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Anodic Stripping Voltametry at Mercury Film  
Deposited on Ultrasmall Carbon Ring Electrodes

by

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**ANODIC STRIPPING VOLTAMMETRY AT MERCURY FILMS  
DEPOSITED ON ULTRASMALL CARBON RING ELECTRODES**

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# ANODIC STRIPPING VOLTAMMETRY AT MERCURY FILMS DEPOSITED ON ULTRASMALL CARBON RING ELECTRODES

## ABSTRACT

Anodic stripping voltammetry of lead and cadmium without deliberately added electrolytes has been studied at ultrasmall carbon ring electrodes following *in situ* deposition of mercury. The stripping of lead has been studied in detail to investigate the dependence of stripping peak current on experimental parameters such as potential scan rate, preconcentration duration, deposition potential, concentration of  $\text{Hg}^+$  during deposition and concentration of  $\text{Pb}^{2+}$ . Anodic stripping voltammetry in solutions without deliberately added supporting electrolyte avoids problems associated with impurities introduced when electrolyte is added. These impurities appear to be highly important when  $\text{Pb}^{2+}$  analysis is carried out in dilute solutions. In addition, a unique effect is observed when relatively low concentrations of  $\text{Hg}^+$  ( $1.0 \times 10^{-6}$  M) are used for the *in situ* deposition step. When low  $\text{Hg}^+$  concentrations are used, the stripping current does not decrease as rapidly as expected as the concentration of  $\text{Pb}^{2+}$  is reduced. The slope of the log-log plot of peak current vs  $\text{Pb}^{2+}$  concentration is significantly less than unity, but the calibration plot is linear and the resulting enhanced peak currents at low  $\text{Pb}^{2+}$  concentrations make stripping analysis possible at extremely low concentrations. Concentrations as low as  $3.2 \times 10^{-11}$  M of  $\text{Pb}^{2+}$  have been examined.

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## INTRODUCTION

Anodic stripping voltammetry (ASV) has always been regarded as one of the most sensitive techniques for trace metal analysis. In general, this technique is a non-destructive method and is applicable to multi-elemental analysis. The part per billion detection limit [1] of stripping analysis is attributable to the preconcentration that takes place during the deposition step. ASV is often carried out with a mercury thin film electrode [2] which provides a large surface area-to-volume ratio and this yields superior sensitivity during voltammetry.

There has also been intense study in the fabrication and development of microvoltammetric electrodes [3-5] during the past decade. Microelectrodes offer a number of attractive features suitable for many electroanalytical applications over conventional-sized electrodes. Small double layer capacitance owing to the small electrode surface area results in diminished electrode charging current. This produces a greater ratio of faradaic to non-faradaic current and can lead to enhanced detection limits [6]. Additionally, the small currents passed by microelectrodes result in negligible ohmic losses and this allows electroanalysis to be carried out in poorly conductive media. This permits the use of systems without any deliberately added supporting electrolyte. Impurities introduced with electrolyte are thus eliminated and the range of potentials accessible for electrochemical measurements can be extended [7]. The combination of small capacitive charging current and small potential drop across the uncompensated cell resistance provides a system where high scan rate cyclic voltammetry is possible. In fact, scan rates above one million  $V s^{-1}$  have been demonstrated [8]. In contrast, at low scan rates ( $< 1 V s^{-1}$ ), edge diffusion [9,10] becomes dominant at

microelectrodes during voltammetry. A steady state diffusional mass transport of electroactive species to the electrode region then arises.

Golas and Osteryoung [11,12] have performed anodic stripping square-wave voltammetry in solutions of  $\text{Pb}^{2+}$  and 0.1 M KSCN with cylindrical carbon-fiber microelectrodes. They observed a linear relationship between anodic stripping peak current and concentration of lead over a range of 0.5 to 4  $\mu\text{M}$ . Sottery and Anderson [13] have demonstrated a technique of short-pulse rapid-scan stripping voltammetry using mercury film carbon-fiber electrodes. Well-resolved peaks were observed for sub-microgram-per-liter levels of lead and cadmium with 60 s deposition time. This technique shows a substantial increase in signal-to-background ratio per unit determination time compared to conventional differential pulse ASV. In another study, Wang and co-workers [14-16] have performed differential pulse ASV using carbon-fiber electrodes in resistive solutions (eg. acetonitrile, methanol, ethylene glycol), in solutions of dilute supporting electrolyte (0.001 M acetate buffer) and aqueous solutions of low ionic strength. In each case, well-defined stripping peaks with no distortion resulting from uncompensated ohmic drops have been observed. Baranski [17] has also described the use of mercury-film microelectrodes for ASV of cadmium and lead in volumes as small as 5  $\mu\text{L}$  with scan rates in the range of 1-100  $\text{V s}^{-1}$ . Jagner and co-workers [18,19] have developed a computerised flow potentiometric stripping method in which automated determinations of lead and cadmium in whole blood were carried out at mercury pre-plated carbon fiber electrodes. Wehmeyer and Wightman [20] have constructed mercury microelectrodes with radii between 2.3 and 7.3  $\mu\text{m}$  using a Pt disk as electrode substrate. In this work, a linear relationship was observed between stripping peak current and concentration of lead over the range of  $7 \times 10^{-10}$  to  $1 \times 10^{-7}$  M, with 0.5-1.5% relative standard

deviation. More recently, Tay *et al.* [21] applied pre-plated mercury on ultrathin Pt ring electrodes for use in flow injection ASV and found that thick mercury deposits were required to prevent problems of intermetallic interferences and peak splitting.

