

Dispersion in Flow Injection Analysis Measured with Microvoltammetric Electrodes

Sir: Measurement of transient changes in chemical concentration may be distorted by dispersive forces. This is especially true in chromatography where the separation achieved on the column can be destroyed by extracolumn broadening (1). In flow injection analysis dispersion dictates the time between samples. The effects of dispersion have been modeled extensively, especially for dispersion in cylindrical tubes (2-5). These models demonstrate that a bolus introduced into a flowing stream will be distorted from its original shape as a result of convective and dispersive forces. However, these models do have limitations. Analytical solutions do not exist for many situations that are operant under normal experimental conditions. In addition, practical design of equipment often precludes theoretical description. Thus, an ideal tool to investigate dispersion in chemical systems would be an infinitely small chemical probe that could be moved inside the dispersion zone. As will be shown, microvoltammetric electrodes approach this ideal; therefore, they provide a useful tool to gain insight into the dispersion processes that occur with loop injectors and conventional on-line detectors.

EXPERIMENTAL SECTION

Flow Injection System. The flow injection system is shown schematically in Figure 1. It consists of a syringe pump, a rotary valve loop injector made of Teflon, and an electrochemical detection system that is interfaced to an IBM personal computer. The pump (Model 940, Harvard Apparatus Co., Millis, MA) with a plastic syringe (20 mL, Pharasel Lab., Glendale, CA) was operated at a flow rate of 0.93 mL min⁻¹. Tubing made of Teflon (0.8 mm i.d.) and couplings (Altex Scientific, Inc., Berkeley, CA) are used throughout the system. A loop injector (type 50, Rheodyne, Inc., Cotati, CA) with an injector volume of 57 or 538 μ L was connected to the detector system with approximately 4 cm of Teflon tubing. A pneumatic actuator (Model 50-01, Rheodyne, Inc., Cotati, CA) coupled with a solenoid valve (Model 38-931, Rheodyne) was triggered by the computer to turn the loop injector in a rapid and consistent manner.

The detector was either an electrochemical channel cell normally used as a detector for liquid chromatography (6) or a microvoltammetric electrode. The channel detector was connected to the Teflon tubing via coupling made of Teflon. When a microvoltammetric electrode was employed, the Teflon tubing from the loop injector was attached to a stainless-steel tube (0.8 mm i.d., 40 mm). The microvoltammetric electrode was centered in the stainless-steel tube, 5.0 mm before the end, with a micromanipulator with 100- μ m resolution.

The locally constructed potentiostat was of conventional, three-electrode design. The time constant of the potentiostat was 10 ms. A saturated calomel reference electrode was used in all experiments.

Microvoltammetric Electrodes. Microvoltammetric electrodes were prepared with the use of carbon fibers inserted into glass capillaries (7). The carbon fiber was cut so that the active sensing area of the electrode is a disk surrounded by a thin wall of glass. Epoxy between the glass and carbon ensures a tight seal. The diameter of the carbon fiber is approximately 10 μ m, and the total diameter of the entire assembly is approximately 20 μ m. The detection volume of a disk-shaped microvoltammetric electrode is a hemisphere whose radius is approximately 6 times the radius of the electrode (8).

Computer Methods. Linear response theory was employed in some experiments to evaluate the degree of dispersion. This approach has been used previously in the analysis of extracolumn band broadening (9). The technique is based on the principle that the response of an input signal distorted by a perturbation is identical with the input signal convoluted with the impulse

response function of the perturbation. This allows the perturbation of the system to be compared with various models of distortion and enables the parameters of these distortion models to be evaluated. The procedure consists of a fast Fourier transform (10, 11) of the input signal and the perturbation's impulse response function, multiplication of the two in the Fourier domain, inverse transformation of the product, and comparison with the measured output wave form.

Reagents. All chemicals were reagent grade and used as received from commercial sources. An aqueous buffer containing 20.0 mM 1-[4-(2-hydroxyethyl)piperazine]ethanesulfonic acid and 150 mM NaCl, adjusted to pH 7.4 with NaOH, was employed. Dopamine (3-hydroxytyramine hydrochloride, Sigma, St. Louis, MO) was used as the test compound, and solutions of the desired concentration were prepared by diluting a stock solution prepared in 0.1 N HClO₄. The diffusion coefficient of dopamine is 6×10^{-6} cm² s⁻¹ (12).

