Application of Square-Wave Voltammetry for Flow Injection Analysis†

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A recent advance in square-wave voltammetry provides a method which can perform potential scanning within seconds, and is thus applicable for detection in a flow system. Although square-wave voltammetry has been applied to the flow injection analysis of additives in food, theoretical work has been lacking in the literature. This paper presents a working equation for the above-mentioned analysis. The results obtained by a theoretical calculation have been shown to give satisfactory agreement with the experimental results. The results for analyses of food are given to illustrate the applicability of the technique for flow injection analysis.

Keywords Flow injection analysis, square-wave voltammetry, automatic analysis, food analysis

Flow injection analysis has become an increasingly important analytical technique in recent years for the automation of chemical analysis due to its simplicity, versatility and availability of instruments, parts and accessories in chemical laboratories. The problem facing the further development of flow injection analysis is the sensitivity and selectivity of the detector for analyzing trace amounts of analytes in an often complicated matrix. Electrochemical detection provides a much needed detector for the above-mentioned purpose due to its sensitivity and selectivity of scanning the potential during detection. However, traditional potential scanning methods are problems since they are flow sensitive and, thus, not amendable to flow injection analysis. The reason is due to the rather long measurement time during electrochemical detection.

The current trend in the development of voltammetric techniques is towards the use of pulse voltammetry due to its short scan time, high sensitivity and good selectivity. This pulse voltammetry technique is particularly suitable for detection in a flowing fluid due to the advantage of running a full potential scan within seconds. Thus, it is less influenced by the effect of a variation in the flow rate of the mobile electrolyte.

Although the experimental details and the analytical results concerning the application of square-wave voltammetry for the flow injection analysis of ascorbic acid has been published, theoretical work under the above-mentioned conditions has been lacking in the literature. Thus, this paper describes the development and verification of a theoretical equation for the transient current response at planar electrodes for a reversible electrode reaction in a flowing fluid:

\[
J(t) = D(\partial C/\partial t)_{t=0} = \frac{[D(C^* - C(0,t))/\delta]}{[\pi t D/\delta^2]^{1/2} + 0.96erf(3.21 t D/\delta^2)^{1/2}},
\]

where \(\delta=3(D/V)^{1/2}(\nu x/U)^{1/2}\); \(\nu\) is the kinematic viscosity; \(U\) is maximum linear velocity of the stream solution; \(C\) denotes the concentration of the electroactive species; \(D\) is diffusion coefficient of the electroactive species; \(x\) is the distance along the planar electrode; \(y\) is the distance from the surface of the electrode; \(t\) is time.

The total current obtained as a result of the diffusional flow to the surface of the planar electrode may be calculated by integrating \(J(t)\) along the surface of the electrode,

\[
I(t) = nFDW \int_0^L J(t) \, dx,
\]

where \(I(t)\) is the total current at time \(t\); \(J(t)\) is the diffusional flux at time \(t\) as a function of \(x\); \(n\) is the number of electrons involved in the electrode reaction; \(F\) is the Faraday constant; \(W\) is the width of the planar electrode and \(L\) is its length. The above equation will be verified experimentally and its application for food

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Experimental

The flow rate of the electrolyte was controlled by a syringe pump with the sample being injected via a sample loop by a 4-way rotary valve. A self-constructed thin-layer electrochemical cell (thickness of 0.34 mm) was used as the detector, with a platinum electrode (4x5 mm²) as the working electrode, Ag/AgCl as the reference electrode and stainless steel as the counter electrode. A square-wave waveform was generated by a microcomputer and superimposed on a self-constructed potentiostat placed near to the electrochemical cell housed in a Faraday cage. The current was sampled by the microcomputer at appropriate times and the peak current for each potential scan was recorded by a Houston Hiplot X-Y digital plotter.

Results and Discussion

The experimental verification of the above equation was performed using the reduction of potassium hexacyanoferrate(III). Current–time curves were obtained at linear flow rates of between 0.1 to 20 cm/s. A comparison of the theoretical calculation and the experimental results showed excellent agreement with the experimental data (Fig. 1).

The application of a pulse voltammetry technique with square-wave voltammetry was investigated for detection in a flow injection analysis of ascorbic acid in soft drinks and fruit juices and for the determination of iodine in food samples. The linear range of this technique for an ascorbic acid analysis was found to range from 2x10⁻⁶ to 6x10⁻³ M, and the detection limit (estimated by ten standard deviations) was 2x10⁻⁷ M. No significant interference was detected for those additives commonly found in juices and drinks samples within their normal concentration ranges. The linear range for an iodide analysis was found to range from 0.1 ppm to 40 ppm iodide, and the detection limit (estimated by three standard deviations) was 0.005 ppm. The effects of 12 potential interferents of inorganic compounds were studied; no significant interference was detected. The method has been applied to the analysis of iodide in seawater, milk powder, cereal and two sea weeds (Porphyra and Laminaria). The results are given in Table 1.

Based on the above study on both theory and applications of square-wave voltammetry for flow injection analysis, the results indicate good agreement between theory and experiment; the technique thus is shown to be applicable to the automatic analysis of food additives in various types of food products.

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References


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