Ultrasmall carbon ring electrodes have been successfully fabricated with total structural diameter approaching  $1\ \mu\text{m}$  [22]. These electrodes appear to have all the advantages of other microelectrodes and are highly useful for voltammetry in ultrasmall environments. In a study of microelectrodes, Bezegh and Janata [23] have developed a diffusional impedance expression for stationary microelectrodes, and have shown that a thin ring electrode can have an effective diffusional area as much as 100 times larger than a microdisk electrode of the same geometrical area. The surface of a ring-shaped electrode is thus more accessible to the diffusing species, resulting in a much higher current efficiency at thin ring electrodes. Bixler *et al.* [24] have also recently employed thin ring electrodes for the determination of 3–6 nM ferrocene samples and thin ring electrodes showed an order of magnitude lower detection limit when compared to microdisk and thin band array electrodes.

In this paper, we present data demonstrating the use of mercury-coated (by *in situ* deposition) ultrasmall carbon ring electrodes for ASV of lead and cadmium. The electrodes used here represent the smallest diameter ( $1\text{--}10\ \mu\text{m}$ ) employed up-to-date for ASV. A major emphasis in this paper is the use of these electrodes to carry out ASV without deliberately added supporting electrolyte. ASV of lead has been studied under these conditions to investigate the dependence of stripping peak current on experimental parameters such as potential scan rate, preconcentration duration, deposition potential, concentration of  $\text{Hg}^+$  during deposition and concentration of  $\text{Pb}^{2+}$ . It should be noted that these experiments could be carried out at small electrodes having geometries other than a ring. Carbon ring electrodes

are used in this work because they have an extremely small tip diameter.

## EXPERIMENTAL SECTION

**Reagents.** Mercury(I) nitrate monohydrate, lead(II) nitrate, potassium nitrate and cadmium nitrate tetrahydrate, purchased from Aldrich Chemical Company, were used without further purification. Stock solutions of 0.10 M  $\text{KNO}_3$ ,  $1.0 \times 10^{-2}$  M  $\text{Pb}^{2+}$ ,  $5.0 \times 10^{-3}$  M  $\text{Hg}^+$  (with 0.5% (v/v) concentrated  $\text{HNO}_3$  added) and  $1.0 \times 10^{-3}$  M  $\text{Cd}^{2+}$  were prepared in doubly distilled water (Corning Mega-Pure MP-3A purification system). Solutions of lower concentrations were prepared by subsequent dilutions of stock solutions. All solutions were purged with nitrogen for 20 minutes prior to voltammetry. After deaeration, a blanket of nitrogen was kept over the solutions.

**Electrodes and Apparatus.** Ultrasmall carbon ring electrodes were constructed as described previously [25,26]. Anodic stripping voltammetry was carried out with a locally constructed low-current three-electrode potentiostat [27] and waveform generator. The electrochemical cell consisted of a 30 mL glass vial, filled to 25 mL, with holes drilled in a plastic cap to facilitate a three-electrode system. A sodium chloride saturated calomel electrode (SSCE) was used as the reference electrode and a platinum wire as the counter electrode. All experiments were carried out in quiescent solutions at room temperature.

**Electrochemical Procedure.** Mercury-coated ultrasmall carbon ring electrodes were prepared by *in situ* deposition of  $\text{Hg}^+$  in the present study. A reduction potential of  $-1.0$  V vs SSCE was applied in the study of ASV of lead and cadmium in  $\text{Hg}^+$ , and  $-0.9$  V in the study of ASV of lead in  $\text{Hg}^+$ . Following a desired preconcentration period, stripping

analysis was performed by scanning the electrode potential to +1.0 V where it was held for 2 min before repeating the experiments. This was to oxidize any remaining mercury from the electrode and also ensured that a clean electrode surface was being employed in each run. In experiments involving analyte solutions of different concentrations, electrodes were rinsed with doubly distilled water before being transferred from one solution to another.

## RESULTS AND DISCUSSION

**Electrode Characterization.** All naked carbon ring electrodes employed in this work were initially tested by voltammetry in a dopamine solution, as described previously [25,26]. Only electrodes which displayed a well-defined sigmoidal voltammogram (not shown), corresponding to the oxidation of dopamine with very little capacitive charging current (typically less than 25 pA), were used in ASV experiments. This result is generally taken as an indication of a good seal obtained between the carbon film and epoxy with negligible fractures and cracks. Occasionally, an electrochemical pretreatment involving cycling the electrode potential between  $-0.20$  and  $+1.85$  V at  $200$  mV s<sup>-1</sup> in the same solution was necessary. This pretreatment activates the carbon surface, giving rise to a more Nernstian sigmoidal wave, as reported previously [26].

To demonstrate the concept of anodic stripping voltammetry at ultrasmall ring electrodes, mercury was deposited *in situ* on carbon ring electrodes. These electrodes have total structural diameters in the 1 to 10  $\mu$ m range and ring thicknesses on the order of 100 nm [25]. The small size of the electrodes precluded visual or microscopic examination of the mercury films or droplets formed; however, experiments demonstrating metal deposition and

stripping from these electrodes, as shown below, provide strong evidence that mercury has been deposited. Ultrasmall electrodes used previously for ASV have been relatively large cylindrical electrodes having lengths in the range of 2 to 10 mm [11-17], relatively large diameter ring electrodes (although ultrathin) [21], or disk-shaped electrodes [20]. The data shown here demonstrate the feasibility of depositing mercury on electrodes having overall ultrasmall dimensions, thus making them highly useful for analysis in microenvironments.

