

# Comparison of Stripping Methods at Thin-film Mercury Electrodes

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When a thin mercury film covered glassy carbon rotating disc electrode (TMFGCRDE) was used in square-wave anodic stripping voltammetric measurements, the highest sensitivity was obtained when the electrode was rotated slowly. The application of advanced analytical instrumentation to such measurements requires the addition of mercury ions to the sample.

**Keywords:** *Thin-film mercury electrode; glassy carbon electrode; rotating disc electrode; square-wave voltammetry; anodic stripping voltammetry*

The determination of toxic trace metals is an important problem in environmental research, marine and aquatic chemistry and clinical and food chemistry.<sup>1</sup> For trace metals capable of forming an amalgam, anodic stripping voltammetry is the most convenient analytical method.<sup>1-4</sup> The highest sensitivity is obtained if a thin mercury film covered glassy carbon rotating disc electrode<sup>1,3,5-21</sup> (TMFGCRDE) in combination with differential-pulse<sup>1,9,12-17,19,20</sup> (DPSV) or square-wave<sup>16,17,21-23</sup> stripping voltammetry (SWSV) is used. The advantages of the TMFGCRDE over a hanging mercury drop electrode are that it provides more effective and stable mass transfer during the accumulation step and very sharp anodic stripping peaks.<sup>1,3,6,7,9,10,13,18,22,23</sup> Pulse voltammetric stripping methods possess an advantage over linear scan stripping in that they discriminate effectively against charging current.<sup>1,9,13,16,17,22-25</sup> The theory of DPSV<sup>26,27</sup> indicates that, in contrast to DP polarography,<sup>28</sup> the sensitivity increases if the period between two successive pulses is equal to the duration of the pulse (*i.e.*, if the DPSV signal becomes similar to the SWSV signal). The theoretical treatment of SWSV at mercury film electrodes has shown that the sensitivity of the method increases proportionally within the square-wave frequency.<sup>22,23</sup> For these reasons, SWSV is superior to DPSV.<sup>16,17,22,23</sup>

In this paper the dependencies of the square-wave, differential-pulse, staircase and reverse-pulse stripping voltammetric peak currents on the rotation rate of the TMFGCRDE during the stripping period are demonstrated. This subject has been discussed several times in connection with linear scan<sup>10,29-31</sup> (LSSV), alternating current<sup>8</sup> (acSV), DPSV<sup>9,13,32</sup> and reverse-pulse<sup>30,32</sup> (RPSV) stripping voltammetric methods. Theoretically, if the rotation rate is very high and the scan rate (LSSV) or frequency (SWSV and DPSV) is low, the peak currents depend linearly on the square root of the rotation rate. On the other hand, if the rotation rate is low and the scan rate or frequency is high, the current is independent of the rotation rate.<sup>8,30-32</sup> In the practical application of the TMFGCRDE the use of forced mass transfer during the stripping period depends on the type of electrical contact on the RDE. If carbon brushes are used for the contact, the electrical noise is very high and the rotation of the RDE must be stopped before the stripping peaks are recorded.<sup>9,10,14-19,29</sup> The mercury contact provides a much lower noise level, so that the electrode can be allowed to rotate during stripping.<sup>6,7,10,11-13,20,21</sup> The rotation increases the LSSV peak currents.<sup>5-7,10,11,20,30,31</sup> The DPSV responses are usually recorded without rotation,<sup>9,13-17,19</sup> although some contrary examples are known.<sup>12,20,21</sup>

## Experimental

The following chemicals were used: NaCl, concentrated HClO<sub>4</sub> (both Merck, Suprapur grade), Pb(NO<sub>3</sub>)<sub>2</sub> and Hg(NO<sub>3</sub>)<sub>2</sub> (both Merck, analytical-reagent grade). The water used for all the solutions was distilled four times, twice using quartz equipment.

