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We present a laboratory experiment, suitable for implementation in analytical chemistry courses at the undergraduate level, that demonstrates the utility of time-based measurements with doublet peaks in flow injection analysis. The measurements are taken with an instrument that incorporates a simple solid-state detector, which has as its source a light-emitting diode (LED) and as its detecting element a photodiode (PD). The system studied here is a simple acid–base titration. The experiment could be adapted to any number of chemical reactions that result in a product that absorbs light of the LED wavelength significantly.

Background

Flow injection analysis (FIA) experiments are attractive for use in teaching laboratories for several reasons. FIA methods use relatively small amounts of reagents and generate relatively small amounts of waste compared to many conventional analytical techniques. The modular nature of the FI manifold lends itself to rapid changes in instrumental configuration, making it possible for students to discover trends on their own and think about what is happening in instruments that often are perceived as "black boxes".

Taking advantage of the ease of performance of flow injection analysis (FIA) experiments and relatively low cost of FIA equipment, Hansen and Ruzicka (*1*) incorporated FIA into student laboratories shortly after it was first described as an analytical technique. Other authors have developed a variety of laboratory exercises based on flow injection analysis (*2–12*). Although peak height is used most commonly for quantitative measurements in flow injection analysis, time-based methods are being utilized increasingly. Measurements of time are less susceptible to errors introduced by noise spikes or source- or detector-drift than are peak-height-based measurements.

Doublet peaks occur in FI systems when the sample species is in excess in the profile center and equivalence occurs at two points, one on the leading edge and the other on the trailing edge of the profile. Initially avoided, due to their detrimental effect on peak-height-based measurements, doublet peaks can be used to advantage in FIA experiments. In essence, the conditions are selected so that during passage through the manifold components the dispersion processes are such that the reagent does not penetrate to the center of the injected bolus by the time the sample zone reaches the detector. For the "well-stirred-tank" model of an FIA system, the basic equation relating the time between doublet peaks, t, to other FI variables is

$$t = (V/Q)\ln\{C^S[\exp(V_i/V) - 1]/C^R\} \quad (1)$$

where V is volume of the mixing chamber, V_i is sample volume, C^S is initial sample concentration, C^R is reagent concentration, and Q is flow rate (*13, 14*). Applications of these time-based doublet peak measurements to flow injection titrations (*14*) and to the determination of stability constants (*15*) have been demonstrated. As in more conventional peak width measurements, the time interval measured is related to the logarithm of the sample concentration, which results in an expanded working range (*14*).

For peak-width or doublet-peak measurements, the detector response need not be linear with concentration. As long as temporal measurements can be made accurately, inexpensive solid-state electronic components can be used, even if they exhibit long-term instability (*16*). Considerable effort in the area of inexpensive solid-state detectors for FIA has been made. A review by Trojanowicz et al. describes the advantages of solid-state detectors, and outlines several of the approaches taken (*17*). Most of these detectors are designed with light-emitting diodes (LEDs) as source elements and phototransistors or photodiodes (PDs) as detecting elements and are used for peak-height-based measurements. Multiple-source detectors also have been developed, including a commercial detector that has been applied to simultaneous FI detection of two (*18*) or three (*19*) chemical species.

One of the most costly components of traditional FI spectrometric systems is the flow cell. Commercially available fused-silica flow cells cost hundreds of dollars. A variety of approaches have been taken to inexpensive flow cells (*12, 17*). We use here simply a 0.9-mm-i.d. Teflon tube.

Experimental

Apparatus

These experiments can be carried out with basic flow-injection analysis apparatus. A schematic diagram is given in Figure 1. A one-channel peristaltic pump is needed, as is a suitable injection valve. We have used a variable-speed pump (Ismatec sa) and a six-port rotary injection valve (Rheodyne). The flow rate with a fixed-speed pump could be controlled through use of different diameter pump tubing, with similar experimental results. Any sample introduction system with suitable adjustable-injection-volume capability could be employed in place of the six-port valve. An integrator (Hewlett–Packard model HP 3394A) was used for data collection. Alternatively, a chart recorder or digital oscilloscope could be employed.

