

Nicholson R S & Shain I. Theory of stationary electrode polarography: single scan and cyclic methods applied to reversible, irreversible, and kinetic systems.

Anal. Chem. **36**:706-23, 1964.

[Chemistry Dept., Univ. Wisconsin, Madison, WI]

The theory of cyclic voltammetry is presented for chemical reactions coupled with electron transfer reactions. A numerical method is described for solving integral equations derived from the appropriate boundary value problems. New correlations make it possible to characterize unknown systems by studying the variation of peak current, half-peak potential, or ratio of anodic to cathodic peak currents as a function of rate of voltage scan. [The *SCI*[®] indicates that this paper has been cited over 895 times since 1964.]

Irving Shain

University of Wisconsin Madison, WI 53706
and

Richard S. Nicholson
Chemistry Division

National Science Foundation
Washington, DC 20550

January 19, 1981

"Our paper deals with a technique that has since become more commonly known as 'cyclic voltammetry.' In cyclic voltammetry one measures the current that flows when a triangularly-shaped voltage is applied to an electrode in an unstirred solution. The shape of the resulting curves—and how they change as a function of triangular wave frequency—provide fundamental information about oxidation-reduction reactions. The method is useful for chemical analysis, basic chemical and biological studies, and applied research on batteries.

"Fifteen years ago we, among others, recognized the tremendous potential of the technique. The problem was that it could only be used empirically, since little in the way of theory existed for relating quantitatively the shape of the curves to the mechanism of the electrochemical reaction. Various attempts at developing theory convinced several workers that the problem was too complex

mathematically to yield analytical solutions, except in the simplest cases. Numerical finite difference solutions tried earlier by one of us (I.S.) had not proved general enough.

"Our (modest) breakthrough came partly from studying a Russian paper¹ that had aroused our interest because the results were not in accord with our intuition (our intuition later proved wrong). From this Russian paper we began to recognize that a useful approach might be the combination of an integral-equation formalism with numerical calculations. The results of the very first calculations were exciting, because we saw that the approach was indeed going to have great versatility. The calculations were so laborious, however, that we quickly sought the help of an electronic computer—an IBM 704 operated by the Midwest Universities Research Association (MURA), then under contract to the Atomic Energy Commission. They kindly let us use the 'graveyard' shift, so we spent many nights in the summer of 1963 solving most of the electrochemical mechanisms of interest.

"We spent the fall of 1963 analyzing the results, devising interpretations, and finally writing the manuscript. While the work itself was mathematical, we tried to organize the manuscript with a nonmathematical user in mind. We were fortunate that the editor and referees who reviewed the paper recognized that the work would be most useful if published as a unit; neither of us has ever had another paper published with so little hassle from the editors. We believe that careful attention to writing the paper is one of the ingredients that has made it a so-called *Citation Classic*. Moreover, in the intervening years electrochemistry has come of age, being broadly adopted as a valuable diagnostic/analytical tool. To a large extent cyclic voltammetry has now replaced classical polarography as the electrochemical tool of choice. Presumably our paper continues to be referenced, so many years later, because it remains a source of most of the basic equations and data for interpreting cyclic voltammetric curves."

1. Gokhshtein A Y & Gokhshtein Y P. *Doklady Akad. Nauk SSSR* **131**:601, 1960.