Differential Pulse Anodic Stripping Voltammetry in a Thin-Layer Electrochemical Cell

Sir: The electrochemistry of thin layers of solution has proved useful for a variety of studies including adsorption at electrodes, kinetics of homogeneous reactions coupled to electrode processes, spectroelectrochemical measurements, and the coulometric determination of n values (*1–3*). For analytical purposes, thin-layer electrochemical cells possess the inherent advantage of small volume capability, experiments having been performed on as little as 5 μl of solution. However, analytical detection limits have been limited to ca. 10^{-5} M by thin-layer coulometry, the electroanalytical technique normally used in conjunction with thin-layer cells (*1–6*).

This communication describes results which demonstrate the feasibility of substantially improving the analytical sensitivity of thin-layer electrochemical cells by using differential pulse anodic stripping voltammetry (DPASV). The pulse voltammetric techniques are among the most sensitive electroanalytical methods. For example, typical detection limits of ca. 300 ng/ml for tetracycline by differential pulse polarography and ca. 0.01 ng/ml for lead by differential pulse anodic stripping voltammetry have been reported (*7, 8*).

EXPERIMENTAL

Apparatus. The thin-layer cell was constructed of Lucite and Teflon as shown in Figure 1. Reference and auxiliary electrodes were isolated from the cell by press-fitted Vycor glass plugs in plastic tubes filled with supporting electrolyte. The polished graphite rod was pressed into the bottom Teflon plate and made even with its surface. Two holes in the top plate permitted solution introduction and evacuation.

The substrate for the mercury film electrode was POCO FXI graphite rod (POCO Co., Dallas, Texas), 0.5-cm diameter, 50-mm length. Wax impregnation was accomplished by immersion of the graphite in molten paraffin under vacuum for 6 h. The electrode end was prepared by polishing on a flat surface with No. 600 grit emory paper followed by cerium oxide powder on rough filter paper and then brought to a mirror-like finish by polishing with alumina (0.05 μm) on felt cloth (Fisher Scientific Co.). These last two steps were repeated each morning before experimentation was begun.

Differential pulse voltammograms were obtained on a Princeton Applied Research Model 174 Polarographic Analyzer. Signals were recorded on a Houston Instrument 2200-5-6 x-y recorder.

Procedure for Metal Ion Determination. One milliliter of pre-electrolyzed supporting electrolyte was drawn through the cell with a vacuum aspirator. This step was repeated between each analysis. Seventy microliters of the solution to be analyzed, containing 20 μg/ml Hg^{2+} ion, was injected into the cell. Deposition at −0.950 V vs. SCE for exactly 60 s followed. The potential was then scanned anodically from −0.950 V to 0.000 V at 5 mV/s with two 50-mV pulses every second.

Reagents. Lead and cadmium solutions were prepared by dilution of 1000 μg/ml atomic absorption standard (Fisher Scientific Co.) with supporting electrolyte. Each solution was made 20 μg/ml in Hg^{2+} ion by the appropriate dilution of 1000 μg/ml atomic absorption standard (Fisher Scientific Co.) Supporting electrolyte used for dilution of metal ion solutions was 1 M in potassium acetate (Baker, Analyzed) and 2 M in acetic acid (E. I. DuPont) at pH 4.0. Supporting electrolyte was pre-electrolyzed at −1.2 V vs. SCE for 48 h. All solutions were prepared with distilled, deionized water.

RESULTS

The objective of this study was to demonstrate the feasibility of using differential pulse voltammetry for analysis in a thin-layer cell. The system selected for evaluation was the well-documented determination of lead and cadmium by DPASV at a mercury film electrode.

The thin-layer electrochemical cell which was developed for this work is shown in Figure 1. The complete cell holds 70 μl of solution with 6 μl actually undergoing electrolysis at the working electrode. The cell thickness is only 0.030 cm, which enables complete electrolysis to be achieved within 1 min with diffusion as the only mode of mass transport as is typical in a thin-layer cell (*1–3*). The volume of solution undergoing electrolysis and the time required for complete electrolysis were determined coulometrically (*5, 6*). POCO FXI spectroscopic grade wax impregnated graphite (WIG) was found to be the best substrate for the mercury film electrode (*9*). A mercury film electrode prepared by simultaneous deposition of the mercury film and metal ions gave more reproducible results than an electrode with a preformed mercury film (*10*). This cell has met our initial criteria of containing a relatively small volume of solution and being easy to fabricate and use.

Figure 2 shows a typical voltammogram of a 50 ng/ml Pb^{2+} and Cd^{2+} mixture. Seventy microliters of the analyte solution was injected into the cell and the Pb^{2+}, Cd^{2+}, and Hg^{2+} were deposited onto the WIG by maintaining the potential at −0.950 V vs. SCE for 60 s. This step also removed dissolved oxygen by reduction to water. Accurate deposition time was necessary due to edge concentration of the analyte into the mercury film (*11*). Pb and Cd were then stripped out of the thin mercury film by DPASV giving the voltammogram in Figure 2. The two oxidation peaks are well-defined and resolution is good. No distortion due to the rather large solution resistance of the thin layer is evident, as the voltammogram compares favorably with that reported in the literature for DPASV on mercury film electrodes in bulk solution (*12*).

