1.2 SUMMARY

Glassy carbon (GC) electrodes modified with hexadecylmethane sulfonate (HDMS) produce much improved signal-to-noise characteristics together with enhanced stability towards amperometric detection of some clinically significant substances, including ascorbic acid, paracetamol and catechol. The HDMS-modified GC electrodes do not alter the reaction mechanism due to the nonelectroactive nature of the modifier; Nevertheless, such modified electrodes offer more reliable results with detection limits in the order of 10^{-4} mol dm^{-3}. Thus, HDMS-modified GC electrodes are employed to quantify the active ingredient in Vitamin-C and Paracetamol tablets (A1, A2).

According to cyclic voltammetric studies, GC electrodes modified with 5,10,15,20-tetraphenylporphyrinatoiron(III) chloride [Fe(III)TPPCl] and 5,10,15,20-tetraphenylporphyrinatocobalt(II) [Co(II)TPP] show the electrochemistry of the Fe(III)/Fe(II), and Co(II)/Co(I) couples, respectively, in aqueous medium between potentials of +0.25 V and -0.50 V vs. the saturated calomel electrode (SCE). When small amounts of certain polar organo-halides are added, the reduction potential of these couples is significantly enhanced and the reversibility is lost. The peak shape and the peak location suggest that the reduction of such substances follow the ECE mechanism, where the reduction product of the metal ion forms an electroactive adduct with the analyte, which then undergoes electrochemical reduction. The current generated during this process is proportional to the bulk concentration of the analyte, indicating the analytical utility of metalloporphyrin-modified GC electrodes as sensors for selected pharmaceutical substances containing organo-halide moieties. In the

absence of metalloporphyrins, these analytes show sluggish electrode kinetics resulting in little or no activity, demonstrating the electrocatalytic ability of metalloporphyrin modified GC electrodes.

The electrocatalytic ability of metalloporphyrin-modified GC electrodes is stereo-specific. For instance, the electrochemical behavior of 2-, 3- and 4-bromobenzoic acids at GC electrodes modified with Fe(III)TPPCl, which acts as a catalyst for the reduction of bromobenzoic acids, is different from each other depending on the location of the substituent. The catalyst offers a significant reduction current for 4-bromobenzoic acid compared to that for 2- and 3-bromo derivatives, indicating that Fe(III)TPPCl-modified glassy carbon electrodes selectively catalyze 4-bromobenzoic acid in the presence of the other two derivatives (A3, A4).

More importantly, the sensitivity of detection of some selected clinically significant substances, including chloroquine phosphate and diethyl carbamazine at metalloporphyrin-modified GC electrodes is further improved by employing steady-state amperometric techniques. Optimization of analytical parameters such as solvent composition, potential of operation, type and concentration of the electrolyte, method of coating, type of coating material, etc. is performed wherever possible. Quantification of the active ingredient in commercial drugs (Chloroquine Phosphate-SPC, Avlochlor, Heterosan, Benocide) is carried out under optimized conditions (A5 - A7). It is advisable to perform the analysis for a sufficient number of trials in order to treat the results statistically.