A stripping voltammogram for lead deposited from a quiescent solution of  $2.0 \times 10^{-7}$  M  $Pb^{2+}$  in the presence of  $1.0 \times 10^{-6}$  M  $Hg^{+}$  and 0.10 M  $KNO_3$  (pH 3.0) ( $KNO_3$  is added as a supporting electrolyte here) is shown in Figure 1(a). In this experiment, the lead amalgam is oxidized at  $-0.46$  V followed by an unknown peak at 0.0 V and, finally, the oxidation of mercury at  $+0.41$  V. The peak at 0.0 V appears to be a copper impurity since it increases in magnitude when  $Cu^{2+}$  is deliberately added to the solution. Very sharp lead stripping peaks are observed in all cases and this is generally obtained with microelectrodes where the small volume of amalgam is easily stripped off of the electrodes [3]. Mercury deposits on glassy carbon electrodes are known to exist as isolated droplets, the size and location of which strongly depend on the potential of deposition [28]. It is probable that mercury behaves in a similar manner on the carbon ring surface, forming some number of mercury droplets. The stripping process from an *in situ* mercury-coated carbon ring electrode may then arise from a single or a very low number of these mercury droplets. However, considering the small surface area of the electrode, it is unlikely that effects from the formation of mercury droplets can be observed electrochemically and we have been unable to observe the mercury coated electrode surface by conventional microscopy. The mercury stripping peak current from the electrode

used in Figure 1(a) is reproducible with an average value of  $189 \pm 10$  pA ( $n=5$ ) at  $400 \text{ mV s}^{-1}$ .

### **Anodic Stripping Voltammetry in the Absence of Deliberately Added Supporting Electrolyte**

ASV is among the most sensitive methods for determination of trace metal ions in aqueous solutions. When conventional-sized electrodes are used, the large currents passed during metal reduction and preconcentration step require a relatively large concentration of supporting electrolyte. In contrast, microelectrodes can be employed in resistive media [30-32]. In this context, the use of ultrasmall mercury electrodes provides a means to carry out stripping analysis in resistive solutions.

Figure 1(b) shows a stripping voltammogram obtained at the same mercury-coated carbon ring electrode in a blank solution consisting of  $1.0 \times 10^{-6} \text{ M Hg}^+$  in doubly distilled water (i.e. without deliberately added supporting electrolyte). This voltammogram reveals only stripping peaks due to oxidation of an apparent copper impurity in solution at 0.0 V and mercury at +0.40 V. Note that no observable trace of lead is detected in the potential range of -0.5 V to 0.0 V in this blank solution. A stripping voltammogram obtained in  $2.0 \times 10^{-7} \text{ M Pb}^{2+}$  in  $1.0 \times 10^{-6} \text{ M Hg}^+$  is depicted in Figure 1(c). Three peaks, at -0.44 V, -0.06 V and +0.34 V for the stripping of lead, copper and mercury, respectively, are observed in this system as was observed in the system with added  $\text{KNO}_3$  (pH 3.0). The mercury stripping peak current in the presence of  $\text{KNO}_3$  is approximately six times larger than that in absence of  $\text{KNO}_3$ . This might be due to more favorable kinetics of oxidation of mercury in acidic media. In contrast, the lead stripping peak current doubles in magnitude

when stripping is carried out in absence of supporting electrolyte compared to that in the presence of  $\text{KNO}_3$ . We speculate this to be the result of a higher coverage of lead on the electrode surface when the condition is less favorable for oxidation of mercury. It should be pointed out here that the concentration of  $\text{Hg}^+$  employed in this work is five times higher than that of  $\text{Pb}^{2+}$ , instead of the more usual value of 152 [2]. However, no distortion of peaks or other unusual observations resulting from this lower  $\text{Hg}^+$  concentration have been obtained in this work, except that the slope of the calibration plot of lead stripping peak current vs concentration varies with the  $\text{Hg}^+$  concentration (vide infra). In aqueous solutions containing no deliberately added supporting electrolyte, peak widths at half height for lead stripping voltammograms are 63, 91, 116 and 153 mV for scan rates of 100, 200, 400 and 800  $\text{mV s}^{-1}$ , respectively. Peak widths at half height for voltammograms in solutions containing 0.1 M  $\text{KNO}_3$  (pH 3.0) as supporting electrolyte are 31, 38, 63 and 100 mV at 100, 200, 400 and 800  $\text{mV s}^{-1}$ , respectively. Relatively sharp lead stripping peaks are thus still obtained in experiments without deliberately added supporting electrolyte.

#### **Effect of Deposition and Stripping Conditions in Absence of Deliberately Added Supporting Electrolyte**

**Effect of scan rate.** ASV in a solution of  $2.0 \times 10^{-7}$  M  $\text{Pb}^{2+}$  and  $8.0 \times 10^{-7}$  M  $\text{Cd}^{2+}$ , in the presence of  $1.0 \times 10^{-6}$  M  $\text{Hg}^+$ , has been studied at an ultrasmall carbon ring electrode. In three experiments, deposition of  $\text{Hg(Pb,Cd)}$  amalgam on the electrode has been carried out at  $-1.0$  V for 5 min. Scan rates in the range of 100 to 400  $\text{mV s}^{-1}$  have been employed. Voltammograms of lead and cadmium obtained at scan rates of 100, 200 and 400  $\text{mV s}^{-1}$  are displayed in Figure 2. A log-log plot of stripping peak current for lead and cadmium vs scan rate yields slopes of 0.88 and 0.65, respectively. These results are in agreement with

Baranski's results [17], where values of 0.86 (for lead) and 0.84 (for cadmium) were obtained using rapid scan ASV.