The sample solution of the analyte is loaded into a loop. When the valve is switched manually, the carrier stream is diverted so that it comes into contact with the injected sample. Dispersion of the reagent and sample occurs as the sample passes through the reactor and, if appropriate conditions of reagent and carrier stream concentrations, injec-

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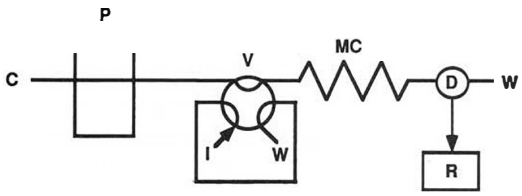

Figure 1. Schematic diagram of FI instrument. P is a peristaltic pump; V is a valve; C is the carrier stream; I is the sample injection port; D is the LED-PD detector; R is the data readout (integrator); W is the waste. MC represents manifold components in which injectate and carrier solutions mix. It could be an open tubular reactor, coiled for convenience (as was used in the experiments described here), or it could be a tank or mixing chamber with stirring.

tion volume, and reactor dimensions are chosen, the dispersion and reaction results in the development of a doublet-peak profile. In these experiments, a true mixing chamber is not used as the reactor. Instead, a slightly coiled 600 mm length of 0.9-mm inner diameter tubing (Chemplast Inc., Chemfluor, Teflon spaghetti tubing) is employed. Use of a tube for the reactor has the advantage of simplifying the system but does result in deviation from theory (*14*). The well-stirred-tank model assumes that the injected sample undergoes dispersion only in the mixing chamber. Such dispersion results in a concentration-time profile for the sample in which both rising and falling edges are described by exponential functions (*13*). If the actual reactor does not behave as a well-stirred tank, then the concentration-time equations are not truly exponential functions, and Δt will not be related logarithmically to the sample concentration.

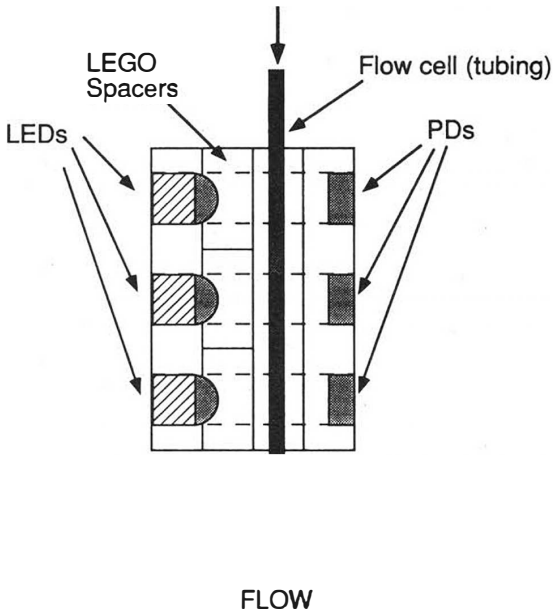

Figure 2. Detector design (not to scale).

After passing through the reactor, the sample bolus reaches the in-house-built detector. Changes in transmittance of the flowing stream are measured by the detector, and the signal is sent to the integrator. The integrator notes the "retention time"—designed for use in chromatographic systems—of each peak, to the nearest 0.001 min. Values for Δt are calculated manually from the difference in time between the doublet peaks.

Detector Design

Figure 2 represents the detector design. The source and detector components are mounted in LEGO blocks, which provide detector configuration flexibility. One red, one yellow, and one green ultrabright LED (Newark Electronics) are mounted sequentially along the "flow cell", which is a segment of the same 0.9-mm inner-diameter tubing used in the FI manifold. On the other side of the flow cell from each LED is a PIN photodiode detector component (Newark Electronics). For the experiments listed here, only one LED-PD pair is used at a time. The signal from the PD is sent through a current-to-voltage converter. As the carrier solution is passed through the flow cell, the negative voltage is offset to zero (because the integrator will not accept negative signals) and the signal is sent to the integrator. When an absorbing species passes through the detector, a decrease in the amount of light transmitted results in a decrease in negative voltage. The integrator sees this as a positive signal. Figure 3 shows the circuitry used to control the LED and PD and to perform the current-to-voltage conversion and offset voltage adjust. The total cost of the components needed to build the entire detector and controller is less than $50.

