

The chronoamperometry: The Cottrell's equation (2) (27)

The chronoamperometry and the Cottrell equation is used in laboratory tests devices for the measurement of weak concentration of biochemical values. This technique was also used for the measurement of the serotonin (49) (50).

In chronoamperometry, the working electrode potential is suddenly stepped from an initial potential to a final potential, and the step usually crosses the formal potential of the analyte. The solution is not stirred. The initial potential is chosen so that no current flows (i.e., the electrode is held at a potential that neither oxidizes nor reduces the predominant form of the analyte). Then, the potential is stepped to a potential that either oxidizes or reduces the analyte, and a current begins to flow at the electrode. This current is quite large at first, but it rapidly decays as the analyte near the electrode is consumed, and a transient signal is observed. If the point in time when the potential is stepped is taken as time zero, then the Cottrell equation describes the how the current, I , decays as a function of time, t :

Cottrell equation and mathematical transformation for the calculation of the concentration in the EIS System

F = Faraday constant (96500 C/mole)

A = Electrode area (en cm²)

C_0 = Ionic concentration (mol/ cm³)

n = number of electrons per molecule

D = Diffusion coefficient (cm²/ s)

t = Measurement time in seconds

Although the current decay may appear to be exponential (in the case of adsorbed redox species), it actually decays as the reciprocal of the square root of time. This dependence on the square root of time reflects the fact that physical diffusion is responsible for transport of the analyte to the electrode surface.