The effect of scan rate on  $\Delta$ SV in solutions of only  $2.0 \times 10^{-7}$  M  $\text{Pb}^{2+}$  and  $1.0 \times 10^{-6}$  M  $\text{Hg}^+$  has also been studied. Here, a reduction potential of  $-0.9$  V has been applied and the scan rate ranges from 100 to 800  $\text{mV s}^{-1}$ . This range of scan rates is limited to those where edge diffusion of material to the electrode predominates. A plot of peak current vs scan rate for lead oxidation shows a linear relationship with a slope of  $0.53 \text{ pA s mV}^{-1}$  and an intercept of  $1.0 \times 10^2$  pA. The correlation coefficient obtained was 0.998. This linear dependence on scan rate clearly indicates a diffusion-controlled rate-determining step in the stripping process at these electrodes in the absence of deliberately added supporting electrolyte. A relatively large intercept (i.e. approaching slower scan rates) is obtained here and can be attributed to a continuous deposition of  $\text{Pb}^{2+}$  as the potential is scanned from the deposition potential to the peak potential, while the solution remains quiescent during both deposition and stripping steps. The amount of lead deposited can be substantial at ultrasmall electrodes owing to enhancement of mass transport relative to electrode surface area resulting from edge diffusion. Similar observations have been reported for differential pulse anodic stripping voltammetry at mercury-coated carbon fiber electrodes [16].

**Effect of Preconcentration Duration.** The effect of preconcentration duration on lead stripping peak current has been studied using a solution of  $2.0 \times 10^{-7}$  M  $\text{Pb}^{2+}$  in  $1.0 \times 10^{-6}$  M  $\text{Hg}^+$ . Preconcentration has been carried out at  $-0.9$  V and voltammograms recorded at a potential scan rate of  $400 \text{ mV s}^{-1}$ . Preconcentration duration has been varied between 60 and 300 s in this work. As expected, a linear relationship between stripping peak current and preconcentration duration is obtained. The slope and intercept are calculated to

be  $0.99 \text{ pA s}^{-1}$  and  $25 \text{ pA}$ , respectively, with a correlation coefficient of 0.999. A corresponding log-log plot yields a slope of 0.82, compared to 1.02 for lead obtained by Baranski [17] in a solution mixture of  $\text{Pb}^{2+}$  and  $\text{Cd}^{2+}$ .

**Effect of Deposition Potential.** A solution of  $2.0 \times 10^{-7} \text{ M Pb}^{2+}$  in  $1.0 \times 10^{-6} \text{ M Hg}^{+}$  has been employed to study the dependence of lead stripping peak current on deposition potential in solutions without deliberately added supporting electrolyte. Voltammograms have been obtained at a scan rate of  $400 \text{ mV s}^{-1}$  following a 5-min preconcentration and deposition at potentials between  $-0.7$  and  $-1.0 \text{ V}$ . The magnitude of the stripping peak current remains essentially unchanged when the deposition potential is varied between  $-0.8$  and  $-1.0 \text{ V}$ . In contrast, the corresponding peak current decreases by approximately 50% when the deposition potential is set at values more positive than  $-0.8 \text{ V}$ .

**Effect of  $\text{Hg}^{+}$  Concentration.** Since the deposition and preconcentration of metal ions described in this paper is performed simultaneously with  $\text{Hg}^{+}$  deposition, it is important to examine the relationship between  $\text{Hg}^{+}$  concentration and stripping voltammetry. In these experiments, the deposition potential has been set at  $-0.9 \text{ V}$  with a 5-min preconcentration interval in a  $2.0 \times 10^{-7} \text{ M Pb}^{2+}$  solution. The dependence of lead stripping current on  $\text{Hg}^{2+}$  concentration has been evaluated in solutions of  $1.0 \times 10^{-6}$ ,  $1.0 \times 10^{-5}$  and  $1.0 \times 10^{-4} \text{ M Hg}^{+}$  and will be discussed further in the next section. In general, well-defined stripping peaks for both lead ( $2.0 \times 10^{-7} \text{ M Pb}^{2+}$ ) and mercury are obtained at  $400 \text{ mV s}^{-1}$  when at least  $1.0 \times 10^{-6} \text{ M Hg}^{+}$  is present. The magnitude of the lead stripping peak current is constant when the concentration of  $\text{Hg}^{+}$  is changed from  $1.0 \times 10^{-4} \text{ M}$  to  $1.0 \times 10^{-5} \text{ M}$ . There is a decrease of approximately 40% in the lead stripping peak current when  $\text{Hg}^{+}$  concentration is decreased from  $1.0 \times 10^{-5} \text{ M}$  to  $1.0 \times 10^{-6} \text{ M}$  in solutions containing  $2.0 \times 10^{-7} \text{ M Pb}^{2+}$ .

