

From pages 39-41 of GDC thesis – “I. Shain, private communication”

Shain has been investigating oscillographic polarography of selenium(IV) at a hanging mercury drop electrode. He finds three waves similar in appearance to those obtained by Lingane and Niedrach at the DME. The three waves, however, occur at all pH values. The first wave is an overall four-electron process, resulting in formation of mercuric selenide, as found by Lingane and Niedrach. The second wave is the result of reduction of selenious acid to selenide. A slow reaction between the selenide and the selenious acid in the diffusion layer to form elemental selenium reduces the overall reduction of biselenite ion ( $\text{HSeO}_3^-$ ) to selenide, followed by the same reaction as in wave two. In acid solutions, this third wave is depressed by another reaction:  $\text{H}^+ + \text{HSeO}_3^- = \text{H}_2\text{SeO}_3$  (kinetic current). Shain also has evidence for selenite ( $\text{SeO}_3^{2-}$ ) being reduced to selenide, but this occurs at a potential more cathodic than the reduction of hydrogen ions.

Shain has also conducted cyclic oscillographic studies at the hanging mercury drop electrode. On sweeping at 100 cycles per second, he obtains three different peaks for three complete cycles. On the first cycle, a peak is observed which is due to the reduction of  $\text{HSeO}_3^-$  to  $\text{Se}^{2-}$ . The third cycle then gives a reduction peak caused by reduction of the mercuric selenide formed in the previous cycle. As the c.p.s. rate is decreased, reaction of selenide with the incoming selenium(IV) occurs in the diffusion layer to form the element, and the wave in the second cycle does not appear.

Shain has also developed, concurrent with the work presented here, a cathodic stripping method for determining selenium at the hanging mercury drop electrode. He preelectrolyzes on the plateau of the first wave for 5 to 10 minutes at pH 3.0. The potential is subsequently scanned cathodically, giving rise to a peak by reduction of the mercuric selenide formed on the electrode surface. A limit of determination of about  $10^{-7}$  M selenium is found.