

## CHANGING CURRENT COMPENSATION IN AC AND DC POLAROGRAPHY

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The limit of detection by AC and DC polarographic techniques ( $5 \times 10^{-5}$  M, Ca 50ppm) is set by the nonlinear variation of charging current (CC) with potential. The detection limit should, in principle, be improved if the CC is either compensated or eliminated. Such an attempt seems worthwhile because, it could make these techniques useful for the analysis of trace constituents without the necessity of preconcentration.

Many compensation methods have been suggested in the past, for improving the detection limit of DC polarography. Most of them achieve only partial compensation, a few that are efficient are cumbersome and hence are not of use to the practicing analyst. A new simple compensation technique is described. This makes use of an *in situ* measurement of double layer capacity at each potential for the on-line calculation of charging current and subtracting the same from the measured cell current at the same potential. A hardware realisation of the same is presented. Experimental results with the prototype of CC compensated DC polarograph show the detection limit to be  $5 \times 10^{-8}$  M (Ca 0.005ppm).

In sinusoidal AC polarography, CC ( $i_c$ ) is given by

$$i_c = -AC_{dl} \frac{d}{dt} (E_s \sin \omega t)$$

( $C_{dl}$  = double layer capacitance

$A$  = area of the electrode

$E_s \sin \omega t$  = applied ac potential)

The CC should, therefore, tend to zero when  $\frac{d}{dt} (E_s \sin \omega t) \longrightarrow 0$  i.e., when the applied a.c. potential is maximum or minimum. A corollary from the above analysis is: *the cell current, if measured at the maximum or minimum of the applied ac potential will be free from charging current.* This simple and elegant technique has not been used so far. A hardware implementation of this principle employing the box car integration technique is described. The phase selective polarography (PSP) and the new current sampling method are compared. It is shown that this newer technique gives signals that are  $\frac{\pi}{2}$  times larger than those of PSP. The detection limit of the current sampled AC polarography is  $5 \times 10^{-8}$  M (Ca 0.005ppm).

**Keywords :** Current Compensation; AC & DC Polarography; Box Car Integration

**Discussion**

- R. NARAYAN (*Indian Institute of Technology, Madras*) : 1. Why do different ions ( $\text{Cd}^{2+}$ ,  $\text{Ni}^{2+}$  etc) have different detection limits? 2. Can  $\text{O}_2$  be eliminated at the extent that it does not interfere? 3. How do you prepare standard solutions of such low concentration? What is the purity of water?
- S. R. RAJAGOPALAN (*National Aeronautical Laboratory, Bangalore*) : The differences noted in the detection limit of various ions (of same valency) arises from (i) differences in the diffusion current constant (ii) reversibility of the reduction and (iii) the magnitude of  $E_{1/2}$ . The factors (ii) & (iii) influence the detection limit since the charging current compensation and elimination is not 100 per cent.
2. Complete elimination is possible only by adding reducing agent like ascorbic acid. Removal of  $\text{O}_2$  by bubbling  $\text{N}_2$  or  $\text{H}_2$  does not proceed to completion.
3. Solutions have been prepared with conductivity water using Spec pure and AR chemicals in polythene ware. Solutions of required concentration are obtained by dilution of concentrated standard solution.
- V. K. VENKATESAN (*Central Electrochemical Research Institute, Karaikudi*) : a. What is the frequency of the a.c. used for *in situ* (differential capacity) charging current determination in the improvement of D.C. Polarograph? b. What is the frequency range in which the charging current compensation in a.c. polarography is applicable if there is any limitation?
- S. R. RAJAGOPALAN : a. The frequency was 220Hz. b. In principle there is no limitation. The upper limit of frequency that can be employed would depend on the maximum frequency that can be handled by the potentiostat.
- G. A. TEDORADZE (*Institute of Electrochemistry, Academy of Sciences of the USSR, Moscow*) : Are you sure that charging current does not change in the depolarizer solution?
- S. R. RAJAGOPALAN : In our method, the charging current is not separately measured with base electrolyte and subtracted from polarographic current. The charging current is monitored in the medium, base electrolyte + depolariser and compensated continuously and automatically.
- B. M. GRAFOV (*Institute of Electrochemistry, Academy of Sciences of USSR, Moscow*) : What is the reason you do not use redoxkinetic effect for detection of small concentration?
- S. R. RAJAGOPALAN : We did not use redoxkinetic effect for the following reasons :
1. The instrumentation is more complex.
  2. Our aim is to use the polarographic analysis for the trace analysis of technical materials. Quite a volume of information on the D.C. and A.C. polarographic behaviour of various ions (inorganic and organic) is available. Information on redoxkinetic or Faradaic rectification by redox system, is quite limited. Improving the detection limits of D.C. & A.C. polarography could therefore lead to the immediate use of these methods in the industrial laboratory. This view prompted us to develop improved D.C. and A.C. polarographs described here.