

## APPLICATION OF AREA UNDER THE C.V-CURVE OF CYCLIC VOLTAMMOGRAMS IN THE QUANTITATIVE ANALYSIS

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The utilization of areas under the curves of cyclic voltammograms and sampled dc (TAST) were explored for quantitative analysis. Areas were measured by (a) graphic integration, (b) paper doll, (c) triangulation, (d) B x H formulae, and (e) rectangulation methods. This method (areas under curves) was found to be more sensitive and accurate at lower concentration ( $10^{-5}$  mM) compared to peak current measurements method.

**Key words:** Cyclic Voltammograms, Sampled d.c. Area under CV Curve. Convolution Sweep Voltammetry.

### INTRODUCTION

Polarography and cyclic Voltammetry along with other electrochemical techniques have been used both for quantitative and qualitative analysis of electroactive substances [1]. Polarography, in its simplest form, in particular, has been, from its very inception, most extensively used in quantitative analysis. Its variation, the pulse technique, is also being used for the quantitative analysis. In contrast, the triangular wave cyclic voltammetry has not been much used for quantitative analysis although the linear scan voltammetry has been used for such a purpose [2].

In polarography and linear scan voltammetry, diffusion  $i_d$  (the plateau) and peak currents  $i_p$  respectively are used for quantitative analysis the currents  $i_d$  or  $i_p$  being proportional to the concentration of the electroactive species in the bulk. Such current-concentration plots can be used conveniently to  $10^{-3}$  to  $10^{-4}$  molar concentrations of electroactive substances. For more dilute solutions, techniques like normal and differential pulse stripping voltammetry are used. The sampled dc (TAST) method is also being used under the same conditions and with the same results. It is surprising that the area under the curves of triangular wave cyclic and sampled d.c. voltammograms have rarely been explored in quantitative analysis.

An exception is the adsorption processes where the area under the cyclic voltammogram is used to determine the amount adsorbed [2b]. If found suitable, the use of the area under the curve may add another useful (routine) tool to analytical chemistry in the quantitative analysis of electroactive substances. In this paper we propose to present the results of our exploratory work on the possible use of areas under curve of cyclic voltammograms in quan-

titative analysis. The results thus obtained are compared with those obtained from the use of peak current.

It may be noted that the present work is equivalent to convolution sweep voltammetry [2c].

### MATERIALS AND METHOD

Depending upon the nature of the curve, the areas under the curve for quantitative analysis purpose can be determined by [3, 4] (a) graphic integration, (b) paper doll, (c) triangulation, (d) (B x H) formulae and (e) rectangulation method. Besides, an electronic integrator can also be used (help from a minicomputer can be taken).

The graphical integration method involves the integration of the number of squares within the voltammograms. In the triangulation method a triangle is constructed by drawing tangents to the sides of the peak; the area of the triangle is then determined. In (B x H) formulae method the area is found by determining the height and the width at one-half width and multiplying them, while in the rectangulation method, the area of each rectangle under the "stair" is determined and added.

### RESULTS AND DISCUSSION

In the present work areas under the curves for cyclic and sampled dc (TAST) voltammograms [4] were determined using the above mentioned methods. Since 1, 3 dinitrobenzene gives text book-reversible voltammograms in non-aqueous system (dimethyl-formamide, acetonitrile), this system was used for the present purpose. Of course aqueous systems with electroactive species could also be used for the same purpose.

For concentration ranges 0.003 mM to 2mM, the plots are given in Figs. 1-6. These Fig. also include the error involved in each measurement. It was found that for concentration range  $5 \times 10^{-4}$ M or above there is little choice; however, for the concentration range lower than  $5 \times 10^{-5}$ M or lower,  $i_p$  gives considerable larger error