The electrode system consisted of a glassy carbon rotating disc working electrode (GCRDE), an Ag - AgCl (saturated NaCl) reference electrode and a platinum wire counter electrode. The construction of the GCRDE has been described previously.<sup>11,13</sup> The glassy carbon disc (diameter 6 mm, surface area 0.283 cm<sup>2</sup>; Tokai Electrode Manufacturing, Tokyo, Japan) was sealed in polycarbonate resin tubing and polished to a mirror finish. The tubing was fixed to a stainless-steel shaft which rotated inside an electrode holder. A noise-free mercury contact was used. The electrode was driven by a synchronous electric motor with a continuously changeable rotation rate of between 843 and 4402 rev min<sup>-1</sup>. Each day, before the experiments, the GCRDE was cleaned by re-polishing with a soft tissue and conditioned by charging to +0.4 V *versus* Ag - AgCl for 30 s. The voltammetric cell (volume 100 ml) was made from PTFE. The reference and counter electrodes were isolated in separate compartments.

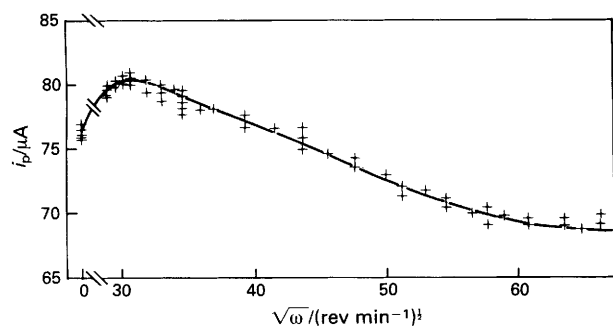
The solutions were de-aerated with extra-pure nitrogen for 20 min prior to measurements; a nitrogen atmosphere was maintained thereafter. The working electrode was rotated during the de-aeration period.

The TMFGCRDEs were formed as described previously.<sup>6,7,10,13</sup> Mercury(II) nitrate was added to the sample solution at a concentration of  $4 \times 10^{-5}$  M for *in situ* formation of the mercury film on the glassy carbon substrate. The initial film formation was performed by the accumulation of mercury at -0.9 V *versus* Ag - AgCl for 20 min. The electrode was rotated at a rate,  $\omega_{acc}$ , of 2623 rev min<sup>-1</sup> during this period. Thereafter, the film grew during each subsequent cathodic deposition stage. In situations where the mercury film had to be maintained at a constant thickness during a series of measurements, the initial film formation was followed by the subsequent transfer of the TMFGCRDE into a sample solution containing no mercury ions.

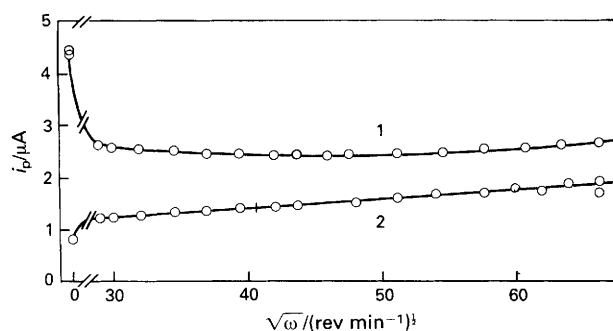
Anodic stripping measurements of  $5 \times 10^{-8}$  M Pb<sup>2+</sup> were performed in 0.55 M NaCl, pH 3 (HClO<sub>4</sub>), supporting electrolyte. Lead amalgam was accumulated at an accumulation potential,  $E_{acc}$  of -0.8 V *versus* Ag - AgCl for an accumulation time,  $t_{acc}$ , of 2 min, during which the TMFGCRDE was rotated at 2623 rev min<sup>-1</sup>. The anodic scan was preceded by a 30-s "rest" period ( $t_{rest}$ ) during which the rotation of the electrode was decreased by reducing the rheostat or stopped by switching the motor off.