Voltammograms having large charging current, broad lead stripping peak and unobservable mercury stripping peak were obtained when a  $\text{Hg}^+$  concentration of  $1.0 \times 10^{-7}$  M was used. When the concentration of lead exceeds that of mercury, more  $\text{Pb}^{2+}$  is expected to be reduced onto the carbon surface with relatively smaller mercury coverage, resembling ASV at naked electrodes. ASV at naked ultrathin ring electrodes has been attempted previously and has been found to yield irreproducible results [29]. Anodic peaks for lead were also observed to have diminished abruptly under similar but not identical conditions at a rotating glassy carbon electrode [2]. Although improvement in sensitivity and a predictable calibration plot (vide infra) for the determination of lead can be achieved with higher  $\text{Hg}^+$  concentration ( $> 1 \times 10^{-6}$  M), a large  $\text{Hg}^+$  concentration is undesirable because this results in a large mercury stripping current and a relatively thick film of mercury reduces the concentration of metal amalgam deposited in the film. The higher concentration of  $\text{Hg}^+$  may also become an additional source of introducing impurities into the system. Voltammograms obtained in solutions of  $1.0 \times 10^{-5}$  M and  $1.0 \times 10^{-4}$  M  $\text{Hg}^+$  appear to have more noise associated with the measured current, presumably due to stripping of a thicker layer of mercury from a small electrode surface area. The baseline between stripping peaks displays a periodic oscillation that can reach peak-to-peak amplitudes of approximately 10 pA. In experiments with conventional-sized electrodes, a 152-fold excess of  $\text{Hg}^+$  over  $\text{Pb}^{2+}$  in concentration [2] is usually maintained in order to avoid saturation of amalgam and/or stripping of non-homogeneous deposits. In contrast, only a 5-fold ratio has been used in this work, but no complications have ever been observed during the stripping process with carbon ring electrodes. The relative ease of stripping the small quantity of material might minimize the above problems when ultrasmall electrodes are used relative to macroelectrodes. It should

also be pointed out that no observable problems of intermetallic interferences (between lead-copper, lead-cadmium, copper-cadmium) or peak splitting have been encountered under conditions employed in this work. Although the lead stripping peak current varies with  $\text{Hg}^+$  concentration, this should not present a difficulty in practical applications as long as the  $\text{Hg}^+$  concentration is kept constant throughout an analysis.

**Effect of  $\text{Pb}^{2+}$  Concentration.** Anodic stripping analysis of lead at the small carbon ring electrodes has been examined at a series of  $\text{Pb}^{2+}$  concentrations from  $4.0 \times 10^{-10}$  M to  $2.0 \times 10^{-7}$  M, in  $1.0 \times 10^{-6}$  M  $\text{Hg}^+$  and in the absence of added electrolyte. In these experiments preconcentration has been carried out at a potential scan rate of  $400 \text{ mV s}^{-1}$ . The resulting log-log plot for stripping peak current vs  $\text{Pb}^{2+}$  concentration is linear with a slope of 0.42 ( $\log(\text{pA M}^{-1})$ ) and a correlation coefficient of 0.999. This range of concentrations is comparable to that obtained by Wehmeyer and Wightman [20] using mercury-coated ultrasmall Pt disk electrodes in 0.1 M  $\text{KNO}_3$ . However, it is interesting to note that there is only a small change in stripping peak current as a function of concentration. A slope of less than unity might be expected for the plot of  $\log(\text{current})$  vs concentration under these conditions since mass transport of  $\text{Pb}^{2+}$  both to and from the electrode is likely to be affected by migration. A slope of 0.92 (correlation coefficient = 0.989) is obtained for the calibration plot of lead stripping peak in  $1.0 \times 10^{-6}$  M  $\text{Hg}^+$  and  $5.0 \times 10^{-3}$  M  $\text{KNO}_3$  (pH 3.0) as supporting electrolyte. The low slope of the calibration plot (0.42) is only observed when a low concentration of  $\text{Hg}^+$  is employed for *in situ* deposition in solutions without added electrolyte. Solutions of  $\text{Pb}^{2+}$  ranging in concentration from  $2.0 \times 10^{-9}$  M to  $2.0 \times 10^{-7}$  M and with higher  $\text{Hg}^+$  concentration have been examined. The log-log calibration plots for peak current vs  $\text{Pb}^{2+}$  concentration were linear with slopes of 0.77 and 1.05, and correlation coefficients

of 0.993 and 0.997, respectively, for  $\text{Hg}^+$  concentrations of  $1.0 \times 10^{-4}$  M and  $1.0 \times 10^{-5}$  M. Although the slopes of the calibration plots vary with  $\text{Hg}^+$  concentration, the plots are linear indicating that reproducible stripping analysis can be carried out in solutions with a constant  $\text{Hg}^+$  concentration. We have further investigated stripping voltammograms in blank solutions containing only  $1.0 \times 10^{-6}$  M  $\text{Hg}^+$  in doubly distilled water at eight ultrasmall carbon ring electrodes. It was found that, apart from the apparent copper impurity oxidation peak and the mercury stripping peak, there was either no observable lead stripping peak ( $n=5$ ) or only a very small peak (approximately 40 pA) ( $n=3$ ) at  $-0.46$  V.

The low background stripping current observed in solutions without added electrolyte prompted us to attempt ASV of lead at extremely low concentrations. Figure 3 depicts an anodic stripping voltammogram of  $3.2 \times 10^{-11}$  M  $\text{Pb}^{2+}$  in  $1.0 \times 10^{-6}$  M  $\text{Hg}^+$  at a freshly cleaved 8  $\mu\text{m}$  diameter carbon ring electrode, after a preconcentration duration of 10 min at  $-0.9$  V. The voltammogram that was obtained by scanning the potential at a rate of  $400 \text{ mV s}^{-1}$  resulted in a peak current of 560 pA. Repeated experiments at  $3.2 \times 10^{-11}$  M  $\text{Pb}^{2+}$  yielded an RSD of 6% ( $n=3$ ). It is important to note that the 560 pA current observed correlates well to that observed at higher concentrations, despite the fact that the examples shown here have similar currents (see Figure 1(c) and Figure 3). The 8  $\mu\text{m}$  diameter electrode used in the  $3.2 \times 10^{-11}$  M  $\text{Pb}^{2+}$  solution has an estimated surface area 17 times larger than that of the 2  $\mu\text{m}$  diameter electrode used in the  $2.0 \times 10^{-7}$  M  $\text{Pb}^{2+}$  solution. When considered with the 0.42 slope of the log-log calibration plot obtained for stripping analysis in  $1.0 \times 10^{-6}$  M  $\text{Hg}^+$  and the relative preconcentration durations, the currents are expected to be of similar magnitude. Using a 2  $\mu\text{m}$  diameter electrode and a 5 min preconcentration duration, one expects a 500 pA stripping peak in  $2.0 \times 10^{-7}$  M  $\text{Pb}^{2+}$  solution and with a log-log calibration

plot slope of 0.42, the calculated current for an 8  $\mu\text{m}$  diameter electrode in  $3.2 \times 10^{-11}$  M  $\text{Pb}^{2+}$  is also approximately 500 pA.