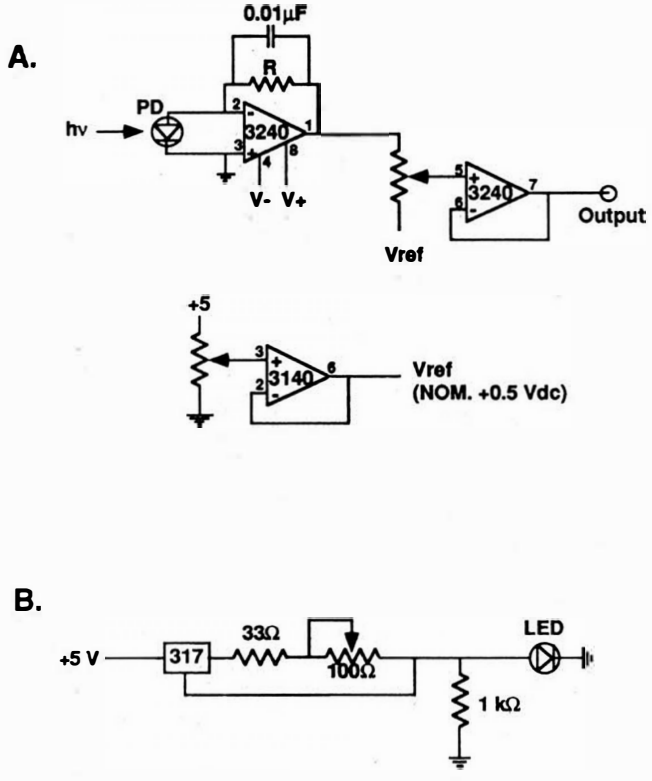

Figure 3. Circuit design for detector operation. **A.** Photodiode (PD) signal current-to-voltage conversion and amplification, and voltage offset circuitry. Resistor R has a value of 10^7 Ω for PD opposite yellow and green LEDs, value of 10^6 Ω for PD opposite red LED. **B.** Adjustable current regulators for light-emitting diode (LED). All three LED circuits are identical.

Reagents and Analytical Solutions

All solutions were prepared in distilled, deionized water. The carrier stream used was 1.0×10^{-5} M HCl and 6.0×10^{-6} M bromothymol blue. An approximately 0.5 M NaOH solution was prepared by dissolving solid NaOH in water. NaOH solutions of lower concentration were prepared by dilution of this NaOH stock solution. Acidic solutions of bromothymol blue are yellow and do not absorb appreciably in the wavelength region of the LEDs. Its alkaline solutions are deep blue in color and absorb light from the LEDs. Many other chemical reactions whose reagents do not absorb in the wavelength region of the LED sources and whose products absorb light in the LED range would be suitable for use with this detector.

Procedure

The student assembles the FI manifold and connects it to the tubing that enters the LED-based detector. If manual experience with FI systems is desired, the students cut and flange all tubing needed for the experiment.

The volume of each sample loop can be measured by placing it in the manifold, filling it with an alkaline solution of known concentration, injecting this sample into a flowing stream of water, collecting the effluent, and titrating with a standard acid solution. The flow rate at a given pump setting and pump tubing size can be calculated from the time needed to collect a given volume (5 mL or less should be sufficient) of effluent into a graduated cylinder. A more accurate method would be to measure the mass of liquid delivered within a known period of time.

Once these operating values are known for the FI system, the FIA experiments can proceed. First, the student chooses a mid- to high-range concentration of analyte (we used 4.81×10^{-2} M NaOH), and a relatively large sample loop volume (here, 807 μL), and varies the flow rate used. Next, the flow rate is held constant (at a relatively low

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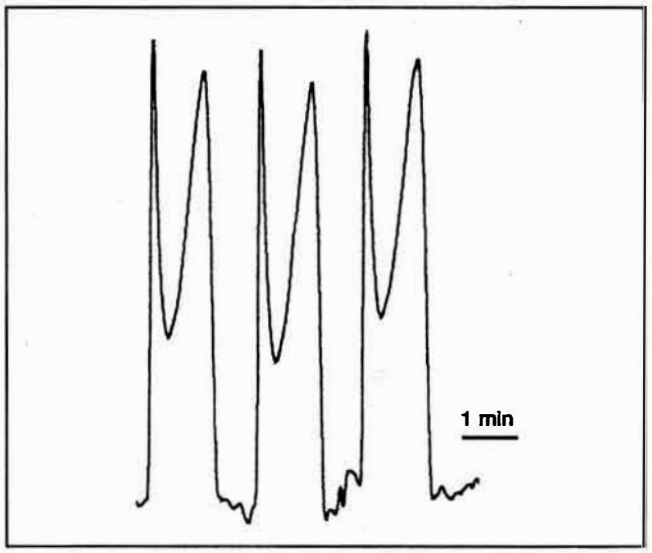

Figure 4. Typical doublet peaks obtained in this experiment. Three injections of a 536-μL sample of 4.81×10^{-2} M NaOH into a carrier stream containing 6.0×10^{-6} M bromothymol blue and 1.0×10^{-5} M HCl flowing at a rate of 1.27 mL/min. Note that noise and drift in baseline do not affect the measurement of Δt.