Princeton Applied Research (PAR) 384B and 174A polarographic analysers connected to a Bausch - Lomb DMP-40 digital plotter and a Hewlett-Packard 7045A *x - y* recorder, respectively, were used. The PAR 174A analyser was partially

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**Fig. 1.** Square-wave stripping voltammetry of  $5 \times 10^{-8}$  M  $\text{Pb}^{2+}$  in 0.55 M NaCl, pH 3 ( $\text{HClO}_4$ ). Dependence of peak currents on the square root of the electrode rotation rate ( $\omega$ ) during the anodic stripping scan. Thin mercury film covered (*in situ*) glassy carbon rotating disc electrode ( $4 \times 10^{-5}$  M  $\text{Hg}^{2+}$  added to the sample; initial accumulation of mercury for 20 min at  $-0.9$  V). Lead amalgam accumulation:  $t_{\text{acc}} = 2$  min;  $E_{\text{acc}} = -0.8$  V versus Ag - AgCl;  $\omega_{\text{acc}} = 2623$  rev  $\text{min}^{-1}$ ;  $t_{\text{rest}} = 30$  s. Stripping conditions: square-wave frequency,  $f = 100$  Hz; peak amplitude,  $a = 60$  mV;  $dE = -2$  mV



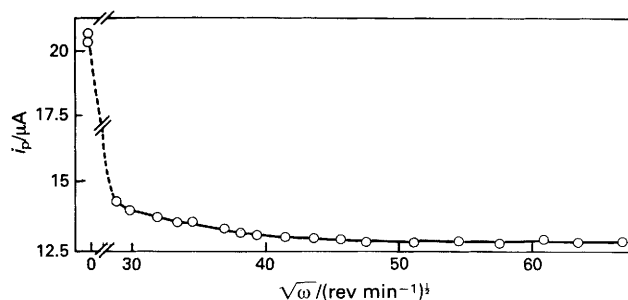
**Fig. 2.** 1, Differential-pulse and 2, staircase stripping voltammetry of lead. Dependence of peak currents on the square root of the electrode rotation rate during the anodic stripping scan. 1:  $t_d = 0.5$  s; pulse duration,  $t_p = 57$  ms;  $\Delta E = 30$  mV;  $dE = -2$  mV. 2:  $dE = -4$  mV;  $dt = 0.1$  s (scan rate,  $v = 40$  mV  $\text{s}^{-1}$ ). All other parameters are as in Fig. 1

adapted to allow the drop time and pulse duration time to be varied.

## Results and Discussion

The dependencies of the square-wave, differential-pulse, staircase (SSV) and reverse-pulse stripping peak currents on the square root of the TMFGCRDE rotation rate during the stripping period are shown in Figs. 1–3. The SWSV, DPSV and SSV measurements were performed using the PAR 384B polarograph, whereas the RPSV measurements were repeated with the PAR 174A analyser and identical results were obtained.

Apart from SSV, all the results are characterised by the adverse effect of the rotation on the stripping peaks. The staircase voltammetric results are similar to those obtained with LSV.<sup>33–35</sup> The SSV peaks (Fig. 2, curve 2) depend linearly on the square root of the TMFGCRDE rotation rate. This is in good agreement with LSSV theory.<sup>31</sup> In addition, the SSV peaks recorded at the stationary TMFGCRDE are smaller than those recorded at the rotating electrode. In contrast, the DPSV and RPSV peaks (Fig. 2, curve 1 and Fig. 3) are almost independent of the rotation rate, but the peaks recorded at the stationary electrode are much higher than the others. This fact cannot be explained by current theory.<sup>32</sup> In SWSV (Fig. 1), the peak currents decrease as the rotation rate increases. For a square-wave frequency of 100 Hz, the highest peaks appear when the electrode rotation rate is 1000 rev  $\text{min}^{-1}$ . Stopping the TMFGCRDE before stripping also causes a slight reduction in the height of the SWSV peaks.



**Fig. 3.** Reverse-pulse stripping voltammetry of lead. Dependence of peak currents on the square root of the electrode rotation rate during the anodic stripping scan.  $t_d = 0.2$  s; and  $t_p = 57$  ms. All other parameters are as in Fig. 1

Residual currents detected by any of the four stripping methods do not depend significantly on the rotation rate.