It is generally known that heavy metal impurities, such as  $\text{Cu}^{2+}$ ,  $\text{Pb}^{2+}$  etc, can be present in electrolytes [20] (ASV voltammograms obtained in our work always reveal a small lead stripping peak at approximately  $-0.45$  V in a solution containing only  $\text{Hg}^+$  in 0.10 M  $\text{KNO}_3$  (pH 3.0)). It is believed that the absence of deliberately added supporting electrolyte has decreased the levels of these metal ions and hence permitted the determination of lead concentrations as low as those reported in this work. In fact, even lower concentrations of  $\text{Pb}^{2+}$  in the absence of deliberately added supporting electrolyte should be detectable by this methodology. Thus, a double implication is present for this work. First, ASV can be carried out at very sensitive levels under conditions where an added electrolyte is not desired (i.e. impurities). Second, the absence of electrolyte and a low  $\text{Hg}^+$  concentration appear to result in an ASV process where enhanced stripping currents are observed in extremely dilute solutions of  $\text{Pb}^{2+}$  and subsequently the trace analysis of  $\text{Pb}^{2+}$  at unheard-of levels is possible. The linearity of the calibration plots makes this methodology highly useful.

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## CREDIT

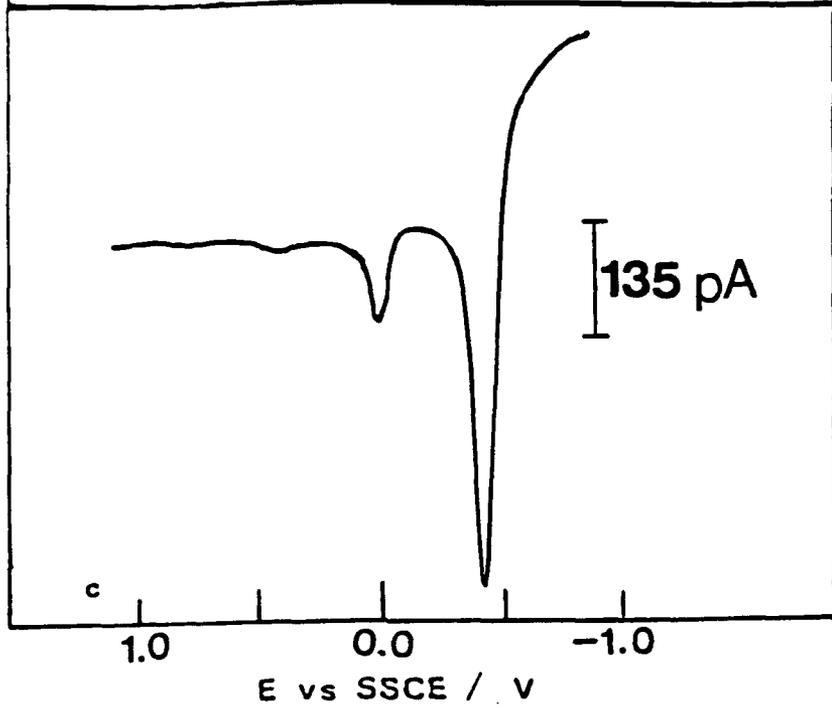
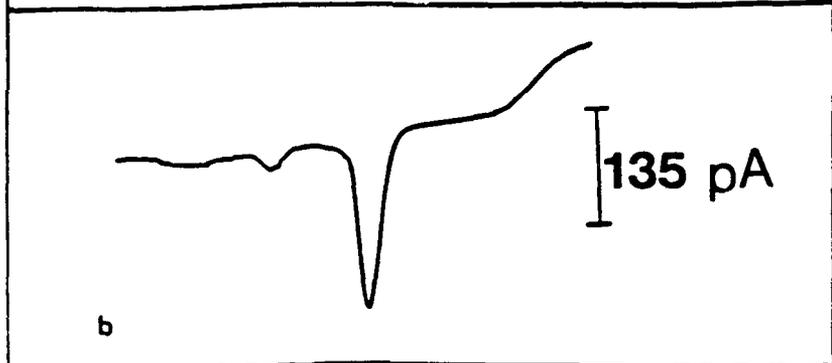
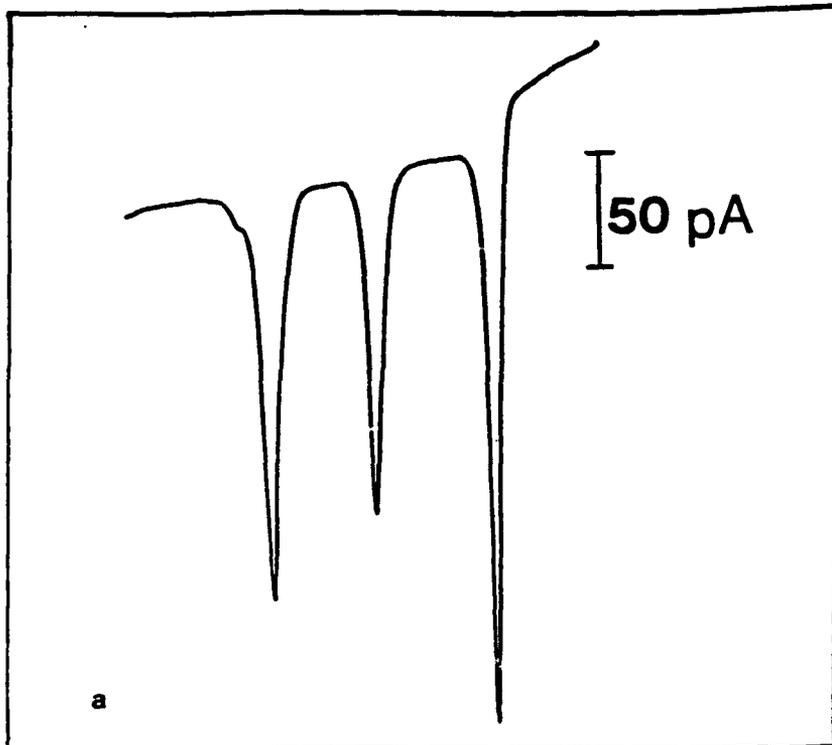
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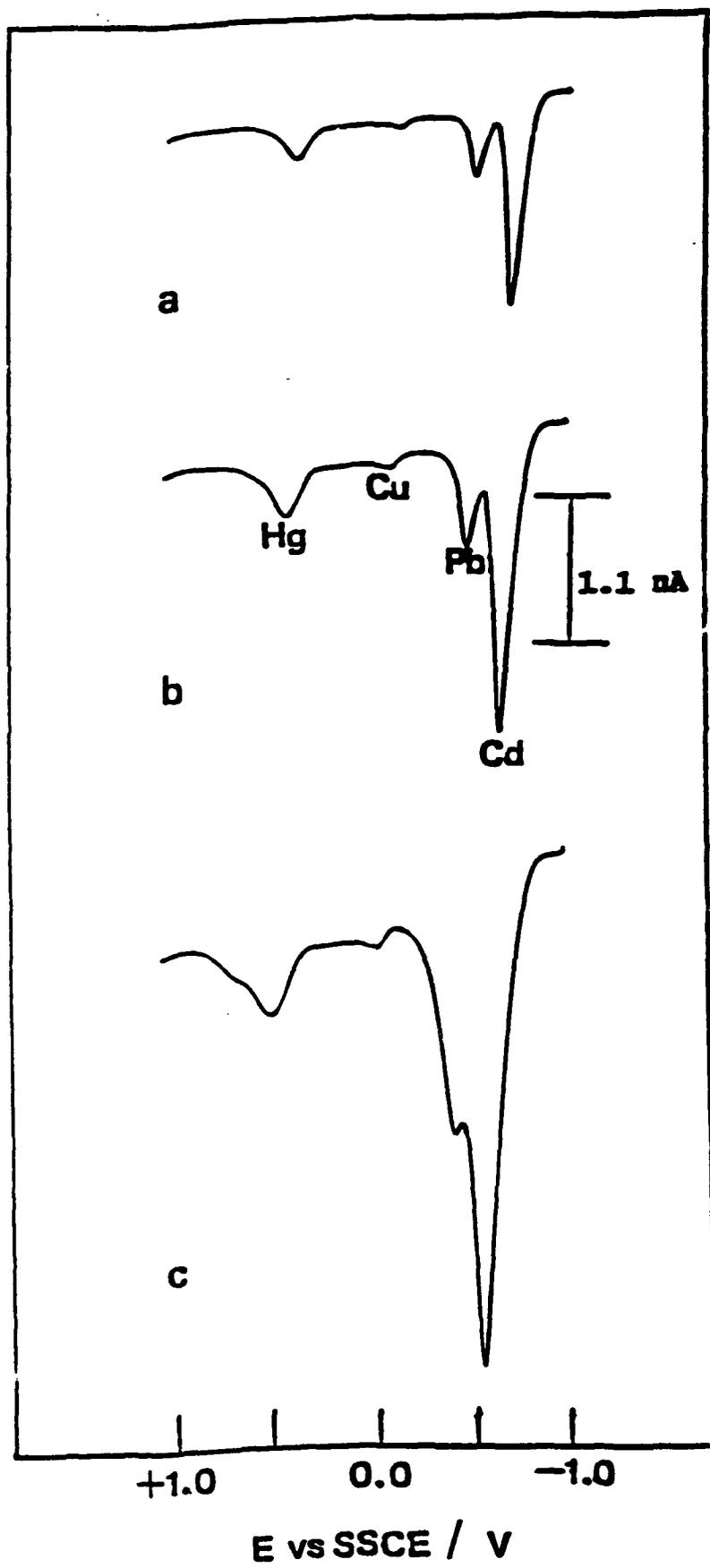
## BRIEF