Table I shows the data for peak height vs. Pb^{2+} and Cd^{2+} ion concentrations which were linear from 25 ng/ml to 500 ng/ml. The standard deviation of the data is well within ac-

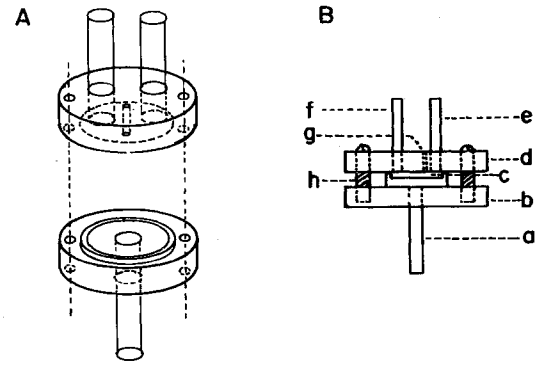

Figure 1. Thin-layer cell

(A) Exploded view of the cell. (B) Side view of assembled cell. (a) Wax impregnated graphite electrode. (b) Teflon bottom plate. (c) Solution. (d) Lucite top plate. (e) Reference electrode salt bridge, Vycor glass plug. (f) Auxiliary electrode salt bridge, Vycor glass plug. (g) Solution entrance ports. Exit port left out for clarity. (h) Screws to hold the cell together

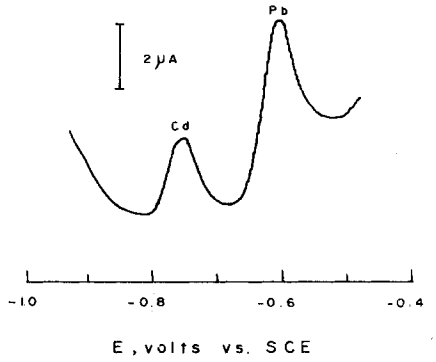

Figure 2. Differential pulse anodic stripping voltammogram of a 50 ng/ml Pb^{2+} and Cd^{2+} mixture in a pH 4.0 acetate buffer with 20 μg/ml of Hg^{2+} at a POCO FXI WIG in the thin-layer cell

Sixty-second deposition at −0.950 V vs. SCE, followed by anodic scan, scan rate = 5 mV/s, two 50-mV pulses every second. $E_{peak,Cd}$ = −0.74 V vs. SCE; $E_{peak,Pb}$ = −0.58 V vs. SCE

ceptable limits for electrochemical trace metal analysis. The detection limit for this method is presently ca. 10 ng/ml. Each analysis took less than 5 min total time.

DISCUSSION

The results presented here for lead and cadmium clearly demonstrate the feasibility of using differential pulse voltammetry to substantially improve the analytical sensitivity of thin-layer electrochemical cells. The detection limit of 10 ng/ml for lead and cadmium is more than two orders of magnitude less than that previously reported by thin-layer coulometry (*1–6*). In addition to good sensitivity, a linear relationship between peak current and concentration was obtained over a wide concentration range. Although lead and cadmium were used in this initial study to demonstrate feasibility, the cell should be applicable to the usual variety of species which are amenable to electroanalysis.

Two anticipated difficulties with the thin-layer cell posed no problem. The relatively large solution resistance which exists in most thin-layer cell designs did not measurably distort the voltammograms, the current levels for differential pulse voltammetry being very low for this concentration range. Problems with memory effects and sample loss due to adsorption on the relatively large surface areas of the cell contacting the analyte were minimized by using Teflon and Lucite for the cell and by carefully rinsing the cell between analyses. Results were unaffected by alternating concentrated and dilute samples.

The thin-layer aspect of the cell enabled complete electrolysis of the 6-μl solution volume in contact with the working electrode to be achieved within 1 min with diffusion as the only mode of mass transport. Consequently, ca. 10% of the analyte in the 70-μl sample could be rapidly deposited into the mercury film without employing the controlled stirring conditions typically used for preconcentration in DPASV. Simultaneous with the deposition step, dissolved oxygen was removed by reduction to water, eliminating the need for nitrogen bubbling. This simplified the procedure and shortened the time required for analysis. Smaller volume cells (ca. 25 μl total volume) have been used effectively (*13*).

Differential pulse voltammetry can also be applied directly to electroactive species in the thin solution layer without preconcentration into the mercury film (*13*). Results with thallium show that reduction of Tl^+ by cathodic differential pulse voltammetry is within a factor of four as sensitive as oxidation of Tl from the mercury film by DPASV. This suggests that problems caused by intermetallic compound formation in the DPASV technique may be avoided in the thin-layer cell by using cathodic differential pulse voltammetry, without a substantial loss in sensitivity.

The thin-layer cell is potentially useful for the analysis of biological samples where sample quantities are sometimes small as in the case of the blood, milk, and organs of small test animals. There the small volume of the thin-layer cell minimizes sample dilution, a step which necessitates greater sensitivity in the analytical technique. This is particularly significant for samples in which dilution cannot be compensated for by preconcentration in a mercury electrode as in conventional DPASV.

Table I. Current Peak Height vs. Metal Ion Concentration

Concentration, ng/ml[a]		Average current, μA		Std dev, μA[b]	
Cd	Pb	Cd	Pb	Cd	Pb
25	25	1.44	2.70	0.06	
50	50	2.37	4.80	0.06	0.08
100	100	5.0_8	8.3_4	0.1_8	0.1_2
200	200	10.5	16.10	0.2_5	0.06
500	500	$23._6$	$37._7$	$2._6$	$1._9$

[a] pH 4.0 acetate buffer as supporting electrolyte with 20 μg/ml Hg^{2+}. 60-s deposition at −0.950 V. Scan to 0.00 V at 5 mV/s with two 50-mV pulses every second. [b] N = 3 for all determinations.

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