RESULTS AND DISCUSSION

The response of a microvoltammetric electrode to a concentration pulse of dopamine introduced by the loop injector is shown in Figure 2. In this experiment the electrode was located approximately in the center of the outlet tube and was approximately 6 cm from the leading edge of the injection loop. The measured current is a direct measure of the temporal concentration change at the tip of the electrode. The distortion from a rectangular shape results from dispersive forces introduced by the loop injector and transport tubing in the flow system. The mechanisms of dispersion can be evaluated by the Peclet number (2, 3), which has a value of greater than 40 000 for the system described here, and the dimensionless time (τ), which is 0.01. For these values axial and radial diffusion are negligibly small compared to convective dispersion mechanisms.

Experiments of this type can be employed to evaluate the temporal distortion of the injected bolus caused by the volume of a conventional detector. In these experiments we used the amperometric liquid chromatographic detector designed in this laboratory (6). The metal tube for the microvoltammetric electrode was removed, and the amperometric detector was connected to the tube made of Teflon. The microvoltammetric electrode was then inserted in the center of the exit port of the channel detector (Figure 2). As seen from the current-time curve, the degree of dispersion is greater than that observed at the input. The dispersion was modeled with the convolute and compare technique, with the assumption that the response function of the dispersion arises from the finite volume of the channel detector and, thus, has an exponential form. The input wave form measured with the microvoltammetric electrode (F_b) was convoluted with the mixing chamber response function

$$F_{out} = F_b * e^{-tV/S} \quad (1)$$

where V is the volume flow rate and S is the internal volume of the channel (3.1 μ L). As can be seen in Figure 2, F_{out} agrees extremely well with the measured result.

Further insights into the dispersion introduced by the loop injector can be obtained by mapping the concentration profile across the outlet tube of the injector. These measurements were made at 0.1-mm intervals and provide a measure of the convective dispersion of the injected bolus (Figure 3). The rise time of the current increases as the electrode is moved closer to the wall of the tube. The current at steady state (20

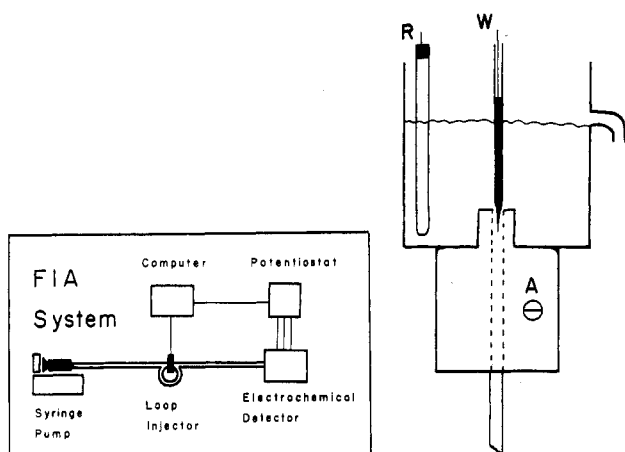


Figure 1. Stainless-steel tube used with the microvoltammetric electrode: Insert, block diagram of the flow injection system.

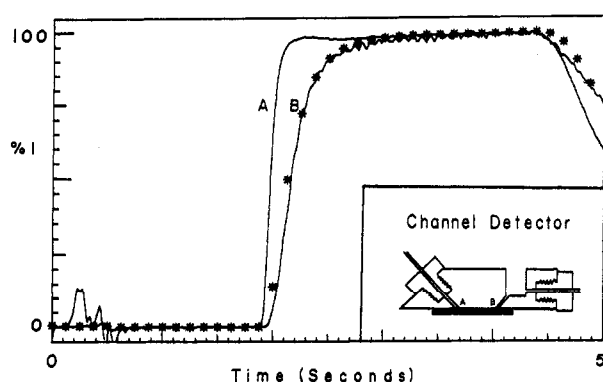


Figure 2. Relative response to a 3-s 10 μ M dopamine pulse for a microvoltammetric electrode before the channel detector (A), a microvoltammetric electrode after the channel detector (B), and a simulated response for a microvoltammetric electrode after the channel detector (asterisk, see text). A diagram of the electrochemical channel detector is shown in the insert.

s) was essentially the same at all positions, which demonstrates that the flow rate dependence of the current is negligible. Thus, the current profile at each position is representative of the temporal concentration changes. The time required to reach half of the steady-state current as a function of position gives a parabolic shape (Figure 3). This is the result expected for dispersion dominated by convection (2, 3).