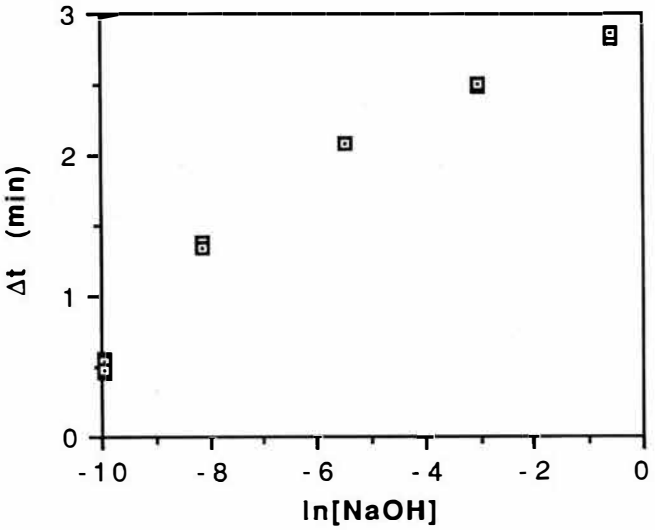

Figure 5. Plot of time between peaks (Δt) versus the natural logarithm of analyte concentration ($\ln[C^S]$).

value, to ensure a relatively broad dynamic range of sample concentrations giving the doublet peaks) and the concentration of analyte is varied for a given sample volume (we used 0.657-mL/min flow rate, and 807-μL sample volume). Finally, the injection volume is varied for a given flow rate and analyte concentration (here, 1.27 mL/min and 4.81×10^{-2} M NaOH). The student should observe significant changes in Δt when each of the parameters is varied. Comparisons between theory and experiment can then be made.

Results and Discussion

A complete set of experimental data collected with the red-LED-based detector pair is given in the table, and some representative doublet peaks are shown in Figure 4. The red LED was chosen as the source, because the absorbance of the basic form of bromothymol blue is greatest in this region of the spectrum. Limited results for the yellow- and green-LED-based detector pairs showed similar trends.

For a fixed sample concentration and injection volume, the flow rate of the system was varied from 0.657 to 3.12 mL/min. When a plot of t versus 1/Q is made, the data fit a straight line ($y = 0.0339 + 1.66\ x$, $R^2 = 1.00$), thereby demonstrating the validity of eq 1.

At low flow rate (0.657 mL/min) and fixed injection volume (807 μL), the concentration of NaOH injected into a stream of acid and indicator was varied from 4.81×10^{-6} M to 0.551 M. Doublet peaks were not observed for the 4.81×10^{-6} M injections. A plot of Δt versus the natural logarithm of the sample concentration is shown in Figure 5. Although eq 1 indicates that this plot should be linear, significant deviation from linearity occurs because the tubing used as the "mixing chamber" does not behave as a proper well-stirred tank (*13, 14*). The data do, however, fit a smooth curve. As a result, the instrument could be used for determination of samples of unknown NaOH concentrations.

At a fixed flow rate and sample concentration, the volume injected was varied from 108 μL to 1.37 mL. Because the volume of the reactor cannot be measured directly (*14*), it is necessary to perform a more "unconventional" curve-

Data Obtained in the FIA Doublet-Peak Experiment

V_i (mL)	C^S (M)	Q (mL/min)	Mean $\Delta t \pm$ Std.dev. (min), ($n = 3$)
0.807	4.81×10^{-2}	0.657	2.495 ±0.005
0.807	4.81×10^{-2}	1.27	1.242 ±0.003
0.807	4.81×10^{-2}	1.89	0.844 ±0.003
0.807	4.81×10^{-2}	2.51	0.635 ±0.003
0.807	4.81×10^{-2}	3.12	0.503 ±0.002
0.807	4.81×10^{-5}	0.657	0.473 ±0.013
0.807	2.95×10^{-4}	0.657	1.360 ±0.013
0.807	4.07×10^{-3}	0.657	2.083 ±0.006
0.807	5.51×10^{-1}	0.657	2.838 ±0.019
1.48	4.81×10^{-2}	1.27	1.965 ±0.010
0.536	4.81×10^{-2}	1.27	1.015 ±0.005
0.322	4.81×10^{-2}	1.27	0.790 ±0.005
0.108	4.81×10^{-2}	1.27	0.531 ±0.007

fit to the data. Some commercially available plotting programs, such as DeltaGraph Professional and Kaleidagraph, allow the user to specify the equation of the curve to which the data is fitted. Using Kaleidagraph, and incorporating the known values for Q, C^R, and C^S (see table), we fit the data points to the following line:

$$y = (7.87 \times 10^{-4}\ V) \ln (481(\exp(x/V) - 1))$$

where $y = t$, $x = V_i$, and V = apparent volume of mixing chamber. The value of V calculated from the data is 126 μL. Alternately, the value of V could be calculated manually from one data point. This calculation does not require sophisticated plotting software, but it does introduce more uncertainty than the fit to all of the data. A plot of t versus $\ln [\exp(V_i/126\ \mu L) - 1]$ results in a straight line, which corresponds to an alternate version of eq 1, with slope V/Q and intercept $(V/Q) \ln [C^S/C^R]$. The equation of the line is $y = 0.480 + 0.125\ x$, $R^2 = 0.998$. It agrees well with both theory and the known values of V, Q, C^R, and C^S.

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