The observed effects may be ascribed to the forced transport of  $\text{Pb}^{2+}$  ions during the stripping procedure. If during an anodic pulse a significant amount of amalgam is re-oxidised, the concentration of  $\text{Pb}^{2+}$  ions near the electrode surface will suddenly be increased. These ions are transported towards the bulk of the solution by diffusion and convection. The transport causes a decrease in the  $\text{Pb}^{2+}$  concentration at the mercury surface. In order to maintain a Nernst equilibrium, additional re-oxidation of the amalgam is required. Hence, the re-oxidation persists throughout the anodic pulse and a certain anodic current can be sampled when it ends. The current is higher if the pulse is shorter or if the convection is faster (the rotation rate is higher). When a cathodic pulse is applied, these  $\text{Pb}^{2+}$  ions are reduced (re-reduced). In DPSV and RPSV the periods between the anodic pulses may be regarded as cathodic pulses of longer duration. The re-deposition effect is more pronounced if the concentration of  $\text{Pb}^{2+}$  ions remaining in the vicinity of the electrode surface is higher, *i.e.*, if the convection is slower (the rotation rate is lower). The cathodic current caused by the re-reduction is also higher if the cathodic pulse duration,  $t_p$ , is shorter. In SWSV and DPSV, the cathodic current is subtracted from the anodic current (*i.e.*, their absolute values are summed). In SWSV both pulses are equally short and the stripping peaks decrease with an increase in the rotation rate because the cathodic components of the responses decrease as the re-deposition decreases. However, with a slowly rotating electrode the peaks are higher than at the stationary TMFGCRDE because moderate convection increases the anodic components without significantly decreasing the cathodic components. The anodic pulses in DPSV and RPSV are both sufficiently long ( $t_p = 57$  ms); hence even moderate convection can decrease the concentration of  $\text{Pb}^{2+}$  ions in the vicinity of the electrode surface to such an extent that their re-deposition during the cathodic pulse is negligible. Hence, the stripping peaks become almost independent of the rotation rate in the range investigated. If the mass transfer is effected by diffusion only, the loss of  $\text{Pb}^{2+}$  ions during the anodic pulse is much smaller, hence their re-reduction can significantly enhance the response (particularly in RPSV). In SSV there are no cathodic pulses. The enhancement of the stripping peaks is caused by an increase in the anodic currents under conditions of forced convection.

That this is true is shown by the dependence of the RPSV peaks on the period between the pulses (Fig. 4). If the drop time ( $t_d$ , the period between the end of two successive pulses) is increased from 0.1 to 1.0 s, the peak currents become about twice as high because of the re-deposition effect. The results shown in Fig. 4 were obtained by anodic stripping at the stationary TMFGCRDE. Varying  $t_d$  has the opposite effect in DPSV: if  $t_d$  decreases, the peak currents increase. This is in agreement with theoretical<sup>26,27</sup> and experimental<sup>13</sup> observations. In both techniques the enhancement of the stripping

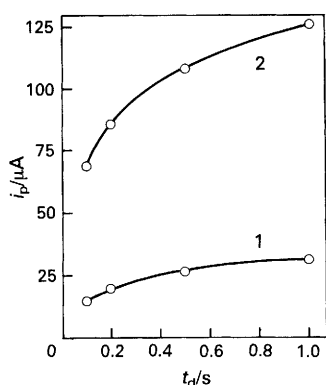


Fig. 4. Dependence of the reverse-pulse stripping peak currents of lead on drop time. The TMFGCRDE was not rotated during the anodic stripping scan. 1,  $t_p = 57$  ms and 2,  $t_p = 27$  ms. All other parameters are as in Fig. 1

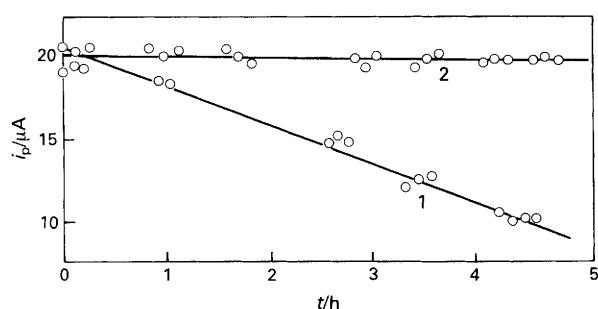


Fig. 5. Stability of the TMFGCRDE (no mercury added to the sample). The RPSV peak currents of lead were recorded repeatedly over a 4-h period and the electrode was not rotated during the anodic stripping scan:  $t_d = 0.2$  s,  $t_p = 57$  ms. 1, The cell was disconnected after each group of three subsequent anodic stripping cycles. 2, The working electrode was charged to  $-0.1$  V versus Ag - AgCl between two successive recordings. All other parameters are as in Fig. 1

peaks can be achieved more effectively by decreasing the duration of the anodic pulse<sup>9,13,36</sup> (compare also curves 1 and 2 in Fig. 4).