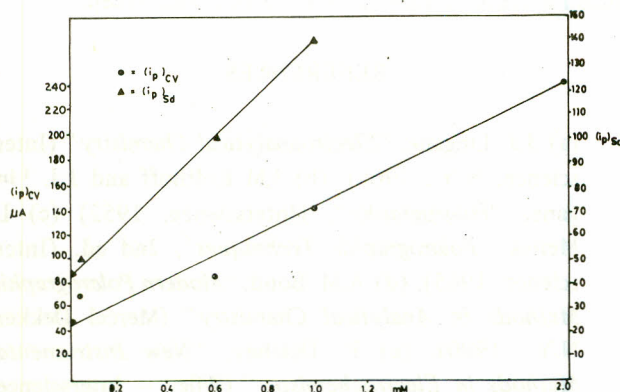


Fig. 1. Concentration (DNB) vs.  $I_p$  for cyclic voltammogram (cv)  $\Phi$  and sampled d.c. (sd)  $\Delta$ .

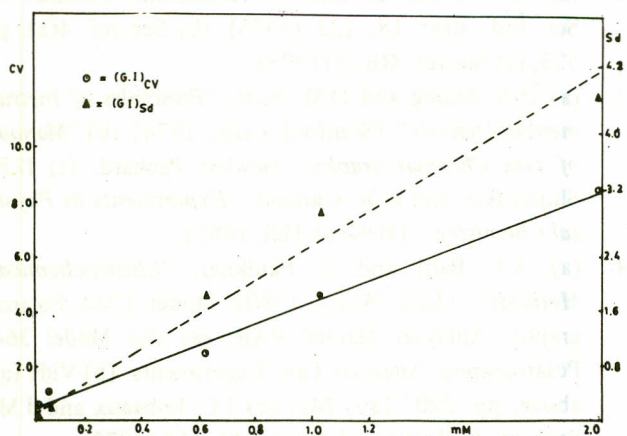


Fig. 2. Concentration (DNB) vs. Area by Graphical Integration cv =  $\circ$ , sd =  $\Delta$ .

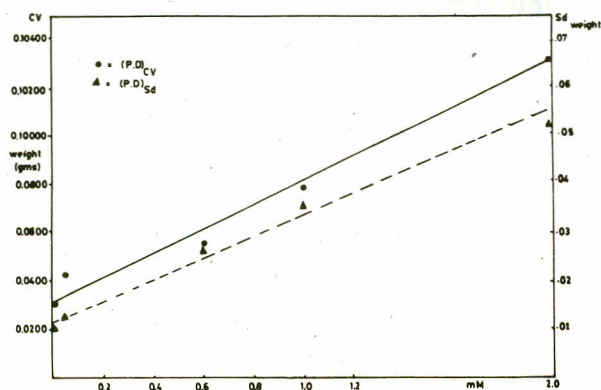


Fig. 3. Concentration (DNB) vs Weight by paper doll. cv =  $\circ$ , sd =  $\Delta$ .

(25 %), as compared to the other methods which give a maximum of 10 %. Besides, these plots show better linearity compared to that for  $i_p$  vs concentration. Surprisingly, the best plot is obtained by triangulation for cyclic voltammogram (Fig. 4).