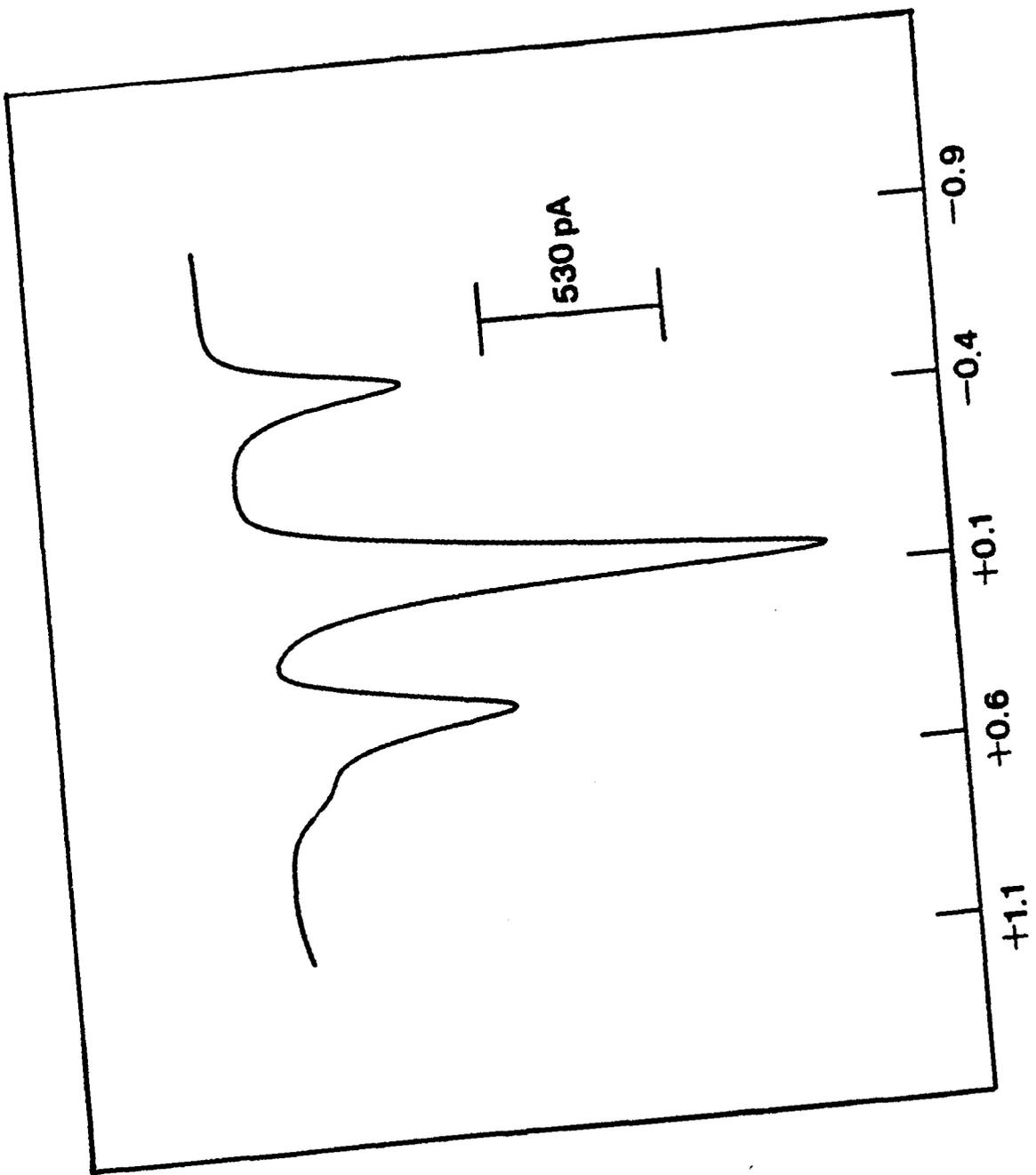
Ultrasmall carbon ring electrodes have been coated *in situ* with mercury which can then be used for anodic stripping voltammetry without deliberately added supporting electrolyte. Concentrations of lead ion as low as  $3.2 \times 10^{-11}$  M have been examined without impurities added in the electrolyte.

## FIGURE CAPTIONS

- Figure 1 Anodic stripping voltammograms at a  $2\ \mu\text{m}$  carbon ring electrodes for (a)  $2.0 \times 10^{-7}\ \text{M}\ \text{Pb}^{2+}$ ,  $1.0 \times 10^{-6}\ \text{M}\ \text{Hg}^{+}$ , and  $0.10\ \text{M}\ \text{KNO}_3$  (pH 3.0) as supporting electrolyte, (b) only  $1.0 \times 10^{-6}\ \text{M}\ \text{Hg}^{+}$  (blank), (c)  $2.0 \times 10^{-7}\ \text{M}\ \text{Pb}^{2+}$  and  $1.0 \times 10^{-6}\ \text{M}\ \text{Hg}^{+}$  (i.e. no supporting electrolyte). Preconcentration potential was set at  $-0.9\ \text{V}$  for 300 s. Scan rate =  $400\ \text{mV}\ \text{s}^{-1}$ .
- Figure 2 Anodic stripping voltammograms of  $2.0 \times 10^{-7}\ \text{M}\ \text{Pb}^{2+}$  and  $8.0 \times 10^{-7}\ \text{M}\ \text{Cd}^{2+}$  at a carbon ring electrode, in the presence of  $1.0 \times 10^{-6}\ \text{M}\ \text{Hg}^{+}$ . Preconcentration potential was set at  $-1.0\ \text{V}$  for 180 s. Scan rate (a) 100, (b) 200 and (c)  $400\ \text{mV}\ \text{s}^{-1}$ .
- Figure 3 Anodic stripping voltammogram of  $3.2 \times 10^{-11}\ \text{M}\ \text{Pb}^{2+}$  at an  $8\ \mu\text{m}$  carbon ring electrode in the presence of  $1.0 \times 10^{-6}\ \text{M}\ \text{Hg}^{+}$ . Preconcentration potential was set at  $-0.9\ \text{V}$  for 600 s. Scan rate =  $400\ \text{mV}\ \text{s}^{-1}$ .







E vs SSCE / V

