has also been known to catalyze hydrolysis reactions. The reaction of bisulfate with dissolved oxygen is given by:

$$2\mathrm{HSO_3^-} + \mathrm{O_2} \rightarrow 2\mathrm{SO^{-4}} + 2\mathrm{H^+} \tag{7.10}$$

Several newer techniques, such as cyclic voltammetry (CV), are now used to identify a proper choice of an antioxidant. The CV is an electrolytic method that uses microelectrodes and an unstirred solution, so that the measured current is limited by analyte diffusion at the electrode surface. The electrode potential is ramped linearly to a more negative potential and then ramped in reverse, back to the starting voltage. The forward scan produces a current peak for any analyte that can be reduced through the range of the potential scan. The current will increase as the potential reaches the reduction potential of the analyte but then fall off as the concentration of the analyte is depleted close to the electrode surface. As the applied potential is reversed, it will reach a potential that will reoxidize the product formed in the first reduction reaction and produce a current of reverse polarity from the forward scan. This oxidation peak will usually have a similar shape to the reduction peak. The peak current, i_p, is described by the Randles–Sevcik equation:

$$i_\mathrm{p} = (2.69 \times 10^5)\, n^{3/2} ACD^{1/2} v^{1/2} \tag{7.11}$$

where n is the number of moles of electrons transferred in the reaction, A is the area of the electrode, C is the analyte concentration (in mol/cm^3), D is the diffusion coefficient, and v is the scan rate of the applied potential.

The potential difference between the reduction and the oxidation peaks is theoretically 59 mV for a reversible reaction. In practice, the difference is typically 70–100 mV. Larger differences, or nonsymmetric reduction and oxidation peaks, are an indication of a nonreversible reaction. These parameters of cyclic voltammograms make CV most suitable for the characterization and mechanistic studies of redox reactions at the electrodes.

The basic components of a modern electroanalytical system for voltammetry are a potentiostat, a computer, and an electrochemical cell. In some cases, the potentiostat and the computer are bundled into one package, whereas in other systems, the computer and the converters and microcontrollers are separate, and the potentiostat can operate independently.

7.4.3 Trace Metals

Trace metal ions can affect the stability and can arise from the bulk drug, formulation excipients, or glass containers. Metal ions can also act as degradation catalysts by their involvement in the production of highly reactive free radicals, especially in the presence of oxygen. The formation of these radicals can be initiated by the action of light or heat and propagate the reaction until they are destroyed by inhibitors or by side reactions that break the chain. Free-radical oxygen species can be generated by transition metals in solutions, such that reactions can be initiated. Because of the involvement of metal ions in degradation reactions, the inclusion of a chelating agent is often advocated.