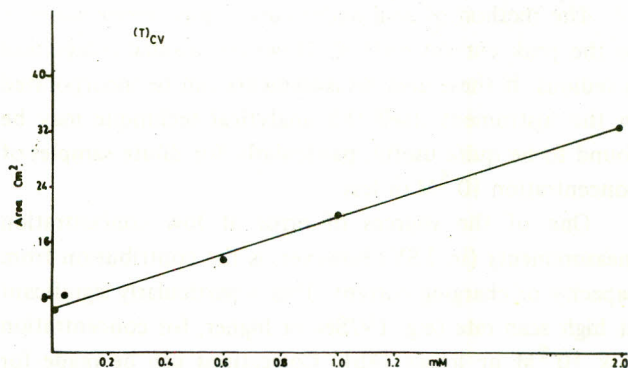


Fig. 4. Concentration (DNB) vs Area by Triangulation. cv

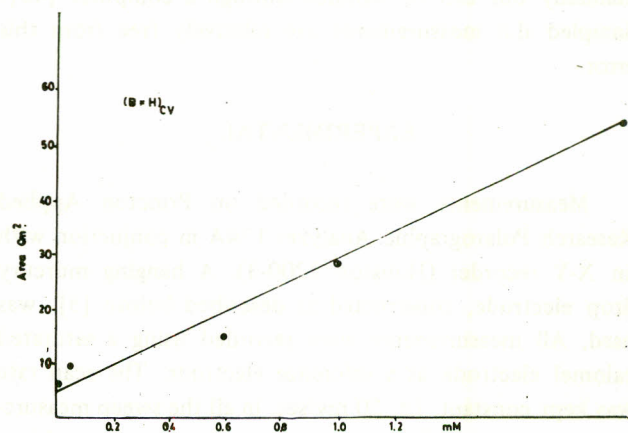


Fig. 5. Concentration (DNB) vs Area by B x H. cv

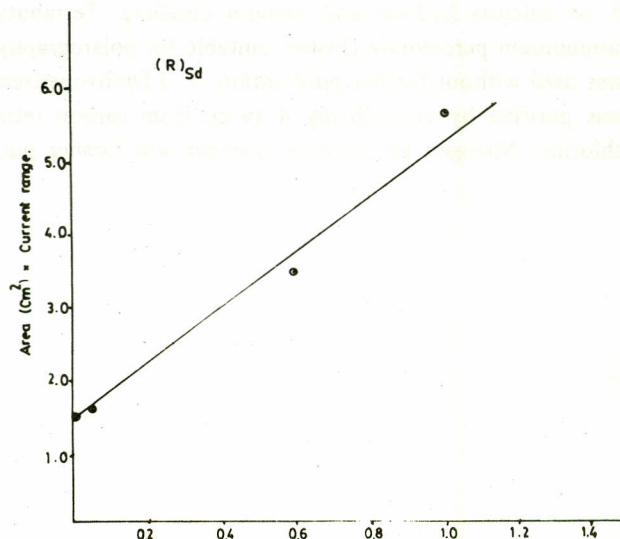


Fig. 6. Concentration (DNB) vs Area Current Range by Rectangulation. sd

For sampled d.c. most of the plots including  $i_p$  give a pretty good straight line. Thus for sampled d.c. technique there is not much choice, except that error in the individual measurement is less in other methods as has been pointed out.

The method of area under curve, thus, seems superior to the peak current method. However, manual integration is tedious. If these area measurements can be incorporated in the instrument itself this analytical technique may be found to be quite useful, particularly for dilute samples of concentration  $10^{-5}$  M or less.

One of the sources of error at low concentration measurements (in LSV) however, is the contribution from capacity or charging current. This is particularly significant at high scan rate (e.g. 1V/Sec or higher, for concentration  $1 \times 10^{-6}$  M or lower [4b]). Corrections can be made for this charging current [4a]. However, it is quite tedious manually but can be handled through a computer [4b]. Sampled d.c. measurements are relatively free from this error.

#### EXPERIMENTAL

Measurements were recorded on Princeton Applied Research Polarographic Analyzer 174A in conjunction with an X-Y recorder (Houston 2200-3). A hanging mercury drop electrode, constructed as described before [5], was used. All measurements were recorded using a saturated calomel electrode as a reference electrode. The scan rate was kept constant, i.e. 50 mv/sec. in all the sweep measurements, while sampled d.c. measurements were carried out as usual [4a]. Acetonitrile (BDH) was purified by keeping it on calcium hydride and vacuum distilling. Tetrabutylammonium perchlorate (Fisher, suitable for polarography) was used without further purification. 1, 3 Dinitrobenzene was purified by crystallizing it twice from carbon tetrachloride. Nitrogen gas from a cylinder was further purified

by passing through a series of traps containing vanadous sulphate over zinc amalgam, solvent and molecular sieve.

Areas under curves were calculated manually based upon the method described before. Paper dolls were cut and weighed on a balance accurate to .01 mg. Several measurements for each sample solution were taken.

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