10 ppm, and Zn = .01 ppm.

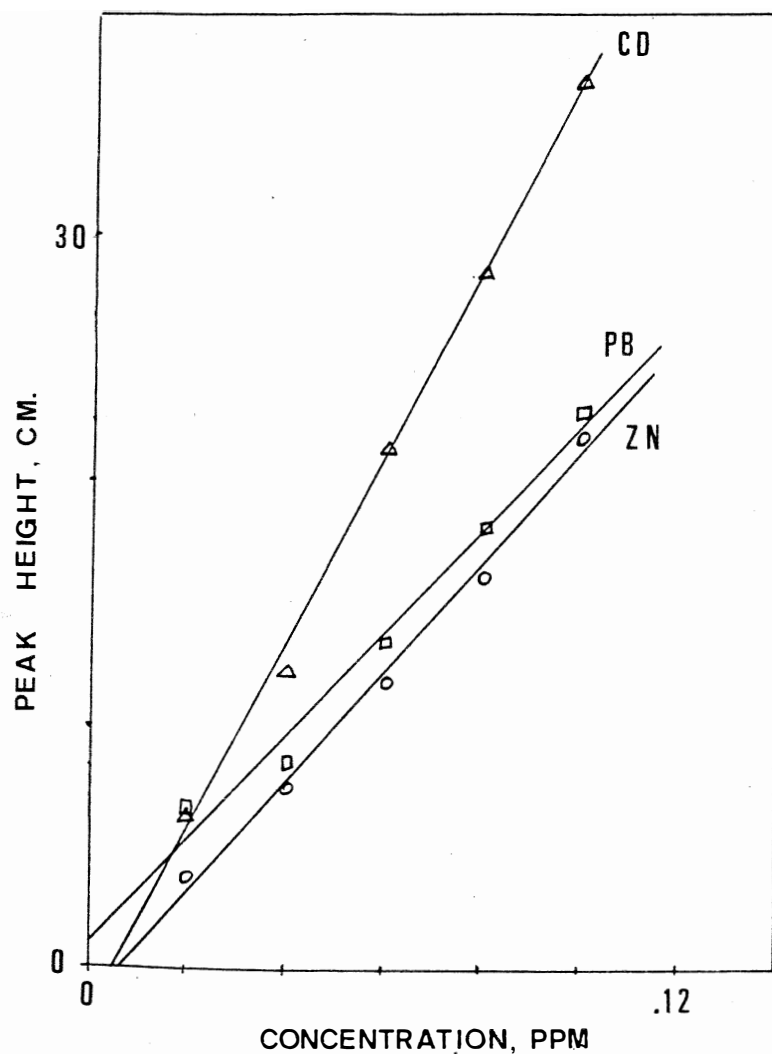


Figure 7. Calibration curves for the simultaneous DPASV analysis of Zn, Cd, and Pb.  $E_{\text{dep}} = -1.2$  V,  $t_{\text{dep}} = 20$  min, pulse height = 30 mV, scan rate = 0.50 V/min. Correlation coefficient ( $r$ ): Cd = 0.9984, Pb = 0.9903, Zn = 0.9969.

*Analyses of Ricefarm Samples.* The mean RSD of duplicate trials (each trial consisting of three to five replicate voltammetric runs) of the different ricefarm samples ranged from 15-19% for Zn, 25-28% for Pb, and 16-23% for Cd. The limits of detection for the three metals in the different samples are given in Table 3.

Table 3. DPASV detection limits for Zn, Cd, and Pb			
<u>Sample</u>	<u>Element</u>	<u>Detection limit, ppm</u>	
		DPASV a	AAS b
Water	Zn	0.02	0.02
	Cd	0.007	0.02
	Pb	0.02	0.2
Core soil (1 meter)	Zn	0.02	0.02
	Cd	0.002	2
	Pb	0.03	10
Surface soil (0-10 cm)	Zn	0.02	0.02
	Cd	0.002	1
	Pb	0.03	0.2
Rice grain (bare)	Zn	0.5	0.005
	Cd	0.05	0.5
	Pb	0.5	5
Plant + hull	Zn	5	0.005
	Cd	0.5	5
	Pb	5	10
<p>a Limit of detection for soil and water samples was taken at twice the average deviation from the mean peak height of the sample having the lowest concentration. However, for the rice samples, it was based on twice the blank signal, since there was only one rice harvest for the study.</p> <p>b AAS detection limits taken from Vicente-Beckett et. al. (10)</p>			

Table 4 gives the analyses of water and soil samples, together with the AAS results (10). In general, mean values of the DPASV method agreed satisfactorily with the AAS studies, and, in some instances (e.g., Cd), provided better estimates of the actual levels of these metals in the ricefarm ecosystem. However, the results for Pb gave poor agreement with the AAS data. Lead contamination, most probably from the atmosphere, was indicated in the highly variable blank analyses. Elevated Pb content in Metro Manila soils have been correlated to atmospheric emissions arising from vehicular fuel combustion (22,23).

Zinc content of the grain and of the rest of the riceplant appeared to be very low (below LOD): even prolonged deposition (up to one hour) did not enhance the stripping signal. The zinc response was not linear (not true with cadmium and lead) when the rice sample was spiked with increasing amounts of a mixture of the three metal standards. These observations suggest some sort of interference, possibly complexation with a matrix constituent or formation of intermetallic compound(s) between zinc and copper (24). Further investigation on this aspect is needed.

Table 4. Analyses of water, soil, and riceplant samples			
Sample/ Sampling date	Element	DPASV Concentration ppm <sup>a</sup>	AAS Concentration ppm
I. Water			
March, 1984	Zn	< .02	< .02
	Cd	< .01	< .02
	Pb	.032 ± .008	< .2
August, 1984	Zn	.10 ± .02	< .02
	Cd	< .01	< .02
	Pb	.123 ± .005	< .2
II. Surface Soil			
June, 1983	Zn	113 ± 33	121 ± 75
	Cd	1.0 ± 0.4	< 1
	Pb	58 ± 22	< 16 ± 1
October, 1983	Zn	36 ± 6	50 ± 1
	Cd	0.55	< 1
	Pb	46 ± 34	< 5
III. Core Soil (1 meter)			
June, 1983	Zn	28 ± 2	27.0
	Cd	2.2	< 2
	Pb	39 ± 31	20
August, 1983	Zn	44 ± 18	32
	Cd	1.0	< 2
	Pb	8.0	< 10
IV. Bare Rice Grain			
November, 1983	Zn	< .5	122
harvest	Cd	< .05	< 0.5
	Pb	< .5	< 5
V. Plant + Hull (w/o grain)			
November, 1983	Zn	< 5.0	11-14
Harvest	Cd	< 0.5	< 5
	Pb	< 5.0	< 10

## Conclusions

This study has established that under ordinary laboratory conditions the ASV method has generally better (i.e., lower) detection limits than AAS. The differential pulse mode (DPASV) provided higher sensitivity and better precision, and required shorter deposition times than the conventional method (ASV). Even lower detection limits may be attained by increasing the deposition time, precisely controlling  $E_{\text{dep}}$  and/or conducting experiments in a clean bench (as in a laminar flow hood). DPASV also allowed for the simultaneous determination of three elements, which is another advantage over the sequential AAS measurements. Moreover, the ASV instrumentation is much cheaper than that for AAS and may easily be home-built (25,26).

Finally, this study has provided some baseline information on the levels of some heavy metals in an agricultural ricefarm, which is presently still inadequate. The levels of Hg, Zn, and Cd in the different components of the ricefarm indicate as yet relatively low pollution.

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