To obtain the total dispersion that would be obtained by a bulk concentration detector, the individual responses were assumed to be representative of the concentration in the ring of the tube in which the electrode was located. Integration of the current over the area of each ring and temporal summation give the bulk change in concentration. Good agreement is obtained when this result is compared to the signal measured from the channel-type amperometric electrode when it was directly connected to the loop injector (Figure 4).

These results demonstrate that microvoltammetric electrodes can be used to measure concentration dispersion. In this system there are several possible sources of temporal distortion, which include the loop injector, transport tubing, and the channel-type detector. However, the results with the microvoltammetric electrode demonstrate that the primary source of dispersion is the transport tubing, while the finite volume of the channel-type detector contributes negligibly to the observed response in agreement with previous reports of dispersion in amperometric detectors (13–15). Although these

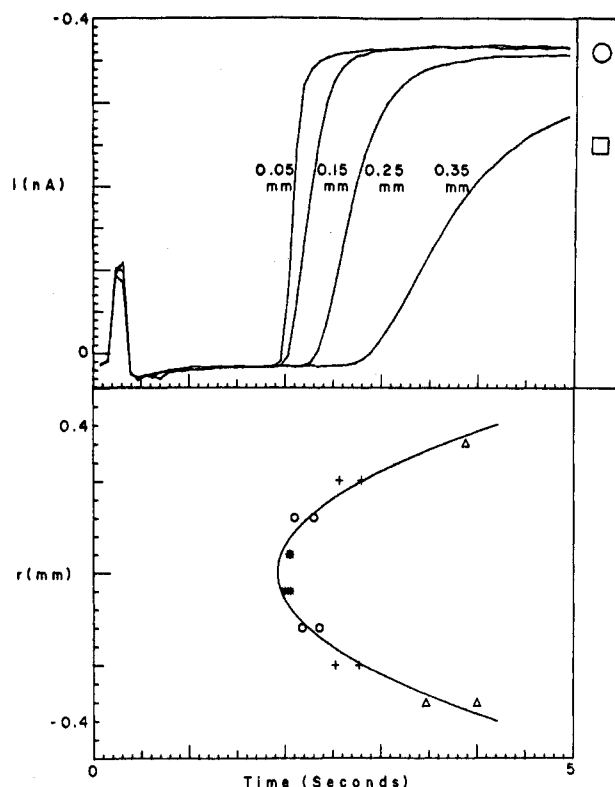


Figure 3. Average current response to a 30-s 20 μ M dopamine pulse measured at different positions from the center of the tube (upper). The average steady-state current for all the positions was measured at 20 s at the specified flow rate (circle) and at zero flow rate (square). Dispersion measured across the tube (lower). The time required to reach half of the steady-state current is plotted against the position of the electrode from the center of the tube. The parabola is the least-squares best fit to the data ($r = 0.967$), and each point represents a single measurement.

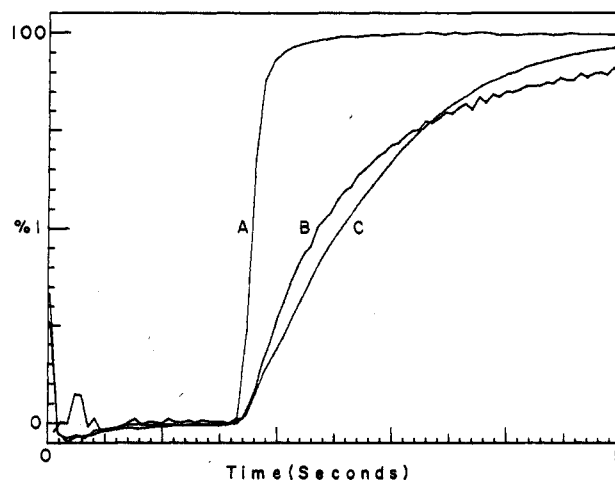


Figure 4. Relative current response to a 30-s 20 μ M dopamine pulse for a microvoltammetric electrode positioned at the center of the tube (A), the channel-type amperometric detector (B), and the total concentration-time profile calculated from the data in Figure 3 (C).

results could be predicted from existing theory, this approach should be useful for exploring less well-defined situations such as turbulent flow or secondary dispersive effects.

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