Our results justify the practice of recording the differential- and reverse-pulse stripping voltammograms at a stationary TMFGCRDE.<sup>9,13-17,19</sup> The increased sensitivity obtained with this procedure is not due to the decreased noise level, as is sometimes stated,<sup>9,29</sup> but is caused by hydrodynamic factors. This practice is also recommended for SWSV, although higher peaks can be obtained if the stripping peaks are recorded at a slowly rotating electrode. However, it may be easier to switch the electric motor off at the end of the accumulation period (using the rest period for quiescing the solution), than to change the electrode rotation rate by altering the rheostat position during the first stage of the rest period.

The application of advanced analytical instrumentation (such as the PAR 384B analyser) to anodic stripping measurements with a TMFGCRDE imposes some restrictions on the choice of the analytical procedure. These instruments disconnect the electrolytic cell from the potentiostat after each anodic stripping cycle. It has been observed that a TMFGCRDE exposed to an open circuit may be ruined if mercury ions are not added to the sample.<sup>19,37</sup> To investigate the stability of a mercury film under open-circuit conditions, the cell was deliberately disconnected several times between RPSV measurements. The PAR 174A polarographic analyser was used. After the initial film formation by electrolysis of  $4 \times 10^{-5}$  M  $\text{Hg}^{2+}$  at  $-0.9$  V for 20 min, the electrode was transferred into a mercury-free sample of  $\text{Pb}^{2+}$  ions. The RPSV peaks were measured several times over a period of 4 h; however, the electrolytic cell was disconnected after each

measurement and connected again immediately before the next measurement. The stripping peaks were recorded at a stationary TMFGCRDE. The results are shown in Fig. 5, curve 1. The results of a control experiment are shown by curve 2. During this experiment, the working electrode was not disconnected, but was continuously charged to  $-0.1$  V versus Ag - AgCl between two successive RPSV cycles. If mercury ions were also added to the sample, the RPSV peak currents were constant throughout the 4-h period regardless of whether or not the cell had been disconnected. The decrease in the peak currents, shown in Fig. 5, curve 1, may be explained by the fact that a film of mercury on glassy carbon consists of numerous very small drops.<sup>38</sup> If the glassy carbon surface is not charged to the controlled potential, but left in an open circuit, it is possible for some of these drops to unite forming larger drops, leaving part of the glassy carbon surface uncovered. It is known that the glassy carbon electrode surface consists of sites of variable activity.<sup>38</sup> Less than half of the geometric electrode surface consists of more active sites on which mercury droplets can be formed when mercury is deposited at low over-voltages. The remainder of the surface is less active and can be activated only if the deposition over-voltage and concentration of mercury ions are both high.<sup>38</sup> Hence it is possible that in an open circuit the droplets formed on the inactive sites become unstable and unite with more stable drops. Therefore, the active surface of the TMFGCRDE may decrease and the stripping peaks diminish. The actual volume of mercury on the glassy carbon surface remains the same after a supposed contraction of the thin layer but, on average, the layer becomes thicker while its active surface area decreases. During the accumulation period the reduction current is linearly proportional to the active area of the film, but not to its thickness. Hence the amount of accumulated amalgam decreases if the mercury film contracts. The stripping peak current depends linearly on the amount of accumulated amalgam.<sup>22,23</sup> The linear proportionality relationship is a function of the film thickness and decreases when the film becomes thicker.<sup>29,39,40</sup> For these reasons, the supposed film contraction would cause a reduction in the stripping peak current. If  $\text{Hg}^{2+}$  ions are present in the sample, the film of mercury regenerates during each cathodic deposition of the lead amalgam and hence the peak currents do not decrease even if the cell is disconnected. It is also possible that in an open circuit the mercury film is oxidised, but in a highly de-aerated solution, kept permanently under a nitrogen atmosphere, this possibility appears to be less probable. In any event if a TMFGCRDE is used with the PAR 384B analyser, the samples should contain mercury ions.

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